

University of Oxford

Department of Chemistry



Layered double hydroxide-based catalysts for thermocatalytic CO₂ conversion

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August 2025

This thesis is submitted in partial fulfilment of the requirement for the degree of
Doctor of Philosophy at the University of Oxford

For my family

Abstract

This thesis explores the development of layered double hydroxide (LDH)-based catalysts for the direct thermocatalytic conversion of carbon dioxide (CO₂) to value-added chemicals, specifically methanol and dimethyl ether (DME). The research contributes to the advancement of low-cost, efficient catalysts designed to utilise CO₂ as a carbon feedstock, thereby supporting defossilisation strategies and facilitating the transition of the chemical industry from a linear to a circular economy.

Chapter 1 provides the contextual foundation for the work by outlining the current challenges and opportunities in CO₂ utilisation. It examines the thermodynamic and catalytic limitations associated with CO₂ conversion, with a particular focus on the production of methanol and DME, two high-value chemicals with a wide range of applications. The chapter introduces LDHs as catalyst precursors and discusses how hierarchical structures such as core-shells can enhance catalyst performance.

In Chapter 2, the synthesis and characterisation of a bifunctional ZSM5@Cu_{1.3}ZnAl core-shell catalyst—derived from an LDH-coated zeolite precursor—for the direct conversion of CO₂-to-DME (CTD). Catalytic testing was carried out in a fixed-bed reactor operating at 3 MPa, between 220 – 300 °C and a weight hourly space velocity (WHSV) of 44,000 mL/g_{cat}·h (CO₂/H₂/N₂ 24:72:4). The bifunctional catalyst demonstrated high DME productivity with a maximum space time yield (*STY*_{DME}) of 0.72 g_{DME}/g_{cat}·h. Further experiments revealed the importance of an oxidising calcination atmosphere in activating the catalyst for efficient CTD conversion.

Chapter 3 investigates the impact of residual sodium content and the ZSM-5:LDH ratio on the performance of the core-shell catalyst. Although sodium had a minimal influence

on the methanol productivity of the LDH-derived $\text{Cu}_{1.3}\text{ZnAl}$ catalyst ($0.27 - 0.29 \text{ g}_{\text{CH}_3\text{OH}}/\text{g}_{\text{cat}}\cdot\text{h}$), it had a considerable impact on the performance of the bifunctional catalysts. Results from CO_2 hydrogenation experiments revealed that $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$, with a 1:1 ZSM-5:LDH ratio, remained the most active catalyst under the conditions of $P = 3 \text{ Mpa}$, $T = 260 - 340 \text{ }^\circ\text{C}$, $WHSV = 18,000 \text{ mL}/\text{g}_{\text{cat}}\cdot\text{h}$, and $\text{CO}_2/\text{H}_2/\text{N}_2 = 24:72:4$. These findings underscore the importance of precise control over the core-shell precursor morphology in determining the catalytic performance of the resulting catalyst.

Chapter 4 describes the synthesis and characterisation of a series of Zr-incorporated hydrotalcite-like materials to investigate the role of Zr as a promoter for $\text{Cu}_{1.3}\text{ZnAl}$. CO_2 hydrogenation tests of Zr-incorporated $\text{Cu}_{1.3}\text{ZnAl}$ led to improved CTM activity at higher Zr loadings ($\text{CZA-Zr}_{0.5} = 0.33 \text{ g}_{\text{CH}_3\text{OH}}/\text{g}_{\text{cat}}\cdot\text{h}$, $\text{CZA-Zr}_{0.75} = 0.33 \text{ g}_{\text{CH}_3\text{OH}}/\text{g}_{\text{cat}}\cdot\text{h}$). Subsequently, Zr was incorporated into the *in-situ* coprecipitation of the core-shell. The remainder of the chapter discusses its performance relative to the original $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$ core-shell catalyst.

Chapter 5 provides a summary of the key findings presented throughout the thesis and outlines potential directions for future research. Chapter 6 describes the analytical techniques and synthesis methods used in the Chapters 2 to 4. Additional data and supplementary information referenced in the main text are included in the Appendices.

Acknowledgements

As lengthy as this thesis already is, I'd still like to take a moment to acknowledge just *some* of the people who have made this work possible. This list is by no means exhaustive, and for many, their contributions, not just to this work, but to my life, could fill a volume of its own.

To Professor Dermot O'Hare, thank you for welcoming me into your group and for your guidance over the years. To Dr Chunping Chen and Dr Zoë Turner, I'm grateful for your support, not only while you were part of the group but also after.

Thank you to Dr Lina Chen, Dr Louis Morris, and Dr Niko Jenek, for being such lovely members of the group. Massive thanks goes to Dr Roland Turnell-Ritson. You've been instrumental in getting me over the finish line for this thesis and for that I am so grateful. Thank you as well to Phani Karamched, Graham Wyatt and Gerardo Martinez Alanis at the DCCEM for their microscopy advice and training, and to Robert Jacobs for advising me on surface analysis techniques.

To Dr Molly Li, thank you so much for giving me the opportunity to conduct my research as a member of your group in Hong Kong. Without it, this work would not have been possible. To Tsz Ching Chan (*Rosanna*) and Lin Yashan (*Echo*), thank you girls for making my time in Hong Kong so great, it really wouldn't have been the same experience without you. A special, big thanks goes to Li Jiangtong, not just for the great work you did in the early stages of the hydrogenation tests, but also for being such a good teacher and friend. Thank you for helping me get set up when I first arrived, and for looking after me whilst I was there. I hope we can share a meal together soon!

To members of the O'Hare group, past and present, it's been a pleasure being a part of the lab shenanigans. Thanks to the organometallics crew for giving the rest of us a break from LDHs. Apologies for the many, many, brucite-like layered structures we subjected you to. Thank you to Katherine Laney for helping me get settled when I first joined. Also, thanks to Tiger Yang for your help on TOPAS-related nonsense and Georgia Stonadge for reactor-related nonsense, and Linet Wairimu Ng'ang'a for your encouragement. To Joshua McConnell, I'm glad we didn't scare you away after your Part II, you've been a

lovely addition to the group and we're expecting big things from you. Matt Williams, I'll never forget bumping into you at that ABBA night all those years ago. I have tried to forget every other night out we've been on. I maintain we have never sent anything to each other on Instagram ever (<3). To Alexander Evans, from one Tesco-meal-deal-warrior to another, I hope you no longer need to make it 'upgraded'. Thank you for getting me up and down two different mountains in one piece, introducing me to new music and permanently messing up my YouTube algorithm. To Sam Roberts. What can I say, S4's not been the same without you. We've missed your hugs, your laugh, and your calming energy. Here's to more nights out in London. Emma Southall, you best not be reading this whilst you got a centrifuge going. Thank you so much for all your encouragement and emotional support both in and out of the lab. Your resilience is inspiring, and you're one of the most dedicated researchers I know. And yes, before you ask, we can get ice cream later.

Shoutout to Jevon Marsh, my fellow CRL survivor and wine bar king. I wish you all the love in the world as you start your new chapter.

They say home is where the heart is, and I've been very fortunate to have had such wonderful flatmates over the years. For the great BBQs and movie nights in Coventry thank you to Katie Pickering, Noelig Hallez and Elizabeth Haycox (and Mink). For the D3 crew at Balliol College, although there's been a lot of turnover in the past three years, every iteration of our floor has been an experience. Shoutout to our ex-Head Chef Jenny Shearer and my fellow oat-and-sultana-cookie-connoisseur Tabea Sieper. Also, to Charlie Clark for inundating us with canned peas. To Jeffery Pendleton, thank you for your exquisite cooking and matcha. Thank you as well to Jyothsna Gurumurthy and Alina Nicheperovich for bringing such warmth to the flat, you are two of the sweetest people I know and it's been a joy to live with you both. Ivana Kuric, you are sunshine in human form, and I can't wait to celebrate with you later. To Misha Schmal thanks for being a great gym-and-yap buddy and to Elyse Cox thank you for giving me shelter on my great American tour.

To Arthur Cullen and Alfie Ellis, thanks for still being around after 14 years. It's been alright I guess. To Adam John Ellison. Thank you for the many years of friendship and support, I wish you the best of luck and success.

Special shoutout to Anne-So Fayet, Stephanie Cheng, Holly Struttaford-Fowler, Magda Krynicka, and Carmen Luong. You guys are an inspiration, and I feel so fortunate we all met through our shared love for dance. Here's to more projects, bubble teas and KBBQs in the future.

To Anna Fiteni and Kate Benjamin. Turns out women can be gorgeous, intelligent and hilarious at the same time, who knew? You guys have shown me a lot of love over the years and now that I'm done, I look forward to making more memories together. Kate, thank you for your support and for keeping me sufficient in Vitamin C with the regular supply of fresh fruit whilst I've been writing up.

To my fellow Warwick University survivors, Siddhartha "Tren" Singh, Archie "Bitcoin miner" Powell, Sophie "Tap" Kempston, Natasha "Fitbit" Patel, Shivani "So Basically" Rughani, and Sam "The Invincible" Turpin, I see a great many trips to the pub in the future so watch this space my loves. To Amy Ho, you are sugar, spice and everything nice, your positivity is infectious, and you are such a joy to be around. To Sean Sung Eun Choi. My dear, thank you for being one of my biggest cheerleaders and for continuing to support me across different continents. May we finally be reunited in the same country for longer than just a weekend.

Dominic Sandhu. Forever my 'Doctor Ken', if being an academic weapon wasn't your day job, you'd make bank as a comedian. You've always been easy to talk to and you're such a kind-hearted person. Share the hair care treatment and the recipes for the rest of us. Nick Smart. You and I could've gone places you know. It's so obvious, you're my number one. I was busy thinking about how thoughtful you are as a person and how much I appreciate you in my life and as a trusted friend and adviser. When I go to the club, I wanna see you buying those Desperados. I'll never forget that, *boom clap*, the sound of your ankle hitting the floor. And really at the end of the day, I only wrote this acknowledgement for you. To Riona Deveraux. My partner in crime. I'm so happy to say we got there in the end. I'm forever grateful for everything you've done for me over the past few years, and I feel so lucky that we met and that I can call you, my friend. My experience at Oxford would not have been the same without you and although I'm heartbroken you're leaving us for bigger, better things, I'm so happy to see you flourish as the talent that you are. Next round of Guinness is on me.

And last, but my no means least, I'd like to thank my family for their unwavering support over the years. To Aunty Tona and Uncle David, thank you for always looking out for us. To Kimi, I may not be able to carry you anymore, but it's hard when I'm also carrying the title as the most boring cousin. Hate to say it kid, but you're gonna have to try harder to fill these dusty boots. To Grandma, some of my fondest memories are of us living with you and Grandpa. Although we've been away for some time now, you're always in our hearts and I'm so happy I get to celebrate the end of this degree with you.

To the Coulthard Clan, I know we're not a sentimental bunch but just bear with me. Sarah, it's been a pleasure seeing you grow into the woman you are now. We traded fist fights for brunches and long yap sessions. Without a doubt, I would not have been able to make it through this PhD without you. You are the most beautiful, kind and caring soul I know. You are loved and adored by so many people, myself included, and I hope you know how lucky I consider myself to have you as my sister. Ma, it couldn't have been easy moving all the way from Singapore to the UK for us. You have always gone above and beyond to support my studies throughout the years, and I can't begin to express my admiration for your generosity and kind spirit. Dad, your optimism in the face of adversity is something that I greatly admire, and I hope I can take whatever comes next in the same stride as you. Mum and dad, you've always been my biggest supporters. I hope the culmination of this work goes some way to make up for the sacrifices you made to get me here. Time to celebrate with some hot pot and a cold one. I love you all.

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Nomenclature

Å	Angstrom
°C	Degrees Celsius
ΔH°	Standard enthalpy change
ΔG^θ	Standard Gibbs free energy change
AMOST	Aqueous miscible organic solvent treatment
ASF	Anderson-Schulz-Flory
BEA	Beta zeolites
BECCS	Bioenergy carbon capture and storage
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Haleda
C ₁	Single carbon
C ₂₊	Multicarbon products
CAGR	Compound annual growth rate
Cat	Catalyst
CC	Climate change
CCC	Climate change committee
CCS	Carbon capture and storage
CCU	Carbon capture and utilisation
CHA	Chabazite
CIF	Crystallographic information file
CO ₂	Carbon dioxide
CPMAS	Cross-polarization magic angle spinning

CTD	CO ₂ -to-DME
CTM	CO ₂ -to-methanol
CZA	Cu/ZnO/Al ₂ O ₃
DAC	Direct air capture
DCCEM	David Cockayne Centre for Electron Microscopy
DFT	Density functional theory
DI	Deionised water
DME	Dimethyl ether
DPMAS	Direct polarization magic angle spinning
DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy
dTGA	First derivative of thermal gravimetric analysis curve
EDX	Energy dispersive X-ray spectroscopy
EPR	Electron paramagnetic resonance
eV	Electron volt
EXAFS	Extended X-ray absorption fine structure
FAU	Faujasite
FER	Ferrierite
FID	Flame ionisation detector
FT	Fischer-Tropsch
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maximum
g	Gram
GC	Gas chromatography
GHG	Greenhouse gas

GHSV	Gas hourly space velocity
GOF	Goodness of fit
h	Hour
SEM	Scanning electron microscopy
HR-TEM	High-resolution transmission electron microscopy
Htl	Hydrotalcite-like
ICP-OES	Inductively coupled plasma atomic emission spectroscopy
IZA	International zeolite association
kJ	Kilojoules
LCA	Life-cycle assessments
LDH	Layered double hydroxide
LDO	Layered double oxide
LPG	Liquid propane gas
MFI	Mobile-five
Min	Minutes
MOF	Metal organic framework
mol	Mole
MOR	Mordenite
mmol	mmol
MPa	Mega pascals
MR	Membered-rings
Mt	Mega tonne
MTD	Methanol-to-DME
MTG	Methanol-to-gasoline

MTO	Methanol-to-olefins
NMR	Nuclear magnetic resonance
P	Pressure
PMMA	Poly(methyl methacrylate)
ppm	Parts per million
PXRD	Powder X-ray diffraction
RWGS	reverse water gas shift
SAPO	Silicoaluminophosphates
S_{BET}	Specific surface areas
$S_{\text{CH}_3\text{OH}}$	Selectivity of methanol
S_{DME}	Selectivity of DME
S_{External}	External surface area
S_{Micro}	Micropore surface area
SMSI	Strong metal support interactions
S_{Product}	Selectivity of a product
ssNMR	Solid state nuclear magnetic resonance
STEM	Scanning transmission electron microscopy
STY	space time yield
STY_{DME}	DME space time yield
T	Temperature
t	Tonnes
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis

TPAOH	Tetrapropylammonium hydroxide
TPD	Temperature programmed desorption
TPR	Temperature programmed reduction
UV-Vis	Ultraviolet-visible
V_{Micro}	Micropore volume
WHSV	Weight hourly space velocity
WLRs	Weight loss regions
XANES	X-ray absorption near edge structure
XPS	X-ray photoelectron spectroscopy
Y_{DME}	Yield of DME
ZSM-5	Zeolite Socony Mobil-5

1

Introduction

1.1: Overview

Anthropogenic activities occurring since the Industrial Revolution have led to a dramatic rise in atmospheric CO₂ concentrations.¹ The acceptance of human emissions as the primary driver of climate change has led to major CO₂ mitigation efforts in recent years.² Simultaneously, increasing attention has been directed toward the development of methods for transforming CO₂ into high-value chemicals and fuels to shift the reliance on fossil fuels in pursuit of a sustainable, circular economy.⁴

The following chapter provides the contextual background underpinning the work in this thesis. It begins by outlining the global challenges associated with CO₂ emissions and introduces the concept of a circular carbon economy where CO₂ is repurposed as a valuable chemical feedstock. It then explores the thermodynamics associated with CO₂ conversion, followed by a discussion of the energetics and catalysts involved in CO₂-to-

methanol (CTM) and CO₂-to-dimethyl ether (CTD) conversions. Key catalysts for the CTM and CTD pathways are reviewed, highlighting their mechanisms, efficiencies, and limitations. Subsequent sections discuss layered double hydroxides (LDHs), their structural features and the potential advantages of incorporating LDHs into core-shell architectures toward CO₂ conversion.

1.2: CO₂ utilisation and the transition to net-zero

Since the beginning of the Industrial Revolution, atmospheric CO₂ concentrations have increased dramatically from a pre-industrial level of approximately 280 ppm, a value that had remained relatively stable for nearly 6000 years of human civilisation (Figure 1.1).⁵ As industrial activity grew, CO₂ emissions began to rise steadily, and by 1950, 230 billion tonnes of extra CO₂ had been emitted by human activity. This continued to climb rapidly, surpassing 977 billion tonnes by 1998. In 25 years, emissions nearly doubled, and by 2023, cumulative anthropogenic CO₂ emissions approached 1.77 trillion tonnes.⁶ Consequently, atmospheric CO₂ levels have now reached nearly 420 ppm, a trend that is expected to continue upward before stabilising.⁷ This increase in CO₂ emissions has direct climate implications. For every 10 ppm rise in atmospheric CO₂, the average global temperature increases by approximately 0.1 °C. Given the scale of these changes, limiting global warming to well below 2 °C above pre-industrial levels remains a pressing challenge. In response, attitudes toward climate responsibility have shifted in recent years, with the public and private sectors increasingly recognising the need for actionable targets to reduce greenhouse gas (GHG) emissions.⁸

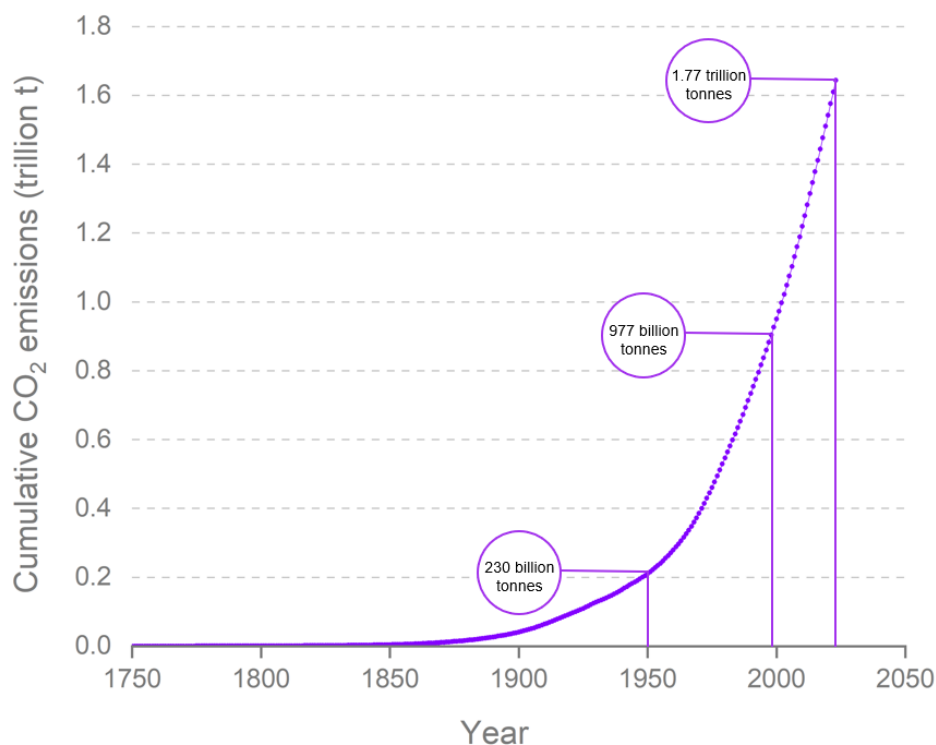


Figure 1.1: Worldwide cumulative CO₂ emissions (trillion tonnes) per year between 1750 to 2023. Global Carbon Budget (2024) – with major processing by Our World in Data.⁶

As a signatory to the 2015 Paris Agreement, the UK is committed to pursuing efforts to limit global temperature rise to 1.5 °C above pre-industrial levels. In alignment with this, the UK has committed to reducing GHG emissions by at least 81% by 2035 relative to 1990 levels. In addition to these international commitments, the UK has also established domestic legally binding climate targets through the Climate Change Act of 2008, legally mandating the reduction of GHG emissions to net-zero by 2050. In its most recent emissions reductions report, the Climate Change Committee (CCC), the UK's independent advisor on climate change policy, described the country's progress as real and quantifiable, noting that emissions fell by approximately 2.5% from 2023 and that the UK remains roughly on track to achieve its climate targets.⁹

The pursuit of net-zero emissions necessitates a shift away from fossil fuel dependency, which in turn demands a transition from the traditional, linear economic model towards a circular economy.^{10, 11} In recognition of this, the UK government established a Circular Economy Taskforce made up of independent experts from industry and academia, to advise on a circular economy strategy for England. Within this context, the chemical industry, which contributes approximately 5% of global GHG emissions has a critical role to play in facilitating this transition. Decarbonisation in this sector can be achieved by moving towards both electrification and defossilisation.^{12, 13} Where the vast majority of chemicals are made using fossil fuel feedstocks, there is a growing opportunity to integrate established carbon capture technologies with emerging carbon utilisation strategies, where CO₂ is used as a non-fossil fuel feedstock for chemical production.^{10, 12}

In this context, carbon capture and utilisation (CCU) has gained increasing attention as a strategy to support emissions reduction and the circular economy. Here, CO₂ is used as a feedstock and is captured either from point sources (i.e. the CO₂ emissions origin, typically at an industrial site) or from Direct Air Capture (DAC).¹⁴ Whilst carbon capture and storage (CCS) projects are concerned with the sequestration of CO₂ emissions, the goal of CCU is to use recycled CO₂ either directly or as a feedstock for the production of value-added chemicals, materials and/or fuels as part of a circular economy.^{14, 15} Thus the feasibility of CCU projects is dependent firstly on the state of CCS technologies which are still in the early stages of implementation.¹⁰ Technological developments in this area alongside increasing investment trends and supportive international government policies suggests an increasing deployment of large-scale commercial CCS projects in the next few years.^{16, 17} For example, final investment decisions have recently been made on CO₂ transport and storage infrastructure in the UK, and new North Sea oil and gas projects are

now required to consider carbon activities before receiving approval.⁹ Furthermore, as infrastructure develops, the cost of CC is expected to decline (mirroring trends observed in the photovoltaics and automotive sectors), likely driving further innovation and deployment in this space.¹⁸

A large portion of CCU research involves catalyst design and engineering (Figure 1.2). Innovations in catalyst design are concerned with tailoring catalysts at the atomic level to optimise the efficacy of the material for CO₂ conversion in terms of activity and product selectivity. Catalyst engineering then focuses on improving the performance of the catalyst by optimising factors such as the reactor design, catalyst shaping (e.g. pelletizing) and scalability. To be commercially viable, the catalyst must be high performing whilst also being cost-effective, durable and suitable for large-scale deployment. Moreover, to achieve net-zero targets, the overall process must be considered, particularly with regard to its energy intensity and source of other reagents involved in CO₂ conversion.

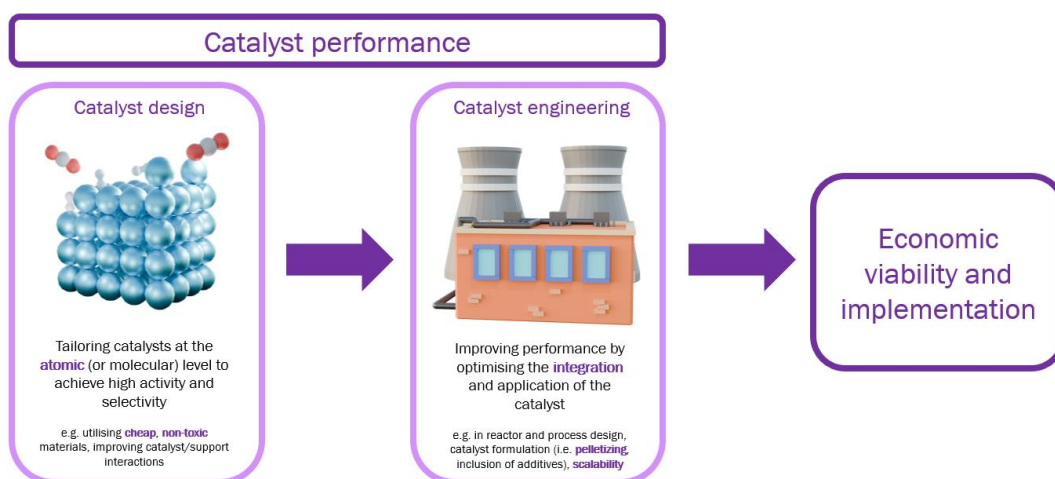


Figure 1.2: Key stages in catalyst development impacting the implementation of CCU technologies.

The utilisation of CO₂ as a feedstock has the potential to improve the economic viability of CCS projects by providing value whilst offsetting emissions in hard-to-abate sectors. Investments in CCU projects, combined with bioenergy carbon capture and storage (BECCS) or DAC can then be used to offset emissions from industries such as aviation, helping to keep in line with net-zero targets.¹⁹ However, the implementation of CCU technologies faces several technical and economic challenges. The capture, transport, storage and transformation of CO₂ are energy intensive processes that may need additional, non-renewable energy sources to meet the demand.¹⁹ As a highly stable molecule, CO₂ typically requires a significant energy input for activation and conversion, with many reactions suffering from sluggish kinetics (the thermodynamics associated with CO₂ conversion will be discussed in the following sections).^{20, 21} Furthermore, CO₂ conversion often requires hydrogen, the sourcing of which must also come from non-fossil fuel feedstocks (e.g. green hydrogen from electrolysis) to ensure overall sustainability.²² From a catalyst design perspective, key challenges include catalyst deactivation, product selectivity and poor performance under industrial conditions. The business case for future CCU projects will also need to include life-cycle assessments (LCAs) for the products generated which necessitates better quality data and an appreciation of the possible environmental impacts of the products.^{20, 23}

Despite these challenges, CCU remains a promising strategy with the potential to make a meaningful contribution to decarbonisation efforts in the chemical sector by providing a domestic, low-carbon alternative to fossil fuels. Thus, CCU can be considered a forward-looking approach for reducing the industry's reliance on fossil fuels, and is predicted to play a larger role in the sector's transition to net-zero.²³⁻²⁵

1.3 CO₂ as a feedstock

CO₂ has been an established feedstock for the industrial synthesis of organics since the beginning of the 19th Century.²⁶ CO₂ can either be used directly without chemical alterations or can be converted into more valuable products (methanol, dimethyl ether (DME), formic acid, urea etc.).^{27, 28} Of the 230 Mt of CO₂ utilised each year, around 42.2 Mt_{CO₂}/year (~18%) is used in its raw form, whilst the majority is transformed into more valuable chemicals, materials or polymers (see Figure 1.3).^{29, 30} In terms of direct utilisation, CO₂ is primarily used in enhanced oil recovery, but it also finds applications within the food and drink industry where it is used for food preservation or carbonation of drinks.³¹ Currently, the largest consumer of CO₂ is the fertiliser industry using over 130 Mt of CO₂ per year for urea production.^{20, 30, 32} Of the remaining CO₂ consumed by industry, a significant proportion (70 Mt_{CO₂}/year) is used in CO₂ mineralisation to produce inorganic carbonates.²⁰ Other chemical products obtained at industrial scale using CO₂ as a raw material include methanol, formaldehyde, DME, formic acid, carbamates, and polymer-building blocks.^{4, 29}

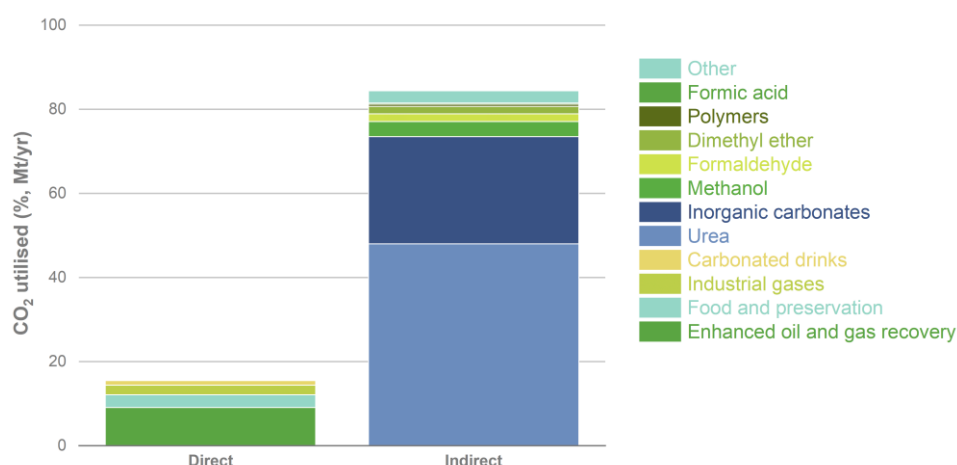


Figure 1.3: Breakdown of direct and indirect uses of CO₂ in industry.

Indirect CO₂ utilisation is an emerging market with significant growth potential. To date, the majority of products that are made using CO₂ are single-carbon (C₁) type chemicals, such as methanol, formic acid, and carbon monoxide.²⁶ Among these, methanol has emerged as one of the most viable CO₂-based products.²⁸ Methanol is a highly versatile platform chemical, with applications in fuel blending, formaldehyde production, acetic acid synthesis and increasingly, in methanol-to-olefins (MTO) and methanol-to-gasoline (MTG) processes.³³⁻³⁵ At present, the majority of methanol is produced from fossil fuels or natural gas sources with only 0.2% of methanol production sourced renewably.³⁵ The transformation of CO₂ to methanol (10 Mt_{CO₂}/year) is a well-researched and established industrial process, and with an international market price of ~450 €/t, it demonstrates how CO₂ can be transformed in an economically viable way.^{29, 36} Increasing global methanol demands in the past year are reflective of the drive for cleaner-burning fuel alternatives within the energy and transportation sectors.³⁷ As an essential component in the chemical industry, switching to renewable methanol synthesised from green hydrogen and recycled CO₂ (i.e. e-methanol) would assist in net-zero/circular economy goals.³⁵

Whilst C₁ products are industrially attractive, there is a growing interest in producing multicarbon (C₂₊) products from CO₂. Multi-carbon (C₂₊) chemicals tend to have greater economic value (see Figure 1.4), higher energy densities and greater application potentials than C₁ products.^{38, 39} Thus establishing CO₂ to C₂₊ conversion is important from the perspective of fundamental research and industrial application.⁴⁰

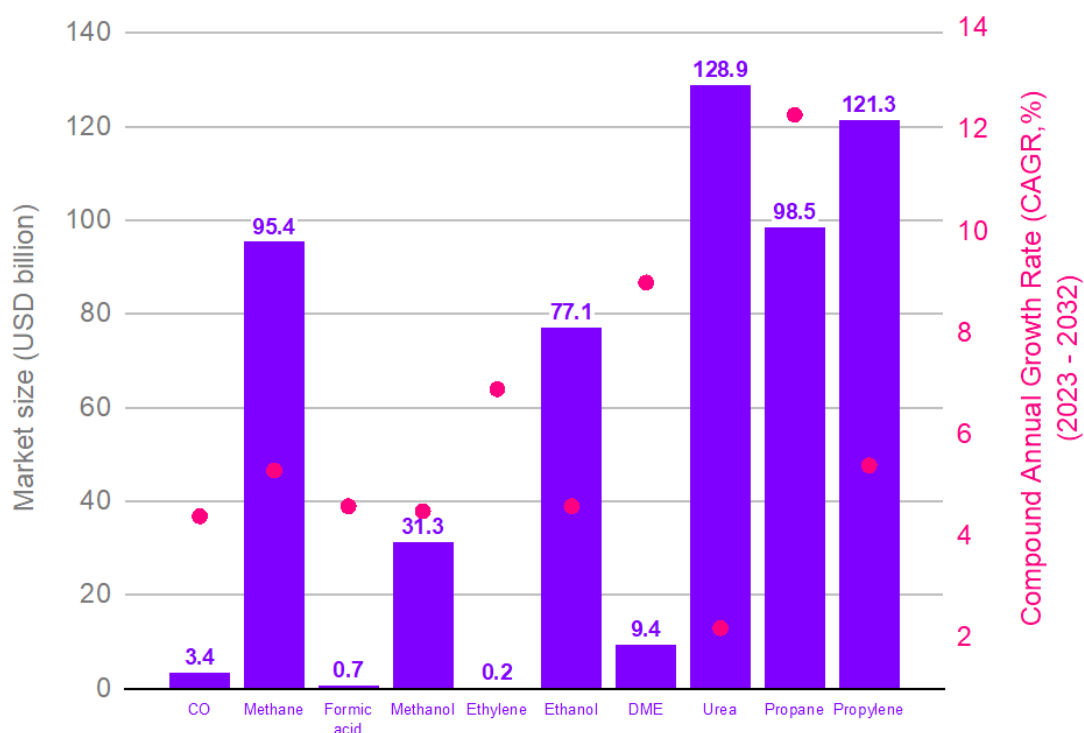


Figure 1.4: Market sizes (billion USD) and compound annual growth rates (CAGRs) of common C₁ and C₂₊ products. Market sizes are based on reported values between 2022 – 2023 whilst CAGR is estimated for the 2023 – 2032 forecasting period.⁴¹⁻⁵⁰

Another possible product from CO₂ conversion is DME, which can be produced from methanol or directly via CO₂ hydrogenation. DME has an international market price of ~520 €/t and has applications as a clean-burning alternative to diesel,⁵¹⁻⁵³ as a non-ozone-depleting propellant in aerosol sprays,⁵⁴ and an intermediate for a variety of chemicals (e.g. dimethyl sulphate, methyl acetate, acetic acid, olefins and gasoline).⁵⁵⁻⁵⁷ At present, the main use of DME is as a blending component with liquid propane gas (LPG) for domestic energy applications such as cooking and heating.⁵⁸ The market for DME is expected to grow significantly in the coming years (with a CAGR of 9% forecasted between 2024 – 2032) particularly in China, Japan and India where governments are promoting low-emission fuel alternatives.^{50, 58} While the production of chemicals from CO₂ is technologically feasible, its commercial viability remains dependent on the

development of more efficient catalysts. In response to the growing demand for DME as a sustainable alternative to diesel, significant research efforts have focused on enhancing the efficiency of catalysts for efficient CO₂-to-DME (CTD) conversion.^{20, 37, 59} In light of this, the following sections discuss the underlying thermodynamics of the reactions governing the conversion of CO₂ to methanol and DME.

1.4 CO₂ conversion

1.4.1 CO₂ thermodynamics

There are several challenges associated with CO₂ conversion. As a non-polar molecule with strong C=O double bonds (~830 kJ/mol), CO₂ has a high activation energy barrier.²¹ The thermodynamic stability of CO₂ (-394.4 kJ/mol), imposes a large energy barrier for activation which is further complicated by poor C–C coupling kinetics are otherwise necessary for complex hydrocarbon formation.^{60, 61}

Entropy also limits CO₂ transformations. For reactions where standard enthalpy change (ΔH°) is negative ($\Delta H^\circ < 0$), and free energy change under standard conditions (ΔG°) is positive, thus product formation under standard conditions is non-spontaneous.²¹ CO₂ conversion can occur at lower temperatures; however, in such cases the carbon atom maintains a +4 oxidation state, producing carbamates, carbonates, urea and its derivatives.⁶² The Gibbs free-energy of formation (ΔG_f°) at standard conditions for several C₁ species, including, methane, formaldehyde, CO, methanol and formic acid, all have positive Gibbs free-energy values ($\Delta G^\circ > 0$) (see Figure 1.5).^{4, 63} Thus, the reaction must be under kinetic control to minimise the formation of the thermodynamically favoured products (e.g. carboxylates). Overcoming the activation barrier requires a

substantial energy input from external sources (i.e. thermal, electrochemical or photochemical), posing significant challenges for the overall energy efficiency of CO₂ conversion.

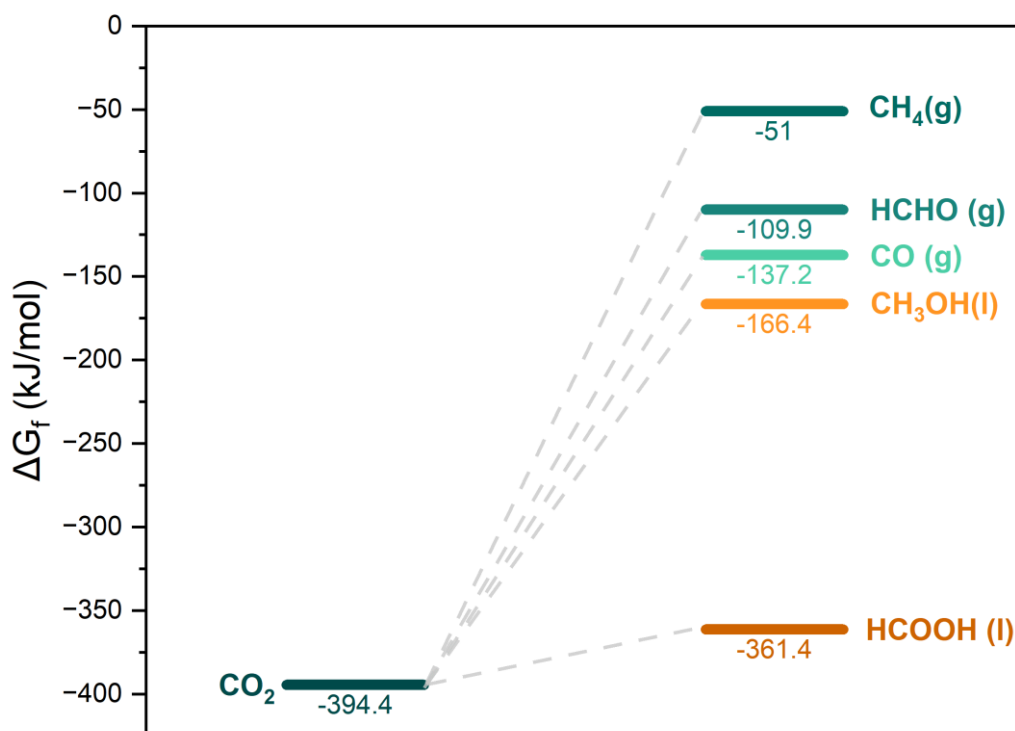


Figure 1.5: Gibbs free-energy of formation (ΔG_f°) of several C₁ species.⁶³

Catalysts are crucial for CO₂ activation and can be used to control the energy barrier in the CO₂ reduction process. Due to the electronegativity difference between the central carbon and adjacent oxygens, CO₂ can react at the electrophilic carbon site (Lewis acid centre) or at the nucleophilic oxygen atoms (Lewis basic character).⁶² With an electron affinity of -0.6 eV and an ionisation energy of 13.8 eV, CO₂ is a better electron acceptor than electron donor, hence CO₂ conversion typically proceeds by nucleophilic attack at the carbon site.^{62, 64} CO₂ activation can be achieved using bases, transition metals or by one electron reduction.⁶⁵⁻⁶⁹ When coordinating to a metal surface, the electron

distribution and geometry of the CO₂ molecules are altered, leading to increased reactivity.²¹

The nature of the catalysts strongly influences the specific reaction pathways and products formed during CO₂ conversion. The following section provides an overview of the various catalytic methods for CO₂ conversion.

1.4.2 CO₂ conversion pathways

The catalytic conversion of CO₂ can be approached in a variety of ways (thermocatalytic, electrocatalytic, photocatalytic etc.).^{4, 70-75} A summary of the different pathways for CO₂ conversion, including their advantages and disadvantages, is highlighted in Figure 1.6. Thermocatalytic conversion is the most traditional and well-established process, with CO₂ to C₁ products having been established in industry for many years. It is a promising pathway as it aligns well with existing infrastructure, making it more readily scalable in the near-term whilst reducing the need for large capital investments.⁵³

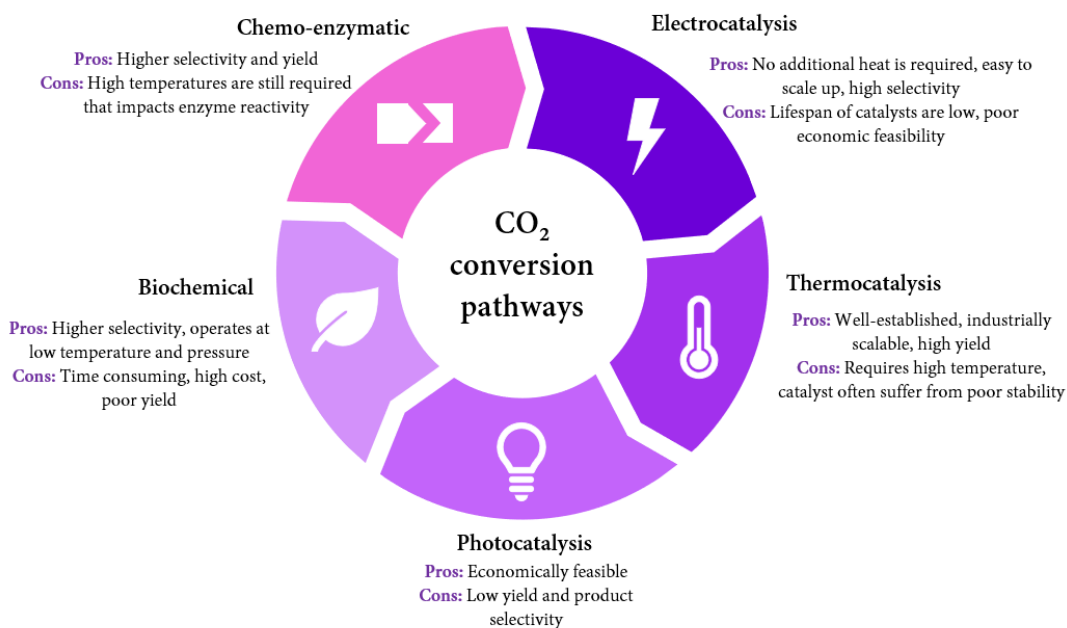


Figure 1.6: A summary of the existing CO₂ conversion pathways.

Large-scale CO₂ to C₂₊ catalysis however, has yet to be realised.^{26, 76} Multicarbon production from CO₂ typically involves cascade reactions where CO₂ is first converted into intermediates which continue to react to form more complex hydrocarbons/oxygenates in subsequent reactions.⁷⁷ From an industrial perspective, achieving CO₂ to C₂₊ conversion necessitates a high-throughput catalyst with high productivity, that is selective and has minimal downstream separation requirements.

When considering the thermocatalytic route there are two commonly researched options for CO₂ conversion to C₂₊ products (particularly for olefin production) which follow distinct reaction pathways: (A) the reverse water gas shift (RWGS)/Fischer-Tropsch (FT) pathway, and (B) the methanol-mediated route (Figure 1.7).⁷⁸ Often described as the indirect pathway, the RWGS/FT route first converts CO₂ and H₂ via the RWGS reaction into CO and H₂O. The resulting CO is then fed to a FT catalyst, typically Fe/Co-based, to produce hydrocarbons, including olefins and paraffins.^{79, 80} Although popular and well-

researched, the drawback of the indirect pathway lies in the poor selectivity of FT catalysts. A major limitation of the FT process is that the product distribution follows the Anderson-Schulz-Flory (ASF) model, favouring the formation of long-chain hydrocarbons over light olefins making it challenging to selectively produce C₂-C₄ olefins at high yield.²⁷

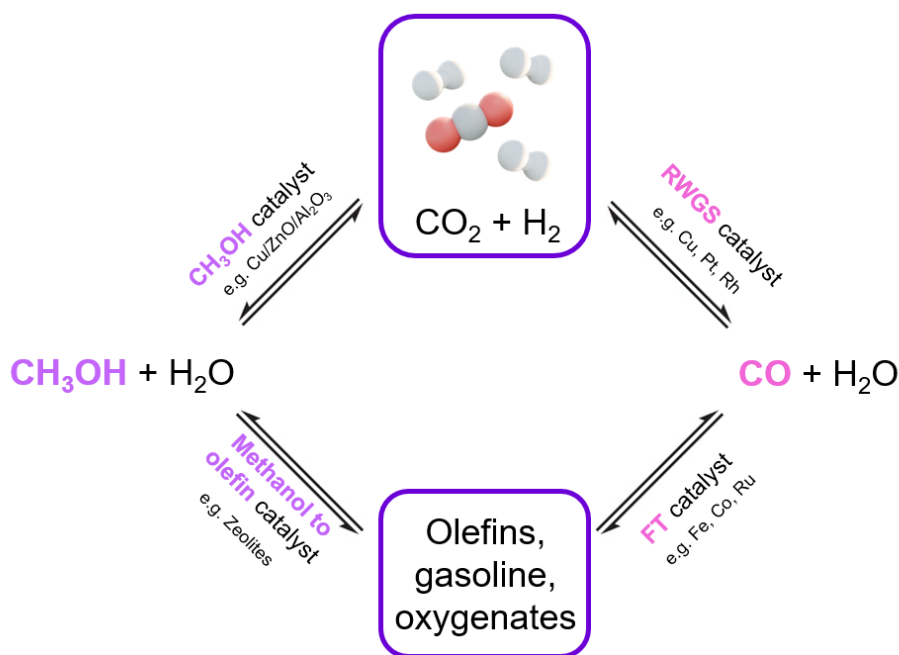


Figure 1.7: The current popular CO₂ conversion to olefins pathways including the RWGS/FT-catalyst route and the methanol-mediated route.

The direct conversion of CO₂ to light olefins (e.g. ethylene, propylene) in a single step process via the methanol-mediated route can bypass the ASF limitations and achieve higher product selectivities.^{81, 82} This methanol-mediated route has also been used to investigate the direct conversion of CO₂ to dimethyl ether (DME).⁸³ Given that DME has applications as both a cleaner fuel alternative and as a platform chemical, utilising CO₂ as a feedstock for DME production offers a compelling economic incentive to shift away from fossil-based resources.⁸⁴ The thermocatalytic conversion of CO₂ to DME via the methanol-mediated pathway offers several advantages. Notably, the process can be

integrated into a single reactor system using a bifunctional catalyst that facilitates both the CO₂-to-methanol (CTM) and methanol-to-DME (MTD) conversion steps.⁸⁵⁻⁸⁷ This setup not only simplifies reactor design, lowering capital expenditure, but also shifts the thermodynamic equilibrium toward greater overall CO₂ conversion by removing methanol *in-situ* via its subsequent transformation to DME.^{83, 88} This approach also has the potential to integrate well with existing industrial infrastructure, reducing the need for retrofitting.

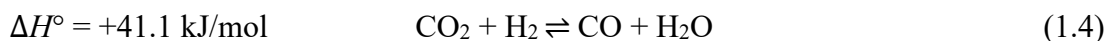
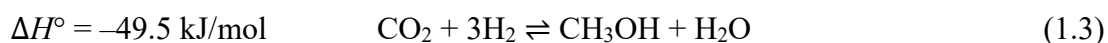
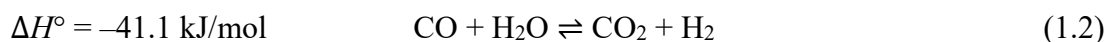
The following section provides a detailed overview of the reaction mechanisms and thermodynamics of the thermocatalytic conversion of CO₂. It first describes the thermodynamics of the CTM process and the reaction pathway over the most widely studied CTM catalyst, Cu/ZnO/Al₂O₃ (CZA). This is followed by a discussion of the roles of copper, zinc oxide, and alumina in CZA, along with an overview of alternative CTM catalysts. The subsequent section will then explore the thermodynamics and reaction pathway of the MTD reaction, including a discussion of frequently used MTD catalysts. Finally, a brief overview of the direct CTD pathway will be provided, highlighting key thermodynamic challenges and current limitations.

1.4.3 The CO₂-to-methanol (CTM) reaction

Conventionally, synthesis gas (syngas), with a composition of CO, H₂ and a small percentage of CO₂, is used to make methanol in a process that's been commercially operated since the 1920s.³³ The industrial production of methanol involves both the initial formation of syngas via steam reforming of methane, a high intensity process requiring high temperatures and pressures (900 °C, 16 – 30 bar).⁸⁹ This is followed by the conversion syngas to methanol (reaction (1.1)) which operates at high pressures (5 – 10 MPa) and modest temperatures (200 – 300 °C).⁹⁰



Experimental evidence has shown that over Cu-based catalysts (the most used catalysts for methanol synthesis), CO in syngas is not directly hydrogenated to methanol.^{91, 92} Instead, CO forms CO₂ as an intermediate via the water gas shift reaction (WGSR, reaction (1.2)) which is then hydrogenated to form methanol and water (reaction (3)).⁹² Hence, the same catalyst and the surface sites can facilitate the syngas and CO₂ hydrogenation pathways.⁹⁰ The main difference lies in the exothermicity which is greater in the case of CO hydrogenation.⁹⁰ This primarily impacts the reactor design, for instance as CO₂ hydrogenation produces less heat, cheaper tube-cooled reactors are used for heat regulation.⁹³



The major considerations for CO₂ hydrogenation are: (i) it is kinetically limited (15 – 20%) as a consequence of the high activation energy associated with CO₂, (ii) it is an exothermic process and (iii) it competes against the RWGS reaction (reaction (1.4)).⁹⁴ Consequently, reaction (1.3) is kinetically favourable at high temperatures but is thermodynamically favourable at low temperatures, with increasing CO formation at higher temperatures. These factors imply a fundamental trade-off in operating conditions for CO₂ hydrogenation. As a result, catalyst design must consider both the activity, selectivity and thermal stability to navigate the thermodynamic-kinetic balance.

Furthermore, the ideal CO₂ hydrogenation catalyst must not only adsorb and activate CO₂, but also stabilise the reaction intermediates to favour the methanol pathway over the RWGS reaction. The catalyst should also facilitate the dissociation of H₂, enabling it to react with the activated CO₂ species/intermediates, thereby promoting the production of methanol over CO. Equally important is the role of metal-oxide supports, which enhance catalyst performance by dispersing the active metal sites, creating interfacial regions, and altering the surface chemistry of the catalyst (e.g. by changing the acidity/basicity or the oxygen vacancy concentration).⁹⁵

1.4.4 CTM catalysts

Cu-based catalysts, specifically CZA-type catalysts, are the most used and well-researched for the CTM reaction.⁹² Typically, CO₂ conversion to methanol over CZA catalysts occurs between 220 – 300 °C.^{33, 90, 92} It is generally accepted that the primary active sites in these catalysts are clusters of metallic Cu⁰ nanoparticles, which play a critical role in adsorbing and dissociating hydrogen.⁹² Besides the Cu⁰ sites, increasing evidence suggests that partially reduced Cu⁺ may also assist CO₂ hydrogenation.⁹⁶⁻⁹⁸ Although its exact role remains debated, it may act as either a structural support stabilising Cu⁰ nanoparticles or as a promoter by facilitating CO₂ adsorption and activation at the metal-oxide interface.^{92, 99, 100} When supported on a metal oxide, the contact between Cu and oxygen at the interface forms an electron-depleted Cu species (Cu^{δ+}) which is crucial for binding and activating CO₂.¹⁰¹ Thus, the nature of the Cu surface is an important consideration. Catalyst performance is closely correlated with the accessible Cu surface area, which emphasises the importance of stabilising Cu⁰ and maximising copper nanoparticle dispersion.^{99, 102, 103} Cu nanoparticles are also prone to sintering, leading to poor catalyst lifetimes.¹⁰⁴ Thus, strategies to inhibit sintering, such

as optimising support interactions and controlling particle size, can improve the overall catalyst performance.

Supports and promoters assist and stabilise the active metal.¹⁰⁰ For CZA catalysts, ZnO primarily acts as a support, separating the active Cu⁰ clusters and improving the dispersion.¹⁰² There is also an additional Cu/ZnO synergy as a result of strong metal support interactions (SMSI) between Cu and ZnO.¹⁰⁵ SMSI between the Cu clusters and ZnO support leads to three effects: it alters the electronic properties of the catalyst, the surface geometry of the catalyst is changed (due to the covering of a thin layer of reducible ZnO_x partially covering the active sites), and dual active sites are formed at the Cu-ZnO support.^{102, 106, 107} These structural interactions between the metal and supports not only influence the stability and dispersion of active sites but also play a role in the reaction mechanism. Hydrogen adsorption occurs on the Cu nanoparticles, whilst CO₂ adsorbs to the metal-oxide or metal-Al sites.¹⁰⁰ Following hydrogen adsorption and dissociation on Cu nanoparticles, atomic hydrogen migrates from copper to ZnO where hydrogenation of the active carbon species occurs (spill-over effect).¹⁰⁰ Meanwhile, Al₂O₃ acts as both a support, improving the stability and thermal resistance of the catalyst, and as a modifier to the ZnO phase.⁹⁰

The three most widely accepted pathways for CTM are the formate, RWGS and *trans*-COOH* mechanisms (see Figure 1.8).^{90, 101} Under the RWGS mechanism, CO₂ is converted to CO which is then hydrogenated to methanol via the formyl (HCO*) and formaldehyde (HCHO*) intermediates.^{108, 109} In the formate pathway, CO₂ binds via the C atom and reacts with an H atom from the dissociation of H₂ over Cu⁰ sites to produce the formate intermediate (HCOO*). Both the RWGS and formate pathways share formaldehyde as an intermediate product however in the case of the formate pathway,

adsorbed CO_2 is thought to interact with surface hydroxyl species on ZnO to form a bicarbonate species which is further hydrogenated to form formaldehyde.^{75, 110} Formaldehyde is then hydrogenated to methoxy (H_2COH^*) and finally to methanol. Lastly, the *trans*- COOH^* mechanism has been proposed for CO_2 hydrogenation on Cu(111) surfaces, in which oxygen in CO_2 binds to hydrogen, forming a hydrocarboxyl species (COOH^*) which subsequently undergoes stepwise hydrogenation to produce methanol.¹¹¹

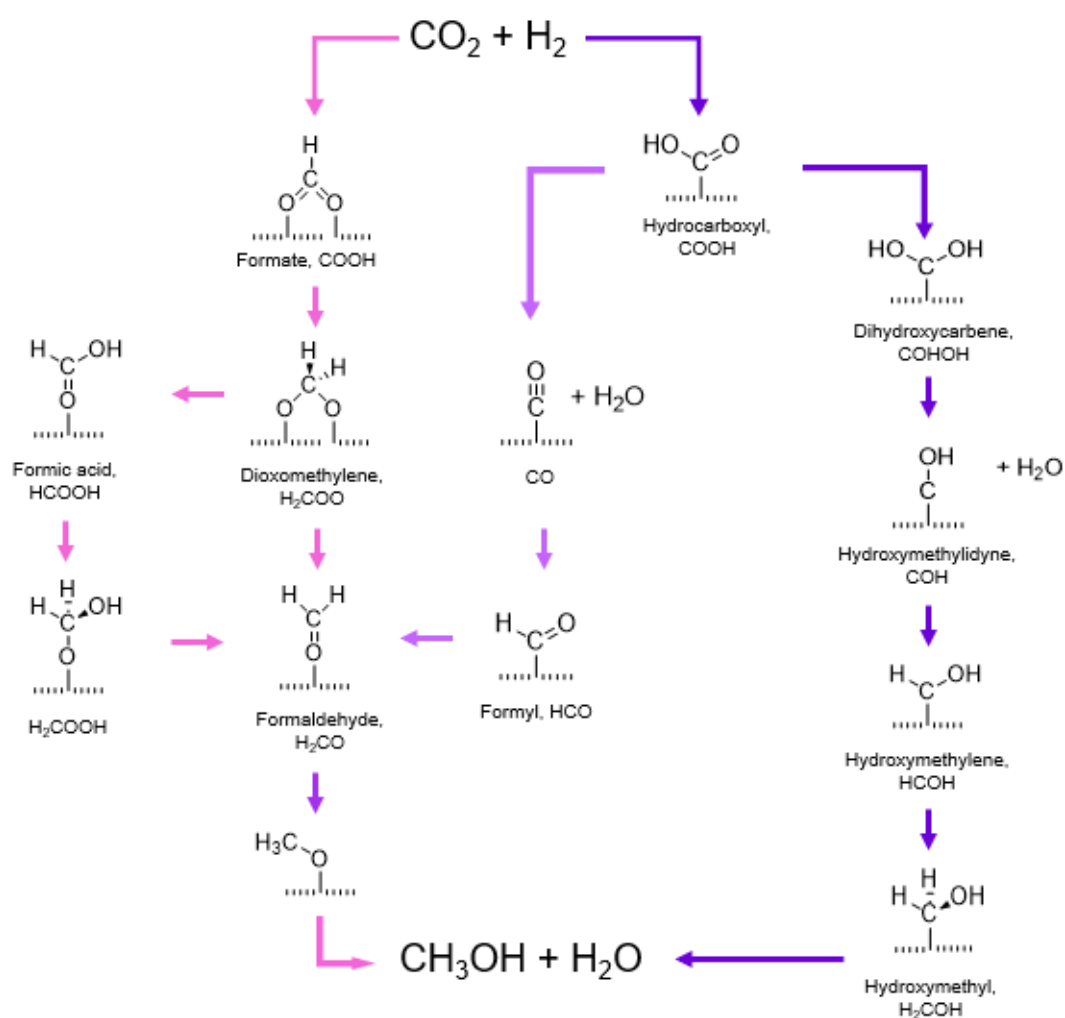


Figure 1.8: Key intermediates in the formate, RWGS and *trans*- COOH^* pathway for CO_2 hydrogenation to methanol.^{90, 101}

From a kinetics perspective, the formation of HCOO and dioxomethylene (H_2COO) intermediates is considered to be rate-limiting in the formate pathway, whereas in the RWGS pathway, the hydrogenation of CO and HCO is rate-limiting. Hence, an ideal CZA catalyst would stabilise the H_2COO species easily whilst binding CO moderately (sufficient to prevent CO desorption but weak enough to prevent CO poisoning) so that both pathways can be facilitated.⁹⁰

In terms of catalyst optimisation, other metal promoters (e.g. Zr, Ga or noble metals like Pt/Pd/Rh/Au,) have also been studied to improve the basicity/reducibility of the catalyst, and have been shown to increase the activity of the CZA catalysts.^{90, 112-114} For instance Zr is a popular promoter for Cu-based catalysts.^{95, 115, 116} Zr enhances the activity of the catalysts by changing the electronic and structural features of the active site. Zr is known to improve Cu nanoparticle dispersion (leading to increased interactions with the metal oxide support), improves the thermal stability of the catalyst (by preventing Cu sintering at high temperatures), and enhances CO_2 activation (by providing basic sites).¹¹⁷⁻¹¹⁹ Cu nanoparticles supported by ZrO_2 also showed good CuO dispersion and oxygen vacancies on the metal oxide support that can stabilise the formate intermediate species.¹²⁰

CTM catalysts are conventionally prepared following calcination and reduction of hydroxycarbonate precursors (which are themselves usually synthesised by coprecipitation).¹²¹ Calcination of the hydroxycarbonate precursors form CuO, ZnO and Al_2O_3 species; reduction under H_2 then generates the active Cu^0 (and Cu^+) nanoparticles.^{90, 110} The activity of CTM catalysts is structure sensitive and since the preparation of CTM catalysts (including the method for synthesising the catalyst precursors) impacts the structure, the method(s) for catalyst generation must be chosen carefully to maximise Cu surface area and introduce greater Cu/ZnO interactions.⁹⁰ The

ratio of Cu/ZnO/Al₂O₃ must also be finely controlled; for instance, the interface between Cu/ZnO is considered to be necessary for the hydrogenation of the active formate species (HCOO*), however at higher Zn content HCOO* coverage on the catalyst surface is too high and leads to catalyst poisoning.^{99, 122, 123} Research in this area has also focused on exploring promoters to improve the stability of the catalyst towards water resistance.^{112, 124} Al in the CZA catalyst is known to be hydrophilic, adsorbing water generated from the RWGS reaction and significantly deactivating the catalyst.¹¹² Zr as a promoter is not only more hydrophobic than Al, but also increases the basicity of the catalyst and is known to improve the stability of Cu⁺ species in reducing environments.^{90, 112, 125}

1.4.5: The methanol-to-DME (MTD) reaction

Industrially, DME is synthesised from syngas (direct route) or derived from natural gas/coal/biomass sources.¹²⁶ In addition to its value as a cleaner fuel alternative and platform chemical, DME is also the initial product prior to C–C coupling in the formation of hydrocarbons, thus in the context of pursuing CO₂ to C₂₊ chemicals, the thermocatalytic conversion of CO₂ conversion towards DME is of particular interest.^{127, 128} In the direct route (from syngas), methanol is formed and immediately dehydrated to DME in a single reactor, which shifts the methanol synthesis equilibrium forward. DME can also be made from the dehydration of methanol (reaction (1.5)) in the presence of an acid catalyst (indirect route). The reaction is exothermic and is therefore favoured at low temperatures.¹²⁹ In the indirect route, the thermodynamic limitations can be overcome by the removal of water which can drive the reaction towards higher DME yields.¹³⁰



Methanol dehydration to DME is an acid-catalysed reaction that typically requires an acidic catalyst such as $\gamma\text{-Al}_2\text{O}_3$,^{88, 131-133} zeolites,^{127, 134-137} silica-alumina,^{138, 139} mesoporous silicates,¹⁴⁰ or heteropoly acids.¹⁴¹ An ideal catalyst for the MTD reaction should have finely tuned acidity—strong enough to activate methanol effectively, but not so strong as to promote side reactions such as excessive hydrocarbon formation or coke deposition—and exhibit high hydrothermal stability to avoid deactivation from water produced during the reaction.¹²⁹

Aluminium oxide (alumina) is a commonly investigated catalyst for the MTD reaction.¹³⁵ Among the various forms of alumina, $\gamma\text{-Al}_2\text{O}_3$ has attracted significant attention as a solid acid catalyst due to its high surface area, thermal stability and surface acidity.^{131, 132} However, a significant drawback of alumina is its hydrophilic nature, making it more susceptible to deactivation.⁸⁸ To overcome this issue, various strategies have been explored to modify alumina.¹³² As an alternative, zeolites are another well-studied class of solid acid catalysts that are often employed for MTD conversion due to their well-defined porous structures, high acidity and resistance to water.^{135, 142}

Zeolites (general formula: $\text{M}_{x/z}[\text{Al}_x\text{Si}_{1-x}\text{O}_2] \cdot q\text{H}_2\text{O}$ where M is the charge balance counter cation (e.g. H^+ , Na^+ , NH_4^+) are microporous aluminosilicates with uniform pore diameters of molecular dimensions.^{143, 144} They are highly porous structures with high surface areas and are size and shape selective for guest molecules.¹⁴⁵ The primary structural unit of all zeolites is corner-sharing AlO_4^{5-} and SiO_4^{4-} tetrahedra which join together to form more complex secondary building blocks (see Figure 1.9). As per Lowenstein's rule, there are no Al–O–Al linkages, only Si–O–Si or Si–O–Al, and as such

the maximum value of x is 0.5.¹⁴³⁻¹⁴⁵ The tetrahedra connect in such a way that cages and channels are formed with pore openings that can range from 6 to 20 membered-rings (MR).¹⁴⁴ The channels can extend along the 1-, 2- or 3-dimensions and allow for the diffusion of molecules through the structure. Zeolites have a variety of framework structures depending on the connections of the tetrahedra; the arrangement of the pores is therefore unique to the type of zeolite and can affect its suitability for different applications.¹⁴⁴ Some examples of commonly used zeolites used in industrial processes include chabazite (CHA), aluminosilicate beta zeolites (BEA), Mobil-five (MFI), mordenite (MOR), faujasite (FAU), and ferrierite (FER) which are summarised in Table 1.1.¹⁴⁵⁻¹⁴⁷

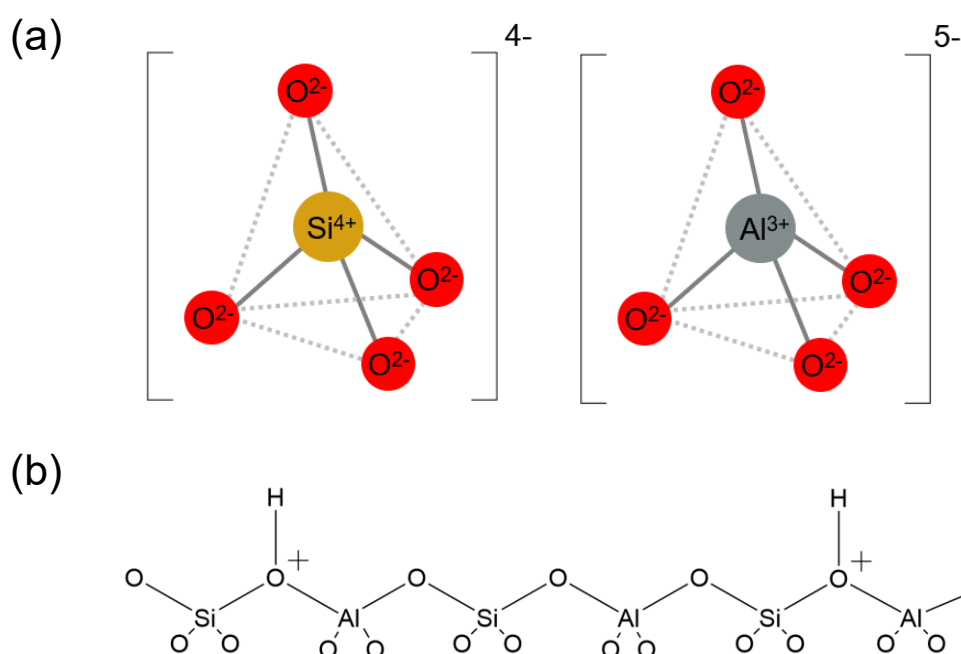
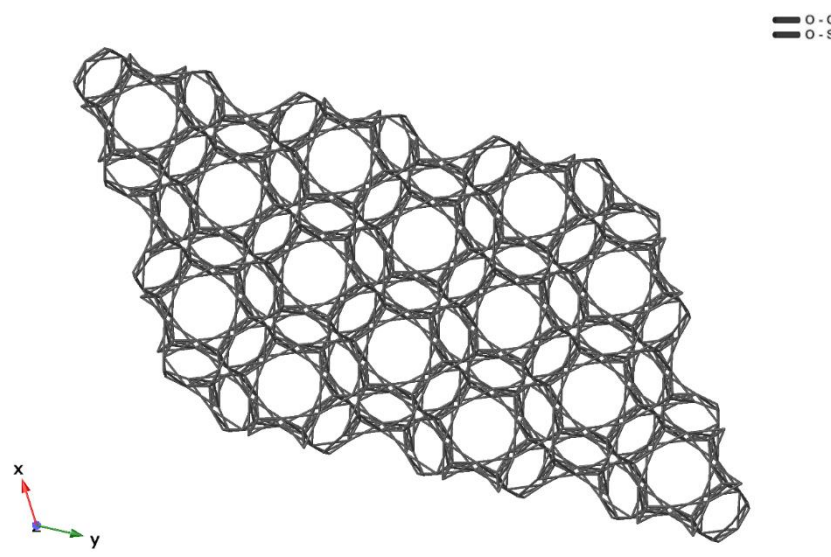
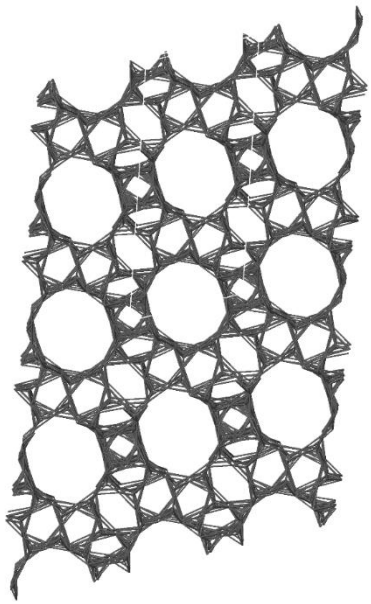
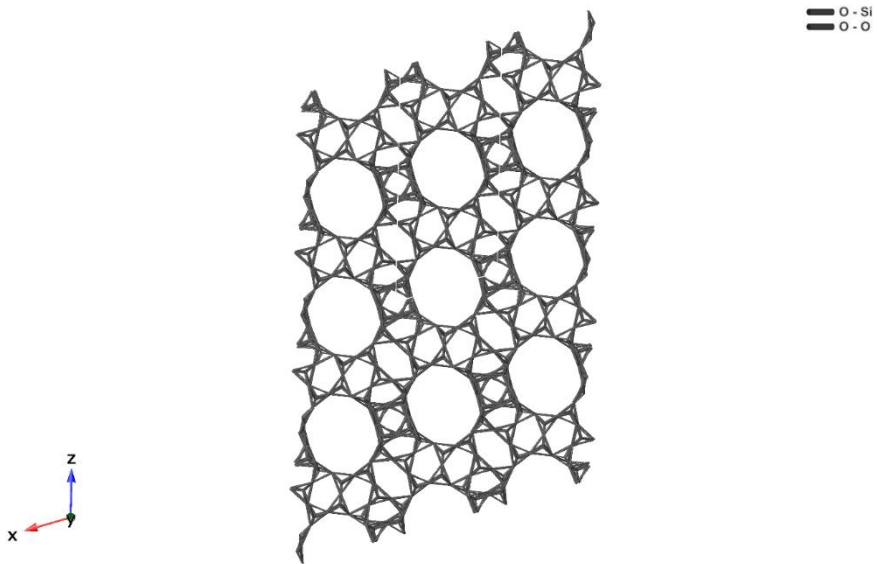


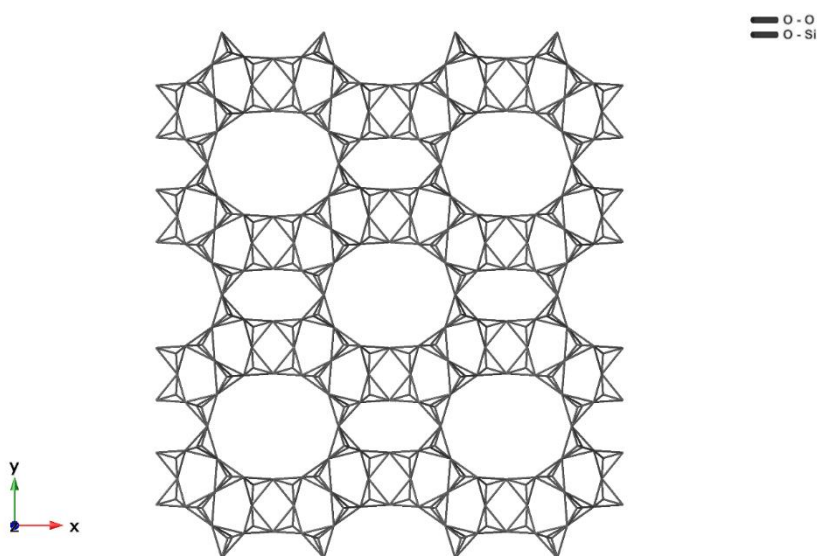
Figure 1.9: (a) Primary and (b) framework linkages of zeolites. (a) depicts the tetrahedral SiO_4^{4-} and AlO_4^{5-} moieties whilst (b) highlights the Si–O and Al–O linkages and Brønsted acid sites in a zeolite.

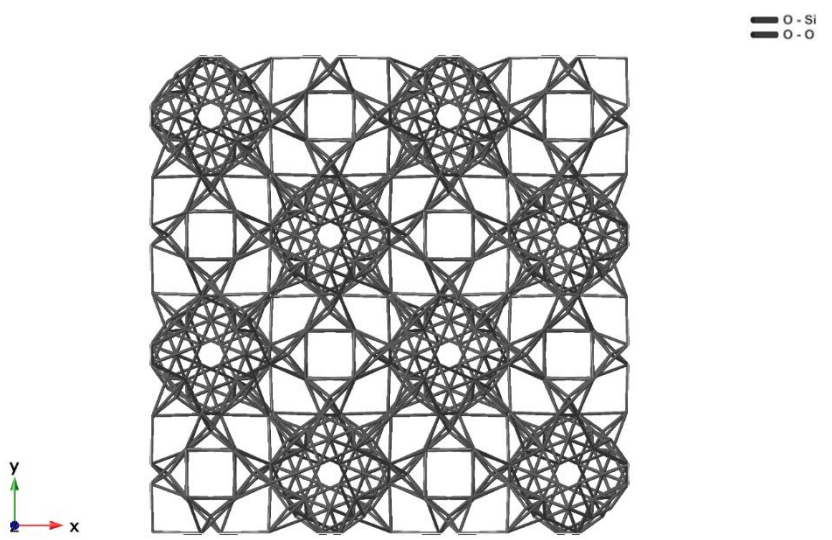
Table 1.1: Zeolite framework types. Framework topology represented with the program CrystalMaker® from the CIF provided by the International Zeolite Association (IZA).

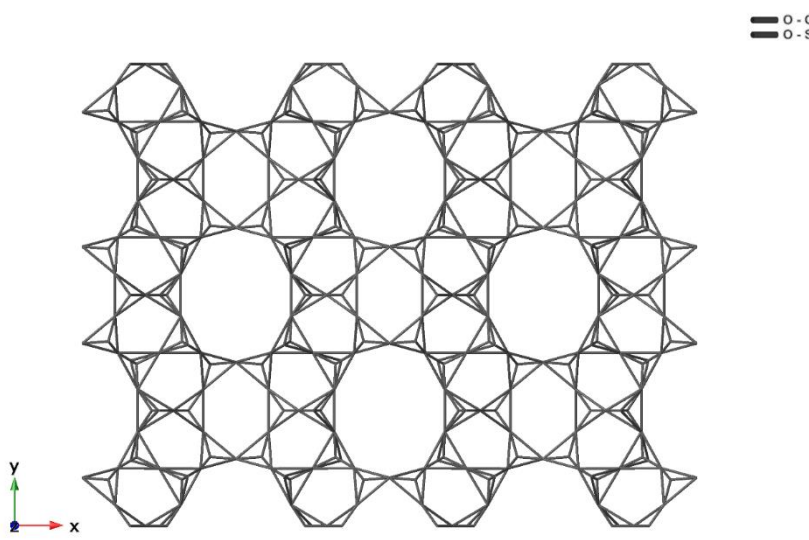
Framework type	Window size	Typical material	Framework images
CHA	$3.8 \times 3.8 \text{ \AA}$ (8-ring)	Chabazite, SSZ-13, SAPO-34	

Framework type	Window size	Typical material	Framework images
BEA	$5.6 \times 5.6 \text{ \AA}$ (12-ring); $6.6 \times 6.7 \text{ \AA}$ (12-ring)	Beta	

Framework type	Window size	Typical material	Framework images
MFI	$5.1 \times 5.5 \text{ \AA}$ (10-ring); $5.3 \times 5.6 \text{ \AA}$ (10-ring)	ZSM-5, silicalite-1, TS-1	

Framework type	Window size	Typical material	Framework images
MOR	$6.5 \times 7.0 \text{ \AA}$ (12-ring); $2.6 \times 5.7 \text{ \AA}$ (8-ring)	Mordenite	

Framework type	Window size	Typical material	Framework images
FAU	$7.4 \times 7.4 \text{ \AA}$ (12-ring)	Faujasite, X, Y, US- Y	

Framework type	Window size	Typical material	Framework images
FER	$4.2 \times 5.4 \text{ \AA}$ (10-ring); $3.5 \times 4.8 \text{ \AA}$ (8-ring)	Ferrierite, ZSM-35	

The molecular dimensions (0.3 – 1.5 nm) of the micropores in zeolites allow for shape selective catalysis.^{145, 148, 149} At the same time, the microporosity of zeolites often causes diffusion limitations of molecules passing through the aluminosilicate network, leading to severe coking and catalyst deactivation.^{150, 151} To overcome this, mesopores (2 – 50 nm) have been introduced into the zeolite to provide better access to the micropores, enhancing the rate of diffusion through the network and ultimately improving the catalytic performance.^{148, 152-154} Desilication, whereby framework silicon is extracted under alkaline conditions, is a common method for generating hierarchical micro- and mesoporous zeolites.^{148, 153, 154} Zeolite desilication should be carefully controlled to avoid excessive framework degradation or dealumination.^{155, 156} MFI zeolites are typically used in zeolite desilication studies and have shown improved catalytic performances post alkaline treatment.^{153, 157}

A wide range of zeolites have been used as solid acid catalysts for the MTD reaction, most commonly in their protonated forms, such as Zeolite Socony Mobil no. 5 (H-ZSM-5),¹⁵⁸⁻¹⁶⁰ H-Y,¹⁶¹⁻¹⁶³ H-MOR,¹⁶⁴⁻¹⁶⁶ H-FER.¹⁶⁷⁻¹⁶⁹ Among them, ZSM-5 of the MFI structural type is one of the most studied acid catalysts for methanol dehydration as it possesses a large number of Brønsted acid sites and is also more resistant to poisoning by water.¹⁷⁰⁻¹⁷² ZSM-5 consists of chains of ten 5-membered ring (pentasil) subunits linked to form sheets which form a 3D framework.¹⁷³ This framework has two perpendicular channel systems, with one running straight and the other progressing in a sinusoidal fashion.¹⁷³ Depending on the reaction conditions, methanol dehydration over ZSM-5 can proceed via an associative or dissociative mechanism (Figure 1.10).¹²⁹ In the associative pathway, two methanol molecules co-adsorb onto neighbouring Brønsted acid sites, where they undergo a concerted reaction to form DME and water. In the dissociative

pathway, the first methanol molecule adsorbs to the catalyst surface, where it is protonated and subsequently loses water to form a surface-bound methoxy species.¹²⁹ The second methanol molecule then acts as a nucleophile attacking the methoxy group, resulting in the formation of DME and the regeneration of the acid site.¹²⁶

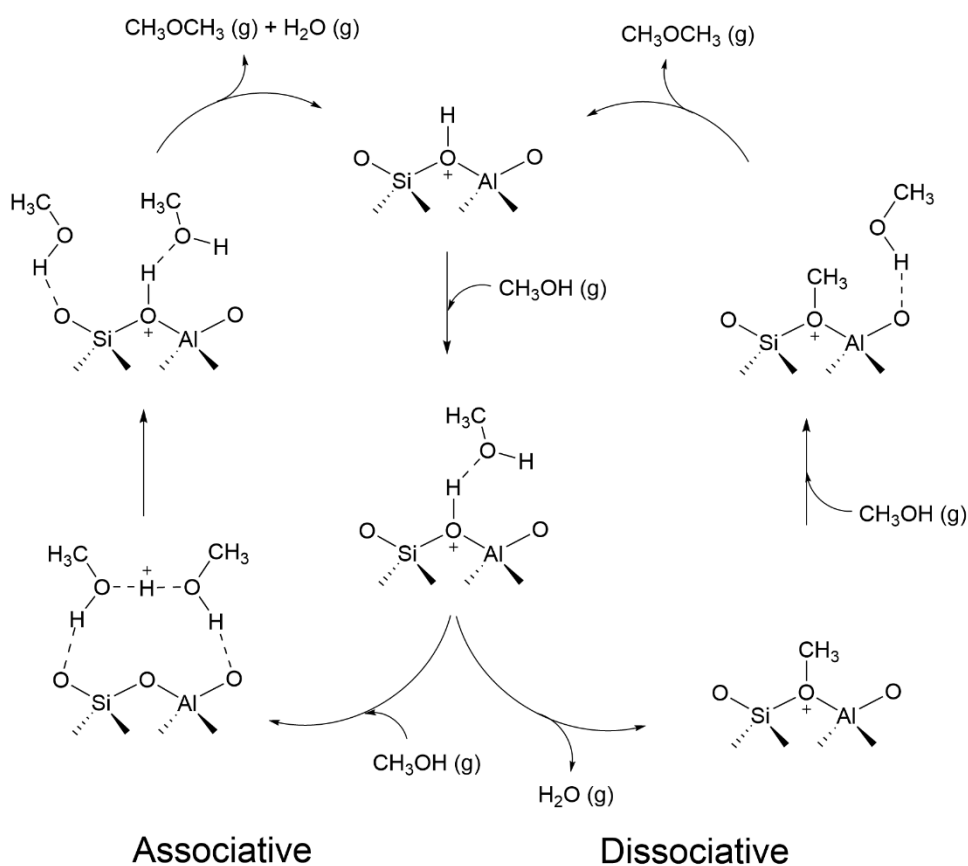


Figure 1.10: Associative and dissociative reaction pathways for the conversion of methanol to DME over H-ZSM-5.

In line with the increasing demands for DME, there has been growing research interest in developing bifunctional catalysts that couple CTM with MTD catalysts, designed to operate in a single-step (see Figure 1.11). The following sections describe the thermodynamic challenges associated with direct CTD conversion.

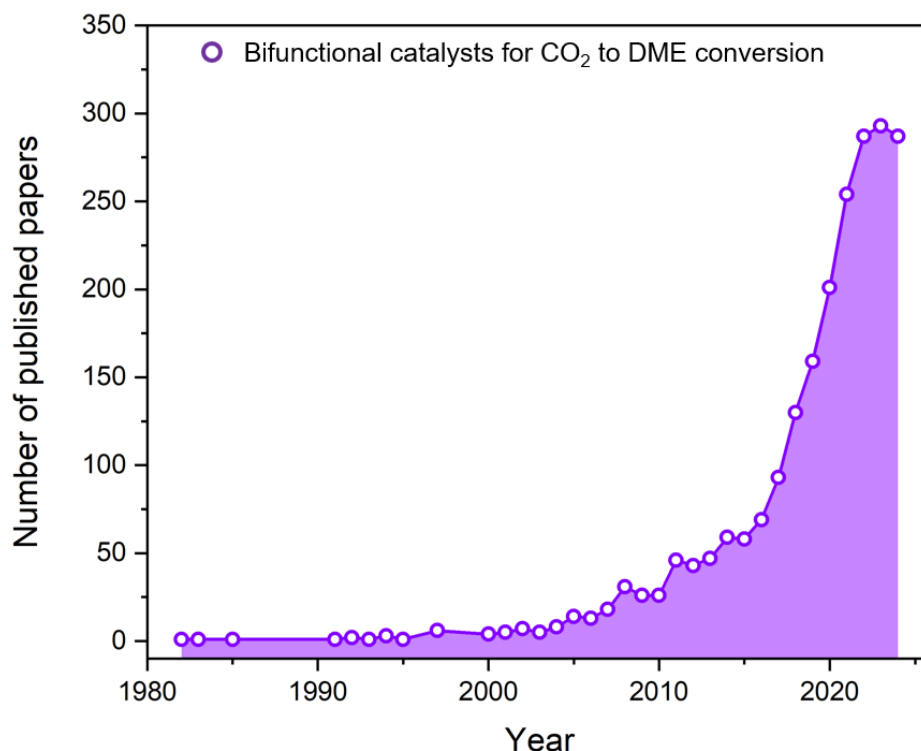


Figure 1.11: Number of published papers related to CO₂ to DME conversion using bifunctional catalysts indexed by Scopus on July 21, 2025.

1.4.5: The CO₂-to-DME (CTD) reaction

From a thermodynamic perspective, designing a bifunctional catalyst employing “conventionally-used” components for the direct conversion of CO₂ to C₂₊ products (whilst achieving high conversion and selectivity) is challenging. The optimum temperature for CO₂ hydrogenation to methanol over CZA catalysts (low temperature range 200 – 300 °C) has poor overlap with the typical conditions used in the MTO conversion over zeolites (between 300 – 500 °C) where higher temperatures are needed to encourage C–C coupling.^{56, 57} In comparison, methanol dehydration to DME can be performed at lower temperatures and has better overlap with the conditions needed to facilitate the CTM reaction.

Besides catalyst design, the thermodynamics of the overall reaction is an important consideration; CO₂ conversion (X_{CO_2}) and the selectivity of a CTD catalyst towards methanol and DME ($S_{\text{CH}_3\text{OH}}$, S_{DME}) changes depending on several factors including the reaction temperature/pressure, the ratio of H₂/CO₂ in the gas stream, and the rate of reactant gas flow over the catalyst.^{27, 174} Based on Le Chatelier's principle we can anticipate that increasing reaction pressures promote X_{CO_2} for the overall CTD reaction which is reflected in the calculated CO₂ equilibrium conversion ($X_{\text{eq,CO}_2}$).^{126, 175} At high temperatures a larger portion of CO₂ molecules overcome their activation energy barrier, however due to reaction (3) being endothermic, the RWGS is favoured, thus higher CO₂ conversion is traded by increasing selectivity to CO (as shown in Figure 1.12).^{126, 175} This is disadvantageous for CTD catalysts designed for the methanol pathway as CO remains unreacted by the zeolite. It follows that an efficient catalyst for C₂₊ product synthesis under a methanol pathway must not only promote methanol formation, but also dehydration/coupling reactions, as well as be operable under the same conditions. Thus, the reaction conditions must be carefully considered.

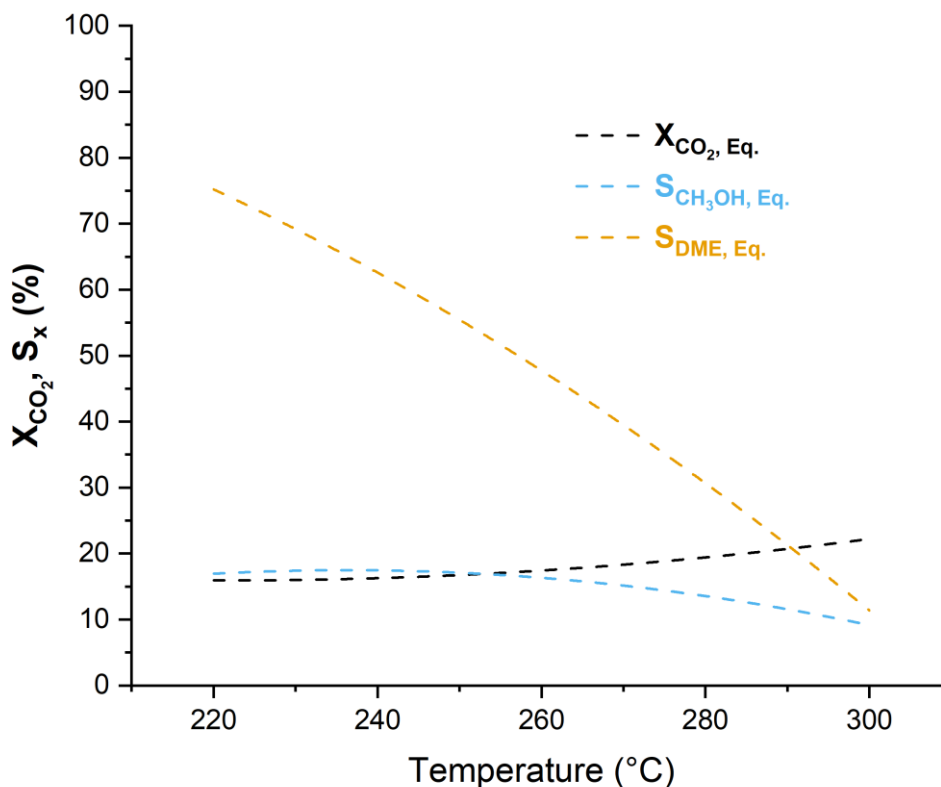


Figure 1.12: Equilibrium CO_2 conversion, methanol and DME selectivity as a function of temperature at $P = 3 \text{ MPa}$, $\text{H}_2/\text{CO}_2 = 3$. Data was taken from reported literature values and recreated.^{171, 175, 176}

Within a single CTD reactor, reactions (2-5) occur simultaneously; hence an efficient bifunctional catalyst should be designed to promote both CTM and MTD processes whilst also minimising the RWGS reaction. Direct CTD has been performed on a variety of hybrid catalysts and contain both metallic and acidic functionalities which are responsible for the CTM conversion and methanol dehydration steps respectively.¹⁷⁷⁻¹⁸⁴ The type of metallic moiety used for the CTM step is chosen based on the same considerations described in section 1.4.2. An acid catalyst is required for the MTD step where the dehydration of CH_3OH occurs on either Brønsted acid sites or Lewis acid-base sites; common acid catalysts include aluminas (e.g. Al_2O_3), metal oxides and H-form zeolites.^{88, 126} For a catalyst with dual functionalities, it is not only important that each phase is optimised for their specific reaction, but that the interactions that might occur

between the phases is beneficial to the overall CTD process. For instance, due to the hydrophilic nature of Al_2O_3 , it is not the most appropriate catalyst to use in tandem with the CTM catalyst; water generated from the RWGS reaction, which is an inevitable occurrence during the CTM reaction, worsens the performance of the Al_2O_3 catalyst and thus the efficiency of the combined CTD catalyst is poorer.^{170, 184, 185} Zeolites, however, exhibit better tolerance to the adsorption of water in comparison to Al_2O_3 -based catalysts and are therefore more appropriate to be used in tandem with a CTM catalyst.¹⁷⁰

Previous research in layered double hydroxide (LDH)-based catalysis has shown the efficacy of a CTM catalyst derived from a CuZnAl-LDH precursor.¹⁸⁶

1.5: Layered double hydroxides

1.5.1: Structural features

Layered double hydroxides (LDHs) are a class of synthetic anionic clays that follow a brucite ($\text{Mg}(\text{OH})_2$)-like structure.¹⁸⁷ Brucite has a CdI_2 layered crystal structure of Mg^{2+} ions octahedrally coordinated to 6 hydroxide ions, where the metal hydroxide layers are stacked on top of each other and held together by hydrogen bonding (Figure 1.13).¹⁸⁸ The partial substitution of Mg^{2+} with Al^{3+} in the metal hydroxy layers leads to the formation of a magnesium-aluminium hydroxycarbonate known as hydrotalcite ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$), which is one of the naturally occurring examples of LDHs. As a result, LDHs are often described as synthetic hydrotalcite-like (HTL) compounds, consisting of two-dimensional (2D), metal hydroxide layers that form a brucite-like layer structure.^{187, 189}

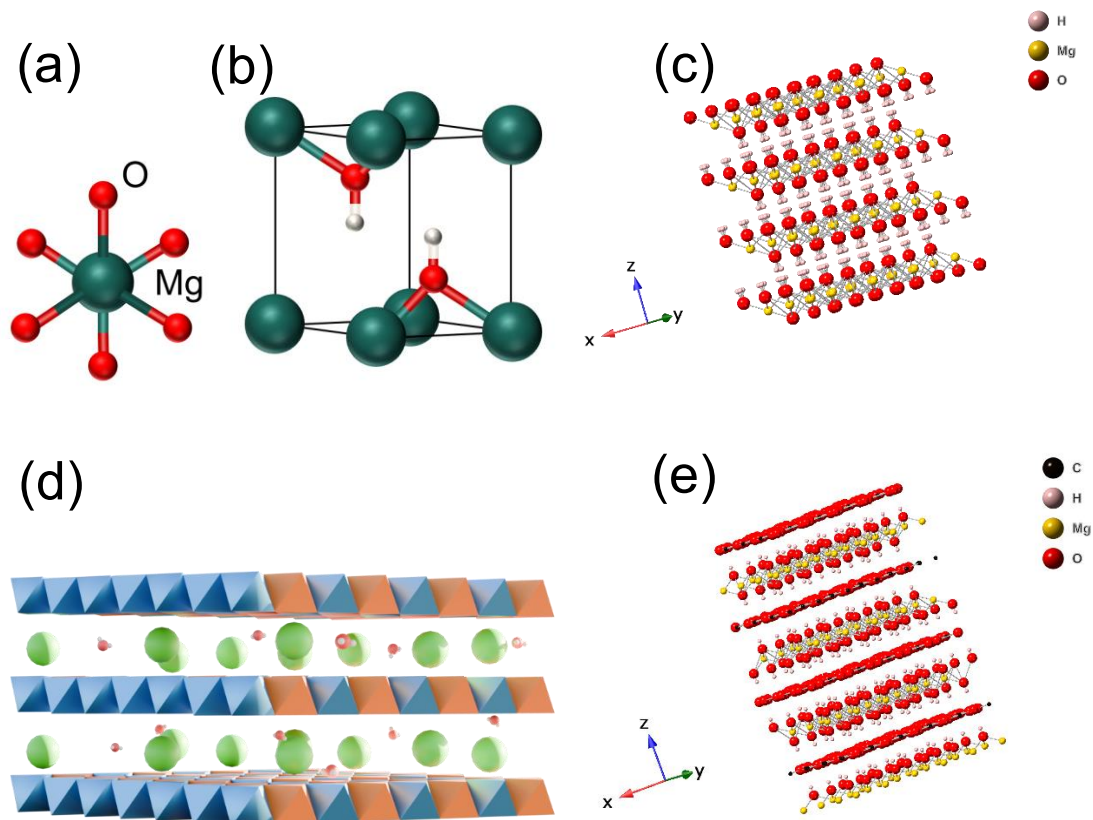


Figure 1.13: Illustrations of (a) stick and ball models of the Mg-O octahedra in brucite, (b) CdI₂ structure of brucite, (c) the brucite structure, (d) representation of the structure of a hydrotalcite and (e) the Mg₆Al₂CO₃(OH)₁₆·4(H₂O) hydrotalcite structure simulated in CrystalMaker.^{190, 191}

The most common form of LDHs may be expressed by the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]A^{n-}_{x/n} \cdot mH_2O$ where M^{2+}/M^{3+} are divalent and trivalent metal cations, and A^{n-} are interlayer anions.^{187, 189, 192} The M^{2+}/M^{3+} metals are coordinated to 6 hydroxide, ions forming octahedral units (see Figure 1.13a).¹⁸⁷ These units are edge-sharing to form an infinite 2D layer.¹⁸⁷ Pure LDH phases may be formed when the M^{2+}/M^{3+} ratio is such that $0.2 < x < 0.33$, although larger ranges have been reported.^{187, 193} Ternary, quaternary and quinary LDHs have also been synthesised where multiple metal cations are incorporated.¹⁹⁴⁻¹⁹⁶

The isomorphic substitution of M^{2+} cations (e.g. Mg^{2+} , Fe^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} , or Zn^{2+}) with the M^{3+} cations (e.g. Al^{3+} , Cr^{3+} , Ga^{3+} , In^{3+} , Mn^{3+} or Fe^{3+}) introduces a net positive charge within the metal hydroxide layers of the LDH.¹⁹⁷ This charge imbalance is compensated by the incorporation of charge-balancing anions (A^{n-}) in the interlayer region. These interlayer anions are randomly distributed along the gallery and can include CO_3^{2-} , NO_3^- , SO_4^{2-} , and ClO_3^- among others.¹⁹³ The resulting layered structure is stabilised by a combination of electrostatic interactions between the anions and the positively charged layers, as well as hydrogen bonding.¹⁹⁸ The water of crystallisation occupies the remainder of the interlayer region.¹⁹⁸ A notable feature of LDHs is the anionic exchange capacity of the interlayer region, which allows for the substitution of interlayer anions with a range of species including organic anions (acetate, carboxylates, formates), chromate (CrO_4^{2-}), permanganate (MnO_4^-), metal complexes and pharmaceutical molecules.¹⁹⁹⁻²⁰⁴

The metal hydroxide layers can adopt different stacking arrangements, resulting in a variety of polytypes (i.e. structures that share the same chemical composition but differ in the sequence and orientation of their layers).¹⁹⁸ The polytypes are classified by two features: the number of sheets per unit cell along the *c*-axis (commonly 1, 2, 3, or 6), and the crystallographic symmetry of the unit cell, which is either rhombohedral (R) or hexagonal (H).^{198, 205} Among the most prevalent polytypes are 3R, a three-layer structure with rhombohedral symmetry, and 2H, a two-layer structure with hexagonal symmetry (see Figure 1.14). Some LDHs exhibit a mixture of stacking sequences and possess a combination of both 2H and 3R polytypes.^{198, 205}

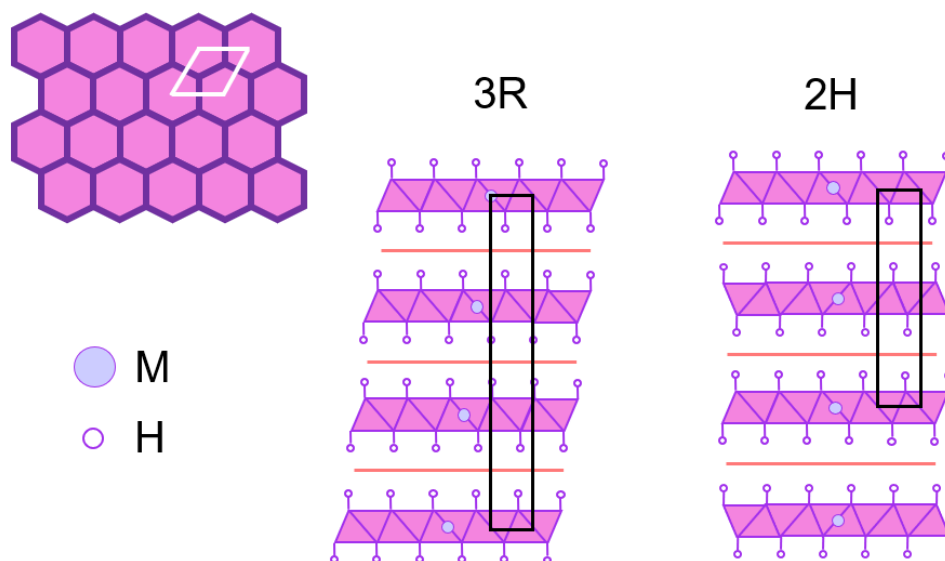


Figure 1.14: Crystal structures of the 3R and 2H polytypes. Image recreated from Zhitova *et. al.*²⁰⁶

Powder X-ray diffraction (PXRD) analysis is one of the most important characterisation techniques for LDH structure determination. The diffraction peaks in a PXRD profile follows Bragg's Law (equation (1.6)) where n denotes the order of diffraction, λ is the wavelength of the X-rays, d is the distance between metal planes and θ is diffraction angle of incidence.^{207, 208} The peak positions in the diffraction pattern provide insight into the unit cell parameters of the crystal structure, while peak broadening may indicate factors such as crystallite size, stacking disorder or structural defects.²⁰⁹ For LDHs, the layered structure gives rise to a set of prominent basal reflection at low 2θ values which are indexed as $(00l)$ planes and correspond to the interlayer spacing.¹⁸⁷

While the position of the Bragg peaks provides information about the crystal structure and symmetry of the contributing phase, the intensity of the pattern reflects the total X-ray scattering from each plane within the crystal structure. This is affected by the type, number and spatial arrangement of atoms within the unit cell. Hence, variations in the intensity, I_{hkl} , of a diffraction peak is related to the chemistry and arrangement of the

atoms in the unit cell. The diffraction intensity equation is summarised in equation (1.7), where $I_{(hkl)\alpha}$ is the intensity of the reflection of hkl in phase α , K_e is the experimental constant, $K_{(hkl)\alpha}$ is the structure factor term, ρ_α is the density of the phase and $\left(\frac{\mu}{\rho}\right)_s$ is the mass absorption coefficient for the sample.²¹⁰

$$n\lambda = 2d\sin\theta \quad (1.6)$$

$$I_{(hkl)\alpha} = \frac{K_e K_{(hkl)\alpha} X_\alpha}{\rho_\alpha \left(\frac{\mu}{\rho}\right)_s} \quad (1.7)$$

Hydrotalcite crystallises in a rhombohedral 3R symmetry, characterised by hexagonal lattice parameters, with a and c calculated using equations (8) and (9) respectively.¹⁸⁷ The (003) reflection in the PXRD pattern is commonly used to estimate the interlayer spacing, as it corresponds to the basal plane repeating unit along the c -axis. By applying Bragg's Law to the 2θ position of the (003) peak, the d_{003} spacing can be calculated (equation (1.8)). This distance represents the thickness of a single layer-repeat unit ($3d_{003}$), which consists of one brucite-like metal hydroxide sheet and its associated interlayer region.¹⁸⁷ This value represents the thickness of one repeating layer unit, comprising one brucite-like metal hydroxide layer and one interlayer spacing. The position of this peak in the PXRD profile can shift depending on the type, size and hydration state of the intercalated anion. For instance, a shift of the (00 l) reflections ((003), (006) etc.) to lower 2θ angles corresponds to a larger interlayer spacing. In contrast, the positions of the (01 l) and (10 l) reflections provide information on the stacking sequence and coherence of the LDH layers.^{187, 198} These reflections are sensitive to stacking faults or turbostratic disorder (a form of structural disorder where the LDH layers are randomly shifted relative to each other, leading to a loss of long-range stacking order along the c -axis whilst maintaining

the integrity of the individual metal hydroxide layers). The (110) reflection, which arises from planes that lie parallel to the basal planes, reflect the arrangement of the metal cations and can be used to determine the average distance between two metal ions in the metal hydroxide layer (equation (1.9)).

$$c = 3d_{003} \quad (1.8)$$

$$a = b = 2d_{110} \quad (1.9)$$

The PXRD profiles can also be used to determine the crystallite dimensions of an LDH.¹⁸⁷ The Scherrer equation (equation 1.10) relates the line broadening of a peak in a diffraction pattern to the coherently diffracting crystallite domain size where: D_{hkl} is the crystallite size perpendicular to the lattice planes being analysed, hkl are the Miller indices of the lattice planes, K is the Scherrer constant, λ is the wavelength of the X-rays, β_{hkl} is the width at half the maximum intensity (FWHM) of the diffraction peak in radians, and θ is the Bragg angle in radians.^{211, 212}

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl}\cos\theta} \quad (1.10)$$

The broadening, symmetry and shape of a diffraction peak is dependent on several instrumental and sample-related effects. For instance, the diffraction peaks may be broader than predicted due to instrumental, grain-size or micro-strain broadening.^{213, 214} Crystallite domain size plays a significant role in this context, as smaller crystallites result in greater peak broadening which are reflected by higher β_{hkl} values. However, for crystallite sizes below 50 nm, instrumental broadening becomes the dominant contributor.²¹³ This is an important consideration when applying the Scherrer equation as it may lead to an overestimation of crystallite domain sizes. In contrast, microstrain and

disorder contribute to diffraction peak broadening which can lead to an underestimation of the domain size. The Scherrer constant (K) is typically 0.9 however, the value may change depending on the morphology of the crystallites, as well as microstrain and defects within them.²¹⁵

1.5.2: LDH preparation and post-synthesis modifications

Several methods exist for preparing LDHs, including co-precipitation, homogeneous urea hydrolysis, sol-gel technique, and reverse micelle microemulsion.²¹⁶ Co-precipitation however, remains the most common method as it is inexpensive, simple, and scalable for industrial applications.²¹⁷ The metal salt solution is prepared in an appropriate solvent (typically water) and the concentrations of metal ions in solution are chosen so the desired M^{2+}/M^{3+} ratio is achieved. It is then added to a basic aqueous solution with the desired interlayer anions whilst the pH is controlled (see Figure 1.15). Controlling the pH ensures that the different metal ions in the metal salt solution precipitate simultaneously.²¹⁸

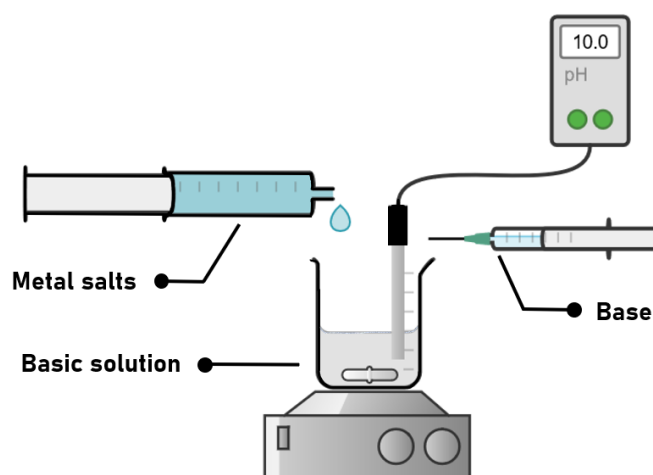


Figure 1.15: Illustration of a common coprecipitation setup for the synthesis of LDHs.

Depending on the nature of the interlayer anion, it may be necessary to conduct the coprecipitation under an inert atmosphere (e.g. N_2). For interlayer anions with low

affinities to the metal hydroxide layer (e.g. Cl^- or NO_3^-), contamination from atmospheric CO_2 dissolving into solution is likely. In contrast, carbonate-intercalated LDHs are easier to synthesise and can be made under air due to the high affinity of CO_3^{2-} and SO_4^{2-} to the metal hydroxide layers.

LDHs synthesised by conventional synthesis methods tend to suffer from “stone-like” aggregation as a consequence of high surface charges and hydrophilicity.²¹⁹⁻²²³ This often results in low surface areas, limiting the performance of the LDH across various applications. LDHs intercalated with either NO_3^- , Cl^- , HCO_3^- , SO_4^{2-} or borate normally commonly exhibit low specific surface areas ranging from 5 – 15 m^2/g .^{219, 224} Carbonate intercalated LDHs can reach relatively higher surface areas (around 110 m^2/g), however the aggregation effect is still observed, limiting their full potential.^{194, 224}

Several techniques have been developed to minimise this effect, including delamination by the aqueous miscible organic solvent treatment (AMOST),^{220, 225, 226} large interlayer anion intercalation,^{227, 228} inhibitor inclusion,²²⁹ and LDH mobilisation onto a supporting material.^{217, 230, 231} For instance, in the AMOST method, the LDHs are washed with solvents such as ethanol, acetone, or methanol after synthesis, disrupting the hydrogen bonding network between the metal hydroxide layers and facilitating delamination (Figure 1.16).^{225, 226, 232} This can result in the formation of ultra-high surface area LDHs with considerably improved performances.^{114, 194, 233, 234}

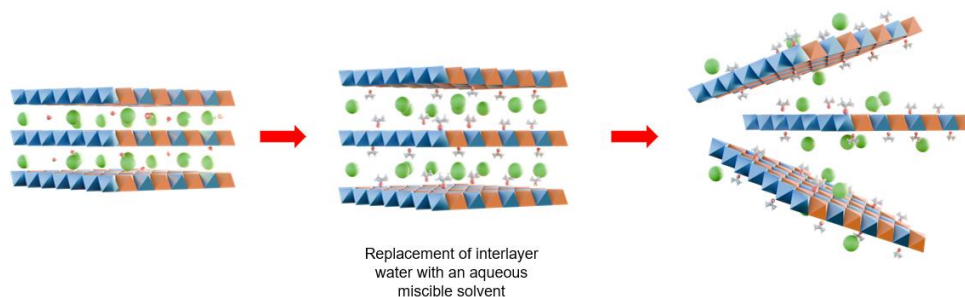


Figure 1.16: Schematic illustrating the post-synthesis treatment of an LDH using the AMOST method.

LDHs are commonly subjected to further treatments post synthesis to tune their structure, composition and/or performance.^{199, 220, 225, 235} For instance, the hydrothermal treatment of LDHs has been known to improve their crystallinity.^{236, 237} Another widely adopted strategy is the calcination of LDHs to form layered double oxides (LDOs), which are mixed metal oxides that possess higher surface areas, enhanced adsorption capacities and greater thermal stabilities compared to their LDH precursors.²³⁸ Due to these properties, LDOs are increasingly used in heterogeneous catalysis, nanoalloy formation, electrode materials and adsorbents.^{114, 235, 239-241} The acid-base properties and thermal behaviour of LDOs are strongly influenced by the parent LDH, which can be tuned by controlling the composition of the LDH precursors.^{242, 243} Calcination typically occurs between 300 – 600 °C, during which water is first removed, followed by the gradual release of hydroxyl groups and interlayer anions, resulting in the collapse of the layered structure.²³⁸ At these temperatures, the metal cations remain octahedrally coordinated to oxides, although some degree of structural disorder is observable in the PXRD profiles as evidenced by broader and less intense diffraction peaks.²⁴⁴ LDOs are also known for their “memory effect”, where the original LDH structure can be reconstructed in the presence of aqueous solutions containing appropriate anions.^{187, 245} However, at temperatures above 600 °C, irreversible formation of spine-type metal oxides can occur.²⁴⁶ The

subsequent reduction of LDOs forms small and thermally stable metal crystallites and can generate SMSI between metal nanoparticles and the supporting metal oxide which enhances the stability of the catalyst.^{187, 197}

1.5.2: Applications of LDHs and their role as catalysts

LDHs have been known for over 150 years and boast a wide range of applications. They have been used as barrier films and sensors,^{247, 248} as well as in water treatment,^{249, 250} drug-delivery,^{251, 252} CO₂ capture,²⁵³⁻²⁵⁵ photochemistry,^{192, 253} electrochemistry,^{60, 61, 256} and thermochemistry.^{82, 216, 257} Due to their highly tuneable morphology, flexible composition (including various metal cations and interlayer species), inexpensive synthesis techniques and low cost of raw materials, LDH-based catalysts are widely used as catalysts.⁸² The versatility of LDH materials can drive catalyst design by tailoring the material to the desired application.

LDHs have attracted significant attention as solid base catalysts due to the high density of surface hydroxyl groups within the metal hydroxide layers.²⁵⁸ In most cases, bulk LDHs undergo post-synthetic treatments to enhance their catalytic performance. For instance, the utilisation of the “memory effect” where the LDH is first calcined to form an LDO and subsequently reconstructed upon exposure to an aqueous environment often results in improved catalytic activity compared to the original bulk LDH material.²⁵⁸⁻²⁶⁰

Recently, the catalytic performance of LDHs has been further enhanced through the development of LDH-based nanocomposites, formed by the integration of LDHs with other materials such as carbon nanotubes,^{261, 262} graphene/graphene oxide,²⁶³⁻²⁶⁵ silica,^{186, 223} and metal oxides.²⁶⁶⁻²⁶⁸ These hierarchical architectures often exhibit synergistic effects arising from improved charge transfer, greater surface accessibility and

multifunctionality, leading to superior catalytic performance.^{223, 269-272} The following section describes the design, synthesis and catalytic application of LDHs-based composites, with a focus on core-shell type morphologies, highlighting their versatility and potential as advanced catalysts.

1.5.3: LDH-based composites and core-shells

Supported LDHs are increasingly utilised in catalysis and constitute a large class of uniquely designed materials. Of the various architectures reported in the literature, the most commonly explored include nanosheet arrays,²⁷³⁻²⁷⁵ needle-like morphologies,²⁷⁶⁻²⁷⁸ as well as yolk-shells and core-shell structures (see Figure 1.17).^{271, 279-284}

In particular, LDH-based catalysts with core-shell type structures, in which two or more functional components are integrated into a single structure.^{82, 186, 208, 284-287} These hierarchical core-shell systems offer several advantages over pure LDH catalysts: (i) LDH platelets grown on supports typically exhibit higher surface areas by minimising platelet stacking and aggregation commonly observed in bulk LDHs; (ii) supported LDHs demonstrated improved resistance to sintering; (iii) the use of catalytically active supports enables the construction of multifunctional catalysts, with each component contributing to the reactivity of the overall material; and (iv) synergistic interactions between the LDH and secondary material(s) have been reported and are shown to enhance the performance of the composite catalyst.^{82, 186, 286}

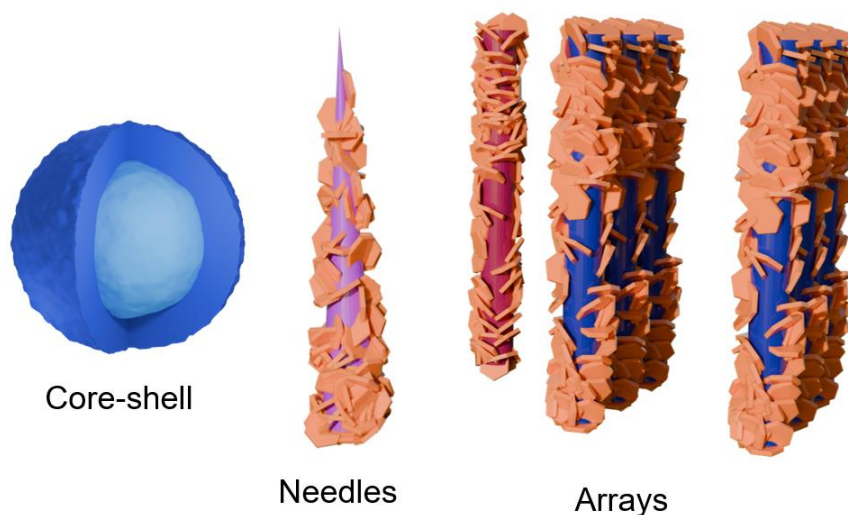


Figure 1.17: Representative structures of some supported LDH-based composites commonly used in catalysis.

A range of different support materials has been used to improve the performance of LDH-based catalysts. These include metal oxide supports (e.g. Al_2O_3 , SiO_2 , TiO_2 , Fe_3O_4),^{267, 272, 288-290} organic supports (polymers, graphene oxide, carbon nanotubes),^{270, 291-294} as well as other more complex composite-type supports (metal organic frameworks, zeolites).^{259, 295, 296} The supports play an important role in promoting the dispersion, stability and accessibility of the active site in the LDH phase, often leading to enhanced catalytic functionality.^{82, 186, 217, 297, 298}

There are several *in-situ* techniques to synthesise LDH core-shell composites including homogenous/non-homogenous coprecipitation,²⁹⁹⁻³⁰¹ hydrothermal/solvothermal,³⁰²⁻³⁰⁴ the sol-gel method,^{305, 306} and metal-organic framework (MOF) etching.^{307, 308} An *in-situ* co-precipitation method developed by Chen *et al.* offers a straightforward and effective approach for the synthesis of LDH-based core-shell structures.^{186, 223, 230, 309, 310} The method allows for the controlled growth of LDHs in the presence of a core material, the coverage of which is dependent on conditions like pH, temperature, stirring speed, drop

rate and ageing time.^{217, 230, 309, 310} Consideration should be made for the compatibility of the LDH and core phase; for instance, zeolites have negative surface charges when dispersed in an aqueous solution and can electrostatically attract positively charged LDH nuclei.²³⁰ Surface aluminium of the zeolites may also act as nucleation point for the growth of Al containing LDHs.³¹⁰

1.5.4: LDHs/LDH-based composites for CO₂ conversion

In recent years, an increasing number of LDH-based catalysts have been designed for either thermocatalytic,¹⁸⁶ electrocatalytic,³¹¹ or photocatalytic CO₂ conversion (Figure 1.18).³¹² Their versatility and high CO₂ adsorption capacity make them attractive as precursor materials.^{313, 314}

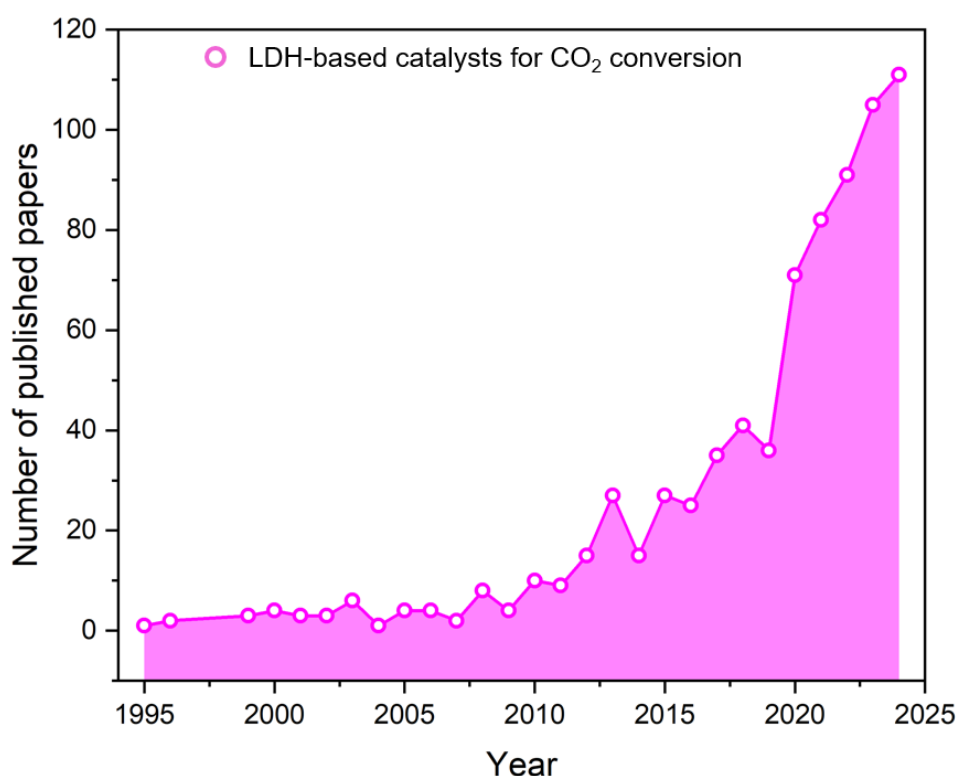


Figure 1.18: Number of published papers related to LDH-based catalyst for CO₂ conversion indexed by Scopus on July 23, 2025.

Numerous studies on Cu-containing catalysts derived from HTL precursors have shown that the HTL phase is beneficial and leads to catalysts containing highly dispersed Cu on metal oxide supports (e.g. ZnO and Al₂O₃).³¹⁵⁻³¹⁸ The high catalytic activity of the HTL-derived catalysts stems from the enhanced physiochemical properties of the mixed metal oxide obtained following the thermal decomposition of HTL precursors. These ex-HTL catalysts are homogeneous with good metal dispersions, small Cu nanoparticle sizes have high resistance to sintering, large surface areas and strong basic properties.^{114, 186, 319-321} For example, Li *et al.* found that the CuZnGa catalyst exhibited high Cu dispersion and large Cu surface areas as determined by N₂O chemisorption during CO₂ hydrogenation to methanol.¹¹⁴ The Cu content and the structure of the precursor LDHs impact the properties and performance of the resulting catalyst.^{114, 320, 322, 323} For instance, Mureddu *et al.* demonstrated that the incorporation of Zr and Ce promoters into CuZnAl LDH precursors altered the acid-base properties and surface hydrophobicity of the activated catalysts, leading to an improvement in the formation of DME during CO₂ hydrogenation.³²²

LDHs have also been incorporated with supports like silica,^{182, 186, 223, 324} MOFs,³²⁵⁻³²⁸ and zeolites for CO₂ conversion.^{322, 329, 330} For example, Zhao *et al.* synthesised Cu/Zn/Al nanocatalysts from LDH/MOF composites for CO₂ hydrogenation to methanol Zhao cited the enhanced Cu dispersion and synergism for the high methanol selectivity (88%).³²⁵ Recently, a silica supported ex-LDH catalyst demonstrated improved catalytic performance compared to its unsupported counterpart.¹⁸⁶ The ES757@Cu_{1.3}ZnAl core-shell catalyst exhibited high methanol productivity, nearly twice that of a commercial Cu/ZnO/Al₂O₃ catalyst and greater than the physical mixture of the CZA and ES757 phases.¹⁸⁶ It was suggested that the directed growth of the LDH on the surface of the

silica core minimised *ab*-face stacking, leading to the improved dispersion of Cu nanoparticles on the surface of the silica and increased interactions with ZnO.¹⁸⁶

1.6: Thesis overview

The aim of this project was to develop novel core-shell composites as bifunctional catalysts for the conversion of CO₂ to DME via the methanol pathway. The work presented in this thesis builds upon previous studies involving CZA-type catalysts derived from LDH precursors, with particular reference to the work by Lyu *et al.*, who demonstrated enhanced catalytic performance using silica-supported CuZnAl core-shell structures for CO₂ hydrogenation to methanol. In Chapter 2, a new core-shell is introduced in which the inert silica core is replaced with ZSM-5 zeolite. ZSM-5 was chosen due to its optimal acid strength (moderate Brønsted acidity which minimises side reactions like hydrocarbon formation), hydrothermal stability, and established performance as a benchmark acid component for DME synthesis studies. This chapter presents the synthesis and characterisation of a hybrid CZA/ZSM-5 core-shell catalyst (ZSM5@Cu_{1.3}ZnAl), designed to function as a bifunctional catalyst that couples the CTM and CTD reactions. The catalytic performance of this material for CO₂ hydrogenation is discussed, alongside a comprehensive analysis of its structural and surface properties. The latter part of the chapter focuses on optimising reaction conditions to enhance DME productivity and evaluate the potential of the core-shell as a high-throughput bifunctional CTD catalyst. Chapter 3 explores strategies to optimise the ZSM5@Cu_{1.3}ZnAl catalyst. Conflicting results in the literature and in previous work by the group suggests that the incorporation of sodium could play an important role in the

performance of the catalyst, where some studies have indicated an improvement in the activity of the CZA and ZSM-5 phases. Thus, Chapter 3 investigates the role of sodium as a promoter for catalytic performance of CZA and the core-shell catalyst as well as its effect on LDH platelet formation. Additionally, the influence of varying the ZSM-5:LDH weight ratio in the core-shell structure is studied to understand how the relative amount of each phase affects the overall catalyst activity in the CTD process. Lastly, Chapter 4 investigates Zr as a promoter for the CZA catalyst. Zr was chosen due to its well-known ability to strengthen metal-support interactions and stabilise Cu nanoparticles. In addition, ZrO₂ has been shown to facilitate CO₂ activation, while its hydrothermal stability makes it suitable for the conditions of DME synthesis. A series of Zr-incorporated CuZnAl-LDHs were synthesised, characterised and evaluated for their CTM performance. The top performing Zr-incorporated LDH was then integrated into the core-shell structure with ZSM-5, and its catalytic behaviour in the direct CTD conversion is evaluated. Collectively, the chapters in this thesis detail the rational design, synthesis and performance of advanced bifunctional core-shell catalysts for CO₂ conversion.

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2

Synthesis, characterisation and catalytic testing of ZSM5/Cu_{1.3}ZnAl catalysts for direct CO₂ to DME conversion

2.1: Introduction

2.1.1: Overview

The following chapter presents the preparation, characterisation and subsequent catalytic testing of hybrid ZSM5/Cu_{1.3}ZnAl catalysts for the direct hydrogenation of CO₂ to dimethyl ether (DME). The introduction provides an overview of CO₂-to-DME (CTD) catalysts reported in the literature, focusing specifically on hybrid catalysts that combine Cu-based, CO₂ hydrogenation catalysts with zeolites.

The main body of the chapter investigates a novel core-shell bifunctional catalyst for direct CTD conversion, which was comprised of a Cu/ZnO/Al₂O₃ (CZA) CO₂-to-

methanol (CTM) shell and a ZSM-5 methanol-to-DME (MTD) core. Previous research in the O'Hare group led to the development of a highly active CZA catalyst for CTM conversion, derived from a $\text{Cu}_{1.3}\text{ZnAl}$ layered double hydroxide (LDH) precursor. This catalyst was adopted in the present study as the CTM phase. A range of analytical techniques were used to characterise the physiochemical properties of the core-shell precursor and activated catalyst ($\text{ZSM5@Cu}_{1.3}\text{ZnAl}$). The activity of the $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ core-shell was then evaluated for the conversion of $\text{CO}_2/3 \text{ H}_2$ to DME over a range of temperatures in a pressurised fixed-bed reactor.

Subsequent chapters focus on optimising both the catalyst activation method and the hydrogenation reaction conditions. These sections explore the influence of the calcination environment and the impact of an increased weight hourly space velocity (WHSV) on the catalytic performance of the core-shell.

2.1.2 CTD catalyst design

DME is a valuable chemical with diverse applications, including its use as a clean-burning fuel alternative, an aerosol propellant, and a platform molecule for producing higher hydrocarbons and oxygenates.¹⁻⁶ In the context of a circular economy, producing DME from captured CO_2 offers a promising route to reducing the chemical industry's reliance on fossil-derived feedstocks.

The formation of DME from CO_2 is a two-step process, involving the initial CO_2 hydrogenation to methanol, followed by the conversion of methanol to DME.⁷ Although the reactions can be performed in two separate chambers, a “one-pot” process where both the CTM and MTD reactions occur simultaneously can overcome the thermodynamic limitations of the MTD reaction (see Chapter 1.4.5 for more details).^{1, 7} Direct CTD

conversion requires a bifunctional catalyst that can facilitate the initial CO₂ hydrogenation (to methanol) and subsequent methanol dehydration (to DME).⁸ The thermodynamic considerations and reaction mechanisms associated with the CTM and MTD reactions over their respective conventional catalysts are described in detail in Chapter 1.4. In summary, an effective CTM catalyst must be capable of activating CO₂ while simultaneously suppressing the competing reverse water gas shift (RWGS) reaction.⁹ For the MTD reaction, the catalyst must selectively convert methanol to DME while minimising the formation of hydrocarbon side products or coke formation.⁷ To achieve direct DME conversion in a single reactor, the bifunctional catalyst must therefore integrate two distinct catalytic phases, typically a Cu-based catalyst for CO₂ hydrogenation to methanol, and an acidic component, such as a zeolite, for methanol dehydration to DME.^{10, 11} Achieving this synergy requires a thermal and chemical compatibility between the phases. Additionally, the method of catalyst preparation plays an important role, where synthesis strategies are designed to optimise the functions of each component.

Cu/ZnO/Al₂O₃ catalysts are one of the most extensively investigated type of CTM catalyst.¹² Here, metallic Cu⁰ nanoparticles act as the active site where H₂ dissociates to form a reactive hydrogen species; ZnO acts as a structural and electronic promoter, dispersing the copper nanoparticles, facilitating CO₂ adsorption and stabilising key reaction intermediates through strong metal-support interactions; Al₂O₃ mainly acts as a support helping to stabilise and disperse the copper and zinc oxide phases.¹³⁻¹⁵

Zeolites are often used as the solid acid catalyst component for methanol dehydration.¹⁶⁻
¹⁸ It follows that, for optimum CTD performance, the zeolite catalyst must not only exhibit strong activity for the methanol dehydration reaction, but also function under the

same conditions as the CTM catalyst. Ideally, this interaction would be synergistic, with the combined catalyst demonstrating better performances than the separated components. Therefore, it is essential to incorporate a zeolite with robust methanol dehydration capabilities. Differences in the pore size and acid site distributions of a zeolite can impact its MTD performance (see Chapter 1.4.5 for more details).¹⁹⁻²² Of the different types of zeolites used in bifunctional catalysts for direct CTD conversion, protonated ZSM-5 (H-ZSM-5) and ferrierite (H-FER) are one of the most widely studied, however other zeolites such as mordenite, faujasite, and SAPO-34 have also been investigated.^{4, 7, 18, 22-24}

A frequently used strategy for the CTD reaction is to combine a Cu-based catalyst (typically of the CZA type but may also include other promoters such as Zr, Fe, Pd etc.) with a zeolite (e.g. ZSM-5, FER).^{11, 25-28} The overall catalytic performance is therefore strongly influenced by the specific combination of metal and acid components. For instance, Mureddu *et al.* investigated different combinations of Zr/Ce promoted CuZnAl catalysts with FER and ZSM-5, identifying CuZnAlZr/ZSM-5 as the most productive catalyst for DME synthesis.²⁹ Table 2.1 provides a summary of the methanol productivities (expressed in terms of the space time yield (*STY*) of DME (*STY*_{DME}) and CO₂ conversions (*X*_{CO₂}) for a selection of hybrid catalysts for direct CTD conversion. It demonstrates the challenge associated with benchmarking, as catalytic performance can be influenced by a range of factors related to catalyst composition and operating conditions.^{17, 30} For instance, in terms of the choice of zeolite, variations in the Si/Al ratios affects the catalyst behaviour, as higher Al content in the framework increases the number of Brønsted acid sites.^{27, 31-37} A well-known disadvantage associated with highly acidic zeolites is their tendency of overproducing carbonaceous deposits which accumulate in

the micropores and reduce long-term catalyst stability.³⁸ Thus, the Si/Al ratio is an important consideration to balance the activity and durability of the bifunctional CTD catalyst.

Table 2.1: Summary of the DME productivities (STY_{DME}) and CO₂ conversion (X_{CO_2}) of Cu-based/zeolite catalysts for the direct conversion of CO₂ to DME.

Catalyst	P (MPa)	T (°C)	CO ₂ fraction	X_{CO_2} (%)	STY_{DME} (g _{DME} /g _{cat} ·h)
Cu/Zn/Al H-ZSM-5 (MSC/ZSM-5) ³⁹	5	260	0.25	30	0.272
Cu/Zn/Al γ -Al ₂ O ₃ (MSC/Y-alumina) ³⁹	5	260	0.25	16	0.002
Cu/Zn/Zr Ga-Sil1 (A + H-Ga-silicate) ⁴⁰	3	250	0.25	19	0.045
CuO-ZnO-Al ₂ O ₃ NaH-ZSM-5 ⁴¹	4	275	0.25	32	0.038
CuO-TiO ₂ -ZrO ₂ H-ZSM-5 ²⁶	3	250	0.233	15.6	0.045
Cu/Zn/Al ZSM5+CNTs ⁴²	3	260	0.25	46.2	0.163
Cu/Zn/Zr FER ²⁸	5	260	0.23	23.6	0.371
Cu/Zn/Al ZSM-5 (CuO-ZnO-Al ₂ O ₃ /NaH-ZSM-5) ³⁰	4	275	0.1111	35	0.325
Cu/Zn/Al γ -Al ₂ O ₃ (CuO-ZnO-Al ₂ O ₃ /Al ₂ O ₃) ³⁰	4	275	0.1111	27	0.110
Cu/Zn/Al Amorphous silica-alumina ⁴³	3	270	0.25	47.1	0.156
Cu/Fe/Zr ZSM-5 ³⁴	5	260	0.1667	28.4	0.079
CuZnZr FER ⁴⁴	5	280	0.23	29	0.687

Catalyst	P (MPa)	T (°C)	CO ₂ fraction	X _{CO₂} (%)	STY _{DME} (g _{DME} /g _{cat} ·h)
CuZnZr FER ²⁷	5	260	0.23	26	0.554
CZA ZSM-5 ³³	3	225	0.25	2.57	0.439
Cu/Zn/Zr H-ZSM-5 ³²	3	240	0.23	16.1	0.430
Cu/Fe/Ce H-ZSM-5 ³¹	3	260	0.2	18.1	0.180
Cu/Zn/Zr SAPO-18 ⁴⁵	3	275	0.25	-	0.373
Cu/Zn/Al ZSM-5 ⁴⁶	3	250	0.25	21.3	0.210
Cu/Zn/Zr FER ⁴⁷	3	260	0.23	21.3	0.297
Cu/Zn/Zr FER ²⁸	5	260	0.23	23.6	0.424
Cu/Zn/Zr FER ⁴⁴	5	280	0.23	30	0.752
Cu/Zn/Zr HMFI ⁴⁸	5	240	0.23	23.6	0.126
Cu/Zn/Zr CBV3024E ²⁷	3	240	0.23	23.6	0.012
Pd Cu/Zr H-ZSM-5 ⁴⁹	5	250	0.23	18.9	0.579

The variation in experimental conditions across different studies makes it challenging to determine which method is the most effective approach for preparing bifunctional CTD catalysts, with several studies reporting correlations between the hybrid catalyst performance and the synthesis strategy.^{25, 50} The bifunctional catalysts can be synthesised in a variety of ways including physical mixing, coprecipitation and metal deposition.^{25, 32, 50-52} For instance, Cu/ZSM-5 hybrid catalysts have been synthesized by coprecipitation, physical mixing, wet mixing and impregnation.^{28, 41, 45, 46}

Based on previously reported bifunctional catalysts in the literature, a hybrid catalyst was designed for the direct hydrogenation of CO₂ to DME. The CTM component of the catalyst consists of a CZA-type material derived from an LDH precursor. As outlined in Chapter 1.5, LDHs are well-established as effective catalyst precursors due to their ability to generate homogeneously dispersed mixed metal oxides upon calcination. In the case of CZA catalysts derived from LDHs, calcination (and subsequent reduction in hydrogen) results in the formation of finely dispersed Cu⁰ nanoparticles.^{53, 54} Previous work in the O'Hare group demonstrated that the activation of a Cu_{1.3}ZnAl-LDH precursor yielded a CZA catalyst with high methanol productivity.⁵⁴ The activity of the catalyst was further improved when the LDH was incorporated as part of a core-shell structure, where the LDH shell was grown around a silicon (ES757) core. The activated core-shell was tested for its CTM performance and demonstrated superior activity in comparison to a commercial CZA catalyst and its physical mixture counterpart. The core-shell approach improved copper dispersion by minimising the aggregation effect of the LDH precursor, an issue often encountered in unsupported LDHs as a consequence of their high surface charges (see Chapter 1.5.3 for more details).⁵⁵ This improved dispersion, in combination

with enhanced metal-support interactions accounts for the synergistic effect observed in the ES757@Cu_{1.3}ZnAl core-shell catalyst.⁵⁴

Building on this concept, the core-shell strategy is extended in this work by replacing the inert silicon core with an active solid acid catalyst. Specifically, ZSM-5 was chosen as the core material due to its well-established reputation and favourable acidic properties for methanol dehydration. From a proof-of-concept perspective, this design raises the question: can a core-shell structure combining a CTM shell with a MTD catalyst core offer a synergetic enhancement of catalytic performance for the CTD reaction? Hence, this approach addresses two key challenges: (a) minimise the aggregation effect commonly observed in unsupported LDH-derived catalysts and (b) increase the interaction between the LDH and ZSM-5 phase to maximise the metal/support interactions.

Using a modified *in-situ* coprecipitation method by Chen *et al.*, a core-shell catalyst precursor was synthesised by directly growing Cu_{1.3}ZnAl-LDHs on a ZSM-5 core.⁵⁶ A 1:1 weight ratio of ZSM-5 to LDH was used as a starting point to screen catalyst compatibility. For comparison, a corresponding physical mixture of the two components was also prepared to assess the potential synergistic effect or potential associated with the core-shell. The precursors were then activated and subsequently evaluated for their performance in the direct CTD reaction. The resultant catalyst was further tested under varying catalyst activation/reaction conditions to evaluate its performance relative to benchmark catalysts reported in the literature.

2.2: Synthesis and characterisation of ZSM5/Cu_{1.3}ZnAl-LDH precursors and catalysts

2.2.1: Preparation of ZSM5/Cu_{1.3}ZnAl-LDH catalyst precursors

The core-shell precursor catalyst was synthesised using a modified coprecipitation technique by Chen *et al.* where Cu_{1.3}ZnAl-LDH platelets were grown in the presence of NH₄-ZSM-5 (“ZSM-5”, Si:Al 23:1).⁵⁶ Basic copper carbonate (CuCO₃·Cu(OH)₂) was used as the copper and carbonate source, and was dissolved in a solution of Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O in a 1.3:1:1 (Cu:Zn:Al) molar ratio. The metal salt solution was then slowly added to a dispersion of ZSM-5 at a rate of 152 mL/hour whilst simultaneously monitoring the pH, which was kept at pH = 10 by the controlled addition of tetrapropylammonium hydroxide (TPAOH). A 1:1 ZSM-5:LDH mass ratio was used as a simplified initial benchmark and assumes that the eventual activation of the hybrid precursor catalyst requires equal catalyst support. The pale-blue product was collected by filtration and is described using the “LDH” suffix, i.e. ZSM5@Cu_{1.3}ZnAl-LDH. A corresponding Cu_{1.3}ZnAl LDH was synthesized using the same coprecipitation method, excluding the zeolite dispersion, and using the same metal salt ratios (Cu_{1.3}ZnAl-LDH). A physical mixture counterpart was also synthesised to investigate the structural changes associated with the *in-situ* coprecipitation technique. Here, the ZSM-5 powder was mechanically mixed (to homogeneity) with Cu_{1.3}ZnAl-LDH in a 1:1 mass ratio. The physical mixture precursor catalyst is also described using the “LDH” suffix, i.e. ZSM5+Cu_{1.3}ZnAl-LDH. For full synthesis methods for the core-shell, LDH and physical mixture synthesis methods consult Chapter 6.2.

2.2.2: Characterisations of ZSM5/Cu_{1.3}ZnAl-LDH catalyst precursors

Powder X-ray diffraction (PXRD) was used for phase identification and structural analysis of the ZSM5@Cu_{1.3}ZnAl-LDH core-shell and ZSM5+Cu_{1.3}ZnAl-LDH physical mixture.

PXRD was initially performed on a Bruker D8 diffractometer to qualitatively identify the LDH and zeolite phases within the hybrid samples. As shown in the resulting patterns (Figure A.1), ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH clearly exhibit the expected Bragg peaks for the crystalline Cu_{1.3}ZnAl-LDH and ZSM-5 (Si:Al, 23:1) phases. The PXRD profile for ZSM5@Cu_{1.3}ZnAl-LDH has maxima corresponding to the (00 l) basal plane Bragg reflections which are indicative of a hydrotalcite-like material. Specifically, the Bragg peaks located at $2\theta = \sim 11.7^\circ$ and $\sim 23.5^\circ$ correspond to the (003) and (006) planes, whilst those at $\sim 33.7^\circ$, $\sim 60.0^\circ$ and $\sim 61.4^\circ$ are attributed to the (101), (110), and (113) reflections.⁵⁷⁻⁵⁹ Peaks associated with ZSM-5 lie between $2\theta = 7 - 9^\circ$ and $23 - 25^\circ$. The peaks at $2\theta \sim 7.9^\circ$, $\sim 8.8^\circ$, $\sim 23.0^\circ$, $\sim 23.0^\circ$, $\sim 24.4^\circ$ correspond to the (101), (200), (501), (151) and (133) Bragg reflections which are typical of MFI zeolites.⁶⁰⁻

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PXRD was also conducted at the I11 Diamond Light Source Synchrotron facility to get high resolution, qualitative data of the materials. The diffraction patterns were then refined using the TOPAS software to extract crystallographic details of ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH and to investigate differences in the crystal structures of the LDH-phase.^{63, 64} Diffraction features from both the LDH and ZSM-5 are observable in the PXRD pattern for ZSM5@Cu_{1.3}ZnAl-LDH (Figure 2.1) and ZSM5+Cu_{1.3}ZnAl-LDH (Figure 2.2) which were confirmed by two-phase Rietveld

refinement (for detailed structural parameters of the refinements, including errors, see Table A.1, see Figure A.2 and Figure A.3 for the Rietveld refinement of ZSM-5 and $\text{Cu}_{1.3}\text{ZnAl-LDH}$).^{57, 60, 65} No other phases were identified in the refinement of either the core-shell or physical mixture.

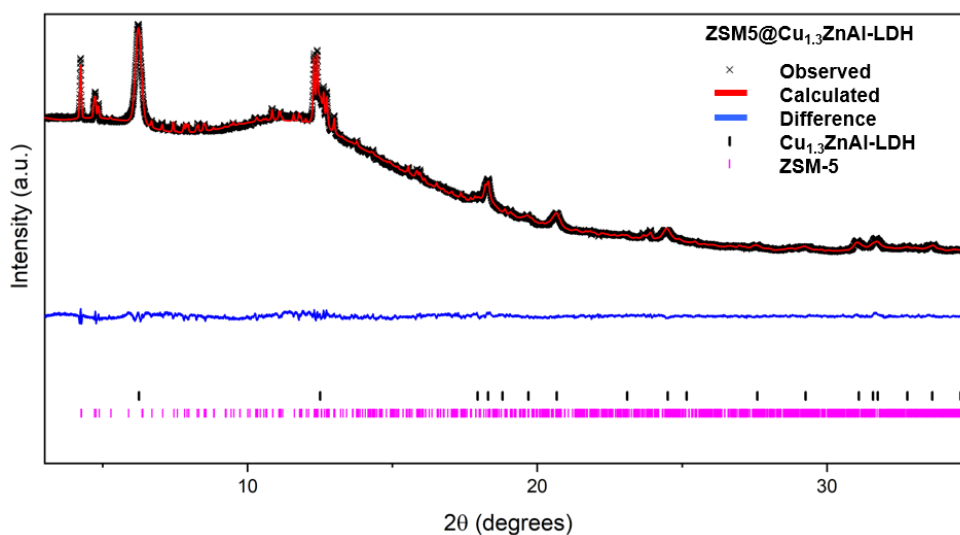


Figure 2.1: Two-phase Rietveld refinement of $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH}$ against ZSM-5 and $\text{Cu}_{1.3}\text{ZnAl-LDH}$. PXRD data was collected at I11 Diamond Light Source.

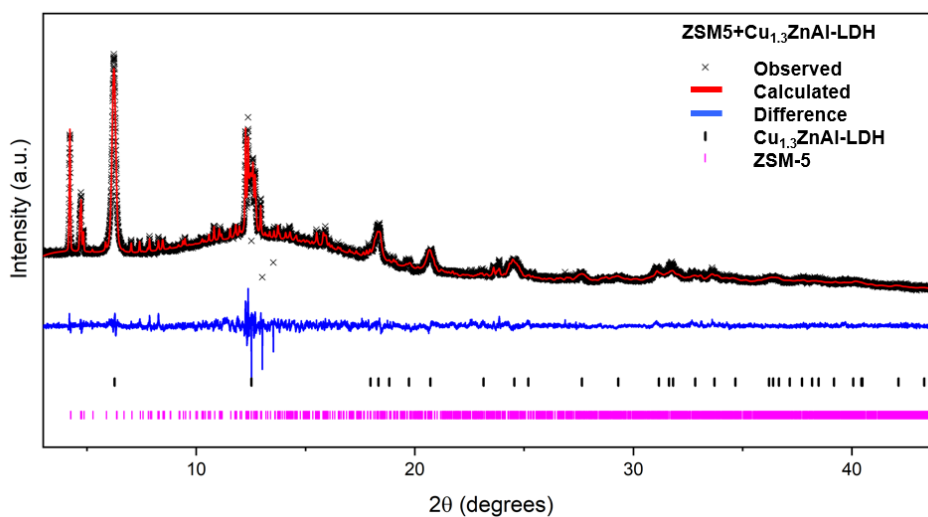


Figure 2.2: Two-phase Rietveld refinement of $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDH}$ against ZSM-5 and $\text{Cu}_{1.3}\text{ZnAl-LDH}$. PXRD data was collected at I11 Diamond Light Source.

The a - and c -lattice parameters were refined for the core-shell and physical mixture samples based on a rhombohedral 3R symmetry unit cell for the LDH.^{57, 59} Where $c = 3d_{003}$, this finds d_{003} as 7.593 Å for ZSM5@Cu_{1.3}ZnAl-LDH and 7.577 Å for ZSM5+Cu_{1.3}ZnAl-LDH, corresponding to values reported for carbonate-intercalated LDHs and are similar to the results of the Cu_{1.3}ZnAl-LDH refinement (7.569 Å, Figure A.4).^{57, 66, 67} The similarity in lattice parameters of ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH indicate there were no major changes to the unit cell dimensions of the Cu_{1.3}ZnAl-LDH phase and that the growth of the LDH in the presence of the zeolite does not affect its crystal structure.

The crystallite domain lengths (D_{003}) and (D_{110}) sizes for the Cu_{1.3}ZnAl-LDH phase within ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH were estimated using the Scherrer equation and are summarised in Table 2.2. The full Scherrer parameters and crystallite domain lengths can be found in Table A.2. A standard method for finding the D_{hkl} of a material is to find the average D_{hkl} of all the peaks in a PXRD profile. However, anisotropy in the crystallites of layered materials often means that the c -axis may be longer than the distance along the ab plane.⁶⁸ In the case of LDHs, stacking faults are also commonplace, leading to non-uniform broadening of the (00 l) reflections.⁶⁹ This is observed for the core-shell, physical mixture and LDH samples where there are considerable differences in the D_{003} and D_{006} domain lengths (Table A.2). Poor signal-to-noise ratios at higher angles combined with instrumental broadening (which increases with 2θ) may lead to an overestimation of the crystallite domain length. Hence, the crystallite domain lengths in the c -axis were determined from the peak width at half maximum for the (003) Bragg reflection rather than an average of the observable (00 l) reflections. The estimated D_{003} length of the core-shell (18.4 nm) was smaller than the

physical mixture (21.4 nm) and LDH (24.6 nm) samples whilst the value for D_{110} was larger (12.4 nm). Meanwhile the domain lengths for ZSM5+Cu_{1.3}ZnAl-LDH and Cu_{1.3}ZnAl-LDH in both the D_{003} (21.4/24.6 nm) and D_{110} direction (9.6/9.3 nm) were similar. Thus, the anisotropy of the Cu_{1.3}ZnAl LDH (defined as the diameter divided by platelet thickness) was higher in the core-shell sample than the physical mixture or pristine Cu_{1.3}ZnAl-LDH. It can be said that the *in-situ* coprecipitation of the Cu_{1.3}ZnAl-LDH in the presence of ZSM-5 particles facilitates thinner, yet wider (in the *ab* plane) LDH platelets. Thus, the core-shell method alters the crystallite growth of the LDH.

Table 2.2: d-spacing and domain lengths of ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH from two-phase Rietveld refinement and Cu_{1.3}ZnAl-LDH from single-phase Rietveld refinement.

Sample	d_{003} (Å)	d_{110} (Å)	D_{003}^a (nm)	D_{110}^a (nm)	Crystalline anisotropy (D_{110}/D_{003})
ZSM5@Cu _{1.3} ZnAl-LDH	7.593	1.541	18.4	12.4	0.7
ZSM5+Cu _{1.3} ZnAl-LDH	7.577	1.537	21.4	9.6	0.4
Cu _{1.3} ZnAl-LDH	7.569	1.534	24.6	9.3	0.4

^aK = 0.9 in Scherrer's equation.

PXRD analysis therefore shows that a carbonate-intercalated Cu_{1.3}ZnAl-LDH was successfully grown in the presence of ZSM-5 with no significant changes to the crystal structure of either the LDH or zeolite phases. Changes in the crystallite sizes calculated from the Scherrer equation suggest that the *in-situ* coprecipitation method generates

thinner $\text{Cu}_{1.3}\text{ZnAl}$ -LDH platelets. Thus, the stacking of the $\text{Cu}_{1.3}\text{ZnAl}$ LDHs is affected by differences in the synthesis conditions. The ZSM-5 core was used as both a support and to direct the growth of Al-containing LDHs where the Al^{3+} sites in the aluminosilicate are expected to act as the nucleation points. However, the formation of thinner platelets may indicate that the presence of ZSM-5 particles interrupts the growth of the LDH, highlighting the sensitivity of the LDH crystallization process to variations in the synthesis conditions.

Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis were used to examine the morphology and elemental composition of the core, shell, core-shell and physical mixture.

As-purchased ZSM-5 particles (Figure 2.3a) are semi-cuboidal with uneven size distributions, varying significantly from 100 nm to micrometres (Figure A.4). The platelet thickness of the LDHs were measured directly from TEM micrographs using the ImageJ software. Measurements were collected from a statistically significant number of platelets across multiple images. The average LDH platelet thicknesses (summarised in Figure A.5) were determined for $\text{Cu}_{1.3}\text{ZnAl}$ -LDH (19.3 ± 8.9 nm), ZSM5@ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH (19.6 ± 7.3 nm) and ZSM5+ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH (26.4 ± 9.3 nm). The relatively large standard deviation in the measured platelet thickness can be attributed to both sampling and projection effects in the TEM analysis. As TEM provides a 2D projection of the particles, platelets that are tilted relative to the electron beam may introduce variability in the apparent thickness. Furthermore, variations in contrast and edge definition make precise determination of platelet boundaries more challenging. The measured thickness may also be overestimated when some particles correspond to small stacks or partially overlapped platelets rather than individual sheets.

PXRD and TEM provided complementary but not identical measures of LDH platelet size. The Scherrer D_{003} crystallite sizes reflect the coherent stacking along the c-axis, whereas TEM thickness are direct, projection-based measurements of physical platelets. Using a shape factor $K = 0.9$, the D_{003} values were 18.4, 21.4 and 24.6 nm for ZSM5@Cu_{1.3}ZnAl-LDH, ZSM5+Cu_{1.3}ZnAl-LDH and Cu_{1.3}ZnAl-LDH respectively. As the crystallite size D is directly proportional to the shape factor K in the Scherrer equation, using $K = 1.0$ (for layered materials) uniformly increases these values by $\approx 11\%$ (20.4, 23.8 and 27.3 nm). The TEM platelet thicknesses (19.6 ± 7.3 , 26.4 ± 9.3 and 19.3 ± 8.9 nm) are broadly consistent with the Scherrer estimates. The core-shell sample shows the closes agreement, while the physical mixture exhibits larger TEM mean thickness (but overlaps the Scherrer range once uncertainty is considered). Given the large spread in TEM measurements and the uncertainties inherent to Scherrer analysis, absolute size values are interpreted cautiously. Both techniques agree that *in-situ* coprecipitation of the LDH in the presence of ZSM-5 yields thinner, more laterally extended LDH platelets than the physical mixture of unsupported LDH, consistent with nucleation of LDH platelets on the zeolite surface and reduced platelet aggregation. The size distribution of the platelets in each sample was similar to those calculated from Scherrer equation which suggests that the particles in the images are largely single crystals.

The ZSM5@Cu_{1.3}ZnAl-LDH core-shell possesses a similar morphology to a previously reported MgAl-LDH/HY zeolite core-shell where the LDH platelets grow vertically from the surface of the zeolite rather than horizontal stacking of the platelets (see the illustration in Figure A.6).⁵⁶

As seen in Figure 2.3b, Cu_{1.3}ZnAl-LDH platelets exhibit a strong tendency to aggregate into larger, dense clusters. This aggregation is characteristic of LDHs due to their high

surface charges and is observed in other non-supported LDHs.^{54, 70, 71} In contrast, this aggregation is significantly reduced in the ZSM5@Cu_{1.3}ZnAl-LDH sample, where the formation of a core-shell structure was achieved. Compared to the physical mixture, ZSM5@Cu_{1.3}ZnAl-LDH exhibits greater LDH coverage around the ZSM-5 particles. The limited coverage in ZSM5+Cu_{1.3}ZnAl-LDH is likely the result of attractive electrostatic forces between the negatively charged zeolite core and positively charged free LDH sheets.⁷² In ZSM5@Cu_{1.3}ZnAl-LDH, the Cu_{1.3}ZnAl-LDH platelets are uniformly distributed over the surface of the ZSM-5 particles, indicating improved dispersion and better control over LDH growth. This supports the effectiveness of the core-shell strategy in mitigating platelet aggregation and promoting closer contact between the LDH phase and the ZSM-5 support.

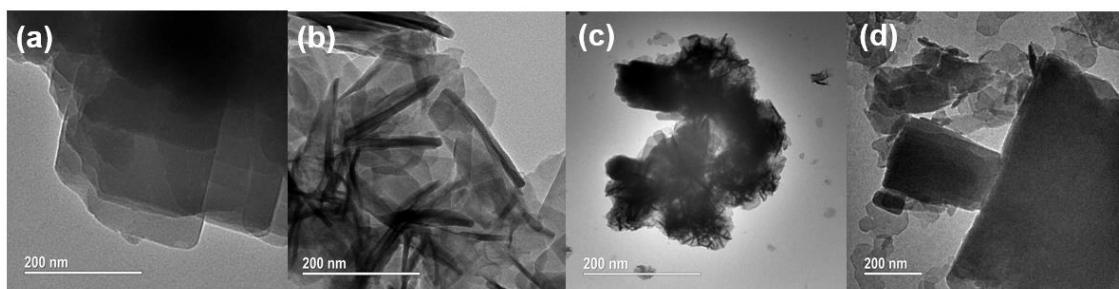


Figure 2.3: TEM images of (a) as-purchased ZSM-5, (b) Cu_{1.3}ZnAl-LDH, (c) ZSM5@Cu_{1.3}ZnAl-LDH, and (d) physical mixture ZSM5+Cu_{1.3}ZnAl-LDH catalyst precursors.

Scanning transmission electron microscopy coupled with Energy-dispersive X-ray spectroscopy (STEM/EDX) mapping was used to image the distribution of Cu/Zn over the zeolites in the core-shell and physical mixture (Figure A.7). The images confirm the presence of Si (magenta) from the ZSM-5 particles and Cu/Zn (blue/orange) from the Cu_{1.3}ZnAl-LDH phase, however, the difference in coverage between ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH was not immediately obvious.

Additionally, Cu was falsely detected in the EDX for pristine ZSM-5 (Figure A.8a). Initially, the samples were loaded into a JEOL2100 TEM using a standard single-tilt holder which uses a brass ring to hold the TEM grids in place. This is the likely source of the copper signals in the EDX mapping of ZSM-5. False signals are a known problem in EDX analysis which occur when spurious X-rays not generated in the region of interest are detected.^{73, 74} If Cu was present in the sample, both the Cu K_{α} peak (at ~ 8 keV) and Cu L_{α} peak (at ~ 0.9 keV) would be seen (as is the case for both the ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH samples, see Figure A.9), however the signal from Cu L_{α} in the holder would be too weak to be detected.⁷⁵ As a consequence, the Cu intensity over the core-shell and physical mixture samples appears to be similarly distributed over the ZSM-5 particles. A reference test was performed using a single-tilt beryllium holder which enables high sensitivity EDX analysis. As shown in Figure 2.4 Cu and Zn were distributed more evenly across ZSM-5 in the core-shell than in the physical mixture. Point analysis was also used to find the approximate elemental wt% at various points across the particles. From this it was determined that (a) no sources of Cu were detected in the pristine ZSM-5, (b) the Si:Al ratio was closer to 12:1 (Figure A.10), and (c) the Cu:Zn ratio for the core-shell was $\sim 1.3:1$ (Figure A.11). The Cu:Zn ratios detected across ZSM-5 in the ZSM5+Cu_{1.3}ZnAl-LDH physical mixture are less uniform than those over the ZSM-5 core in ZSM-5, with areas of lower Cu/Zn detection (Figure A.12).

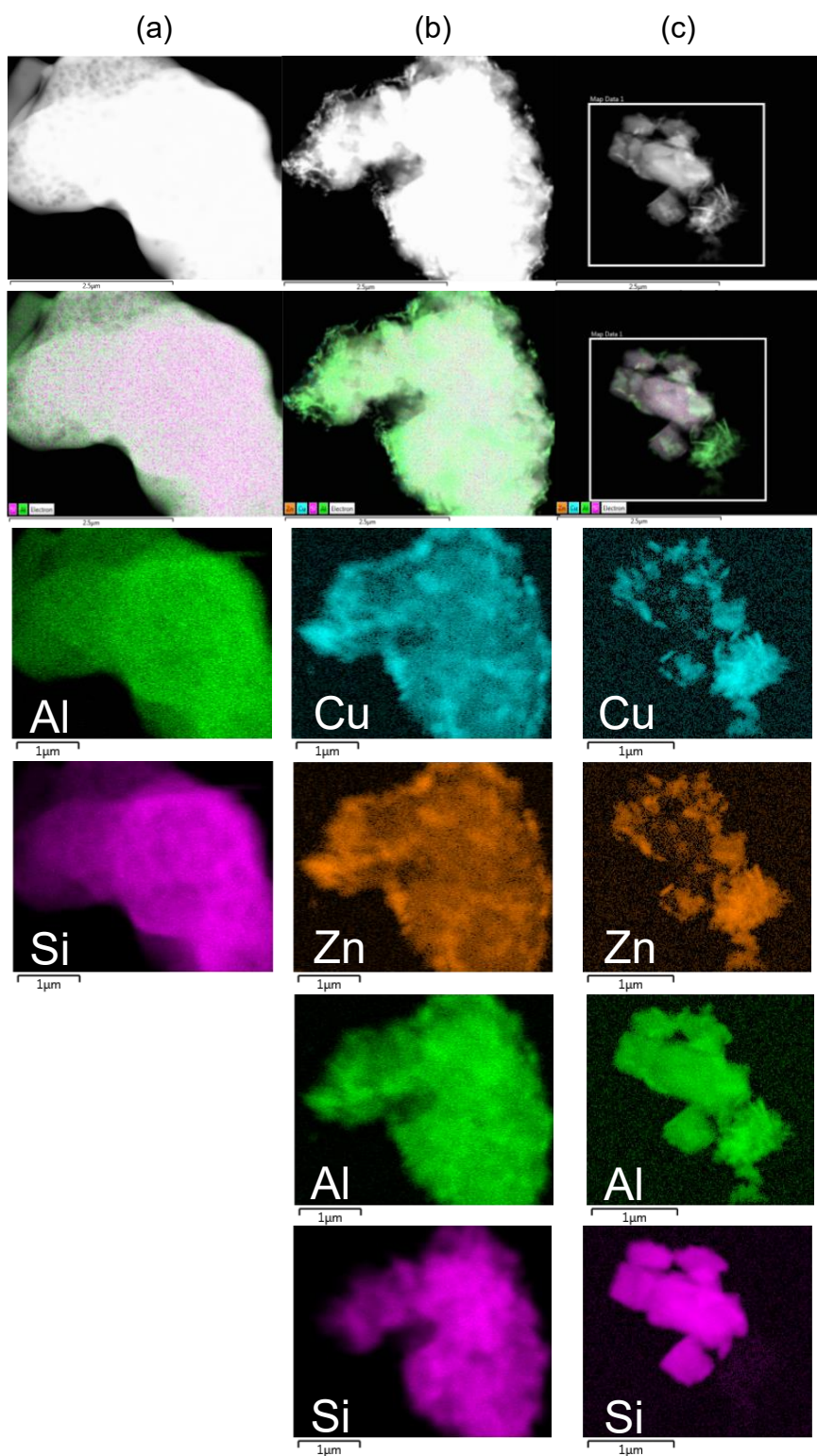


Figure 2.4: STEM/EDX of (a) ZSM-5, (b) ZSM5@Cu_{1.3}ZnAl-LDH and (c) ZSM5+Cu_{1.3}ZnAl-LDH catalyst precursors showing the distribution of on Cu (blue), Zn (orange), Al (green) and Si (magenta). Samples were loaded onto JEOL2100 using a single-tilt beryllium holder.

Together the results suggest that the *in-situ* coprecipitation of $\text{Cu}_{1.3}\text{ZnAl-LDH}$ in the presence of ZSM-5 encourages a more homogeneous dispersion of LDH across the zeolite particles. By physically mixing $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and ZSM-5, some coverage of ZSM-5 is observed (as expected from the compatible surfaces charges) however the distribution of the LDHs over the zeolite is not uniform. Some free LDHs were observed in the TEM images of the core-shell sample which suggests that the core-shell synthesis can be optimised, possibly by altering the 1:1 ratio of ZSM-5:LDH to investigate its effect on LDH coverage. Previous research in core-shell composites have demonstrated the importance of the dropping rate during coprecipitation in minimising free LDHs (see Chapter 1.5.2 for more details), which could be altered to encourage LDH growth around the ZSM-5 core.⁷⁶

In addition to TEM, scanning electron microscopy (SEM), in combination with EDX analysis, was used to investigate the surface overage of LDH over the zeolite core in $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH}$. Whilst TEM images provides 2D projections that are valuable for measuring platelet thickness, SEM shows the 3D surface topography of the materials, allowing for clearer assessment of the uniformity of LDH coverage. SEM images summarised in Figure 2.5 highlight the differences in morphology between pristine $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and ZSM-5. The ZSM-5 sample appears angular and with coffin-shaped crystals of varying sizes that are intergrown into large particles. $\text{Cu}_{1.3}\text{ZnAl-LDH}$ exhibits the characteristic platelet-like morphology, appearing as thin nanosheets that are aggregated into larger clusters ($> 2 \mu\text{m}$). The aggregation observed in the $\text{Cu}_{1.3}\text{ZnAl-LDH}$ sample corresponds to that seen in the TEM images. The surfaces of both $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and ZSM-5 are smooth reflecting the crystalline nature of the phases (as seen in the PXRD analysis).

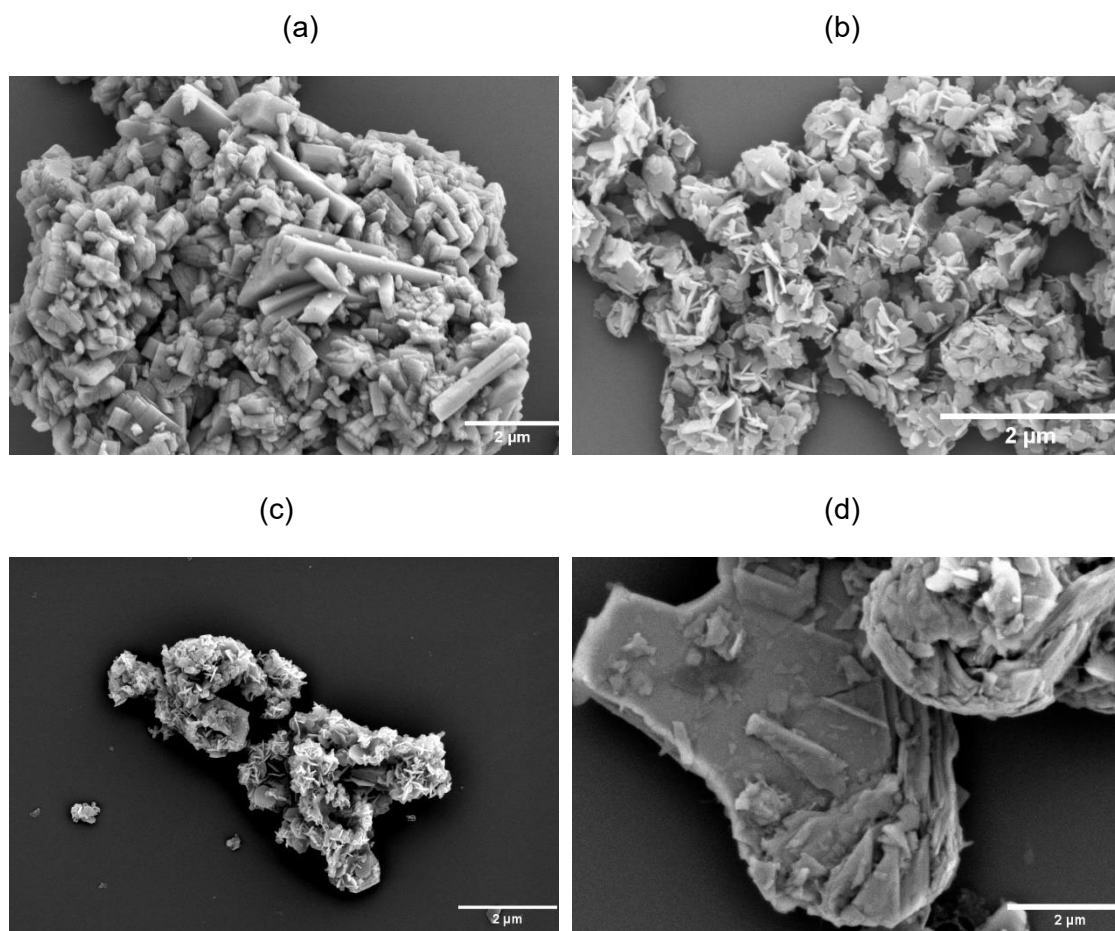


Figure 2.5: SEM images of (a) ZSM-5, (b) Cu_{1.3}ZnAl-LDH, (c) ZSM5@Cu_{1.3}ZnAl-LDH and (d) ZSM5+Cu_{1.3}ZnAl-LDH catalyst precursors.

The coverage of the Cu_{1.3}ZnAl-LDH around ZSM-5 in ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH is as expected based on the TEM micrographs. In comparison to the ZSM5+Cu_{1.3}ZnAl-LDH physical mixture, ZSM5@Cu_{1.3}ZnAl-LDH demonstrates improved coverage where Cu_{1.3}ZnAl-LDH uniformly coats the ZSM-5 surfaces, forming the core-shell structure. This is exemplified in the EDX mapping (Figure 2.6). Si (magenta) in the EDX images of ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH are associated with the ZSM-5 framework. The overlay of the elemental maps shows Cu (blue) and Zn (orange) signals dispersed around the ZSM-5 particles with greater intensity in the core-shell sample than in the physical mixture sample. SEM/EDX images

of ZSM5+Cu_{1.3}ZnAl-LDH therefore reflect the results from STEM/EDX mapping whereby Cu/Zn distribution over the ZSM-5 crystals is patchy and uneven, indicating that there is incomplete coverage in the physical mixture sample.

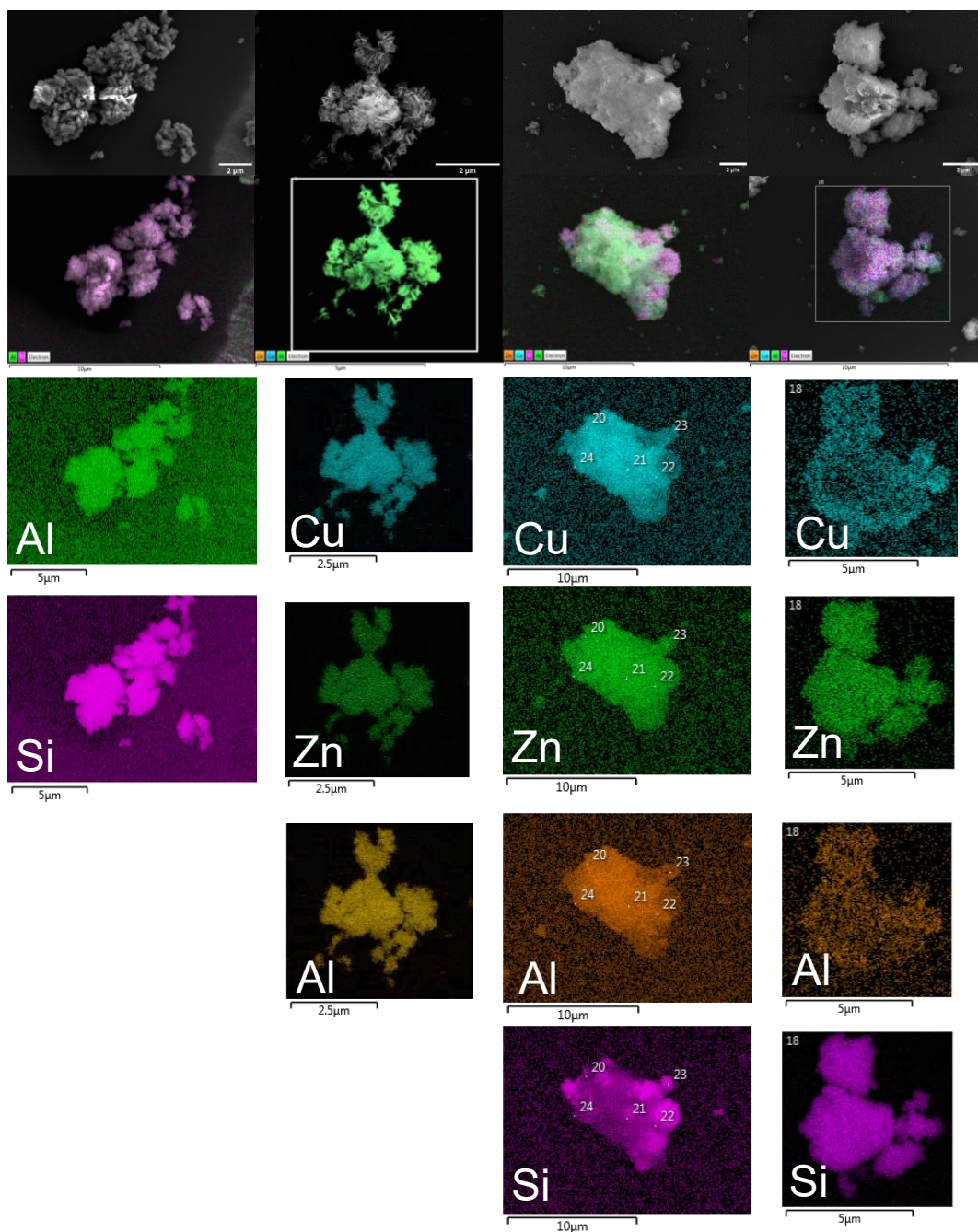


Figure 2.6: SEM/EDX images of (a) ZSM-5, (b) $\text{Cu}_{1.3}\text{ZnAl-LDH}$, (c) $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH}$, (d) $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDH}$ catalyst precursors showing the distribution of on Cu (blue), Zn (orange), Al (green) and Si (magenta).

Point analysis of $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH}$ shows several regions on the ZSM-5 particle where the Cu:Zn ratio is $\sim 1.3:1$ (Figure A.13 and Table A.3). In comparison, the elemental wt% obtained from $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDH}$ (Figure A.14 and Table A.4)

exhibit higher Si intensities, indicating greater Si exposure on the surface of the zeolite in the physical mixture compared to the core-shell precursor catalyst.

Taken in combination with the STEM/EDX images, it can be said that there are observable differences in the morphology of the core-shell and physical mixture precursor catalysts where ZSM5@Cu_{1.3}ZnAl-LDH has a more uniform and continuous coverage of Cu_{1.3}ZnAl-LDH platelets over the ZSM-5 core.

²⁹Si and ²⁷Al solid state nuclear magnetic resonance (ssNMR) spectroscopy was used to determine the coordination environment of the Si/Al species and to detect changes to the zeolite framework after coprecipitation. The ²⁹Si and ²⁷Al ssNMR spectra are summarised in Figure 2.7 and Figure 2.8 respectively.

The ²⁹Si cross-polarization magic angle spinning (CPMAS) NMR spectrum of ZSM-5 shows Si resonances typical for the zeolite. Deconvolution of the spectrum (Figure A.15) identifies three peaks. The resonance band around -112.2 ppm is assigned to the tetrahedrally coordinated (Q⁴) Si(OSi)₄ sites (i.e. Si(OAl)₀) with a shoulder at -116.0 ppm, together with a peak at -106.5 ppm which is observed in samples with high Al content and corresponds to Q⁴ species of the type Si(OSi)₃(OAl) (i.e. Si(OAl)₁).⁷⁷⁻⁸⁰ The deconvoluted spectra for ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH show broader features, with six sites detected in the core-shell and five in the physical mixture. This suggests that the presence of the Cu_{1.3}ZnAl-LDH in both samples interacts with the ZSM-5, altering the Si environments. The shifts in the peak positions and the different number of sites suggests that the nature or extent of interaction varies in the two composite samples. This reflects the complexity of the interfacial interactions occurring at the zeolite surface.

The peaks occurring at -106.7 ppm and -105.7 ppm for the core-shell and physical mixture are assigned to the $\text{Si}(\text{OSi})_3(\text{OAl})$ species, whilst the peaks at -112.9 ppm and -112.3 ppm are related to the $\text{Si}(\text{OSi})_4$ site (Table A.5).⁸⁰ The slight shift in the $\text{Si}(\text{OSi})_3(\text{OAl})$ peak might be due to the interaction with Cu/Zn from the LDH in close proximity to the zeolite, however interpretation of the peaks is challenging due to the broadness of the NMR signals. This is a consequence of paramagnetic Cu^{2+} enhancing the spin-spin relaxation, resulting in broader ^{29}Si signals in the NMR spectrum.⁸¹

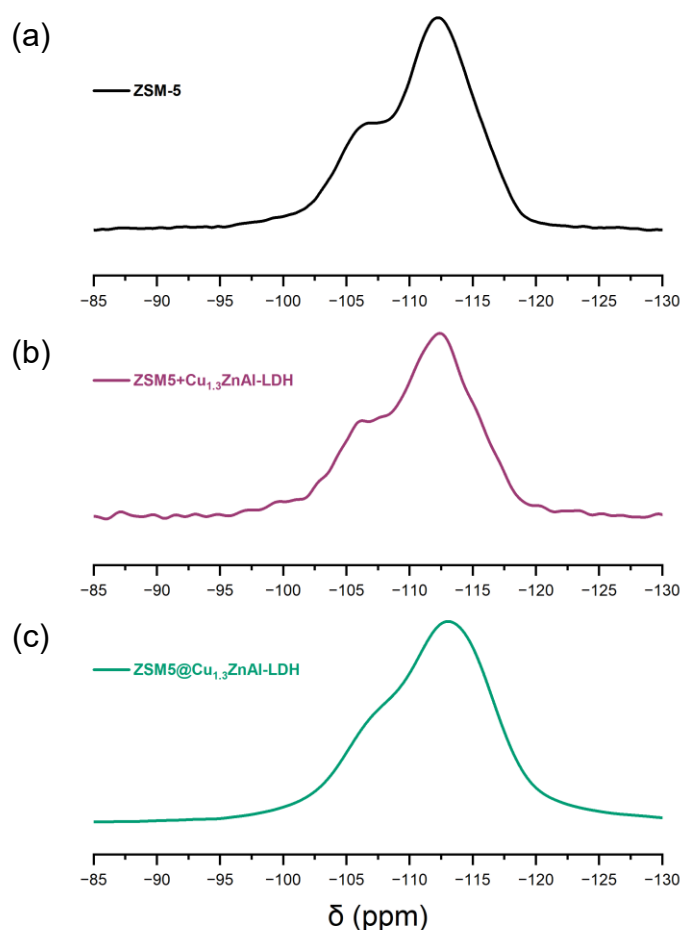


Figure 2.7: ^{29}Si solid-state CPMAS NMR spectra of (a) ZSM-5, (b) ZSM5+ $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and (c) ZSM5@ $\text{Cu}_{1.3}\text{ZnAl-LDH}$.

The ^{27}Al direct polarization MAS (DPMAS) NMR spectra of the samples are shown in Figure 2.8. ZSM-5 exhibits a singular peak at 54.2 ppm which corresponds to a tetrahedrally coordinated AlO_4 .⁷⁸ There were no other bands in the 0 – 50 ppm region which suggests there were no extra-framework aluminium species in the parent ZSM-5.^{78, 82} This peak is present in the core-shell and physical mixture samples; however, it is shifted more upfield in the core-shell (53.8 ppm). This shift may indicate that Cu^{2+} or Zn^{2+} ion exchanged in the zeolite framework during coprecipitation, leading to a distortion of the local Al environment.

The peak at 9.4 ppm in the core-shell is associated with octahedrally coordinated Al in AlO_6 within the LDH metal hydroxide layer.⁸³⁻⁸⁵ Similar to the ^{29}Si NMR spectrum, the peaks in the ^{27}Al NMR spectrum for the LDH are broad due to the influence of paramagnetic Cu^{2+} .^{86, 87} Deconvolution of the core-shell shows two peaks associated with Al species in the LDH phase (Figure A.16) between –89 and –208 ppm. Due to the Cu^{2+} distortion within the LDH layers, the electric field gradient measured at the Al sites is significantly altered leading to multiple Al environments.⁸⁵ Wu *et al.* have suggested that peaks in this high-frequency region of the spectrum may correspond to tetrahedrally coordinated Al species (AlO_4) located at the edges of the LDH.⁸⁸ Due to the Jahn-Teller effect, paramagnetic Cu^{2+} tends to avoid neighbouring regularly coordinated AlO_6 octahedra, leading to local structural distortion.^{88, 89} This distortion, combined with the high aluminium concentrations found near the LDH edges may promote a transformation from octahedral to tetrahedrally coordinated aluminium.⁸⁸ Peaks associated with AlO_6 and AlO_4 are also observed in the ^{27}Al NMR spectrum for the physical mixture (Table A.6). In the case of the core-shell sample, where the LDH is grown from the surface of the aluminosilicate core, such interfacial interactions are likely to enhance this effect,

with higher concentrations of Al at the LDH-zeolite boundary. This is reflected in the ^{27}Al NMR data, where the relative intensity of the peak at -207.8 ppm (associated with the distorted AlO_4 species) is greater in the core-shell sample compared to the same peak in the physical mixture (Table A.6). This difference indicates there are stronger interactions at the LDH-zeolite interface in the core-shell structure.

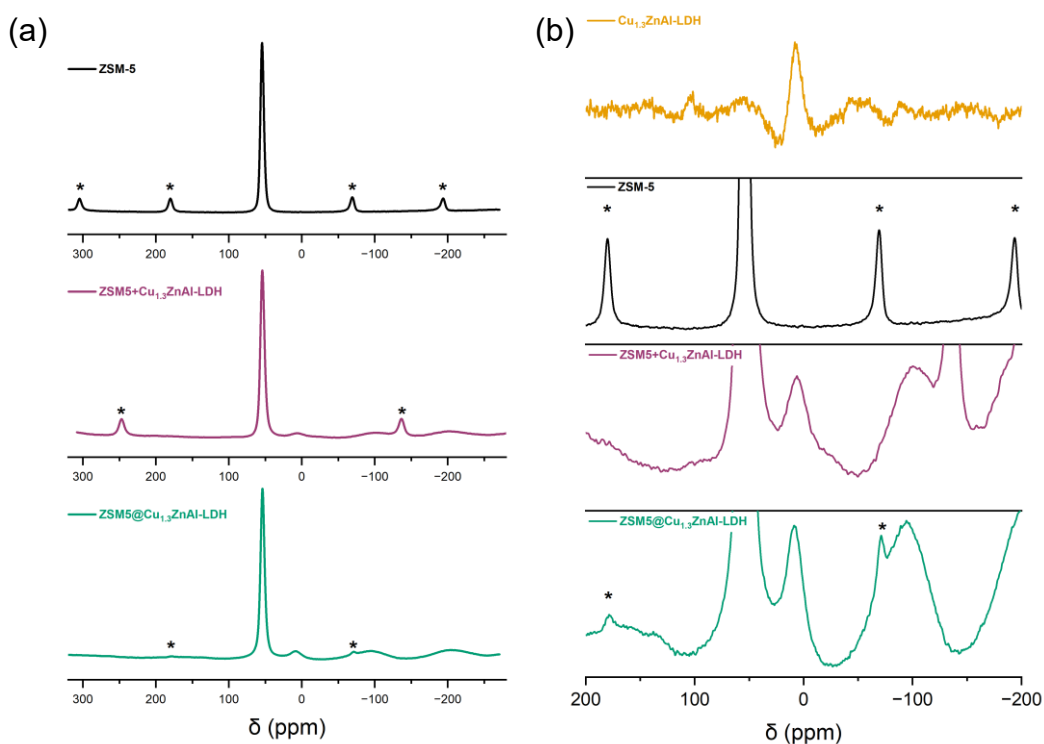


Figure 2.8: ^{27}Al solid-state DPMAS NMR spectra of (a) ZSM-5, ZSM5+ $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and ZSM5@ $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and (b) the enlarged region between $-200 - 200$ ppm for $\text{Cu}_{1.3}\text{ZnAl-LDH}$, ZSM-5, ZSM5+ $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and ZSM5@ $\text{Cu}_{1.3}\text{ZnAl-LDH}$. * indicates the spinning sidebands.

^{29}Si solid state NMR (ssNMR) analysis confirmed that the ZSM-5 framework in the core-shell was unchanged following coprecipitation, whilst the ^{27}Al SSNMR verified that $\text{Cu}_{1.3}\text{ZnAl-LDH}$ was integrated into the core-shell and physical mixture samples.

Inductively coupled plasma atomic emission spectrometry and carbon/hydrogen/nitrogen (ICP-OES/CHN) analysis of the precursor core-shell and physical mixture show that the Cu:Zn:Al ratios are in agreement with the 1.3:1:1 molar ratio used in the reaction (Table 2.3). This indicates that ZSM-5 was not digested in the preparation for the ICP-OES analysis. Full zeolite digestion is difficult to achieve on account of its robust structure and tends to require hydrogen fluoride for full digestion. In this case nitric acid was used (see Chapter 6.1.5) which likely resulted in full digestion of the LDH phase but no digestion of the zeolite. As a result, the Si and Al wt% of the zeolite were not accounted for, and the Si/Al ratio cannot be determined from this analysis. Only the Cu:Zn:Al ratio of the LDH can be quantified.

Table 2.3: ICP-OES/CHN elemental analysis of the LDH, core-shell and physical mixture precursors

Sample	Cu (wt%)	Zn (wt%)	Al (wt%)	Cu:Zn:Al	C (wt%)	H (wt%)	N (wt%)
ZSM5@Cu _{1.3} ZnAl-LDH	14.11	10.02	4.43	1.45:1.00:1.07	2.34	1.89	0.47
ZSM5+Cu _{1.3} ZnAl-LDH	12.73	10.08	4.20	1.30:1.00:1.01	1.71	1.97	0.95
Cu _{1.3} ZnAl-LDH	26.17	19.00	7.45	1.42:1.00:0.95	2.02	2.59	0
ZSM-5	-	-	-	-	0.10	0.11	1.49

Carbon/hydrogen/nitrogen (CHN) analysis indicates that ZSM-5 contained nitrogen species alongside small amounts of carbon and hydrogen. Based on the FTIR analysis (see the following section), the pristine ZSM-5 did not have residual organic templates, hence the nitrogen and hydrogen species detected in the CHN analysis is likely from the NH_4^+ counterion. The detection of some carbon may suggest a different carbon containing impurity present in the sample, however, considering the results from PXRD and SSNMR analysis, the impurity does not significantly affect the structure of the zeolite. The detection of carbon species in $\text{Cu}_{1.3}\text{ZnAl-LDH}$ (2.02%) confirms that the LDH is carbonate-intercalated. With no nitrogen species detected in $\text{Cu}_{1.3}\text{ZnAl-LDH}$ the presence of nitrogen in $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH}$ and $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDH}$ arises from the ZSM-5 phase (the pristine ZSM-5 used in the reaction is of the ammonium form). The ICP-OES/CHN results are therefore consistent with expectations.

Fourier transform infrared spectroscopy (FTIR) was used to identify the functional groups of the $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH}$ core-shell catalyst precursor. The FTIR profile of $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH}$ was compared against $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDH}$, $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and ZSM-5 and are shown in Figure 2.9.

The profile for ZSM-5 shows bands at ~ 1200 , 1041 and 788 cm^{-1} which are characteristic of the SiO_4 tetrahedron units within a zeolite.⁶² More specifically the absorption band at 1213 cm^{-1} is associated with Si–O asymmetric stretching vibrations of structures with four chains of 5-membered rings arranged around a two-fold screw axis, the peak at 1041 cm^{-1} with the internal asymmetric stretching vibration of Si–O–T (T = Si/Al), and the peak at 788 cm^{-1} with the symmetric stretching of T–O in the external linkages.⁶² The absence of stretching bands in the $2980 - 2880\text{ cm}^{-1}$ region, typically associated with C–H functional groups, suggests the commercial ZSM-5 is free of residual organic

templates (e.g. TPAOH is a common organic template used in the synthesis of MFI zeolites). A small peak at 3635 cm^{-1} is usually assigned to the acidic Si-(OH)-Al hydroxyl group which decreases in relative intensity when replaced by NH_4^+ . In this case it is likely to be from the bending vibration of adsorbed NH_4^+ on acidic sites.⁹⁰ The absorption band around 1450 cm^{-1} can also be associated with the bending mode of the bound ions, in this case NH_4^+ , to the acid sites.⁹¹ Although the peak at 1629 cm^{-1} appears in a similar position as the H_2O bending peak in the LDH (Figure A.17), the lack of a broad O-H peak between $3670 - 2760\text{ cm}^{-1}$ suggests the transmittance is due to the N-H bending of free NH_3 physisorbed to the zeolite.⁹¹ For comparison, ZSM-5 was calcined at $500\text{ }^\circ\text{C}$ for 3 hours to synthesize the protonated H-ZSM-5. H-ZSM-5 is usually generated by calcination at high temperatures ($\geq 500\text{ }^\circ\text{C}$) for several hours leading to the decomposition of organic molecules and the formation of the protonated zeolite.^{18, 92} This can be seen in the FTIR profile of H-ZSM-5 (see Figure A.18) where the peaks associated with $\text{NH}_3/\text{NH}_4^+$ (3635 , 1629 , and 1450 cm^{-1}) species are absent.

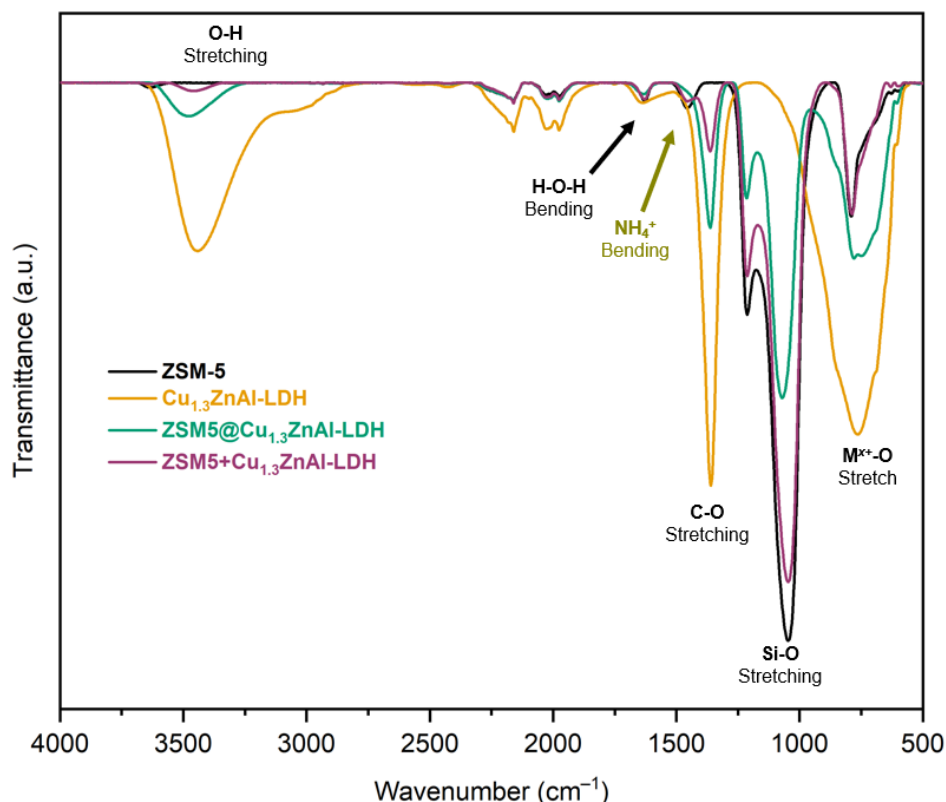


Figure 2.9: FTIR profiles of the catalyst precursors ZSM5@Cu_{1.3}ZnAl-LDH, ZSM5+Cu_{1.3}ZnAl-LDH, Cu_{1.3}ZnAl-LDH, and ZSM-5.

The Cu_{1.3}ZnAl-LDH sample demonstrates peaks that are characteristic of an LDH. Transmittance observed between 3670 and 2760 cm⁻¹ corresponds to the O-H stretching of hydroxyl groups on the LDH layers and of water within the interlayers; the peak at 1630 cm⁻¹ is also due to H₂O bending.⁵⁷ The peak at 1360 cm⁻¹ is indicative of the asymmetric stretching of interlayer carbonate ions (ν_3 -CO₃²⁻ stretching) in the LDH, whilst the broader peaks around 780 cm⁻¹ are likely a combination of the CO₃²⁻ bending mode and lattice vibrations (i.e. M^{x+}-O, M^{x+}-OH and O-M^{x+}-O).^{93, 94}

A summary of the transmittance peaks can be found in Table 2.4 and demonstrates that the majority of the peaks associated with the LDH and ZSM-5 phases are present in the core-shell and physical mixture precursor samples. The 3635 cm⁻¹ peak (originating from

ZSM-5) is present only in the case of the physical mixture which suggests a change in the environment of the Brønsted acid sites. This may be due to ion-exchange between NH_4^+ and $\text{Cu}^{2+}/\text{Zn}^{2+}/\text{Al}^{3+}$ ions occurring during the coprecipitation of ZSM5@Cu_{1.3}ZnAl-LDH. ZSM5+Cu_{1.3}ZnAl-LDH also has a small broad peak between 3569 – 3332 cm⁻¹ from the O-H stretching of hydroxyl groups in the LDH phase. The weak peak at 1630 cm⁻¹ is present in both the physical mixture and the core-shell arising from the NH_4^+ groups in the ZSM-5 phase.

Table 2.4: Summary of FTIR absorbance frequencies and associated functional groups for ZSM5@Cu_{1.3}ZnAl-LDH, ZSM5+Cu_{1.3}ZnAl-LDH, Cu_{1.3}ZnAl-LDH, and ZSM-5.

Sample	Frequency (cm ⁻¹)	Functional group
ZSM5@Cu _{1.3} ZnAl-LDH	3639 – 3226	O-H stretching
	1630	H ₂ O bending / NH ₃ bending
	1360	$\nu_3\text{-CO}_3^{2-}$ stretching
	1213	SiO ₄ tetrahedron units
	1041	Si–O–T (T = Si or Al)
	780	CO_3^{2-} bending mode, $\text{M}^{x+}\text{-O}$, $\text{M}^{x+}\text{-OH}$ and $\text{O-M}^{x+}\text{-O}$ lattice vibrations

Sample	Frequency (cm ⁻¹)	Functional group
ZSM5+Cu _{1.3} ZnAl-LDH	3635	NH ₄ ⁺ bending
	3569 – 3326	O-H stretching
	1630	H ₂ O bending / NH ₃ bending
	~1450	NH ₄ ⁺ bending
	1360	ν_3 -CO ₃ ²⁻ stretching
	~1210	SiO ₄ tetrahedron units
	1041	Si–O–T (T = Si or Al)
Cu _{1.3} ZnAl-LDH	780	CO ₃ ²⁻ bending mode, M ^{x+} –O, M ^{x+} –OH and O–M ^{x+} –O lattice vibrations
	3670 – 2760	O-H stretching
	1630	H ₂ O bending
	1360	ν_3 -CO ₃ ²⁻ stretching
	780	CO ₃ ²⁻ bending mode, M ^{x+} –O, M ^{x+} –OH and O–M ^{x+} –O lattice vibrations

Sample	Frequency (cm ⁻¹)	Functional group
ZSM-5	3635	NH ₄ ⁺ bending
	1629	N-H (free NH ₃) bending
	~1450	NH ₄ ⁺ bending
	~1200	Asymmetric stretching vibration
	1047	Internal asymmetric stretching vibration of Si–O–T (T = Si/Al)
	788	Symmetric stretching of the T–O in external linkages

Results from the FTIR analysis largely confirm that the functional groups associated with both the Cu_{1.3}ZnAl-LDH and ZSM-5 phase are present in the hybrid precursor CTD catalysts. The analysis also suggests that some ion exchange has occurred in the zeolite core of ZSM5@Cu_{1.3}ZnAl-LDH as a consequence of the coprecipitation method used to synthesize the core-shell.

The thermal stabilities of ZSM5@Cu_{1.3}ZnAl-LDH, ZSM5+Cu_{1.3}ZnAl-LDH, Cu_{1.3}ZnAl-LDH and ZSM-5 were evaluated by thermogravimetric analysis (TGA) and are shown in Figure 2.10. For ZSM-5, a weight loss of 8.2% between 30 – 250 °C is attributed to the loss of surface-adsorbed water and water trapped within the pores of the zeolite.³⁵ A subsequent weight loss of 2.2% between 300 – 500 °C is associated with decomposition of organic molecules.¹⁹ These weight loss regions (WLRs) are more easily

observable in the dTGA profiles. The weak, broad peak in the second WLR suggests that the pristine ZSM-5 is largely template free, with the weight loss likely resulting from the decomposition of NH_4^+ . At this temperature, the protonated H-ZSM-5 zeolite is formed. H-ZSM-5 was synthesised from the calcination of the pristine NH_4 -ZSM-5 at 500 °C for 3 h, reflecting the eventual catalyst activation conditions. The synthesised H-ZSM-5 was also characterised by TGA and showed only one WLR (9.7%) between 30 – 250 °C with a similar residual weight (89.6%) as ZSM-5 (see Figure A.19). This demonstrates the high thermal stability of ZSM-5 and suggests that the catalyst activation conditions generates the protonated form of the zeolite which is required for the MTD reaction.¹⁹

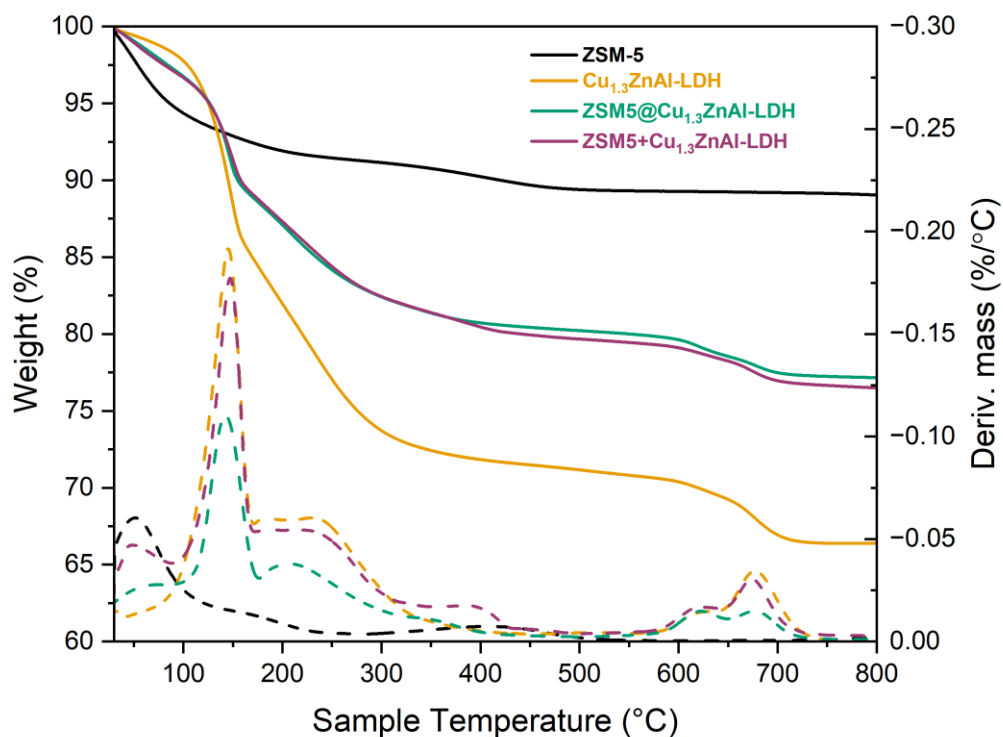


Figure 2.10: TGA and dTGA curves of the core-shell and physical mixture ($\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH}$ and $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDH}$) in comparison to the pure ZSM-5 and $\text{Cu}_{1.3}\text{ZnAl-LDH}$.

The dTGA profile of $\text{Cu}_{1.3}\text{ZnAl-LDH}$ displays several weight loss events that are typical for LDHs.⁹⁵ The first WLR occurs below 100 °C and is associated with the loss of weakly

adsorbed water on the crystal surface (0.5%).^{96, 97} The rapid weight loss seen in the dTGA profile between 100 – 200 °C (17.7%) is attributed to the loss of interlayer water.^{96, 97} Thermal events observed between 200 – 400 °C are associated with lattice dehydroxylation and partial decomposition of the interlayer carbonate anions with a weight loss of 10.1%.^{97, 98} At these temperatures, the LDH transforms into LDOs.⁹⁹ A CuAl_2O_4 spinel phase is often reported for CZA LDHs calcined at temperatures above 400 °C.^{65, 100, 101} The last weight loss of about 4.8% occurs between 500 – 800 °C and is due to desorption of strongly held CO_3^{2-} anions leading to the full decarbonation of the LDH.^{99, 102} Calcination of the LDH above 400 °C leads to collapse of the layered structure forming amorphous mixed metal oxides.⁶⁵ Thermal decomposition studies in combination with *in-situ* FTIR analysis of CuZnAl LDHs have suggested that the material in this temperature region is an $\text{M}^{2+}\text{M}^{3+}\text{O}_y(\text{CO}_3)_2$ oxycarbonate.¹⁰³ The two peaks observed in the dTGA may be due to $\text{M}^{2+}\text{M}^{3+}\text{O}_y(\text{CO}_3)_2$ with different thermal stabilities although the determination of these species is unclear.^{103, 104} This effect has been observed in other Cu containing LDHs.¹⁰⁴

TGA confirms the presence of both the LDH and zeolite phases in ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH. WLRs for ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH that occur between ambient temperature and 200 °C are attributed to the loss of physisorbed water from the from the LDH and ZSM-5, between 200 – 400 °C to the dehydroxylation of the LDH layers and decomposition of charge compensating anions, and lastly between 500 – 800 °C to the full decarbonation.^{58, 67, 105} The two peaks observed in the dTGA associated with the decomposition of oxycarbonate intermediates are present in both hybrid samples.

ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH displayed similar weight losses in each region with a residual weight of ~77.3% (consult Table A.7 for full summaries of the weight loss percentages). This corresponds to a ZSM-5:LDH ratio of 1:1.1, which closely matches the 1:1 weight ratio used in both the core-shell synthesis and the physical mixture. This suggests that: (a) coprecipitation of the LDH in the presence of ZSM-5 does not affect the yield of LDH (as the approximate weight of the LDH in the core-shell sample matches the anticipated amount based on the synthesis of Cu_{1.3}ZnAl-LDH), (b) the preparation of ZSM5+Cu_{1.3}ZnAl-LDH produces a well-mixed sample, and (c) ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH possess similar thermal stabilities.

N₂ adsorption studies were conducted to investigate the textural properties of the catalyst precursors. The t-plots for nitrogen adsorption at 77 K were used to estimate the Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) and micropore volumes (V_{micro}) which are summarised in Figure 2.11 (see Table A.8 for additional details).

Pristine ZSM-5 is observed have the largest overall S_{BET} (382 m²/g) which is primarily due to the substantial micropore surface area (339 m²/g). This is characteristic of the microporous structure of zeolites.⁶¹ Conversely, the low S_{BET} value exhibited by Cu_{1.3}ZnAl-LDH (62 m²/g) is dominated by the external surface area (44 m²/g). The poor internal surface area and low V_{micro} (0.008 m³/g) of Cu_{1.3}ZnAl-LDH is indicative of the aggregation effect in pure LDH, which forms stone-like particles (as demonstrated in the SEM images) with low surface areas.^{70, 106-108}

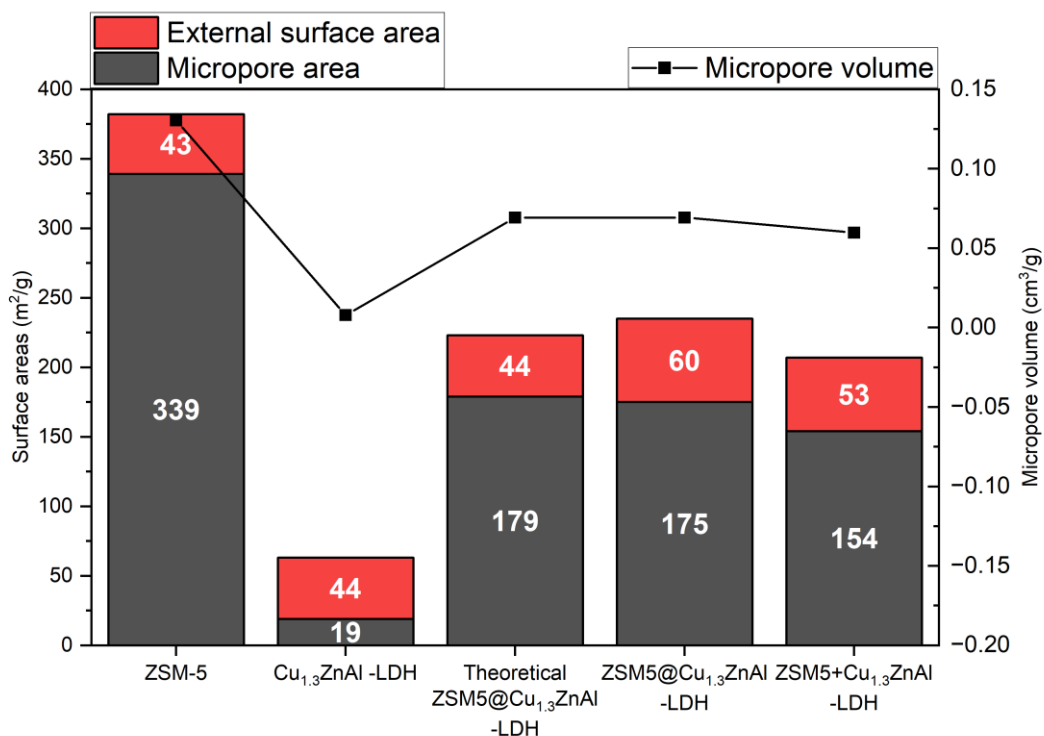


Figure 2.11: N₂ BET surface areas and micropore volumes of the ZSM-5, Cu_{1.3}ZnAl-LDH, ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH precursors. The grey and red bars show the estimated micropore surface area and external surface area respectively, while the line plot shows the estimated micropore volume of the samples.

Similar to ZSM-5, the micropore surface area (S_{Micro}) of ZSM5@Cu_{1.3}ZnAl-LDH (175 m²/g) is the main contributor to overall surface area (235 m²/g). Based on the surface area values for ZSM-5 and Cu_{1.3}ZnAl-LDH, values for the external surface area (S_{External}), S_{Micro} and V_{Micro} were calculated for a theoretical hybrid mixture with a 1:1 LDH:ZSM-5 ratio. Whilst the S_{Micro} for the core-shell is in good agreement with the theoretical S_{Micro} , the external surface area of the core-shell sample (60 m²/g) is higher than expected. Although the S_{External} of the physical mixture (53 m²/g) is slightly lower than the core-shell, the difference is minimal and the external surface areas of the hybrid samples is assumed to be the same. ZSM5@Cu_{1.3}ZnAl-LDH demonstrates improved surface areas compared to the physical mixture due to the lower micropore surface areas in

ZSM5+Cu_{1.3}ZnAl-LDH which may indicate that platelet aggregation occurs more readily in the physical mixture sample.

N₂ adsorption-desorption isotherms were used to identify the porosity type of the catalyst precursor materials (Figure 2.12). The LDH displays a type II isotherm with an H3 hysteresis loop at high relative pressure indicating a macroporous adsorbent with poorly defined pore shapes/sizes.¹⁰⁹ This is due to the slit-like mesopores/macropores in the LDH and is consistent with similar LDHs reported in literature.^{70, 110, 111} At low relative pressure ZSM-5 demonstrates a classic type I isotherm that is indicative of a microporous material.¹¹⁰ Thus, in the case of the hybrid core-shell/physical mixture compounds, both the type I ($< 0.3 (p/p^0)$) and type II ($> 0.3 (p/p^0)$) isotherms are observed. At high relative partial pressures ZSM-5 displays a small type IV hysteresis loop which arises from mesoporous interstitial spaces between single crystal agglomerates.¹¹² This is also observed in the ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH samples.

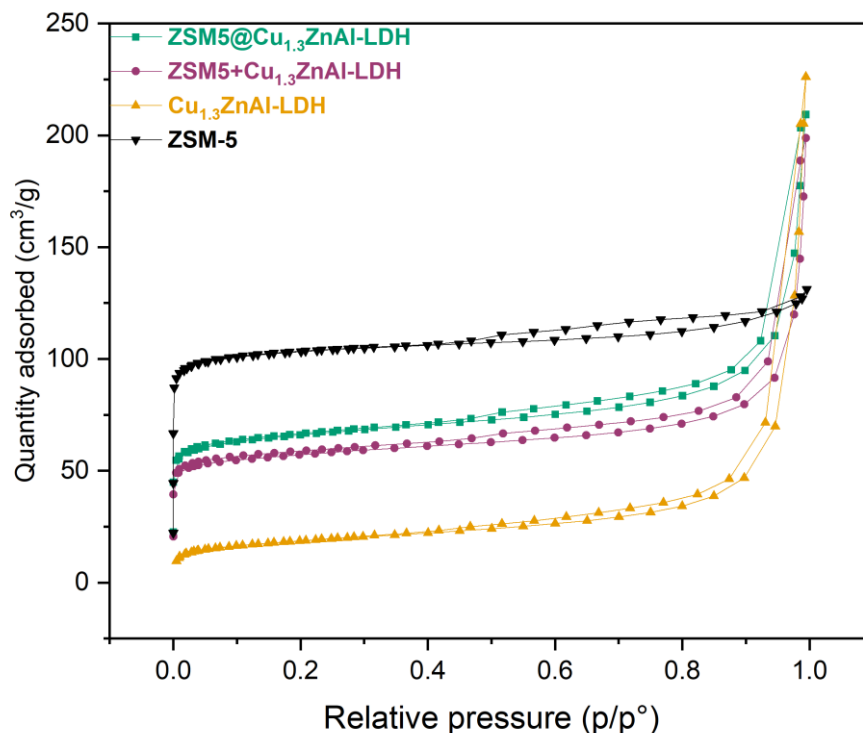


Figure 2.12: N_2 adsorption isotherms of ZSM-5, $Cu_{1.3}ZnAl$ -LDH, ZSM5+ $Cu_{1.3}ZnAl$ -LDH and ZSM5@ $Cu_{1.3}ZnAl$ -LDH.

The Barrett-Joyner-Haleda (BJH) model was applied to the adsorption branch of the isotherms and was used to determine the mesopore size distribution of the samples (Figure 2.13a). The broad distribution profile for $Cu_{1.3}ZnAl$ -LDH indicates that the pore sizes in the LDH are non-uniform. This is likely due to intense platelet aggregation in the LDH which is typically observed in LDHs on account of the high surface charges of the metal hydroxide layers.^{54, 70, 71, 113} Adsorption between 2 – 50 nm suggests there are mesopores between stacked nanoplatelets of the LDH, whilst pores larger than 50 nm are associated with macropores and is typical of an LDH of this type.^{54, 106, 114, 115} Based on the high N_2 uptake for pore sizes in the meso- and macropore dimensions it can be said that the majority of the pores in the LDH are macroporous whereas pristine ZSM-5 is largely microporous. ZSM5+ $Cu_{1.3}ZnAl$ -LDH demonstrates a slightly broader

distribution profile in the macropore region than for ZSM5@Cu_{1.3}ZnAl-LDH which suggests that the pore sizes in the physical mixture are less uniform than the core-shell. The density functional theory (DFT) model was used to determine micropore size distribution and was applied to the adsorption branch of the isotherms (Figure 2.13b). As anticipated no microporosity was observed for Cu_{1.3}ZnAl-LDH whereas ZSM-5 presented one major micropore size with a 0.4 nm radius (which is consistent with sizes reported in the literature).¹¹⁶ The micropore size distribution of ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH was compared against ZSM-5. The hybrid samples also showed an average micropore diameter of 0.4 nm stemming from the ZSM-5 core and demonstrated similar pore size distributions when compared against each other. The lack of peaks at 0.6 nm or 1.1 nm suggests some micropore blocking might have occurred. The generation of new peaks at 0.9 nm and 1.3 nm may be due to the interaction of the LDH with the surface of the ZSM-5 core.

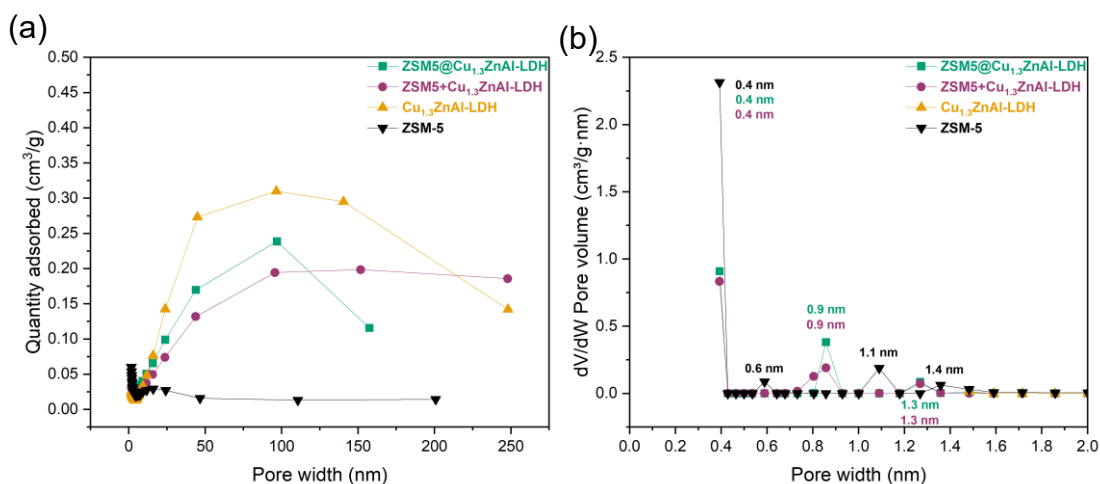


Figure 2.13: (a) BJH pore size distribution and (b) DFT size distribution of ZSM-5, Cu_{1.3}ZnAl-LDH, ZSM5+Cu_{1.3}ZnAl-LDH and ZSM5@Cu_{1.3}ZnAl-LDH.

It should be noted, however, that for more accurate micropore size determination, N₂ is not the preferred adsorbate due to the limitations of N₂ adsorption at low p/p^0 .¹¹⁷ Ar

physisorption at 87 K is often used as an alternative to nitrogen for BET analysis of microporous materials such as zeolites, due to its lack of quadrupole moment.¹¹⁸ From this it may be possible to more accurately determine the extent of ion-exchange/pore blocking within the micropores of ZSM-5 as a consequence of the coprecipitation method.

These observations suggest that the directed growth of LDH on the ZSM-5 core reduces LDH platelet aggregation and thus increases the overall surface area. In comparison to the physical mixture, the ZSM5@Cu_{1.3}ZnAl-LDH core-shell demonstrates greater external and internal surface areas. The data also suggests that the coprecipitation method does not cause significant micropore blocking in the ZSM-5 core which is crucial to ensure effective mass transport through the zeolite.

2.2.3: Characterisation of activated ZSM5/Cu_{1.3}ZnAl catalysts

ZSM5@Cu_{1.3}ZnAl was designed as a hybrid CO₂ hydrogenation-methanol dehydrogenation catalyst for direct CO₂ conversion. The catalyst is generated following the calcination and subsequent reduction of the ZSM5@Cu_{1.3}ZnAl-LDH precursor. As previously discussed, the synthesis method of the bifunctional CTD catalyst can influence its catalytic performance. Accordingly, the method used to activate the catalyst from its precursor must also be carefully considered. However, the wide variation in reported procedures, such as the range of calcination temperatures used for copper-based/ZSM-5 bifunctional catalysts, presents a challenge in establishing an optimum activation method.^{29, 42, 119} The conditions used in this work follow a similar method to previous work published in the O'Hare group concerning a ES757@Cu_{1.3}ZnAl core-shell catalyst for CTM conversion.⁵⁴

ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH catalyst precursors were ex-situ calcined in air at 500 °C for 3 hours. At 500 °C, LDHs undergo dehydration and decarbonylation forming LDOs, thus, all calcined samples are described using the ‘LDO’ tag e.g. Cu_{1.3}ZnAl-LDO or ZSM5@Cu_{1.3}ZnAl-LDO and were dark green in colour. The calcined samples were then reduced in H₂ for 2 hours at 260 °C (2 °C/min) to match the *in-situ* reduction conditions that would be used to generate the catalyst (see Chapter 6.2.5). The active catalysts are described without the ‘LDH’ suffix, e.g. Cu_{1.3}ZnAl (activated LDH), ZSM5@Cu_{1.3}ZnAl (activated core-shell) and ZSM5+Cu_{1.3}ZnAl (activated physical mixture) and are all black powders.

PXRD patterns of the fresh core-shell, physical mixture and LDH-derived catalysts are summarised in Figure 2.14. Reflections from the sample holder appear as a sharp Bragg reflection $2\theta = 6.5^\circ$ and a broad region between $2\theta = 15 - 40^\circ$. The profile for Cu_{1.3}ZnAl shows indistinguishable peaks that suggest a homogenous dispersion of metal/metal oxide species and is characteristic of mixed oxide materials.¹²⁰ Based on the results from hydrogen temperature programmed reduction (H₂-TPR), it is anticipated that the majority of the CuO species formed following calcination of the Cu_{1.3}ZnAl-LDH precursor would have been reduced to metallic Cu⁰ nanoparticles at 260 °C. Whilst the broad peak between $2\theta = 25 - 35^\circ$ arises from the PXRD sample holder, the peak between $2\theta = 35 - 40^\circ$ may be due to partially reduced Cu₂O and/or oxidised CuO. However, due to the amorphous character of the catalyst, the extent of which these species are present in the sample remains unclear. The peak at $2\theta = 43.3^\circ$ can be attributed to the (111) facet of Cu⁰ and suggests a large portion of the sample has been reduced.¹²¹

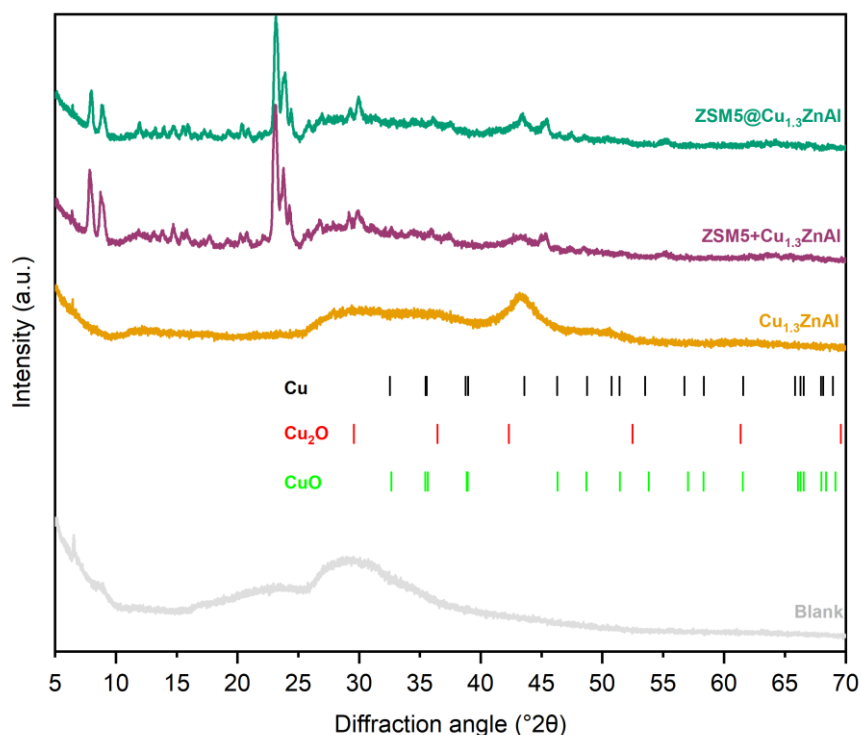


Figure 2.14: PXRD profile of the ZSM5@Cu_{1.3}ZnAl, ZSM5+Cu_{1.3}ZnAl and Cu_{1.3}ZnAl catalysts against a blank scan of the sample holder. The Cu, Cu₂O and CuO reflection ticks were taken from the simulated diffraction patterns in CrystalDiffract.

No changes were observed in the peaks associated with the ZSM-5 phase in the activated hybrid catalysts compared to pristine ZSM-5 suggesting that the structure of the zeolite is maintained following calcination and reduction (Figure A.20). The broad Cu⁰ (111) peak at $2\theta = 43.3^{\circ}$ is observed in both the core-shell and physical mixture catalysts which suggest that the catalyst preparation method was capable of reducing the CuO species formed following calcination. No major differences were observed in the PXRD patterns between the hybrid catalysts.

The morphology and nanostructure of the reduced catalyst was investigated by TEM characterisation. As shown in Figure 2.15 small black copper nanoparticles were widely distributed on LDO platelets. The sphere-like nanoparticles had narrow particle size

distributions and increased on the order of $\text{Cu}_{1.3}\text{ZnAl}$ (6.4 nm) < $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ (7.4 nm) < $\text{ZSM5+Cu}_{1.3}\text{ZnAl}$ (9.7 nm). The lattice fringes with d-spacing 2.08 Å and 2.81 Å were observed in all samples and are associated with the (111) and (101) lattice planes of Cu^0 and ZnO respectively (see Figure A.21 for the ZnO(101) plane in $\text{Cu}_{1.3}\text{ZnAl}$). The measured lattice spacings of 2.47 Å and 2.60 Å are attributed to the (101) and (002) crystal plane of ZnO. Cu(111) was the most predominant facet for the Cu phase which is in agreement with the results from PXRD analysis. Facets associated with the Al_2O_3 phase were not observed and is indicative of its amorphous structure.

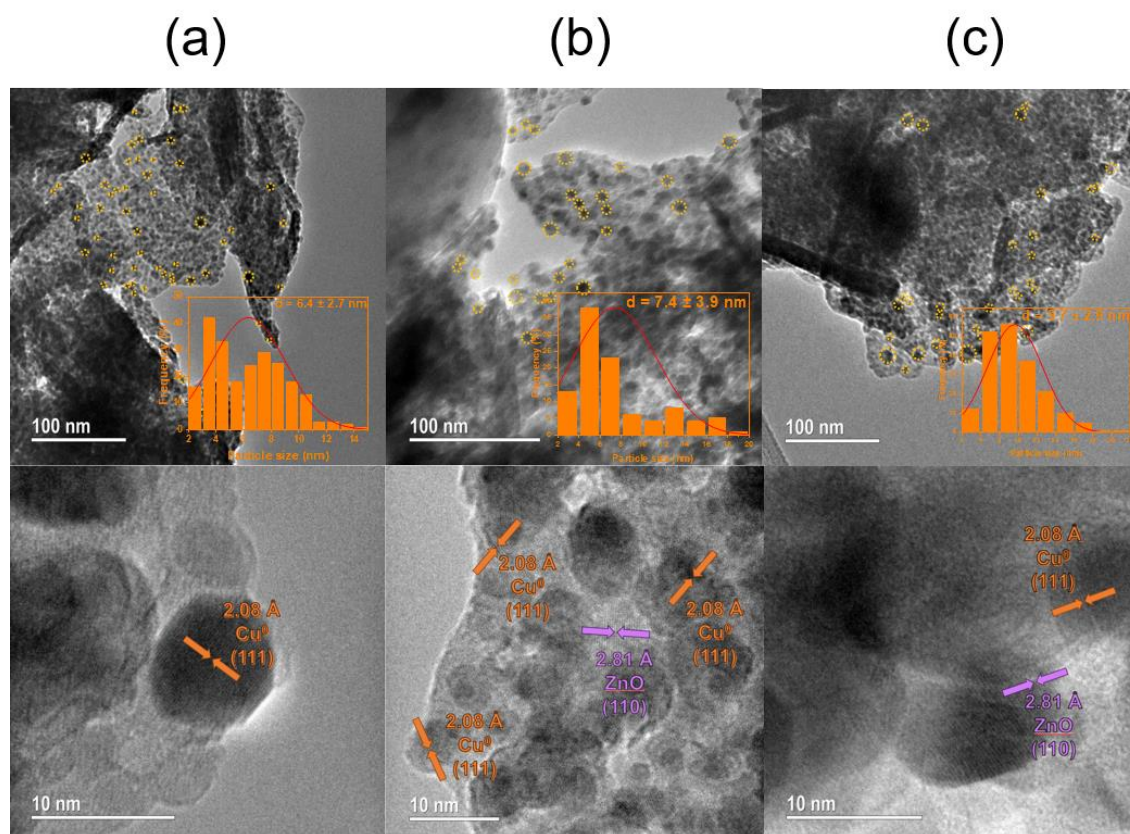


Figure 2.15: TEM images of the activated catalysts (a) $\text{Cu}_{1.3}\text{ZnAl}$, (b) $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$, and (c) $\text{ZSM5+Cu}_{1.3}\text{ZnAl}$.

The TEM micrographs show that the Cu nanoparticles in the catalysts are embedded in the LDO nanosheets and that there is an intimate contact between the Cu and ZnO phases.

It is widely known that the Cu/ZnO interface plays an important role in the methanol synthesis activity of CZA-type catalysts.¹²² Facets for Cu₂O or spinel ZnAl₂O₄ phases have been reported in other CZA catalysts which were not noticed here. High-resolution TEM (HR-TEM) can enable clearer visualization of lattice fringes, allowing for more accurate determination of interplanar spacings and a more precise evaluation of phase purity.

Temperature programmed desorption (TPD) analysis is a technique used to monitor the desorption of a molecule from the surface of a material as a function of temperature. The stronger the interactions between the molecule and the surface, the higher the temperature of desorption. By using CO₂ or NH₃ as the desorbing molecule, the basicity and acidity of the catalysts can be investigated. For information regarding the CO₂/NH₃-TPD method, see Chapters 6.1.8 and 6.1.9.

In the hydrogenation of CO₂ over CZA type catalysts, H₂ adsorption and dissociation occurs on Cu⁰ sites whilst CO₂ adsorbs on the surface of the ZnO/Al₂O₃ support.¹²³ The introduction of the aluminosilicate core may affect the basic properties of the CZA phase in the hybrid catalysts. Hence, CO₂-TPD was conducted to investigate the basicity of the CZA phase of the active core-shell catalyst, providing insight into how the material interacts with the reactant CO₂. The desorption profiles of the CO₂-TPD study for the ZSM5@Cu_{1.3}ZnAl, ZSM5+Cu_{1.3}ZnAl, Cu_{1.3}ZnAl and H-ZSM-5 catalysts are summarised in Figure 2.16. The quantitative data calculated from the deconvoluted spectra (Figure A.22) can be found in Table 2.5.

Only one desorption peak was observed in the CO₂-TPD profile for H-ZSM-5 which suggests that only one type of weak basic site is present in the sample. For zeolites these

sites are associated with the negatively charged lattice oxygen atoms.¹²⁴ Meanwhile the CO₂-TPD profile for Cu_{1.3}ZnAl demonstrates that the LDH-derived catalyst possesses weak (desorption below 260 °C), medium (desorption between 260 °C and 440 °C) and strong (desorption above 440 °C) basic sites. CO₂-TPD studies of CZA catalysts have typically attributed low temperature desorption with weak basic sites originating from Brønsted basic OH groups.^{125, 126} Previous work in the O'Hare group has confirmed that hydroxyl groups are present even after thermal treatment of the LDH at elevated temperatures.¹²⁷ The medium strength basic sites are associated with moderate metal-oxide pairs (Zn–O, Al–O) and the strongly basic sites are associated with coordinatively unsaturated O^{2–} ions.^{125, 126, 128} Features from H-ZSM-5 and Cu_{1.3}ZnAl appear in the CO₂-TPD profile for ZSM5@Cu_{1.3}ZnAl, where three major peaks associated with weak, medium and strong basic sites are observed.

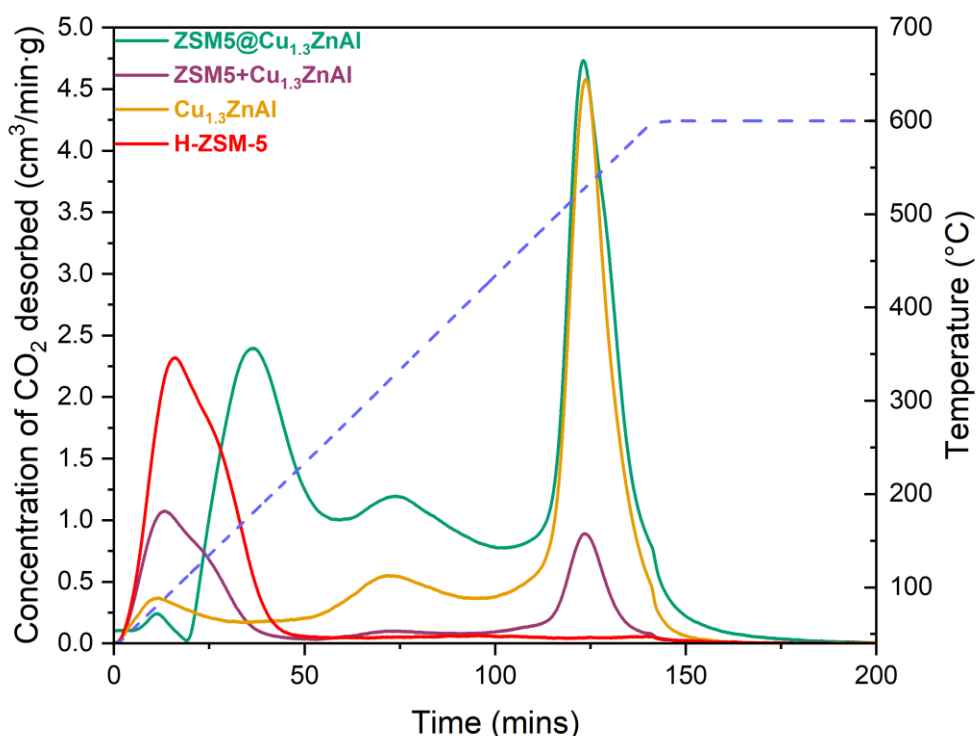


Figure 2.16: CO₂-TPD of ZSM5@Cu_{1.3}ZnAl, ZSM5+Cu_{1.3}ZnAl, Cu_{1.3}ZnAl and H-ZSM-5.

Table 2.5: Quantitative data of CO₂ chemisorption measurements for H-ZSM-5, Cu_{1.3}ZnAl, ZSM5@Cu_{1.3}ZnAl and ZSM5+Cu_{1.3}ZnAl.

Sample	CO ₂ uptake (cm ³ /g)	$T_{1,\text{CO}_2}^{\text{a}}$ (°C)	$T_{2,\text{CO}_2}^{\text{b}}$ (°C)	$T_{3,\text{CO}_2}^{\text{c}}$ (°C)
H-ZSM-5	51	91	-	-
Cu _{1.3} ZnAl	113	71	318	530
ZSM5@Cu _{1.3} ZnAl	199	180	329	526
ZSM5+Cu _{1.3} ZnAl	44	89	324	528

^a T_{1,CO_2} , temperature of maximum CO₂ desorption below 260 °C. ^b T_{2,CO_2} , temperature of maximum CO₂ desorption between 260 °C and 440 °C. ^c T_{3,CO_2} , temperature of maximum CO₂ desorption above 440 °C.

Based on the CO₂-uptake found for H-ZSM-5 (51 cm³/g) and Cu_{1.3}ZnAl (113 cm³/g), the CO₂ capacity for ZSM5+Cu_{1.3}ZnAl (44 cm³/g) was far lower than anticipated. Conversely, ZSM5@Cu_{1.3}ZnAl exhibited higher CO₂-uptake (199 cm³/g) than the combined CO₂ capacity of Cu_{1.3}ZnAl and H-ZSM-5 (164 cm³/g). The temperature of maximum desorption below 260 °C (T_{1,CO_2}) for the core-shell catalyst occurs at a higher temperature (180 °C) than ZSM5+Cu_{1.3}ZnAl suggesting that the strength of the weak basic sites in ZSM5@Cu_{1.3}ZnAl are improved. In ZSM5@Cu_{1.3}ZnAl, ZSM5+Cu_{1.3}ZnAl and Cu_{1.3}ZnAl, the temperature of maximum desorption between 260 – 440 °C (T_{2,CO_2}) and the temperature of maximum desorption above 440 °C (T_{3,CO_2}) occur at similar temperatures, however the intensity of T_{3,CO_2} is far greater in the core-shell compared to the physical mixture catalyst. This suggests that the nature of the strong basic sites in the CZA phase of ZSM5@Cu_{1.3}ZnAl remains largely unchanged and that the strong basic

sites of the hybrid catalysts originate from the CZA phase and not the H-ZSM-5 core. $\text{Cu}_{1.3}\text{ZnAl}$ does not possess a large number of weak basic sites (as indicated by the poor intensity of the T_{1,CO_2} (71°C) peak) which suggests that the weak basic sites in the hybrid catalysts originate from H-ZSM-5.

The results from CO_2 -TPD chemisorption experiments demonstrate that: (i) basic sites are present in all catalysts; (ii) the $\text{Cu}_{1.3}\text{ZnAl}$ phase possess weak, medium and strong basic sites which are also present in the hybrid catalysts; (iii) the generation of the core-shell catalyst $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ alters the weak basic sites associated with the $\text{Cu}_{1.3}\text{ZnAl}$ phase and improves the overall basicity of the catalyst.

It is not yet clear why the CO_2 capacity, and thus the basicity, of $\text{ZSM5+Cu}_{1.3}\text{ZnAl}$ is poorer than expected. Further work should be done to investigate the type of basic sites present in the LDH-derived phase. Pyrrole FTIR spectroscopy, whereby pyrrole is used as a probe molecule, is a common technique for determining the nature of basic sites.⁸³

Following the generation of methanol from CO_2 , an acidic catalyst is required to convert methanol into DME. Thus, NH_3 -TPD experiments were conducted to evaluate the strength of the acidic environments on the catalysts' surface. The results from the experiments are summarised in Figure 2.17.

The NH_3 -TPD profile for H-ZSM-5 shows two regions of desorption which is reflective of the profiles observed in the literature.¹²⁹⁻¹³¹ Typically, NH_3 -TPD experiments of protonated zeolites show a low temperature peak between 170 °C – 280 °C and a high temperature peak between 370 °C – 440 °C (associated with weak and strong NH_3 adsorption respectively).¹³⁰ Proton-exchanged zeolites like H-ZSM-5 possess both Brønsted and Lewis type acid sites. The Brønsted acid type sites in H-ZSM-5 are the

bridging hydroxyl groups of the Si–(OH)–Al unit and are considered as the main catalytic site.^{132, 133} The Lewis acid type sites in H-zeolites are typically associated with under-coordinated aluminium species, however there is still some ambiguity over their structure. Following dehydroxylation at elevated temperatures, Yakimov *et al.* used 1D/2D MAS NMR spectroscopy to identify the Lewis acid sites of protonated mordenite as tricoordinated Al adjacent to a siloxane bridge.^{129, 133} Lewis acid sites may also be introduced following treatments like dealumination or by heteroatom incorporation (e.g. Ti, Sn, Zr, Mg).^{132, 134} The low temperature peak of H-ZSM-5 has a T_{1, NH_3} at 100 °C with a shoulder at 180 °C (Table 2.6); peaks in this temperature region are associated with weakly adsorbed NH₃ on the catalyst surface and are not considered to be catalytically important.¹³⁵ Previous studies have suggested that the ammonia species desorbing at low temperatures are those that are hydrogen bonded to NH₄⁺ ions (conjugate acid) coordinated to lattice O atoms (conjugate base) in the H-zeolite.^{130, 136} Extra framework aluminium species like Al(OH)₂⁺ and Al(OH)₂²⁺ have also been described as having weakly acidic character.^{137, 138} The high temperature peak is associated with NH₃ bound to both strong Brønsted and strong Lewis acid sites.¹³⁰ Whilst NH₃-TPD can distinguish sites by sorption strength, it is not possible to separate the peaks by Brønsted or Lewis type. Further FTIR studies can be conducted to differentiate between the sites.

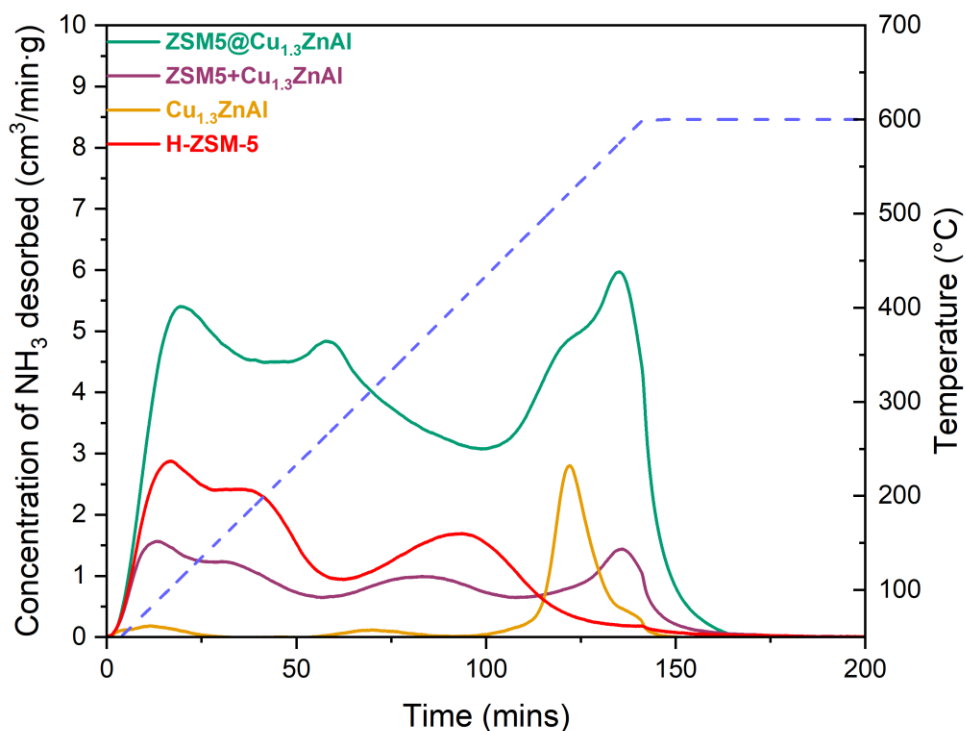


Figure 2.17: NH_3 -TPD profiles of $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$, $\text{ZSM5+Cu}_{1.3}\text{ZnAl}$, $\text{Cu}_{1.3}\text{ZnAl}$ and calcined ZSM-5 (H-ZSM-5).

Table 2.6: Quantitative data of NH_3 chemisorption measurements for H-ZSM-5, $\text{Cu}_{1.3}\text{ZnAl}$, $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ and $\text{ZSM5+Cu}_{1.3}\text{ZnAl}$.

Sample	NH_3 uptake (cm^3/g)	T_{1,NH_3}^a ($^\circ\text{C}$)	T_{2,NH_3}^b ($^\circ\text{C}$)	T_{3,NH_3}^c ($^\circ\text{C}$)
H-ZSM-5	189	100	407	-
$\text{Cu}_{1.3}\text{ZnAl}$	49	78	308	522
$\text{ZSM5@Cu}_{1.3}\text{ZnAl}$	566	113	264	575
$\text{ZSM5+Cu}_{1.3}\text{ZnAl}$	145	88	362	575

^a T_{1,NH_3} , temperature of maximum NH_3 desorption below 260 $^\circ\text{C}$. ^b T_{2,NH_3} , temperature of maximum NH_3 desorption between 260 $^\circ\text{C}$ and 440 $^\circ\text{C}$. ^c T_{3,NH_3} , temperature of maximum NH_3 desorption above 440 $^\circ\text{C}$.

Cu_{1.3}ZnAl shows some weak (desorption below 260 °C) and strong (desorption between 260 °C and 440 °C) acid sites, as well as one intense peak at 525 °C which corresponds to very strong interactions between NH₃ and the catalyst surface. Thus, the Cu_{1.3}ZnAl catalyst is observed to have only one type of very strong acidic site. CZA catalysts in the literature tend to show only one peak at low temperatures which are associated with the desorption of NH₃ hydrogen bonded to hydroxyl groups on the surface of the catalyst.¹³⁹ Following calcination at 500 °C, dehydroxylation of the LDH precursor might explain the poor intensity of the peaks in the low temperature region. The nature of the strong acidic site in Cu_{1.3}ZnAl should be investigated by pyridine FTIR.

Quantitative data was calculated from the deconvoluted spectra of the materials (see Figure A.23). From this, the NH₃ capacity of ZSM5@Cu_{1.3}ZnAl (566 cm³/g) was found to be far greater than either ZSM5+Cu_{1.3}ZnAl (156 cm³/g) or the combined capacity of Cu_{1.3}ZnAl and H-ZSM-5 (238 cm³/g). The broadness of the peaks suggests that desorption occurs across a variety of acidic sites with different strengths. Simultaneous desorption of NH₃ from acid sites with comparable strengths often lead to overlapping peaks within TPD profiles and is observable in the spectrums of all the materials.

The temperature of maximum desorption above 440 °C (T_{3,NH_3}) for ZSM5@Cu_{1.3}ZnAl and ZSM5+Cu_{1.3}ZnAl occurs at the same temperature (575 °C). A shoulder at 534 °C is also observed in the hybrid catalysts and occurs at a similar temperature to T_{3,NH_3} of Cu_{1.3}ZnAl (522 °C). Whilst this may be due to NH₃ adsorption to Lewis acidic Al³⁺-O²⁻-Cu or Al³⁺-O²⁻-Zn²⁺ sites in the CZA phase, it is also possible that the thermal conductivity detector (TCD) was detecting CO₂ gas produced from the decarbonisation of the LDO above 500 °C. As part of the catalyst preparation method, the samples are calcined at 500 °C prior to reduction. Based on the TGA profiles (Section 2.2.2), at

500 °C only partial decarbonisation of the LDH phase has occurred, with full decarbonisation initiating at temperatures close to 600 °C. The TCD detects any compounds with a different thermal conductivity to the carrier gas (in this case He) and as such is unable to distinguish between NH₃ and CO₂. The TGA results suggest that the majority of gas detected above 440 °C arises from NH₃ desorption at very strong acidic sites. As was the case for the CO₂-TPD analysis of the materials, the exact nature of the acidic sites is unknown and should be probed using pyridine FTIR for full characterisation.

For the weak desorption region, the peak shape of the NH₃-TPD profile for ZSM5+Cu_{1.3}ZnAl resembles that of H-ZSM-5, with T_{1,NH_3} occurring at ~100 °C and a shoulder occurring at ~170 °C. These two peaks are shifted to higher temperatures in the NH₃-TPD profile for ZSM5@Cu_{1.3}ZnAl which suggest there are stronger sites in the core-shell sample. The peak that appears at 264 °C for ZSM5@Cu_{1.3}ZnAl does not appear in the patterns for H-ZSM-5, Cu_{1.3}ZnAl or ZSM5+Cu_{1.3}ZnAl. This might suggest that the interaction between the H-ZSM-5 and Cu_{1.3}ZnAl phases in the core-shell sample results in new medium-strength acidic sites in the active catalyst. As mentioned previously, the acidic sites in a zeolite can be altered by heteroatom incorporation/dealumination which may have occurred during the coprecipitation (based on previous characterisation of the ZSM5@Cu_{1.3}ZnAl-LDH precursor). This may have trapped Cu²⁺/Zn²⁺ species or extra framework or generated more Al³⁺ species within the zeolite leading to the generation of new Lewis acid type sites.¹⁴⁰

NH₃-TPD analysis shows that a variety of acidic sites are present in the hybrid catalysts. Based on the peak shapes of H-ZSM-5 and Cu_{1.3}ZnAl, the majority of the acid sites found in the core-shell and the physical mixture is located in the zeolite phase. The combination

of H-ZSM-5 and Cu_{1.3}ZnAl may lead to the generation of strong acidic sites that are present in both the core-shell and physical mixture. The core-shell and physical mixture catalysts therefore possess different distributions of acidic sites, with the core-shell demonstrating higher NH₃ uptake and overall greater acidity. This suggests that the acidic properties of the hybrid catalysts are affected by the synthesis method (i.e. coprecipitation vs physical mixing).

N₂ adsorption studies were also conducted to investigate the surface area and pore-size distribution of the active catalysts.

A summary of the S_{Micro} , S_{External} and V_{Micro} of the catalysts (taken from the t-plots of nitrogen adsorption at 77K) can be found in Figure 2.18 and Table 2.7. The active core-shell (263 m²/g) and physical mixture (280 m²/g) catalysts had higher surface areas than the theoretical S_{BET} of the hybrid catalyst (based on the combined S_{BET} for H-ZSM-5 and Cu_{1.3}ZnAl (216 m²/g)). This was due to increases in both the S_{External} and S_{Micro} of the hybrid catalysts which suggests that the combination of the two phases facilitates higher surface area catalysts by improving the external and internal micropore surface areas. V_{micro} for ZSM5@Cu_{1.3}ZnAl (0.074 cm³/g) and ZSM5+Cu_{1.3}ZnAl (0.078 cm³/g) were also greater than V_{micro} of the theoretical hybrid catalyst (0.062 m³/g). This may be due to the generation of new micropores between the CZA and zeolite phases. ZSM5+Cu_{1.3}ZnAl possesses a slightly higher S_{External} (90 m²/g) than ZSM5@Cu_{1.3}ZnAl (78 m²/g), whilst the S_{Micro} for both catalysts are similar and fall within the error associated with BET measurements.

The S_{BET} , S_{External} and V_{micro} values estimated for H-ZSM-5 was similar to that for pristine ZSM-5 which suggests that calcination of the zeolite does not significantly alter its

textural properties (see Figure A.24 for comparisons between precursor and catalyst materials). For $\text{Cu}_{1.3}\text{ZnAl}$, catalyst activation significantly improved the overall S_{BET} of the material, which is expected based on previous research in calcined LDHs.^{106, 141} The core-shell and physical mixture catalysts demonstrate higher overall surface areas than their precursors. As there were no significant changes to the surface area of H-ZSM-5 (from its precursor ZSM-5), the higher S_{BET} values observed for the hybrid catalysts have been ascribed to surface area improvement in the CZA phase and new interactions between the CZA and zeolite phases. For the core-shell catalyst, S_{External} increases by only 30% in comparison to the 74% increase observed for the physical mixture catalyst. Likewise, S_{Micro} increases by 5% for $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ but by 23% for $\text{ZSM5+Cu}_{1.3}\text{ZnAl}$. Based on TEM images, $\text{ZSM5+Cu}_{1.3}\text{ZnAl}$ was described as having reduced LDOs in close proximity to ZSM-5 particles, whereas for $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ the reduced LDOs predominantly lay on the surface of the core. The close interaction between the CZA and zeolite phases in $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ may have slightly impacted the surface area of the material.

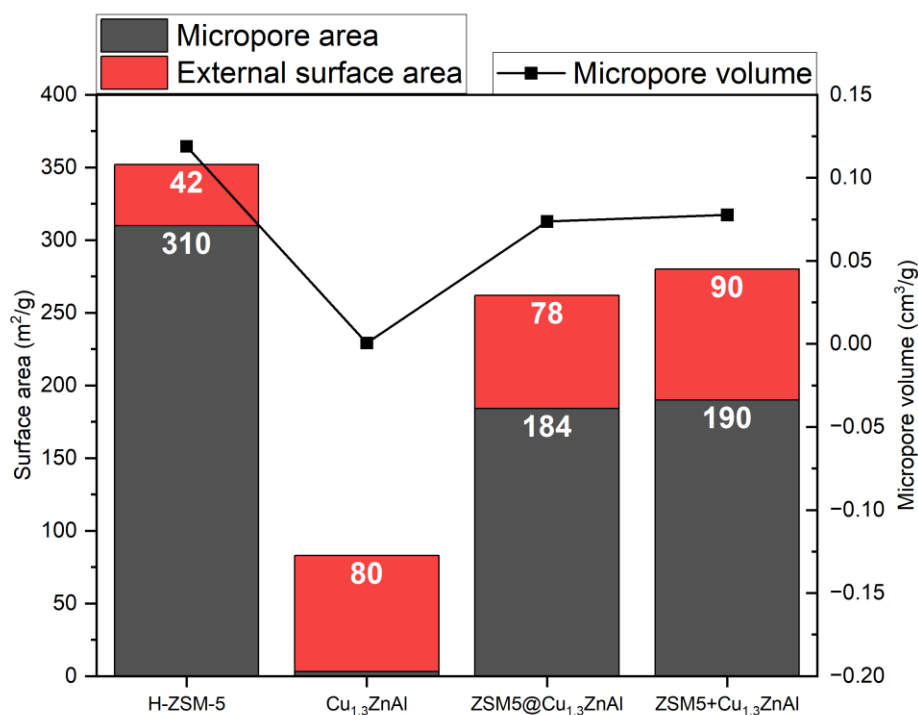


Figure 2.18: N₂ BET surface areas of activated ZSM5@Cu_{1.3}ZnAl, ZSM5+Cu_{1.3}ZnAl, Cu_{1.3}ZnAl and H-ZSM-5 catalysts. The grey and red bars show the estimated micropore surface area and external surface area respectively, while the line plot shows the estimated micropore volume of the samples.

Table 2.7: Textural properties of activated ZSM5@Cu_{1.3}ZnAl, ZSM5+Cu_{1.3}ZnAl, Cu_{1.3}ZnAl and H-ZSM-5 catalysts.

Sample	S_{External} (m ² /g)	S_{Micro} (m ² /g)	S_{BET} (m ² /g)	V_{Micro} (cm ³ /g)
ZSM5@Cu _{1.3} ZnAl	78	184	263	0.074
ZSM5+Cu _{1.3} ZnAl	90	190	280	0.078
Cu _{1.3} ZnAl	80	3	83	0.005
H-ZSM-5	42	310	352	0.119

The N₂ adsorption-desorption isotherms of the catalysts are presented in Figure 2.19a. H-ZSM-5 displays the same type of isotherm as ZSM-5 (see Section 2.2.2). High N₂ uptake at low relative pressure (< 0.3 (p/p^0)) with a type I isotherm (which plateaus at medium relative pressures) is indicative of a highly microporous material with low external surfaces.¹⁴² Isotherms of this type are typical for zeolites.^{61, 142, 143} A small type IV hysteresis loop is also observed at high relative pressure (> 0.5 (p/p^0)) which suggests there is some mesoporosity in H-ZSM-5.¹⁰⁹ For ZSM-5, the mesoporosity was ascribed to the interstitial spaces between crystal agglomerates and is assumed to be the same mesoporosity observed in H-ZSM-5.¹¹² Compared to its precursor, the Cu_{1.3}ZnAl catalyst showed a similar type II isotherm with H3 hysteresis loop with a much higher N₂ uptake at high relative pressure.¹⁰⁹ This suggests a significant increase in the amount of slit-like mesopores/macropores in the LDH-based catalyst and is consistent with the large increase in S_{BET} .

The isotherms for ZSM5@Cu_{1.3}ZnAl and ZSM5+Cu_{1.3}ZnAl show characteristics of both the zeolite and CZA phase. N₂ uptake at $p/p^0 < 0.3$ suggests the hybrid catalysts possess microporosity (from the H-ZSM-5 core) and uptake at $p/p^0 > 0.5$ indicate mesoporosity from the CZA phase. N₂ uptake for ZSM5+Cu_{1.3}ZnAl was slightly higher which is consistent with the S_{BET} values previously described.

Average pore diameters of the catalysts were obtained by applying the BJH model to the adsorption branch of the N₂ isotherm and are summarised in Figure 2.19b. Compared to the pore sizes of Cu_{1.3}ZnAl-LDH, Cu_{1.3}ZnAl has a much narrower pore size distribution with sizes between 2 – 50 nm, i.e. the range indicative of mesopores, whereas the LDH had a higher distribution of macropores. Pore size distribution in the mesopore range appears to be similar for ZSM5@Cu_{1.3}ZnAl and ZSM5+Cu_{1.3}ZnAl. Figure 2.19c shows

the micropore size distribution of the catalysts obtained using the DFT model on the adsorption branch of the N_2 isotherm. The 0.4 nm micropores dominating in ZSM-5 (as described in Section 2.2.2) is present in H-ZSM-5, ZSM5@Cu_{1.3}ZnAl and ZSM5+Cu_{1.3}ZnAl. The 0.6, 1.1 and 1.4 nm micropores found in ZSM-5 are also present in H-ZSM-5 which again suggests there are no major structural changes to the micropore region of the zeolite following catalyst activation. Changes to the microporosity in the core-shell and physical mixture catalysts are therefore associated with the interactions between the CZA and ZSM-5 components. Comparing the micropore size distribution of the catalysts to the precursor materials, it can be seen that catalyst activation leads to a loss of the 0.9 nm size micropore present in ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH. It also generates 1.4 nm micropores that are associated with micropores within the zeolite. 1.2 nm micropores are only found in ZSM5@Cu_{1.3}ZnAl which suggests that these micropores stem from the interaction between the CZA and H-ZSM-5 phase and not from the core.

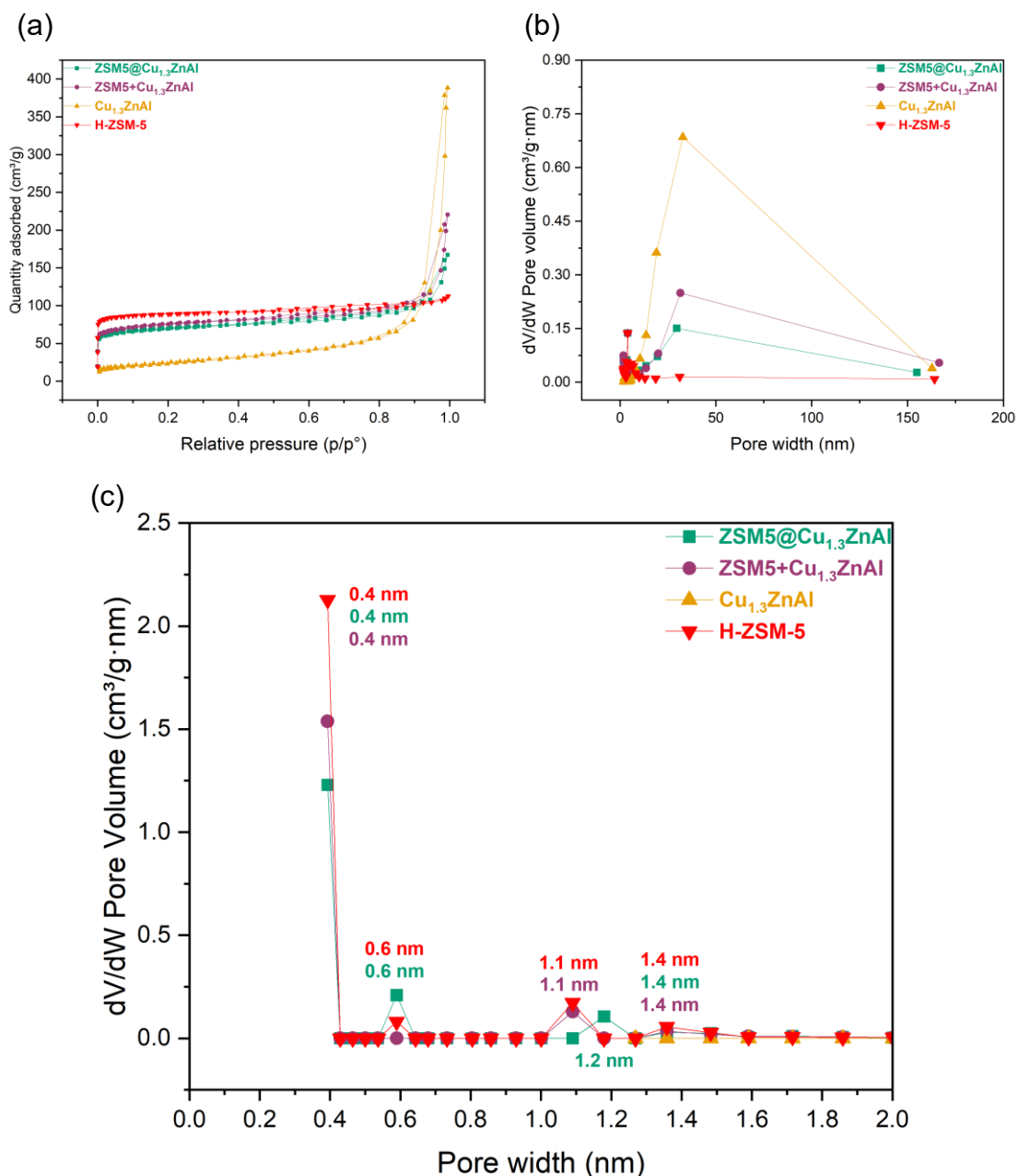


Figure 2.19: (a) N₂ adsorption isotherms, (b) BJH pore size distribution, (c) DFT micropore size distribution of the active ZSM5+Cu_{1.3}ZnAl and ZSM5@Cu_{1.3}ZnAl, Cu_{1.3}ZnAl and H-ZSM-5 catalysts.

Results from the N₂ adsorption study suggest that whilst there are some changes to the micropore region between the core-shell and physical mixture catalysts, the textural properties between the core-shell and physical mixture catalysts are similar. It also demonstrates that the combination of the H-ZSM-5 and CZA phases by either method generates high surface area catalysts. The conversion of the LDH into the active catalyst

following calcination and reduction significantly improves the overall surface area of the LDH-based catalyst. This improvement in the CZA phase was reflected in the higher external surface areas of the hybrid catalysts. ZSM5+Cu_{1.3}ZnAl demonstrated higher overall surface areas and larger pore volumes than the ZSM5@Cu_{1.3}ZnAl which was possibly due to the greater aggregation between the H-ZSM-5 and CZA phases in the core-shell catalyst. Lastly, the results suggest that the microporosity of the zeolite core is largely preserved, with only a few changes to the micropore size distribution between ZSM5@Cu_{1.3}ZnAl and ZSM5+Cu_{1.3}ZnAl. Crucially, no major micropore blockage is observed in the core-shell catalyst which is crucial for efficient mass transport during CO₂ hydrogenation.

The characterisation of the activated catalysts therefore shows that the combination of the ZSM-5 phase with the Cu_{1.3}ZnAl phase generates hybrid catalysts with high overall surface areas with even dispersions of small Cu⁰ nanoparticles.

2.3: CO₂ hydrogenation performance of ZSM5/Cu_{1.3}ZnAl catalysts

Following *ex-situ* calcination in air at 500 °C, the calcined catalysts were loaded into a fixed-bed reactor and reduced *in-situ* under H₂ flow. Approximately 0.1 g of catalyst was reacted under CO₂:H₂:N₂ (24:72:4) flow with a weight hourly space velocity (WHSV) of 18,000 mL/g_{cat}·h and the products of the hydrogenation were analysed by GC. For full details of the testing method see Chapter 6.5. In the case of bifunctional catalysts designed for “one-pot” conversions the reaction conditions need to be considered in a way that encourages both CTM and MTD reactions whilst also suppressing the RWGS formation.

Based on the reaction conditions used for other hybrid CTD catalysts the temperature range for the CO₂ hydrogenation was tested between 220 – 300 °C.

The results for the hydrogenation of CO₂ on ZSM5@Cu_{1.3}ZnAl and ZSM5+Cu_{1.3}ZnAl are summarised in Figure 2.20 and Table 2.8. Space time yields were calculated using equation (6.4) in Chapter 6.5. Both catalysts produced a mixture of DME, methanol and CO, with the highest DME space time yields (STY_{DME}) observed between 260 °C – 280 °C. This is consistent with the optimum temperatures for direct CTD conversion reported in the literature.^{39, 42, 51, 144} Furthermore, no hydrocarbon products were observed under the adopted experimental conditions. The product selectivity of the hybrid catalysts was similar, where the selectivity towards DME (S_{DME}) decreases with increasing temperature, whilst CO selectivity (S_{CO}) steadily increased. This correlates with the thermodynamics associated with the initial CTM conversion and the competing RWGS reaction.¹⁴⁵ As the RWGS reaction is an endothermic process it becomes favoured at higher temperatures leading to greater CO production. The low conversion observed in the catalysts may be due to the poor kinetics of CO₂ conversion at lower temperatures and possibly competitive adsorption of CO₂ and CO (formed from the RWGS reaction).⁴² The results for ZSM5@Cu_{1.3}ZnAl and ZSM5+Cu_{1.3}ZnAl reflect the trends seen in similar catalysts where CO₂ conversion (X_{CO_2}) increases with temperature.^{28, 33, 42, 44} Hence, the conversion-selectivity relationship creates a volcano-like plot of S_{DME} , whereby the highest space time yields are observed when the competing RWGS reaction is minimised whilst the CO₂ conversion is maximised (Figure 2.20c). The STY_{DME} calculated for ZSM5+Cu_{1.3}ZnAl (0.41±0.05 g_{DME}/g_{cat}·h) was found to be greater than that of ZSM5@Cu_{1.3}ZnAl (0.37±0.03 g_{DME}/g_{cat}·h), however, the space time yields for the physical mixture catalyst was observed to have a larger margin of error. The error in the

DME STYs was evaluated through repeated experiments and was found to range between 10 – 20%. Therefore, a minimum error of 10% is assumed for all reported STY values in this work.

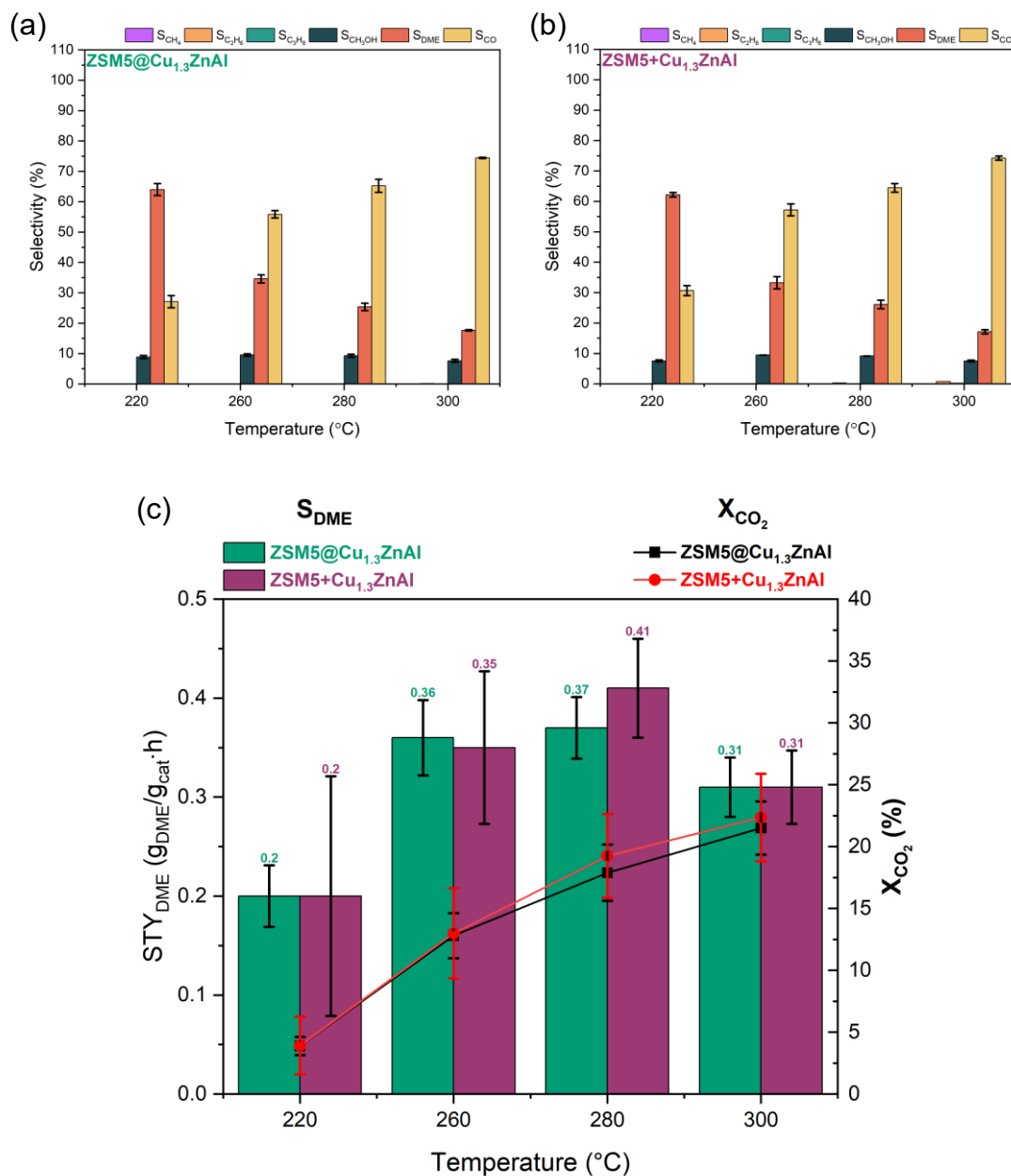


Figure 2.20: Product distribution of CO₂ hydrogenation reaction over (a) ZSM5@Cu_{1.3}ZnAl and (b) ZSM5+Cu_{1.3}ZnAl catalysts as a function of temperature (220 – 300 °C); (c) STY_{DME} and CO₂ conversions for ZSM5@Cu_{1.3}ZnAl and ZSM5+Cu_{1.3}ZnAl. Reaction conditions: $P = 3.0$ MPa; CO₂:H₂:N₂ = 24:72:4; WHSV = 18,000 mL/g_{cat}·h, carbon balance 97.70% – 102.45%.

Table 2.8: CO₂ hydrogenation results for ZSM5@Cu_{1.3}ZnAl and for ZSM5+Cu_{1.3}ZnAl.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)			Yield (%)	<i>STY</i> _{DME} (g _{DME} /g _{cat} ·h)
			<i>S</i> _{DME}	<i>S</i> _{CH₃OH}	<i>S</i> _{CO}	<i>Y</i> _{DME}	
ZSM5@Cu_{1.3}ZnAl	220	3.9±0.7	64.0±1.1	8.9±0.3	27.1±1.2	2.5±0.4	0.20±0.03
	260	12.8±1.8	34.6±1.3	9.5±0.4	55.8±1.2	4.4±0.6	0.36±0.04
	280	18±2	25.4±1.2	9.3±0.5	65.2±1.2	4.5±0.5	0.37±0.03
	300	22±2	17.6±0.2	7.6±0.5	74.4±0.2	3.8±0.3	0.31±0.03
ZSM5+Cu_{1.3}ZnAl	220	4±2	62.2±0.7	7.6±0.3	30.7±1.6	2.4±1.2	0.2±0.1
	260	13±4	33.3±2.0	9.45±0.04	57.2±2.0	4.3±1.4	0.35±0.08
	280	19±3	26.1±1.4	9.14±0.03	64.5±1.4	5.0±0.8	0.41±0.05
	300	22±4	17.1±0.7	7.5±0.3	74.2±0.7	3.8±0.7	0.31±0.04

^aReaction conditions: *P* = 3.0 MPa, CO₂/H₂/N₂ = 24:72:4, and *WHSV* = 18,000 mL/g_{cat}·h⁻¹.

The methanol selectivity ($S_{\text{CH}_3\text{OH}}$), S_{DME} and X_{CO_2} of the hybrid catalysts were compared against calculated thermodynamic equilibrium values collected from the literature and summarised in Figure 2.21.^{8, 32, 146} $S_{\text{CH}_3\text{OH}}$ of the catalysts is maintained across the temperature range at a threshold value between 7 – 10% which approaches the calculated equilibrium values and is observed in other hybrid catalysts (9 – 17%).^{28, 44} This suggests that the rate of methanol synthesis is in competition with methanol dehydration to form DME. Likewise, the S_{DME} and X_{CO_2} approach equilibrium values which suggests that the catalysts are under kinetic control.^{32, 44, 146}

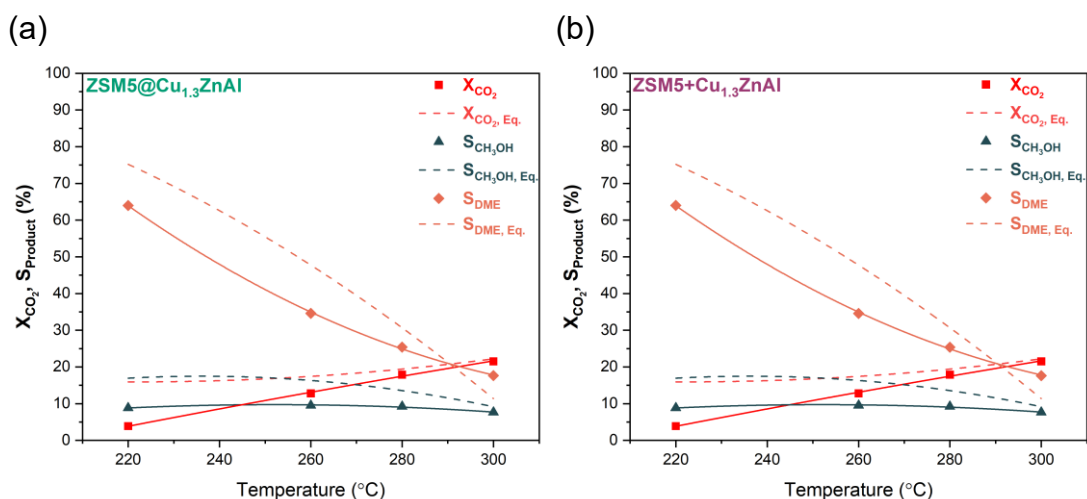


Figure 2.21: Summary of experimentally determined X_{CO_2} , S_{DME} and $S_{\text{CH}_3\text{OH}}$ of (a) ZSM5@Cu_{1.3}ZnAl and (b) ZSM5+Cu_{1.3}ZnAl compared to reported equilibrium conversion ($X_{\text{CO}_2, \text{Eq.}}$) and equilibrium selectivities of methanol ($S_{\text{CH}_3\text{OH}, \text{Eq.}}$) and DME ($S_{\text{DME}, \text{Eq.}}$) for CO₂ hydrogenation to DME.

In another hydrogenation test, calcined Cu_{1.3}ZnAl-LDO and ZSM-5 were loaded into the fixed-bed reactor and separated by a thin layer of quartz wool to understand how the complete separation of the catalyst phases might affect the overall CO₂ hydrogenation performance. Due to the poor CO₂ conversion of the hybrid catalysts between

220 – 240 °C, the temperature range was set between 260 – 340 °C. The results are summarised in Figure 2.22 and Table 2.9. Whilst the X_{CO_2} values at 260 °C (8.84%) and 280 °C (13.72%) were greater than the core-shell or physical mixture catalyst, the selectivity of the catalysts towards DME was significantly impacted and decreased rapidly as the temperature increased. The highest STY_{DME} was observed at 260 °C (0.28 g_{DME}/g_{cat}·h), with no DME production observed at temperatures at and above 300 °C. This suggests that close interaction between the CZA and H-ZSM-5 catalyst phases is necessary to facilitate DME formation.

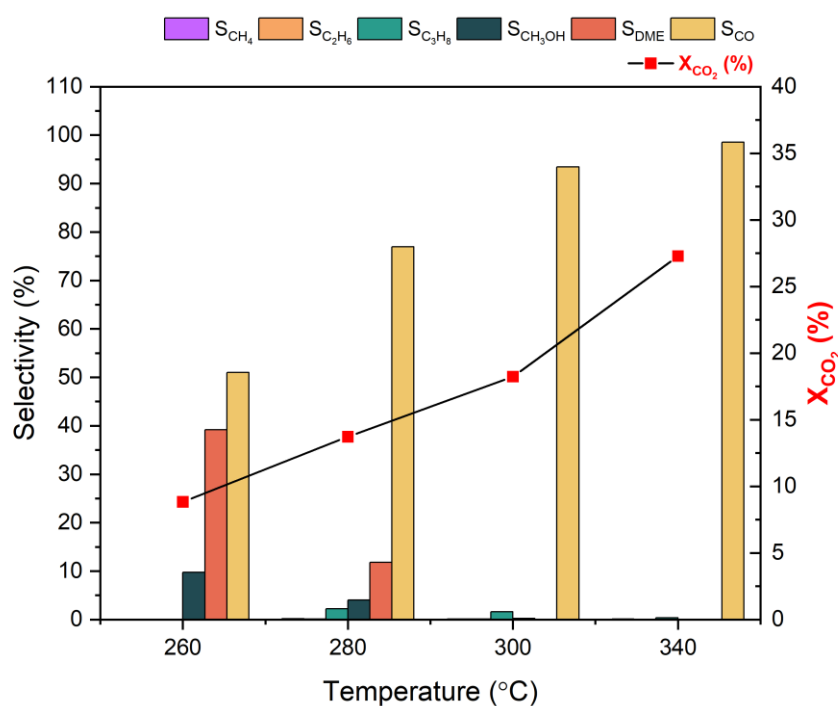


Figure 2.22: Product distribution of CO_2 hydrogenation reaction over fully separated $\text{Cu}_{1.3}\text{ZnAl}$ and H-ZSM-5 as a function of temperature (260 – 340 °C). Reaction conditions: $P = 3.0$ MPa; $\text{CO}_2:\text{H}_2:\text{N}_2 = 24:72:4$; $WHSV = 18,000$ mL/g_{cat}·h, carbon balance 97.89% – 101.44%.

Table 2.9: CO₂ hydrogenation results for fully separated Cu_{1.3}ZnAl and H-ZSM-5.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)			Yield (%)	STY_{DME} (g _{DME} /g _{cat} ·h)
			S_{DME}	S_{CH_3OH}	S_{CO}	Y_{DME}	
Fully separated ZSM5/Cu _{1.3} ZnAl	260	9	39	10	51	3	0.28
	280	14	12	4	77	2	0.13
	300	18	-	-	93	-	-
	340	27	-	-	99	-	-

^aReaction conditions: $P = 3.0$ MPa, CO₂/H₂/N₂ = 24:72:4, and $WHSV = 18,000$ mL/g_{cat}·h.

Results from the fixed-bed tests show that the combination of the $\text{Cu}_{1.3}\text{ZnAl}$ and H-ZSM-5 components as a hybrid catalyst facilitates the formation of methanol, DME and CO. The complete separation of the catalysts negatively impacts the CTD performance and the close contact between CZA and H-ZSM-5 is necessary to achieve high DME productivity. Whilst the error associated with the product selectivities are minimal, the error in the X_{CO_2} is considerable, especially in the case of $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl}$. The difference in X_{CO_2} between hydrogenation experiments may be due to improper mixing of the physical mixture catalyst compared to the core-shell $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$. Hence, the core-shell $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$ catalyst has a more consistent DME productivity than the physical mixture catalyst.

It is not clear why the performance of the core-shell and physical mixture catalysts is similar although there are differences in the surface areas, acidity and basicity. In both cases, CO_2 was converted to a mixture of CH_3OH , DME and CO and demonstrated good DME productivities.

2.4: Optimising CO_2 hydrogenation performance of $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$

CO_2 hydrogenation over the $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$ - catalyst showed relatively high DME productivity. This promising performance motivated further investigation into strategies to enhance the catalyst's activity. A wide range of factors could be systematically modified to influence catalytic behaviour, for instance, a potential avenue for improvement involves the separate optimization of the CZA and H-ZSM-5 catalyst

phases. The incorporation of promoters such as Na, Ga, Zr, for example, may alter the performance of the CZA phase by modifying metal dispersion, reducibility, or surface basicity.^{47, 147, 148} Similarly, various structural and compositional features of the zeolite component can be tuned to influence its catalytic efficacy.^{62, 124, 149} Prior studies have highlighted that the Si/Al ratio, and thus the acidity, of the zeolite strongly affects its function as a solid acid catalyst.^{36, 150-152} Furthermore, more the particle size and uniformity of the ZSM-5 crystals have been shown to influence methanol dehydration activity.¹⁴²

The catalyst activation method also plays an important role in determining the final physiochemical properties of the catalyst.^{28, 42, 153, 154} The parameters associated with calcination, including temperature, heating rate, gas flow rate, and calcination atmosphere, influence the structural properties of catalysts.¹⁵⁵⁻¹⁵⁸ For instance, the formation of LDOs from the thermal decomposition of LDHs is an important step that improves the properties of the LDH-based catalyst.^{57, 65, 159, 160} Likewise, the method and conditions used for catalyst reduction (i.e. temperature, reduction duration, and flow rate) can impact the performance of the material.^{153, 154}

In addition to catalyst design and preparation, it is also important to consider the operating conditions under which CO₂ hydrogenation is performed. One of the major challenges in comparing the performance of CTD catalysts across studies is the variability in reaction conditions. Changes to pressure, reactant flow rate, or feed gas composition has been known to affect the catalyst performance.^{8, 146, 161, 162}

Here catalyst preparation method and the reaction conditions of the CO₂ hydrogenation was investigated. Specifically, the effect of the calcination atmosphere during

ZSM5@Cu_{1.3}ZnAl activation, as well as increasing the reactant flow rate to achieve a higher WHSV comparable to industrial standards were examined.

2.4.1: Calcination atmosphere

Calcination is a common post-synthesis treatment to improve the catalytic properties of a material. It is well known that the calcination conditions affect the final physiochemical properties of the catalyst and must be chosen in a way that enhances the properties of the catalyst. In the work presented so far, the catalyst precursors were calcined in a tube furnace under air flow (50 mL/min) and heated to 500 °C at a ramp rate of 2 °C/min, holding for 3 hours before cooling to room temperature. At 500 °C the Cu_{1.3}ZnAl-LDH phase is transformed into the LDO and the ZSM-5 phase undergoes thermal decomposition to form the protonated H-ZSM-5.

Several publications have noted an impact on catalytic performance based on the calcination atmosphere due to structural differences in the catalysts following treatment in either an oxidising (O₂/air), reducing (H₂) or inert (N₂/Ar) environment.^{156-158, 163-167} The ideal calcination atmosphere is clearly dependent on the catalyst composition as well as the reaction the material is catalysing. For example, N₂ calcination of a Co₃O₄ toluene oxidation catalyst led to more uniform particle distribution and lower temperature reducibility resulting in an improved catalyst activity compared to the air or O₂ treated sample.¹⁶⁷ Kikhtyanin *et al.* found differences in the hydrogenolysis capability of CuZn catalysts depending on the calcination atmosphere, with greater CuO/ZnO contact observed in the catalyst pre-treated in an oxidising atmosphere.¹⁶⁴ Gao *et al.* demonstrated how a Cu/Al₂O₃ catalyst for furfural hydrogenation had enhanced conversion and selectivity when treated in N₂ as opposed to O₂.¹⁵⁷ Characterisation of the

catalysts suggested the N₂-treated Cu/Al₂O₃ had a larger number of Cu⁺ and Cu⁰ species which facilitated the hydrogenation.¹⁵⁷ The textural properties of H-ZSM-5 is also sensitive to the calcination conditions although studies in this area typically focus on the effect of temperature. Studies investigating the effect of calcination atmosphere on ZSM-5 performance is lacking. Serrano *et al.* demonstrated that hierarchical ZSM-5 calcined in a two-step N₂-air treatment presented higher activity across several reactions.¹⁶⁸ Whilst Bai *et al.* showed how their PtSnNaMg/ZSM-5 catalyst exhibited the highest activity when calcined in flowing air, Lai *et al.* found that catalytic activity of a Fe-ZSM-5 catalyst was improved when prepared under an N₂ atmosphere.^{169, 170}

The variation in conclusions makes it challenging to predict which calcination environment facilitates the performance of the catalysts synthesised in this work. The following sections investigate the effect of calcination atmosphere on the catalytic properties and structural characteristics of O₂- and N₂-treated ZSM5@Cu_{1.3}ZnAl catalysts in comparison to air-treated ZSM5@Cu_{1.3}ZnAl for the direct CTD hydrogenation.

2.4.1.1: Effect of calcination atmosphere on CO₂ hydrogenation performance

ZSM5@Cu_{1.3}ZnAl-LDH was synthesised following the modified coprecipitation method outlined in Chapter 6.2.2. The sample was then *ex-situ* calcined in a tube furnace under O₂ or N₂ flow (50 mL/min) for 3 hours before loading approximately 0.1 g of the treated ZSM5@Cu_{1.3}ZnAl-LDO into a fixed-bed reactor. The sample was then reduced *in-situ* at 260 °C (2 hours, 2 °C/min) and reacted under CO₂:H₂:N₂ (24:72:4) flow (18,000 mL/g_{cat}·h) at 3 MPa between 260 – 300 °C. For full details consult Chapter 6.5.

CO₂ hydrogenation results, summarised in Figure 2.23 and Table 2.10, clearly shows that N₂ treatment significantly impacts the eventual performance of the core-shell catalyst. Some DME production was observed in the high temperature range (300 – 340 °C) however CO₂ conversion was notably worse for the N₂-treated catalyst in comparison to air-treated ZSM5@Cu_{1.3}ZnAl. O₂-treated ZSM5@Cu_{1.3}ZnAl performed similarly to the air-treated core-shell catalyst (0.37 g_{DME}/g_{cat}·h), with the highest methanol productivity occurring at 280 °C (0.38 g_{DME}/g_{cat}·h) (see Table A.9). Although X_{CO_2} for O₂-calcined ZSM5@Cu_{1.3}ZnAl (18.3%) is greater than for air-calcined ZSM5@Cu_{1.3}ZnAl (17.9%), based on the error associated with X_{CO_2} , the difference in conversion between the O₂- and air-treated core-shell catalysts is considered to be minimal. S_{CO} of N₂-treated ZSM5@Cu_{1.3}ZnAl is nearly 100% at lower temperatures (260 – 280 °C) and stays above 70% as the temperature increases. This suggests that the RWGS dominates. Much higher temperatures (340 °C) are required for N₂-treated ZSM5@Cu_{1.3}ZnAl to achieve similar X_{CO_2} values (4.5%) as the air-treated ZSM5@Cu_{1.3}ZnAl (220 °C, 3.9%). Interestingly, no methanol was observed in the product gas stream of N₂-treated ZSM5@Cu_{1.3}ZnAl. In comparison, O₂-treated ZSM5@Cu_{1.3}ZnAl produces methanol at the threshold value (~10%) up until 300 °C, after which methanol productivity considerably decreases. This suggests that where DME production occurs (at 300 and 340 °C), all of the methanol generated by the CZA phase is converted into DME.

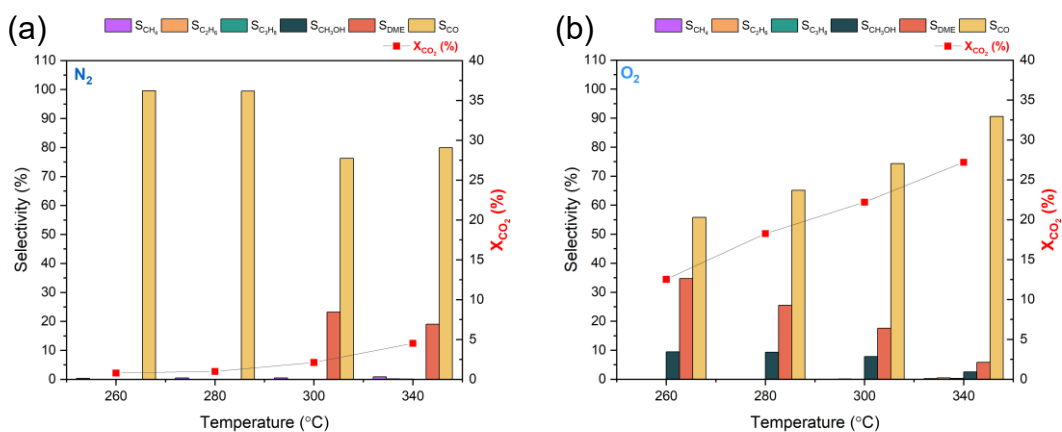


Figure 2.23: Product distribution of CO₂ hydrogenation reaction over (a) N₂-calcined ZSM5@Cu_{1.3}ZnAl and (b) O₂-calcined ZSM5@Cu_{1.3}ZnAl catalysts as a function of temperature (260 – 340 °C). Reaction conditions: $P = 3.0$ MPa; $\text{CO}_2:\text{H}_2:\text{N}_2 = 24:72:4$; $\text{WHSV} = 18,000$ mL/g_{cat}·h, carbon balance (a) 99.70 – 100.11%, (b) 98.16 – 99.55%.

Table 2.10: CO₂ hydrogenation results for the ZSM5@Cu_{1.3}ZnAl catalyst pre-treated in N₂/O₂.

Calcination environment	Temperature (°C)	Conversion (%)	Selectivity (%)			Yield (%)	STY_{DME} (g _{DME} /g _{cat} ·h)
			S_{DME}	S_{CH_3OH}	S_{CO}		
N ₂	260	0.8	0	0	99.6	0	0
	280	1.0	0	0	99.5	0	0
	300	2.1	23.2	0	76.2	1.6	0.13
	340	4.5	19.0	0	79.9	3.6	0.29
O ₂	260	12.5	34.7	9.46	55.8	4.3	0.35
	280	18.3	25.5	9.31	65.1	4.7	0.38
	300	22.2	17.6	7.83	74.3	3.9	0.32
	340	27.2	5.9	2.53	90.6	1.6	0.13

^aReaction conditions: $P = 3.0$ MPa, CO₂/H₂/N₂ = 24:72:4, and $WHSV = 18,000$ mL/g_{cat}·h.

The results from the CO₂ hydrogenation tests suggest that an inert environment has a considerably negative impact on the function of ZSM5@Cu_{1.3}ZnAl to act as a CTD catalyst. The highest methanol production for the ZSM5@Cu_{1.3}ZnAl catalyst can be found for the air- and O₂-treated catalyst at 280 °C (at ~0.38 g_{DME}/g_{cat}·h).

To understand how the physiochemical properties of ZSM5@Cu_{1.3}ZnAl changed in response to the calcination atmosphere used in the catalyst preparation method, the N₂-, O₂- and air-treated ZSM5@Cu_{1.3}ZnAl were characterised by H₂-TPR, BET, and CO₂/NH₃-TPD techniques.

2.4.1.2: Discussion

The reduction of copper oxide species to metallic Cu⁰ is an important step in the activation of CZA catalysts. There are several factors that may change the reducibility of copper species in a CZA-type material, including copper dispersion and support interaction effects which may alter the electronic properties of the copper.¹⁷¹⁻¹⁷³ Thus, the reducibility of copper species in the core-shells were investigated by hydrogen temperature programmed reduction (TPR). The precursor samples were *ex-situ* calcined at 500 °C (2 °C/min) for 3 hours prior to the TPR experiment (for full details consult Chapter 6.1.10). As air-calcined and O₂-calcined ZSM5@Cu_{1.3}ZnAl-LDO demonstrated similar CO₂ hydrogenation performances, and in the interest of time, H₂-TPR was performed on O₂- and N₂-calcined ZSM5@Cu_{1.3}ZnAl-LDO. The TPR peaks summarised in Figure 2.24 demonstrate the reducibility of the calcined catalyst precursors.

The reduction of copper species in CZA-type catalysts usually occurs between 180 – 400 °C, consequently TPR analysis was conducted from ambient temperature up to 400 °C.¹⁷⁴⁻¹⁷⁶ Direct comparisons linking the identity of copper species to temperature

regions of hydrogen consumption are challenging because the reducibility of copper species varies depending on the chemical composition of the CZA catalyst and the methods used for catalyst synthesis/activation. *In-situ* spectroscopic techniques (e.g. FTIR) could be used to aid the identification of copper species.¹⁷⁷ Here the peaks have been assigned to copper species based on results reported in the literature.

In the case of Cu_{1.3}ZnAl-LDO, two reduction peaks were observed between 120 – 280 °C which indicate that at least two kinds of reducible copper species were present in the sample (see Figure A.25 for deconvoluted peaks). The first peak at approximately 190 °C corresponds to the reduction of highly dispersed CuO species to Cu₂O, whilst the second, more intense, peak with a maximum at ~230 °C is associated with the reduction of Cu₂O to Cu⁰.¹⁷⁴ ZnO and Al₂O₃ have very high reduction temperatures (> 700 °C), and is unlikely to be the species undergoing reduction at 400 °C. Thus the peaks in the TPR profiles were attributed to the reduction of copper oxide species.^{178, 179} The reduction temperatures for Cu_{1.3}ZnAl-LDO are comparable to that of other hydrotalcite- and non-hydrotalcite-like CZA materials and are observed to be on the lower end of the reduction temperature range.^{83, 101, 171, 174, 180} CuO with smaller particle sizes are more easily reduced to Cu⁰ compared to bulk CuO, hence, the lower temperature reduction observed for Cu_{1.3}ZnAl-LDO suggests that the calcination method used here generates well-dispersed CuO species.¹⁸¹

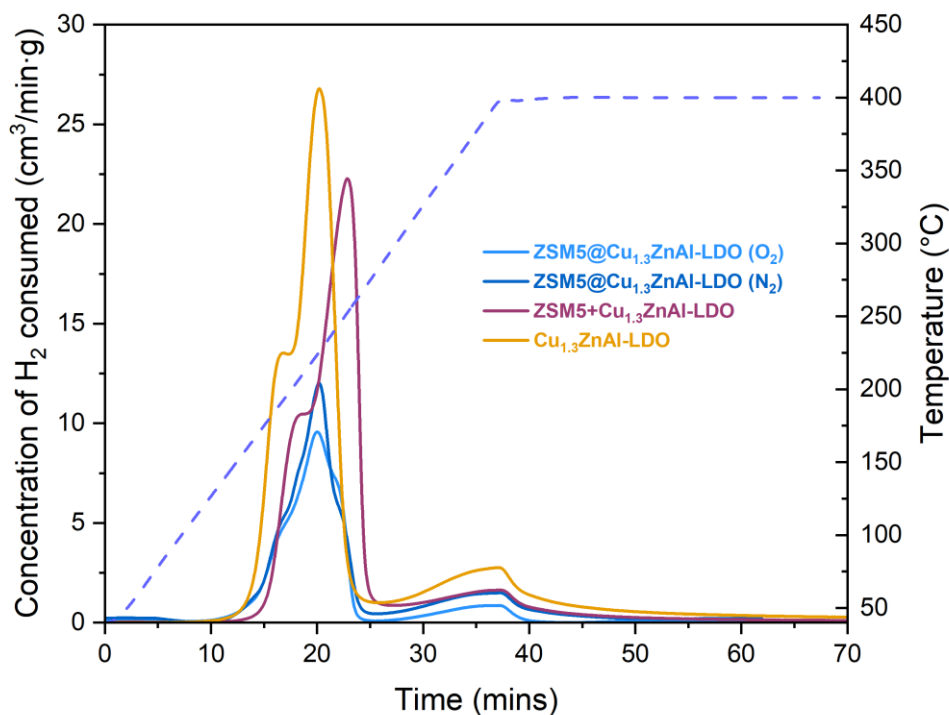


Figure 2.24: H₂ TPR profile of O₂ and N₂-calcined ZSM5@Cu_{1.3}ZnAl-LDO against the physical mixture ZSM5+Cu_{1.3}ZnAl-LDO and Cu_{1.3}ZnAl-LDO.

The TPR profile of both O₂ and N₂-calcined ZSM5@Cu_{1.3}ZnAl-LDO are similar to each other and are divergent from the ZSM5+Cu_{1.3}ZnAl-LDO and Cu_{1.3}ZnAl-LDO samples. In both core-shell samples, reduction starts at approximately 130 °C and reaches a maximum at 220 °C. Deconvolution of the peaks between 220 °C and 280 °C suggests there are at least three peaks (see Figure A.25), although there is significant overlap between them making it challenging to identify the reducing species. TPR studies of high silica, copper-loaded MFI zeolites have shown similarly complex TPR profiles; these overlapping peaks had been ascribed to the presence of multiple copper environments, including [Cu–O–Cu]²⁺, CuO, Cu²⁺, Cu⁺ and isolated Cu²⁺ species, with overlapping reduction temperatures.¹⁸² TPR studies of CZA catalysts have suggested that the lowest temperature peak comes from the reduction of CuO crystallites to Cu⁰, followed by the

reduction of CuO species with strong interactions with Zn/Al and/or free Cu^{2+} trapped within the zeolite to Cu^+ , and lastly by Cu_2O and isolated Cu^+ reduction to Cu^0 .^{173, 183-188} Studies involving hydrotalcite-derived CZA catalysts describe the main reduction as that of Cu^{2+} ions in octahedral sites in $(\text{Cu}, \text{Zn})\text{Al}_x\text{O}_y(\text{CO}_3)_z$ compounds followed by reduction of CuO species.^{100, 176, 189}

The most intense peak in the TPR profiles of N_2 and O_2 -calcined $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDO}$ occurs at the same temperature as $\text{Cu}_{1.3}\text{ZnAl-LDO}$ (225 °C). Although the reduction profile for $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDO}$ has the same shape as the profile for $\text{Cu}_{1.3}\text{ZnAl-LDO}$, the peaks are shifted to higher temperatures, with the first reduction peak at ~210 °C and the maximum peak at 250 °C. Whilst the temperature shift is small it may suggest there is poorer copper oxide dispersion in the physical mixture catalyst. The similar peak shapes between $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDO}$ and $\text{Cu}_{1.3}\text{ZnAl-LDO}$ suggests that physical mixing of the two phases does not change the type of copper species generated during calcination of the physical mixture catalyst. This supports the notion that different reducible copper species are present in the $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDO}$. The low intensities of the peaks for the core-shell samples in comparison to $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDO}$ or $\text{Cu}_{1.3}\text{ZnAl-LDO}$ indicates that there are fewer exposed Cu^{2+} on the surface of the catalyst. Jing *et al.* observed a similar effect and suggests this was due to the formation of a CuAl_2O_4 spinel phase hindering the interaction between Cu^{2+} and H_2 .¹⁰⁴

For all samples, the majority of reduction occurs by 280 °C, although a small asymmetric peak is also observed as the temperature approached 400 °C. Some CZA based catalysts have reported hydrogen consumption at high temperatures (> 400 °C) which have been attributed to the reduction of a spinel CuAl_2O_4 phase formed during the calcination

process.^{100, 190} Facets of the CuAl_2O_4 spinel (e.g. 2.45 Å, 2.65 Å or 1.54 Å for the (311), (220) and (511) planes respectively) were not noticed in the TEM of $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ (Section 2.2.3).¹⁹¹ HR-TEM allows for easier identification of the lattice fringes and should be used to further investigate the catalysts. PXRD analysis of $\text{Cu}_{1.3}\text{ZnAl-LDO}$, $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDO}$ and $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDO}$ should also be conducted to help confirm the presence of any additional phases in the calcined sample.

Results from the H_2 -TPR analysis suggests that the majority of the Cu species in the catalysts were reduced after H_2 reduction at 260 °C. The complexity of the TPR profiles suggests additional copper species were present in the core-shell samples that weren't present in $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDO}$. As there were no major differences in performance between $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ and $\text{ZSM5+Cu}_{1.3}\text{ZnAl}$, the differences in the reducibility of the core-shell catalysts and the physical mixture catalyst are considered to be negligible. The similarity of the profiles for O_2 - and N_2 -calcined $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDO}$ suggests that the same copper species are present in either sample. Consequently, the differences in catalytic performance are unlikely to be due to variations in the reducibility of the catalysts.

A further study on the effect of reduction parameters on the performance of the catalysts should be conducted. For instance, from the H_2 -TPR profiles hydrogen consumption at high temperatures (> 300 °C) suggests the presence of an additional copper phase that would not have been reduced under the current H_2 reduction method. A range of temperature, ramp rates and hold times could be tested. Further characterisation such as X-ray absorption near edge structure (XANES), extended x-ray absorption fine structure (EXAFS) or UV-Vis could be used to determine the identity of the reducible copper species.¹⁸⁹

The textural properties N_2 -calcined $ZSM5@Cu_{1.3}ZnAl$ were investigated by N_2 BET analysis and the surface areas and pore volumes are summarised in Figure 2.25 and Table 2.11.

Based on the surface areas estimated from the t-plots of nitrogen adsorption at 77 K, N_2 -calcined $ZSM5@Cu_{1.3}ZnAl$ has slightly lower $S_{External}$ ($68 \text{ m}^2/\text{g}$) and $S_{Micropore}$ ($163 \text{ m}^2/\text{g}$) than air-calcined $ZSM5@Cu_{1.3}ZnAl$. $S_{External}$ decreased by 13% and S_{Micro} decreased by 11%. The micropore volume of the N_2 -calcined core-shell catalyst was also observed to be lower than the air-calcined counterpart. Previously, N_2 BET analysis of air-calcined $ZSM5@Cu_{1.3}ZnAl$ and $ZSM5+Cu_{1.3}ZnAl$ showed that both catalysts had higher surface areas than expected. The S_{BET} of N_2 -calcined $ZSM5@Cu_{1.3}ZnAl$ is similar to the expected values, in particular there is very little improvement to the external surface area in comparison to the theoretical $S_{External}$ value ($61 \text{ m}^2/\text{g}$).

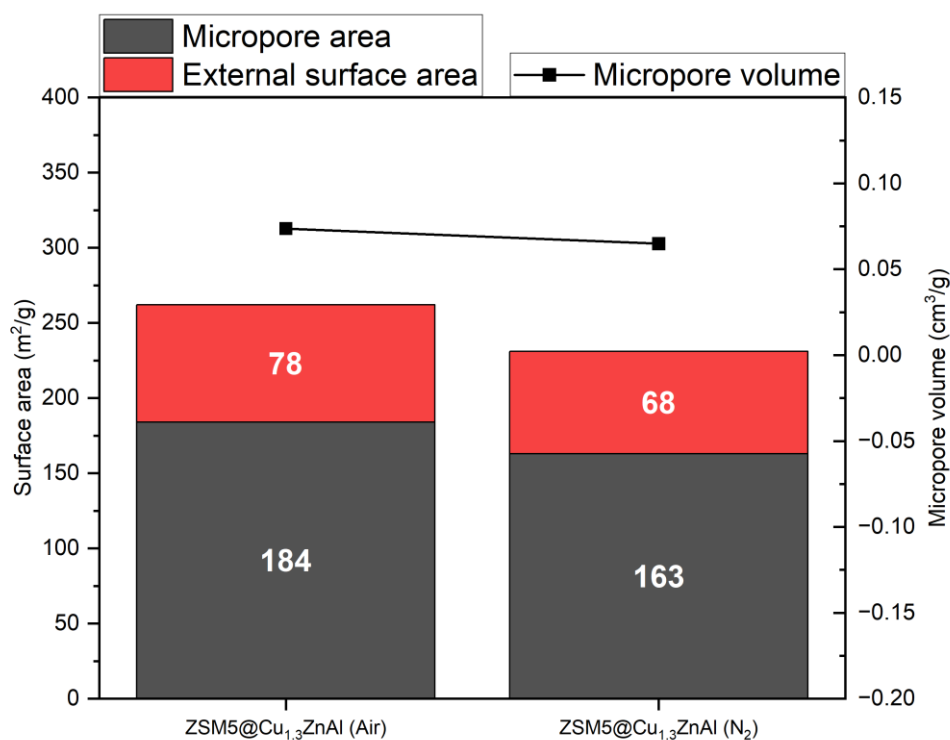


Figure 2.25: N₂ BET surface areas of air-calcined ZSM5@Cu_{1.3}ZnAl against N₂-calcined ZSM5@Cu_{1.3}ZnAl catalysts. The grey and red bars show the estimated micropore surface area and external surface area respectively, whilst the line plot shows the estimated micropore volume of the samples.

Table 2.11: Textural properties of activated ZSM5@Cu_{1.3}ZnAl pre-treated in air, N₂ and O₂.

Calcination environment	S_{External} (m^2/g)	$S_{\text{Micropore}}$ (m^2/g)	S_{BET} (m^2/g)	V_{Micro} (cm^3/g)
Air	78	184	263	0.074
N ₂	68	163	231	0.065

N₂ adsorption isotherms, BJH mesopore size distribution and DFT micropore size distribution of air and N₂-calcined ZSM5@Cu_{1.3}ZnAl are shown in Figure 2.26.

No change is observed in the shape of the N₂ adsorption isotherm of N₂-calcined ZSM5@Cu_{1.3}ZnAl which shows that both zeolite and CZA phases are present in the sample. This is indicated by high N₂ uptake with a type I isotherm at low relative pressures ($p/p^0 < 0.3$), ascribed to the microporosity of the H-ZSM-5 core, and a type II isotherm and H3 hysteresis loop at high relative pressures ($p/p^0 > 0.5$) associated with the slit-like mesoporous/macroporous CZA phase.^{109, 142} Both N₂- and O₂-calcined ZSM5@Cu_{1.3}ZnAl exhibit similar mesopore and micropore size distributions. The differences in the micropore sizes are attributed to the poor sensitivity associated with N₂ adsorption at low relative pressures.^{117, 192}

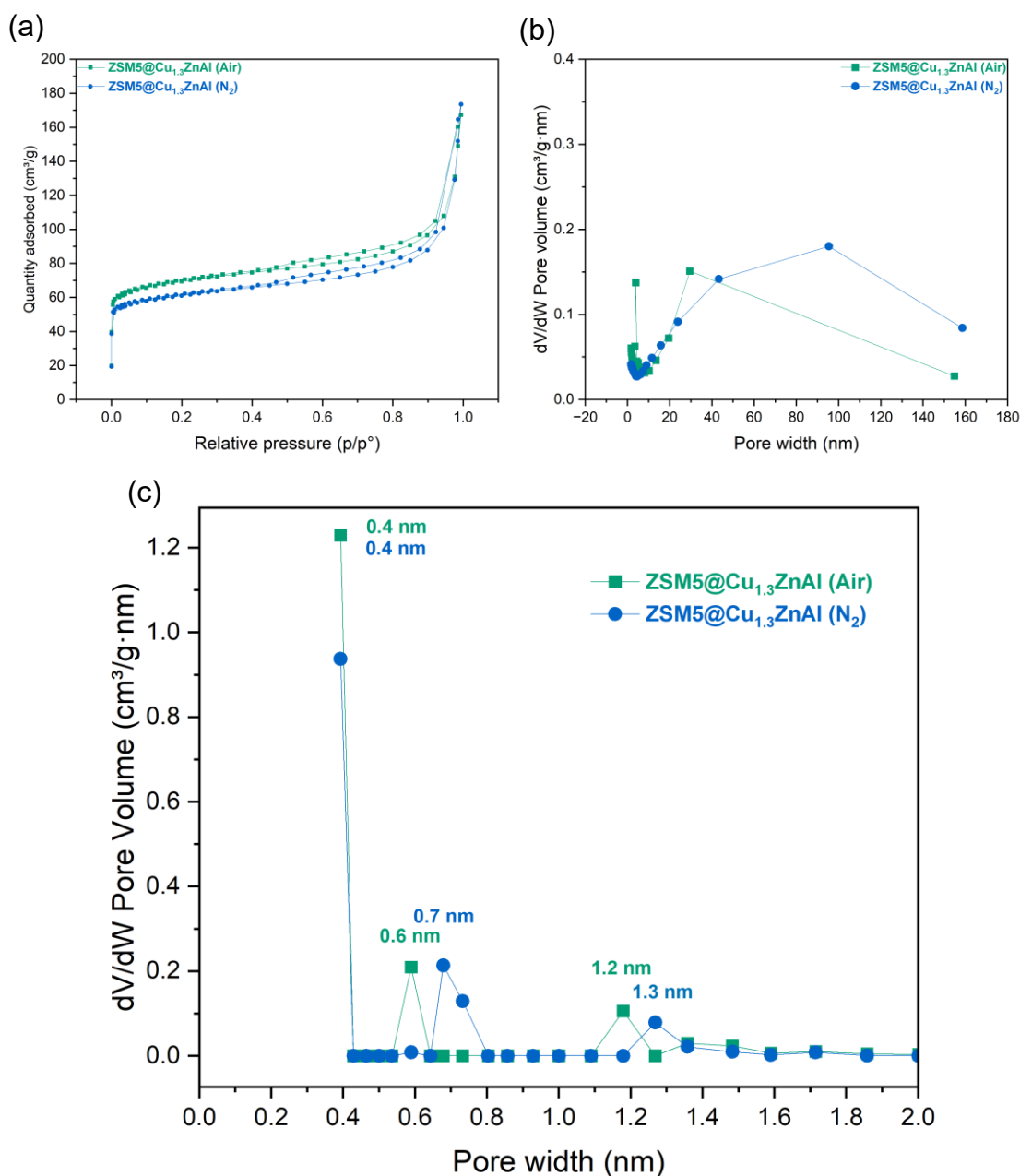


Figure 2.26: (a) N₂ adsorption isotherms, (b) BJH pore size distribution, (c) DFT size distribution of air-calcined and N₂-calcined ZSM5@Cu_{1.3}ZnAl-LDH.

The textural properties of N₂-calcined ZSM5@Cu_{1.3}ZnAl and air-calcined ZSM5@Cu_{1.3}ZnAl are similar. Differences were also observed in the textural properties between air-calcined ZSM5@Cu_{1.3}ZnAl and ZSM5+Cu_{1.3}ZnAl, however, the

performance of the catalysts were similar. Given this context, it is unlikely that the reduced surface area and micropore volume observed in the N₂-calcined ZSM5@Cu_{1.3}ZnAl catalyst are responsible for its poorer performance.

CO₂-TPD analysis was conducted to investigate the basicity of the ZSM5@Cu_{1.3}ZnAl catalysts treated in different calcination environments. Figure 2.27 summarises the desorption profiles for air/O₂/N₂-treated ZSM5@Cu_{1.3}ZnAl. There is a notable difference in the desorption pattern for N₂-calcined ZSM5@Cu_{1.3}ZnAl compared to the air- or O₂-treated catalyst. O₂ and air-calcined ZSM5@Cu_{1.3}ZnAl display a similar pattern with peaks between 40 – 260 °C, 260 – 400 °C and 400 – 600 °C indicating there are weak, medium and strong basic sites. The air- and O₂- calcined ZSM5@Cu_{1.3}ZnAl exhibit similar CO₂ capacities (199 cm³/g and 214 cm³/g respectively) and similar temperatures of maximum CO₂ desorption for each of the three regions (see Table 2.12 for more details). This suggests there are no significant changes to the nature of the acid sites or the acidic capacity of ZSM5@Cu_{1.3}ZnAl when treated in an oxidising atmosphere. By comparison, N₂-calcined ZSM5@Cu_{1.3}ZnAl demonstrates considerably lower CO₂ uptake (43 cm³/g). Based on the deconvoluted CO₂-TPD spectrum of N₂-calcined ZSM5@Cu_{1.3}ZnAl (see Figure A.26), the major differences between the N₂ and air/O₂-calcined core-shell catalysts are: (a) there are very few moderately basic sites (estimated N₂ uptake was 6 cm³/g), and (b) there are at least two different types of weakly basic sites (on account of the two peaks present in the low temperature desorption region). T_{1,CO_2} occurs at 91 °C with a shoulder at 137 °C due to desorption from a slightly stronger basic site. N₂-calcined ZSM5@Cu_{1.3}ZnAl does possess some strong basic sites and interestingly the desorption occurs at slightly higher temperatures (T_{3,CO_2} = 544 °C) than the catalysts treated in an oxidising atmosphere (~527 °C). CO₂-TPD analysis of other

CZA type catalysts have associated weak, medium and strong basic sites with hydroxides, metal-oxide pairs like Zn–O, and coordinatively unsaturated surface O^{2-} groups respectively. Thus, the results indicate that some significant changes have occurred to the metal-oxide pairs and the availability of O_2^- sites on the surface of the catalyst. It also suggests there are changes to the strength of the hydroxyl groups left on the surface of the LDO phase following calcination.

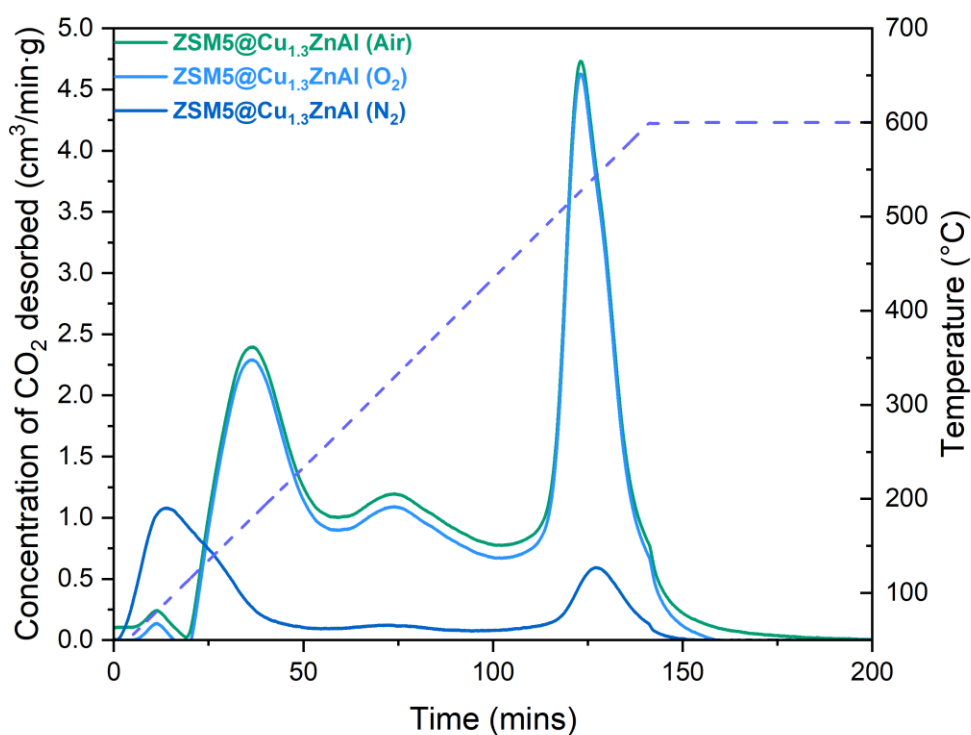


Figure 2.27: CO_2 -TPD of air, O_2 and N_2 calcined $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ catalysts.

Table 2.12: Quantitative data of CO₂ chemisorption measurements for air, O₂ and N₂ calcined ZSM5@Cu_{1.3}ZnAl.

Sample	CO ₂ uptake (cm ³ /g)	$T_{1,\text{CO}_2}^{\text{a}}$ (°C)	$T_{2,\text{CO}_2}^{\text{b}}$ (°C)	$T_{3,\text{CO}_2}^{\text{c}}$ (°C)
Air	199	180	329	526
O ₂	214	178	330	527
N ₂	43	92	328	544

^a T_{1,CO_2} , temperature of maximum CO₂ desorption below 260 °C. ^b T_{2,CO_2} , temperature of maximum CO₂ desorption between 260 °C and 440 °C. ^c T_{3,CO_2} , temperature of maximum CO₂ desorption above 440 °C.

The results suggest that there is a significant impact on the basicity of the core-shell catalyst when pre-treated under N₂ calcination. The profile pattern of N₂-calcined ZSM5@Cu_{1.3}ZnAl more closely resembles the CO₂-TPD profile of H-ZSM-5 (see Section 2.2.3 for more details). Whilst the nature of the basic sites is unknown, the results from the CO₂-TPD analysis in combination with the results from CO₂ hydrogenation tests suggest that N₂ calcination has a considerable impact on the basic sites involved in CO₂ to methanol conversion.

An NH₃-TPD study of O₂-calcined and N₂-calcined ZSM5@Cu_{1.3}ZnAl was also conducted to investigate the effect of calcination conditions on the acidity of core-shell catalyst. The NH₃ desorption profiles were compared against air-calcined ZSM5@Cu_{1.3}ZnAl and the results are summarised in Figure 2.28 and Table 2.13.

The catalysts demonstrated similar NH₃-TPD profiles, with peaks occurring at similar temperature regions. Hence, the weak, medium and strong acid sites identified for air-calcined ZSM5@Cu_{1.3}ZnAl (see Section 2.2.2) are maintained in the O₂- and N₂-treated

catalysts. Differences in the intensities of the peaks associated with the medium and strong acid sites suggest that whilst the same type of acid sites are present in all catalysts, the calcination environment may affect the strength/quantity of those sites. T_{2,NH_3} ($\sim 270^\circ\text{C}$) and T_{3,NH_3} (580°C) for O_2 - and N_2 -calcined $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ occur at similar temperatures to each other. Compared to air-treated $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$, these peaks, associated with medium and strong acid sites, are shifted to slightly higher temperatures which suggests they are slightly stronger. NH_3 uptake for T_{2,NH_3} was also greater for O_2 - and N_2 -calcined $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ which suggests a greater number of medium acid sites was present in the samples. Deconvolution of the peaks (see Figure A.27) suggests there are multiple acidic environments in the O_2 - and N_2 -treated $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ core-shells which is consistent with the NH_3 -TPD profile observed for the air-treated core-shell catalyst. It had been suggested that the complex NH_3 -TPD profile for air-treated $\text{ZSM5@Cu}_{1.3}\text{ZnAl}$ was due to the formation of new acidic sites in the zeolite. The formation of new Lewis acid type sites may have occurred during coprecipitation and is believed to be due to heteroatom incorporation (i.e. trapped $\text{Cu}^{2+}/\text{Zn}^{2+}$ species within the zeolite) and/or the generation of more Al^{3+} extra framework aluminium species.

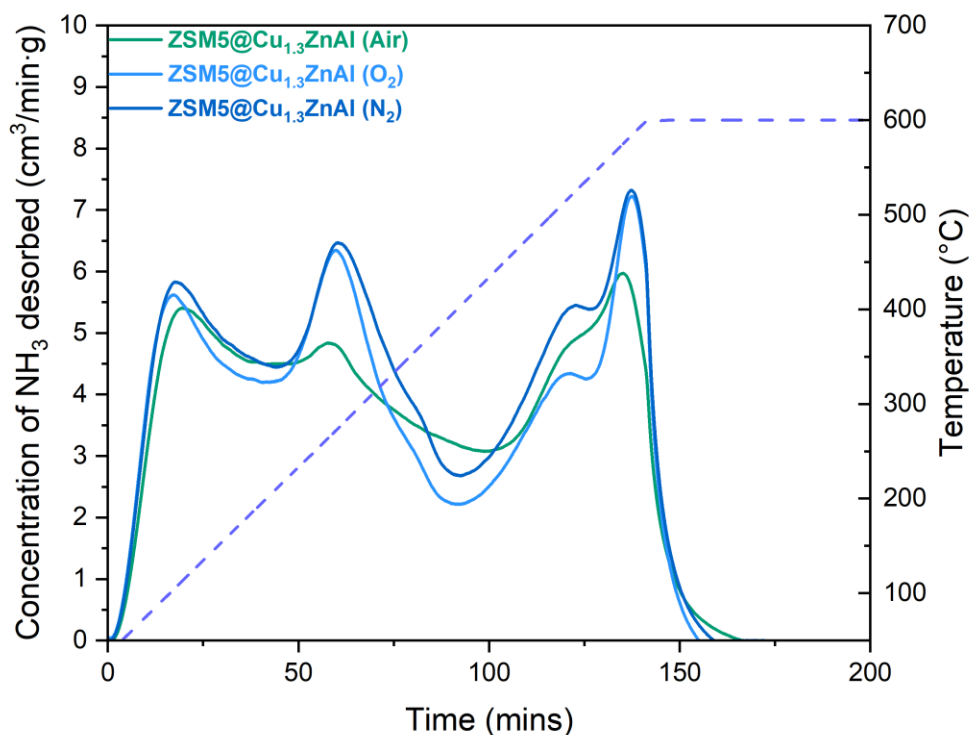


Figure 2.28: NH₃-TPD profiles of air, O₂ and N₂ calcined ZSM5@Cu_{1.3}ZnAl catalysts.

Table 2.13: Quantitative data of NH₃ chemisorption measurements for air, O₂ and N₂ calcined ZSM5@Cu_{1.3}ZnAl.

Sample	NH ₃ uptake (cm ³ /g)	$T_{1,\text{NH}_3}^{\text{a}}$ (°C)	$T_{2,\text{NH}_3}^{\text{b}}$ (°C)	$T_{3,\text{NH}_3}^{\text{c}}$ (°C)
Air	566	113	264	575
O ₂	618	102	273	583
N ₂	678	107	277	583

^a T_{1,NH_3} , temperature of maximum NH₃ desorption below 260 °C. ^b T_{2,NH_3} , temperature of maximum NH₃ desorption between 260 °C and 440 °C. ^c T_{3,NH_3} , temperature of maximum NH₃ desorption above 440 °C.

Characterisation using H₂-TPR, N₂-BET, and NH₃-TPD techniques indicates that the calcination atmosphere used in the catalyst pre-treatment has little effect on the

reducibility, surface area, micropore volume, or acidity of the ZSM5@Cu_{1.3}ZnAl catalyst. Instead, the most notable change is in the basicity. This shift can be attributed to the CZA phase, which is responsible for the catalyst's basic properties and suggests that the calcination atmosphere influences the basic functionality of the catalyst without compromising the acidic sites.

Numerous studies have investigated the active sites of Cu/ZnO/Al₂O₃ catalysts in an effort to describe the mechanism of CO₂ hydrogenation, often highlighting the crucial interaction between Cu and ZnO.^{12, 193-195} There is still much debate as to the nature of the active sites and the specific role of each component within the catalyst. It is generally understood that for CO₂ hydrogenation over a CZA catalyst, hydrogen dissociation occurs on Cu nanoparticles and the close contact of Cu-Zn provides dual binding sites for the activation of CO₂.¹⁹⁶ The CO₂-TPD results demonstrated that CO₂ interacts poorly with N₂-treated ZSM5@Cu_{1.3}ZnAl and there were considerable changes in the moderately strong and strong basic sites. Since these are associated with the metal-oxides and O²⁻ ions on the surface of the catalyst, it is necessary to consider the roles that the ZnO and Al₂O₃ metal-oxide phases play in the activity of the catalyst to explain the poor performance of N₂-treated ZSM5@Cu_{1.3}ZnAl.

Although hydrogen dissociation occurs on the surface of copper nanoparticles, metal oxides with strong Lewis acid-base M–O pairs like Zn–O can assist in the activation of H₂, whereby H⁺ adsorption occurs on lattice O²⁻ sites and H₂ adsorbs on M^{x+} sites. As shown in the H₂-TPR analysis, H₂ interacts with O₂-treated ZSM5@Cu_{1.3}ZnAl in a similar way to N₂-treated ZSM5@Cu_{1.3}ZnAl based on similar H₂ capacities and profile patterns. This tells us that the basic sites that were altered under N₂-calcination doesn't have an impact on the reducibility of the copper species. However, an additional H₂-TPD

experiment could be performed on the activated catalysts to investigate the interaction between the reactant H_2 species and ZSM5@Cu_{1.3}ZnAl. Several studies have suggested that co-adsorbed oxygen has a role to play in the activity of the copper phase.¹⁹⁷⁻¹⁹⁹ The interaction between Cu⁰ and oxygen creates dual adsorption sites that facilitate CO₂ binding and activation.¹⁹⁹ These co-adsorbed oxygen species can originate from the presence of water that dissociates to produce hydroxyl groups. Since moisture was present in all the gas canisters used for air, O₂ and N₂ treatment (see Chapter 6.2.5), calcination in an inert atmosphere likely introduces fewer oxygen species compared to oxidising conditions.

The next phase of research can be divided into catalytic performance tests and advanced characterisation. A key objective is to examine how calcination in an inert atmosphere influences the activity of the Cu_{1.3}ZnAl catalyst independent of the ZSM-5 core. This will help isolate the effects of calcination atmosphere on the CZA component itself. Furthermore, a range of advanced characterisation techniques should be conducted to investigate the nature of the basic metal-oxide sites in N₂-treated ZSM5@Cu_{1.3}ZnAl. *In-situ* XRD can be used to monitor copper phase transitions (i.e. Cu, Cu₂O or CuO) under varying temperatures and gas atmospheres. HR-TEM/EDX can provide detailed information on Cu nanoparticle distribution and the nature of the Cu-ZnO by identifying the exposed crystallographic facets. For surface and oxidation state analysis, X-ray photoelectron spectroscopy (XPS) in combination with XANES and EXAFS can provide information on the oxidation states of Cu and Zn and probe metal-support interactions. Electron paramagnetic resonance (EPR) can also be used to detect and quantify oxygen vacancies in the catalysts, providing information on defect sites which may influence the basicity of ZSM5@Cu_{1.3}ZnAl. Finally, *in-situ* techniques like diffuse reflectance infrared

Fourier transform spectroscopy (DRIFTS) will be crucial for monitoring the adsorption and transformation of CO₂ on the catalyst surface. Together, these techniques will offer a comprehensive understanding of the structural, electronic and surface chemical changes induced by N₂-calcination.

As the O₂ and air-treated ZSM5@Cu_{1.3}ZnAl catalysts exhibited comparable catalytic performance for direct CTD conversion, it was assumed that the choice of oxidising calcination atmosphere had minimal impact on catalytic behaviour. Therefore, for practical reasons, all subsequent catalysts examined in this thesis were calcined under an O₂ atmosphere.

2.4.2: The effect of reaction conditions on CO₂ hydrogenation performance

Provided it did not exceed the limitations of the equipment, the operating parameters used for CO₂ hydrogenation tests were selected based on commonly used conditions in the literature. Undoubtedly, parameters such as the reaction temperature, reaction pressure, feed gas composition, and space velocity have significant impacts on CO₂ conversion and product distribution. This is based on the thermodynamics associated with CO₂ hydrogenation and include CO₂ to methanol, RWGS and methanol to DME reactions. For instance, the reaction temperature range was set between 260 – 340 °C based on the temperatures associated with high DME productivity in Section 2.3 (which also concur with observations in the literature).^{39, 42, 51, 144}

Reaction pressure is an important consideration as it affects the initial CO₂ to methanol conversion; higher pressures are favoured based on Le Chatelier's principle and methanol

selectivity is observed to increase with pressure.²⁰⁰ Although increasing pressure does not have an effect on the methanol dehydration reaction, increasing methanol production at higher pressures may lead to an improvement in the overall CTD conversion. The fixed-bed reactor used in this work was limited to 3 MPa and thus the effect of pressure on the ZSM5@Cu_{1.3}ZnAl catalyst system was not investigated.

The feed gas composition should have a H₂:CO₂ molar ratio of 3:1 based on the equation for CO₂ hydrogenation to methanol (see Section 1.4.1) and is the standard ratio used in the literature. Some studies have shown that the feed gas composition has an impact on CO₂ conversion and selectivity.^{10, 200} The amount of dilutant, i.e. the CO₂ fraction, in the gas composition has also been shown to affect the DME productivity.¹⁰ Initial tests of the ZSM5@Cu_{1.3}ZnAl catalysts were done using CO₂ reactant feeds with higher CO₂ fractions however, due to time constraints, this parameter has not been thoroughly investigated.

Space velocity is a measure of how quickly gas flows through a reactor relative to the amount of catalyst present. It is typically expressed as either weight hourly space velocity (*WHSV*) or gas hourly space velocity (*GHSV*). *WHSV* is defined based on the mass of the catalyst and is given in units of volume of gas flow per gram of catalyst per hour (mL/g_{cat}·h), whereas *GHSV* is defined based on the volume of the catalyst bed and is given in units of volume of gas flow per volume of catalyst per hour (mL/mL_{cat}·h). Previous studies have shown that space velocity has a demonstrable impact on the CO₂ conversion of CZA catalysts, though research in this area is limited and the results are often conflicting.²⁰⁰ For instance, Lee *et al.* showed that higher space velocity gave higher methanol formation rates whereas another study by Koh *et al.* showed CO₂ conversion decreased at higher *WHSV* due to shortened residence time.^{201, 202} Space velocities used

in previous DME studies tend to lie between 800 and 6000 mL/g_{cat}·h. From an industrial perspective, a catalyst that performs effectively at high *WHSV* is desirable as it indicates high throughput, i.e., allowing more product to be generated with less catalyst, thereby reducing operating costs.

The following section describes the results from CO₂ hydrogenation test where *WHSV* was set to 44,000 mL/g_{cat}·h to match the space velocity used by our industrial partners.

2.4.2.1: Effect of *WHSV* on the CO₂ hydrogenation performance

To achieve a space velocity of 44,000 mL/g_{cat}·h, the flow rate of the reactant gas was increased to 74 mL/min. All other parameters were kept the same.

Based on the results summarised in Figure 2.29 and Table 2.14, DME productivity of ZSM5@Cu_{1.3}ZnAl improves when a higher space velocity is used. The activity was compared against the values reported for O₂-calcined ZSM5@Cu_{1.3}ZnAl tested at 18,000 mL/g_{cat}·h which demonstrates how the *S*_{DME} is higher across all temperatures. The highest *STY*_{DME} was found to be 0.78 g_{DME}/g_{cat}·h at 280 °C. CO₂ conversion at higher space velocities was also consistently lower than for ZSM5@Cu_{1.3}ZnAl tested at 18,000 mL/g_{cat}·h. This is likely due to the decreased residence time of reactants over the catalysts due to the high flow rate and has been observed in other catalysts tested at high *WHSV*s. For ZSM5@Cu_{1.3}ZnAl tested at 44,000 mL/g_{cat}·h, the methanol threshold rate stays at about 10% which is consistent with literature values and indicates the reaction is kinetically limited. At 340 °C, *S*_{DME} and *S*_{CH₃OH} decreases significantly to 7.1% and 4.1% and the RWGS reaction dominates. At all temperatures, *S*_{CO} at 44,000 mL/g_{cat}·h is lower than at 18,000 mL/g_{cat}·h which implies that the RWGS reaction is less favoured when a higher flow rate is used.

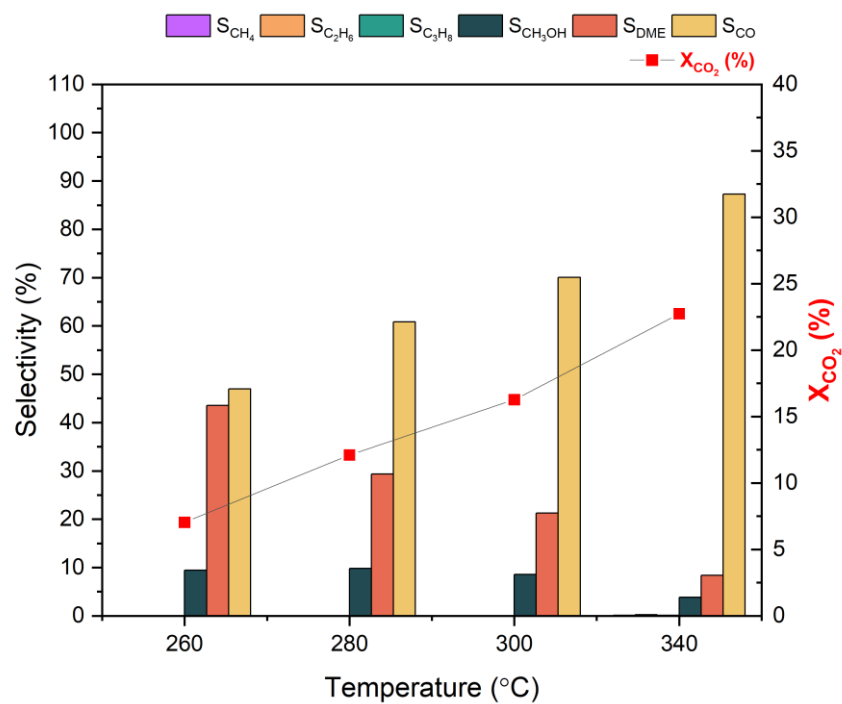


Figure 2.29: Product distribution of CO₂ hydrogenation reaction over ZSM5@Cu_{1.3}ZnAl as a function of temperature (260 – 340 °C). Reaction conditions: P = 3.0 MPa; CO₂:H₂:N₂ = 24:72:4; WHSV = 44,000 ml/gcat·h, carbon balance 99.48 – 100.74%.

Table 2.14: CO₂ hydrogenation results for the ZSM5@Cu_{1.3}ZnAl catalyst at WHSV = 44,000 ml/g_{cat}·h.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)		Yield		<i>STY</i> _{DME} (g _{DME} /g _{cat} ·h)
					(%)		
			<i>S</i> _{DME}	<i>S</i> _{CH₃OH}	<i>S</i> _{CO}	<i>Y</i> _{DME}	
ZSM5@Cu _{1.3} ZnAl	260	8.2	44.7	9.7	45.6	3.7	0.73
	280	13.1	30.0	10.1	59.9	3.9	0.78
	300	17.6	20.5	9.0	70.5	3.6	0.71
	340	23.9	7.1	4.08	88.3	1.7	0.34

^aReaction conditions: $P = 3.0$ MPa, CO₂/H₂/N₂ = 24:72:4, and $WHSV = 44,000$ mL/g_{cat}·h.

There is considerable improvement in the performance of the ZSM5@Cu_{1.3}ZnAl core-shell catalyst for direct CO₂ to DME conversion when reacted at high space velocity. This improvement has yet to be fully investigated, however, it is likely due to the removal of water during the reaction. As described in Chapter 1.4.1, CO₂ hydrogenation to methanol (as well as the RWGS reaction) generates water as a side product. The build-up of moisture is a well-known problem in CO₂ hydrogenation over CZA catalysts, deactivating the catalyst by re-oxidising Cu⁰ (or Cu⁺) species and altering the structure. Some studies have approached this from an engineering perspective, modifying the reactor bed design to facilitate the removal of excess water generated during the reaction. Other research efforts, including the work presented in this thesis, have focused on designing hydrothermally stable catalysts as a way to prolong the lifetime of the catalyst. The following section reviews previous CTD catalysts and compares the activity of the LDH-derived ZSM5@Cu_{1.3}ZnAl core-shell catalyst against those reported in the literature.

2.4.2.2: Benchmarking

Benchmarking CTD catalysts is challenging as studies often report DME productivity using different units or conditions. This lack of standardisation makes it difficult to perform meaningful comparisons across studies and evaluate catalyst performance. The data collected on direct CTD catalysts for benchmarking purposes is therefore not exhaustive. Studies reporting DME productivity as space time yields (in g_{DME}/g_{cat}·h) were included, enabling a performance comparison of ZSM5@Cu_{1.3}ZnAl with other hybrid catalysts tested under similar operating conditions.

The results, summarised in Figure 2.30, highlight how the typical operating conditions for direct CO₂ hydrogenation to DME uses pressures of either 3 MPa or 5 MPa, with generally lower *WHSV* values ranging from 1000 – 4000 NmL/g_{cat}·h. The ZSM5@Cu_{1.3}ZnAl core-shell catalyst investigated in this thesis demonstrates good DME productivity, which further improves at high space velocities. When tested at 44,000 mL/g_{cat}·h, its performance becomes competitive with that of CuZnZr/ferrierite (FER) catalysts. Zr is a commonly used promoter for Cu-based catalysts in the conversion of CO₂ to methanol.^{29, 119, 183, 203, 204} Several factors have been proposed to explain this effect, including improved Cu dispersion, enhanced CO₂ adsorption and activation, improved redox properties and catalyst stability, as well as possible synergistic effects. FER zeolites have also been widely studied as the acid catalyst component in hybrid systems for direct CTD conversion.^{20, 27, 28, 44, 47}

ZSM5@Cu_{1.3}ZnAl tested at 18,000 mL/g_{cat}·h was outperformed by two hybrid catalysts at 3 MPa, a Cu/ZnO/Al₂O₃ and ZSM-5 (CZA/ZSM5) hybrid by Krim *et al.* and a CuZnZr and SAPO-18 (CZZr/SAPO-18) hybrid by Ateka *et al.*^{33, 45} The CZA/ZSM5 catalyst was designed for the one step conversion of CO₂ to DME and had a DME space time yield of 0.439 g_{DME}/g_{cat}·h. The study examined how the textural properties of ZSM-5 influenced the overall CTD conversion. Krim *et al.* combined a commercial CZA catalyst (44.2:17:4.15:0.68 molar ratio of Cu:Zn:Al:Mg) with hollow, nanosized ZSM-5 pre-treated to introduce mesoporosity.³³ The parent nano-ZSM-5 was synthesised by hydrothermal treatment and further modified in an alkaline treatment to produce hollow and hollow/mesoporous variants. Ultimately, the combination of the CZA catalyst with commercial microporous ZSM-5 (Zeolyst Int. CBV 3024E) demonstrated the highest DME space time yield. It should be noted that the CZA and ZSM-5 phases were combined

as separated phases within the reactor (in a 1:3 metal:acid catalyst ratio). The activity of the catalysts was attributed to the Lewis acidity and mesoporosity of the ZSM-5 phase which highlights the importance of the zeolite's acidic properties. Meanwhile, Ateka *et al.* were investigating the promotion properties of Zr/Mn- incorporated Cu/ZnO catalysts and found that the DME productivity of the hybrid CZZr/SAPO-18 catalyst for CTD conversion was the greatest ($0.407 \text{ g}_{\text{DME}}/\text{g}_{\text{cat}}\cdot\text{h}$).⁴⁵ The CZZr phase was made by coprecipitation of the metal salts (2:1:1.5 molar ratio of Cu:Zn:Zr) and SAPO-18 was synthesised by a hydrothermal method; the hybrid catalyst was made by physically mixing the metal and acid catalysts in a 2:1 ratio. The lowest performing catalyst was CZA/SAPO-18 which highlights the promoting qualities of Zr for the conversion of CO_2 to methanol.

ZSM5@Cu_{1.3}ZnAl tested at 44,000 mL/g_{cat}·h ($STY_{\text{DME}} = 0.72 \text{ g}_{\text{DME}}/\text{g}_{\text{cat}}\cdot\text{h}$) outperformed multiple CuZnZr/FER hybrid catalysts operating at high pressure (5 MPa). A CuZnZr/FER catalyst by Bonura *et al.* demonstrated slightly higher DME productivity ($0.75 \text{ g}_{\text{DME}}/\text{g}_{\text{cat}}\cdot\text{h}$) which was attributed to the improved interaction between the CuZnZr and zeolite phase.⁴⁴ The hybrid catalyst was made by the *in-situ* oxalate coprecipitation of CuZnZr (60:30:10, Cu:Zn:Zr molar ratio) in the presence of a home-made FER zeolite (2:1, metal:acid ratio). Surface area and acidity data was unable to justify the superior CTD performance of the CuZnZr/FER catalyst over a CuZnZr/MOR catalyst. However, TEM analysis demonstrated that the interaction of the metal and zeolite phases were considerably worse in the MOR hybrid catalyst, leading to better mass transfer over CuZnZr/FER.⁴⁴

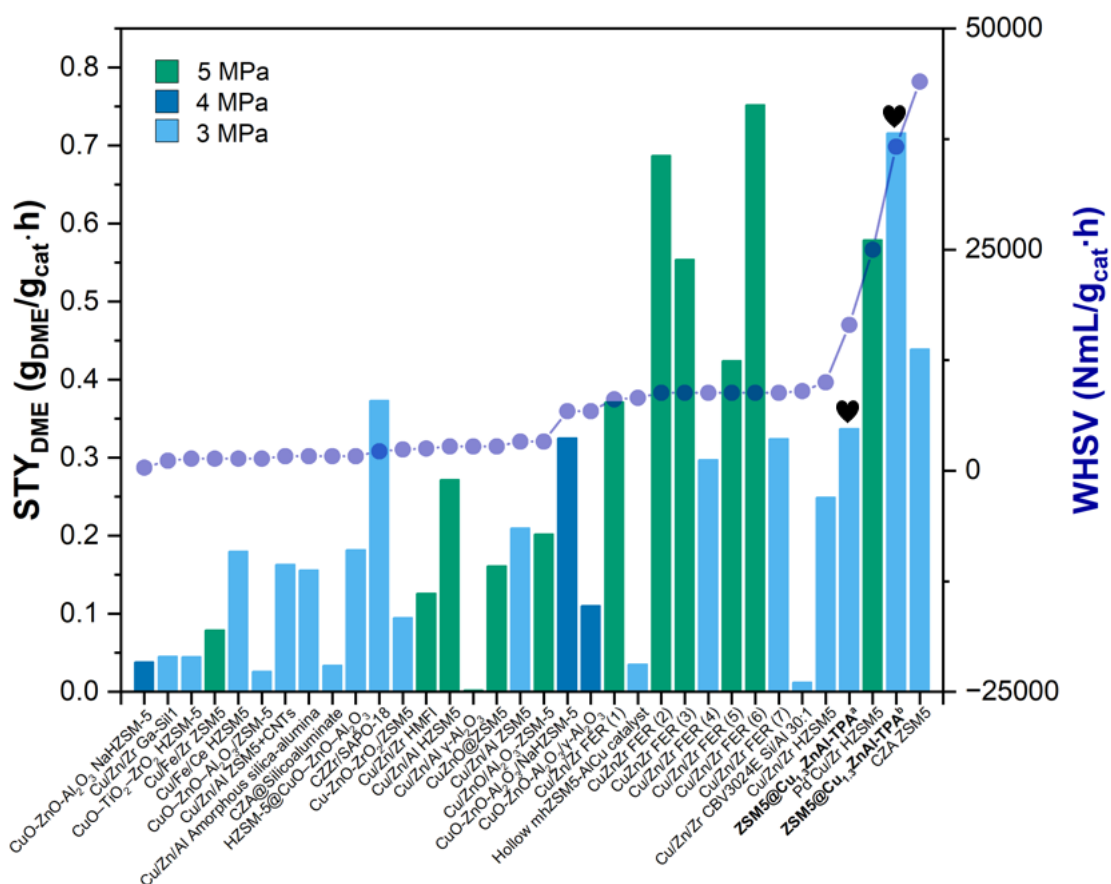


Figure 2.30: DME productivity of reported catalysts toward direct CTD conversion. Results for the work in this thesis are highlighted with ^aair-calcined ZSM5@Cu_{1.3}ZnAl (WHSV = 18,000 mL/g_{cat}·h) and ^bO₂-calcined ZSM5@Cu_{1.3}ZnAl (WHSV = 44,000 mL/g_{cat}·h).

There are many parameters to consider when benchmarking ZSM5@Cu_{1.3}ZnAl against CTD catalysts in the literature. For the catalysts with comparable DME productivities, differences in the synthesis methods (coprecipitation, physical mixing, wet impregnation etc.), catalyst compositions (such as; metal ratios, incorporation of promoters, Si/Al ratios in the zeolite, metal/zeolite ratios), and operating conditions such as CO₂ fraction in the reactant gas stream, space velocities, reactor bed set-up complicate the analysis. The information collected from the literature review suggests that the high DME productivity

of ZSM5@Cu_{1.3}ZnAl is due to the close interaction between the CZA and ZSM-5 phases. TEM in Section 2.2.3 suggested there was also close interaction between the CZA and ZSM-5 in the physical mixture catalyst, which is likely why the performance of ZSM5+Cu_{1.3}ZnAl was similar to the core-shell catalyst. CZA and ZSM-5 were chosen for their electronic compatibility which may be why the phases still interact well in ZSM5+Cu_{1.3}ZnAl.

Based on the results from the literature review, our suggestions for the next study should investigate the CTD performance of ZSM5+Cu_{1.3}ZnAl when reacted at high space velocities (44,000 mL/g_{cat}·h). Zeta potential analysis is also recommended to investigate the compatibility between the CZA and zeolite phases across other zeolites including FER, MOR and SAPO-18.

2.5: Conclusions and future work

In this chapter, an LDH-derived core-shell catalyst ZSM5@Cu_{1.3}ZnAl demonstrated high DME productivity ($STY_{DME} = 0.72 \text{ g}_{DME}/\text{g}_{cat}\cdot\text{h}$) at high space velocities (44,000 mL/g_{cat}·h). The core-shell catalyst precursor was synthesised an *in-situ* coprecipitation method in the presence of the ZSM-5 zeolite, and outperformed several CTD catalysts. The core-shell catalyst demonstrated superior performance when compared against CTD catalysts operating at high pressure. Hence, ZSM5@Cu_{1.3}ZnAl functions as a high throughput direct CO₂ to DME catalyst operable at low pressures, making it an attractive option as an industrially applicable, low-cost catalyst.

When tested at lower space velocities (18,000 mL/g_{cat}·h), the physical mixture counterpart, ZSM5+Cu_{1.3}ZnAl, demonstrated similarly good DME productivity.

Although there were differences in the surface acidity/basicity and surface areas/micropore volumes of ZSM5@Cu_{1.3}ZnAl and ZSM5+Cu_{1.3}ZnAl, the similar performance of the hybrid catalyst for CTD conversion suggests that these differences did not impact the overall performance. To investigate this further, N₂O experiments should be conducted to investigate the Cu surface areas where the DME productivities can be normalised against the exposed Cu surface areas of the core-shell and physical mixture catalysts. An investigation into the stability of the catalysts should also be performed where ZSM5@Cu_{1.3}ZnAl and ZSM5+Cu_{1.3}ZnAl are tested over a prolonged period to monitor the performance with time. It would also be pertinent to test the physical mixture for CTD conversion at a higher *WHSV* of 44,000 mL/g_{cat}·h.

The high DME productivity of ZSM5@Cu_{1.3}ZnAl was possible only when the catalyst had been pre-treated in an oxidising atmosphere. Similarly, more advanced characterisation techniques like the N₂O titration method (to determine the exposed Cu surface area), or XANES/EXAFS experiments (to determine the oxidation states of Cu and Zn and probe metal-support interactions) should be performed on the air-, O₂- and N₂-calcined ZSM5@Cu_{1.3}ZnAl.

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3

Optimisation and preparation of $(\text{ZSM5})_x/(\text{Cu}_{1.3}\text{ZnAl})_y$ catalysts

3.1: Introduction

3.1.1: Overview

In the previous chapter, a novel $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$ core-shell catalyst was developed to convert CO_2 to DME in a single reactor. This bifunctional catalyst was designed to integrate two distinct functional phases: a $\text{Cu}_{1.3}\text{ZnAl}$ shell derived from a layered double hydroxide (LDH) precursor to catalyse the hydrogenation of CO_2 to methanol, and a ZSM-5 core to facilitate the subsequent methanol dehydration to DME. The core-shell approach was chosen to enhance metal-support interactions, improve the dispersion of the Cu^0 nanoparticles in the active catalyst, and potentially achieve synergistic behaviour between the two catalyst phases. The resulting catalyst demonstrated high DME

productivity comparable to other bifunctional CO₂-to-DME (CTD) catalysts in the literature.

Characterisation of the precursor materials revealed subtle structural differences between the core-shell and a corresponding physical mixture, including variations in the LDH crystalline anisotropy. Additionally, evidence of ion exchange within the ZSM-5 core following coprecipitation indicated that *in-situ* LDH formation in the presence of ZSM-5 alters the LDH phase and the zeolite's pore environment.

The standard coprecipitation method for LDHs tends to use sodium-containing reagents (e.g. Na₂CO₃, NaOH). In earlier work by the group, it was observed that using sodium-based reagents in the core-shell coprecipitation left residual sodium in the catalyst, negatively affecting CTD performance. To address this, the synthesis method used in Chapter 2 was modified to exclude sodium-containing reagents. This chapter builds on that foundation by altering the synthesis conditions to optimise the performance of the ZSM5@Cu_{1.3}ZnAl catalyst. The first section examines the sensitivity of the coprecipitation process, specifically how sodium incorporation affects LDH formation, sodium retention and catalyst performance. For brevity “sodium” will be used to refer to “sodium ions”, unless otherwise specified. The second section explores the effect of varying the metal catalyst to acid catalyst ratio within the core-shell to determine the optimal catalyst composition for CTD conversion.

3.1.2 Cu/ZnO/Al₂O₃ and ZSM-5 modifications

Catalyst design for the thermocatalytic conversion of CO₂ to higher-order chemicals (including hydrocarbons, alcohols, olefins and oxygenates) seeks to overcome the inherent thermodynamic stability of CO₂, whilst maintaining high selectivity towards the

desired products.¹⁻³ One promising approach is the use of bifunctional catalysts to directly convert CO₂ to DME in a single reactor via a methanol-mediated pathway (see Chapter 1.4 for a detailed discussion of the underlying reaction mechanisms). Here, a metal oxide catalyst (typically Cu-based) facilitates CO₂ hydrogenation to methanol, which is subsequently dehydrated to DME over a solid acid catalyst (such as alumina or a zeolite).⁴⁻⁹ A widely studied and effective configuration combines the Cu/ZnO/Al₂O₃ (CZA) type catalyst with microporous zeolites such as ZSM-5 or FER.^{7, 10, 11} Hybrid catalysts of this type have shown promising activity for CO₂ conversion under low-temperature conditions. Research in this area is concerned with fine-tuning aspects of the CZA and ZSM-5 phases, both separately and together, to enhance catalytic performance.

One factor that may affect the performance of hybrid CZA/zeolite catalysts is the presence of residual alkali metals, particularly sodium. Previous studies have suggested that sodium can impact both the CZA and ZSM-5 components, albeit through different mechanisms.^{12, 13}

Zeolites are often used as the acid component in bifunctional catalysts for the direct CTD conversion, where they catalyse the methanol dehydration step to form DME.^{5, 14} The aluminosilicates are often incorporated as part of the CTD catalyst design due to their high Brønsted acidity, well-defined microporous structure (which enables size and shape selectivity), and strong hydrothermal stability – an important feature given the formation of water during the CTD process (see Chapter 1.4.5 for further discussion).^{5, 15, 16} Zeolites can be tailored to optimise their acid strength and pore architecture, enabling control over the product selectivity and conferring resistance to coke formation.^{5, 17, 18} For ZSM-5 catalysts, the incorporation of alkali metals has been known to affect the catalytic performance by modifying the acidity of the aluminosilicate.¹⁹ Ion-exchange with alkali

cations, such as Na^+ reduces the Brønsted acid site density and impacts activity in acid-catalysed reactions.²⁰⁻²² Several studies have explored these effects; however, the relationship between sodium content and catalytic performance is not always straightforward.

For instance, Dyballa *et al.* demonstrated that the introduction of alkali metal oxides altered the reactivity of H-ZSM-5, influencing the product selectivity and lifetime of the Na ion-exchanged H-ZSM-5 in the methanol-to-olefins (MTO) reaction.²³ Similarly, Hashiba *et al.* observed that ion exchange of H-ZSM-5 with Na^+ reduced the number of Brønsted acid sites and led to a decreased catalytic activity during the cracking of octene.²⁴ While this study did not focus on the MTO reaction, it provides further evidence of the sensitivity of ZSM-5 to alkali metal modification. Conversely, Vishwanathan *et al.* found that Na^+ incorporation into H-ZSM-5 enhanced the selectivity towards DME (~100%) by suppressing hydrocarbon formation during methanol dehydration.²⁵ These contrasting results highlight how the effect of sodium incorporation is highly dependent on the reaction system and the targeted product: while detrimental in reactions requiring high acid density and open microporosity (e.g. MTO), partial Na^+ exchange may benefit DME synthesis by moderating the acidity and minimising undesired side reactions.

Post-synthetic alkaline treatments are frequently used to generate mesopores in zeolites, thereby enhancing mass transport through the aluminosilicate framework and reducing coke formation during acid-catalysed reactions.^{17, 26} Alkaline desilication, typically carried out using sodium hydroxide, can be designed to selectively remove silicon from the framework, creating mesopores whilst preserving the crystallinity and intrinsic acidity of the aluminosilicate (see Chapter 1.4.5 for more details).^{27, 28} The treatment conditions

(e.g. NaOH concentration, treatment time and temperature) must be controlled to prevent excessive framework degradation.²⁸

The CZA component is widely studied for its high efficiency in CO₂ (and CO) hydrogenation. Efforts to optimise its performance have largely focused on enhancing copper dispersion, increasing metal-support interactions (especially between Cu and ZnO), and improving hydrothermal stability. These properties can be tuned through the incorporation of metal promoters such as Zr, Mg, or Ga, which influences the activity of the catalyst as well as the resistance to sintering or deactivation.^{10, 29-32} In CZA-type catalysts, an excess of residual sodium can impair their catalytic activity.^{33, 34} For example, Kondrat *et al.* investigated the effect of sodium on methanol synthesis over a Cu/ZnO catalyst and reported a decline in methanol yield with increasing Na wt%.³⁵ Similarly, Jun *et al.* demonstrated that the presence of NaNO₃ in a Cu/ZnO/Al₂O₃ catalyst inhibited the CuO-ZnO interaction, ultimately leading to reduced copper dispersion (an important factor in catalytic efficiency) and poorer methanol conversion.³⁶ Wu *et al.* also emphasized the detrimental role of residual sodium in a multicomponent CuZnO-based catalyst, attributing the loss in activity to a reduction in copper surface area.¹³

These findings underscore the importance of minimising residual sodium during catalyst preparation. Initial work in the group demonstrated that a ZSM5@Cu_{1.3}ZnAl core-shell catalyst synthesised via a conventional sodium-containing coprecipitation method exhibited suboptimal CTD performance. Adapting the synthesis to eliminate Na⁺ significantly enhanced the catalyst efficiency in direct CTD conversion. In Chapter 2, the sodium-free method produced a core-shell material with well dispersed Cu⁰ nanoparticles on the ZSM-5 support and achieved DME productivities comparable to other bifunctional CTD catalysts in the literature. This raises key questions for the current chapter: how

sensitive is the coprecipitation method, particularly LDH growth on ZSM-5, to sodium? Furthermore, does the sodium method alter the mesoporosity or acidity of the zeolite through framework desilication or ion exchange? To address these questions, it was necessary to investigate the effect of sodium incorporation and base selection on the precursor synthesis and ultimately the CTD activity of the activated catalysts.

Within the context of optimising the ZSM5@Cu_{1.3}ZnAl catalyst for direct CO₂ to DME conversion, it is also necessary to explore the ideal ZSM-5:LDH ratio. The benchmarking study conducted in Chapter 2.4.2.2 highlighted the wide range of parameters that can influence the performance of hybrid CZA/zeolite catalysts. Reported ratios of CZA to zeolite vary considerably across the literature. For instance, while Naik *et al.* used a 60:40 ratio for a 6CuO-3ZnO-1Al₂O₃/HZSM-5 catalyst, Krim *et al.* used a 1:3 ratio of CZA/ZSM-5.^{7, 37} This was the same for studies using non CZA-type basic catalysts, e.g., Bonura *et al.* used a 2:1 ratio of CuZnZr/FER while Zhang *et al.* used a ratio of 70:30 Pd, carbon nanotube-promoted Cu-ZrO₂/HZSM-5.^{38, 39}

This chapter begins by examining the impact of sodium incorporation (in the core-shell synthesis method) on the performance of the ZSM5@Cu_{1.3}ZnAl hybrid catalyst, assessing whether sodium behaves as an unwanted impurity or acts beneficially as a promoter. This study also provides an opportunity to examine the extent of zeolite desilication in response to the basic conditions used during coprecipitation. The latter part of this chapter attempts to optimise the performance of the ZSM5@Cu_{1.3}ZnAl catalyst by altering the ZSM-5:CZA ratio, whilst also exploring how the degree of LDH coverage over the ZSM-5 core may affect the activity of the final catalyst following activation.

3.2: Synthesis and characterisation of sodium-treated ZSM5/Cu_{1.3}ZnAl-LDH catalyst precursors

3.2.1 Preparation of the catalyst precursors

The synthesis of core-shell materials is sensitive to a variety of parameters, including dropping rate, metal salt concentration and stirring speeds.^{40, 41} To understand how sodium might affect the core-shell precursor and thus the CO₂ hydrogenation activity of the activated catalyst, ZSM5@Cu_{1.3}ZnAl-LDH core-shells were synthesised using two coprecipitation methods which utilise sodium-containing reagents. The coprecipitation of the core-shell catalyst precursor involves the slow addition of a Cu:Zn:Al (1.3:1:1) metal salt solution to a dispersion of ZSM-5 where the pH is simultaneously monitored and controlled by the addition of a base, keeping to pH 10 throughout the reaction. The sodium-free method used to generate the LDH and core-shell samples in Chapter 2 utilised basic copper carbonate (CuCO₃.Cu(OH)₂) as the copper and carbonate source, with tetrapropylammonium hydroxide (TPAOH) to control the pH. A Na-treated counterpart was synthesised by replacing TPAOH with NaOH, and generated a light blue powder referred to as ZSM5@Cu_{1.3}ZnAl-LDH-Na. The ‘standard’ coprecipitation method commonly used to synthesise LDHs uses Na₂CO₃ as the carbonate source and NaOH for pH control.⁴²⁻⁴⁶ To synthesise the Na₂CO₃-treated core-shell, Cu(NO₃)₂.3H₂O, Zn(NO₃)₂.6H₂O and Al(NO₃)₃.9H₂O was added to a dispersion of ZSM-5 and excess Na₂CO₃. The pH was maintained at pH 10 by the addition of NaOH. The light blue powder collected from the standard coprecipitation method is described as ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃. The LDH counterparts were synthesised using similar procedures, but without the ZSM-5 dispersion. Lastly, physical mixtures were made by

combining the LDH counterparts with pristine ZSM-5 in a 1:1 weight ratio. Full details regarding the synthesis of the sodium free core shell (i.e. ZSM5@Cu_{1.3}ZnAl-LDH-TPA) and the ZSM5@Cu_{1.3}ZnAl-LDH-Na and ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ core-shells (as well as the corresponding LDHs) can be found in Chapter 6.3.

To act as controls, ZSM-5 was also treated with basic solutions at pH 10 to replicate the alkaline conditions experienced by the zeolite during coprecipitation. ZSM5-TPA, ZSM5-Na and ZSM5-Na₂CO₃ correspond to ZSM-5 treated in TPAOH, NaOH, and NaOH/Na₂CO₃ (see Chapter 6.3.8).

3.2.2: Characterisations of TPA-, Na- and Na₂CO₃-treated ZSM5/Cu_{1.3}ZnAl catalyst precursors

Two-phase Rietveld refinement was performed on synchrotron powder X-ray diffraction (PXRD) data of ZSM5@Cu_{1.3}ZnAl-LDH-Na (Figure 3.1) and ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ (Figure 3.2) to identify differences in the crystal structures of the LDH-phase in response to the different coprecipitation methods. Full details of the Rietveld refinement and structural parameters of the core-shells are summarised in Table B.1 and are compared against sodium-free Cu_{1.3}ZnAl-LDH-TPA and ZSM5@Cu_{1.3}ZnAl-LDH-TPA.

The (00 l) basal plane Bragg reflections indicative of a hydrotalcite-like material can be seen in the PXRD patterns of both Na- and Na₂CO₃-treated ZSM5@Cu_{1.3}ZnAl-LDH.^{45, 47, 48} These Bragg reflections occur at $2\theta = \sim 6.2^\circ$ and $\sim 12.5^\circ$ which correspond to the (003) and (006) planes respectively. Reflections typical of an MFI zeolite are observed between $2\theta = 3 - 5^\circ$, with the peaks at $2\theta = \sim 4.2^\circ$ and $\sim 4.7^\circ$ corresponding to the (101) and (200) Bragg reflections. The narrow peak width reflects the high crystallinity of the

zeolite, suggesting that there were no significant changes to the core structure following coprecipitation.⁴⁹⁻⁵¹

Lattice parameter a was refined based on a rhombohedral 3R unit cell for the LDH phase in the core-shells and found to be similar across the samples (3.060 Å – 3.080 Å). Lattice parameter c was approximately 22.8 Å for all LDH shells. The similarity in the unit cell parameters demonstrates that all LDH shells share the same crystal structure and are carbonate-intercalated LDHs (based on $d_{003} = 7.580$ Å).^{47, 52, 53} This suggests that residual Na^+ in the ZSM5@Cu_{1.3}ZnAl-LDH-Na and ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ core-shell samples (as determined by ICP-OES analysis) does not occupy the interlayer region of the LDH and that the crystal structure is unaffected by the change in the coprecipitation method.

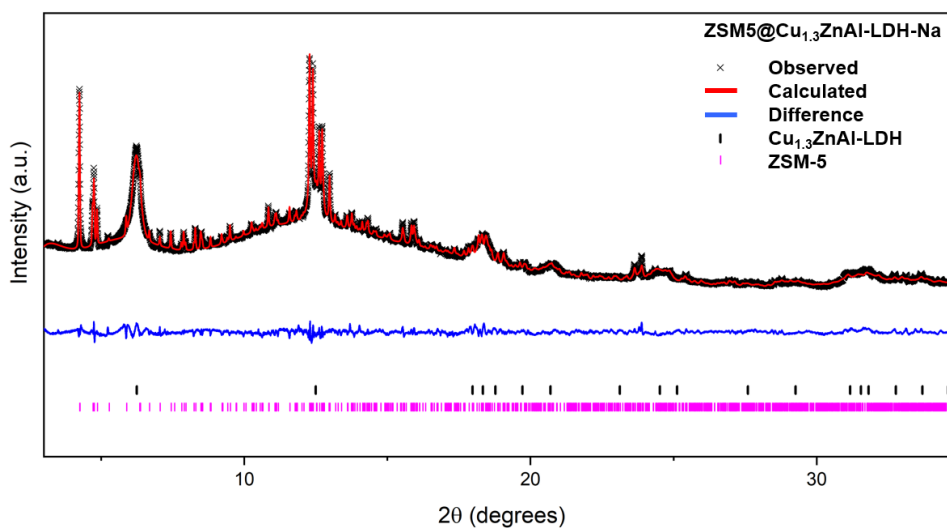


Figure 3.1: Two-phase Rietveld refinement of ZSM5@Cu_{1.3}ZnAl-LDH-Na against ZSM-5 and Cu_{1.3}ZnAl-LDH. PXRD data was collected at I11 Diamond Light Source.

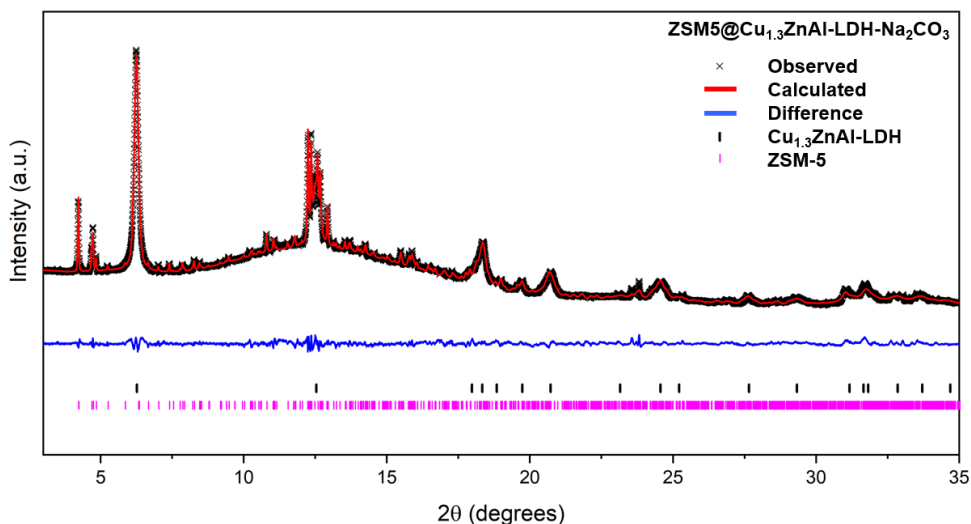


Figure 3.2: Two-phase Rietveld refinement of ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ against ZSM-5 and Cu_{1.3}ZnAl-LDH. PXRD data was collected at I11 Diamond Light Source.

Using the Scherrer equation, the crystallite domain lengths of the Cu_{1.3}ZnAl-LDH phase in the core-shells were estimated and are summarised in Table 3.1 (see Table B.2 for full Scherrer parameters). ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ exhibits the largest D_{003} value (24.9 nm), indicating the highest degree of layer stacking order. In contrast, Na- and Na₂CO₃-treated samples have lower degrees of stacking which suggests that the coprecipitation method influences the crystallite growth of the LDH.

Table 3.1: d-spacing and domain lengths of ZSM5@Cu_{1.3}ZnAl-LDH-TPA, ZSM5@Cu_{1.3}ZnAl-LDH-Na and ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ from two-phase Rietveld refinement. Refinements were performed on PXRD data collected at Ill Diamond Light Source.

Sample	d_{003} (Å)	d_{110} (Å)	D_{003}^a (nm)	D_{110}^a (nm)	Crystalline anisotropy (D_{110}/D_{003})
ZSM5@Cu _{1.3} ZnAl-LDH- TPA	7.593	1.541	18.4	12.4	0.7
ZSM5@Cu _{1.3} ZnAl-LDH- Na	7.597	1.534	12.5	4.8	0.4
ZSM5@Cu _{1.3} ZnAl-LDH- Na ₂ CO ₃	7.569	1.537	24.9	8.9	0.4

^aK = 0.9 in Scherrer's equation.

Due to time constraints, synchrotron data of the Na- and Na₂CO₃-treated Cu_{1.3}ZnAl-LDH was not collected. To compare the PXRD results, the core-shells and corresponding LDHs were analysed using a Bruker D8 ECO diffractometer. Full comparisons of the core-shells, LDHs and base-treated ZSM-5 samples are summarised in Figure 3.3. Rietveld refinements were performed on the PXRD patterns (Figure B.1 – Figure B.9) and the structural parameters are summarised in Table B.3.

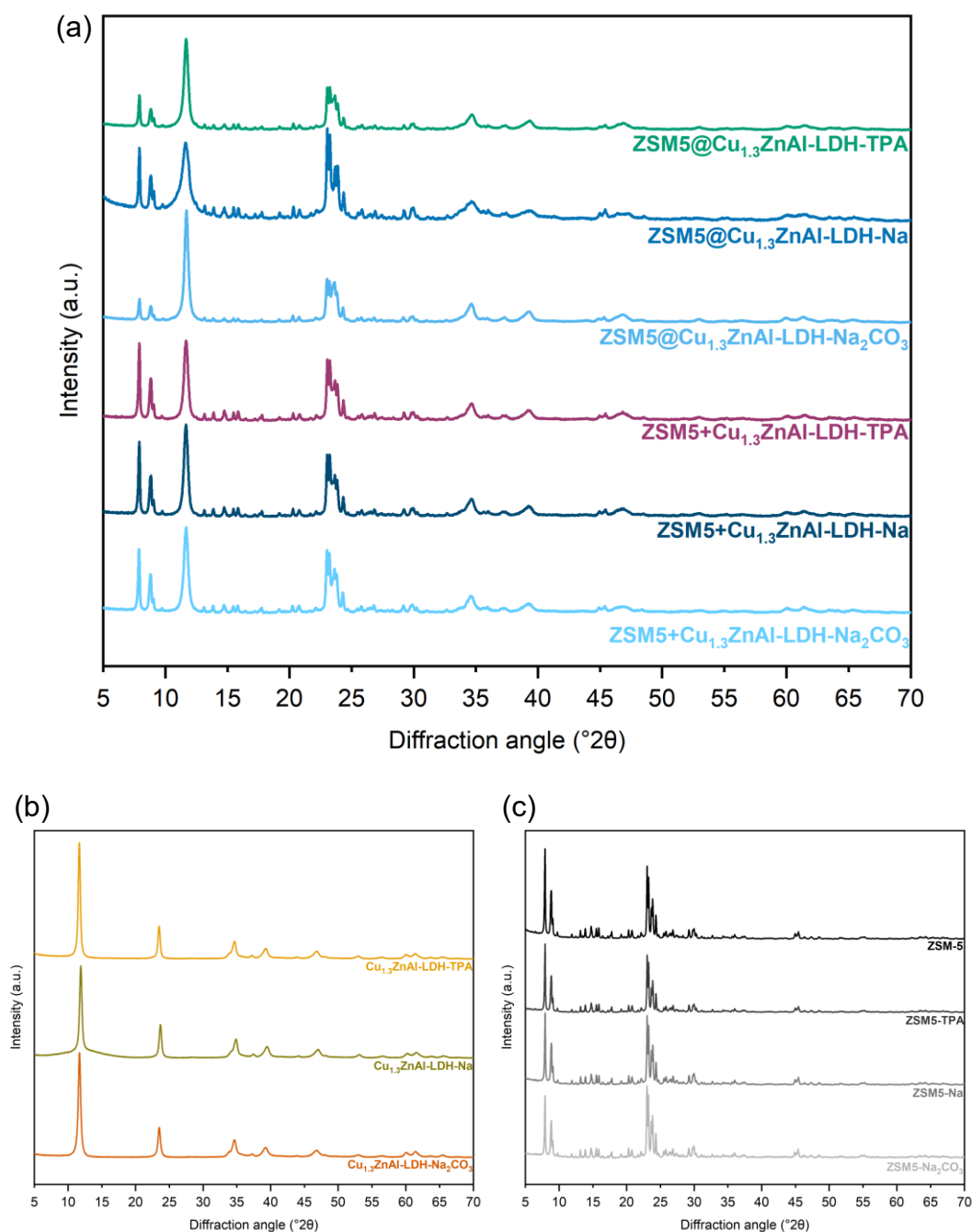


Figure 3.3: PXRD of (a) core-shells and physical mixtures, (b) LDHs and (c) ZSM-5 treated in TPAOH, NaOH and Na₂CO₃. PXRD data was collected on a Bruker D8 ECO diffractometer.

As shown in Figure 3.3a, the PXRD patterns of Na- and Na₂CO₃-treated core-shells are consistent with the expected structures, with peaks that are indicative of the LDH and ZSM-5. Overall, the PXRD data collected using the Bruker diffractometer are in good

agreement with those obtained from synchrotron measurements. All core-shells exhibited similar lattice parameters, consistent with the values derived from the synchrotron data. The refined D_{110} values follow a similar trend: ZSM5@Cu_{1.3}ZnAl-LDH-Na (5.4 nm) > ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ (6.3 nm) > ZSM5@Cu_{1.3}ZnAl-LDH-TPA (7.4 nm). Variations in instrumental broadening between diffractometers (affecting the full width at half maximum (FWHM) of the diffraction peaks) likely contributed to the differences observed in crystallite domain length estimations between the Bruker and synchrotron data.

The PXRD profiles for the physical mixtures were also consistent with expectations. No significant differences were observed in the *a*- or *c*-lattice parameters of the LDH phase across the TPA-, Na- and Na₂CO₃-treated samples (see Table B.3). ZSM-5 and the alkaline-treated samples (ZSM5-TPA/Na/Na₂CO₃; Figure 3.3c) also exhibited similar lattice parameters ($a \approx 20.2$ Å, $b \approx 20.0$ Å, and $c \approx 13.5$ Å) with no change in peak shape in the PXRD profile, confirming that the alkaline treatments did not compromise the crystal structure or crystallinity of the zeolite.

Domain lengths of the core-shells were compared against the physical mixtures and are summarised in Table 3.2. Across all physical mixtures (ZSM5+Cu_{1.3}ZnAl-LDH-TPA, ZSM5+Cu_{1.3}ZnAl-LDH-Na, ZSM5+Cu_{1.3}ZnAl-LDH-Na₂CO₃) the crystalline anisotropy remains similar. In contrast, ZSM5@Cu_{1.3}ZnAl-LDH-Na and ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ are more anisotropic than ZSM5@Cu_{1.3}ZnAl-LDH-TPA. This suggests that among the coprecipitation methods tested, only the sodium-free approach facilitates the growth of larger LDH crystallites.

Table 3.2: Domain lengths of Na- and Na₂CO₃-treated core-shells, physical mixtures and LDHs from two-phase Rietveld refinement. Refinements were performed on PXRD data collected on a Bruker D8 ECO diffractometer.

Sample	D_{003}^a (nm)	D_{110}^a (nm)	Crystalline anisotropy (D_{110}/D_{003})	Sample	D_{003}^a (nm)	D_{110}^a (nm)	Crystalline anisotropy (D_{110}/D_{003})
ZSM5@Cu _{1.3} ZnAl- LDH-Na	17.0	5.4	0.3	ZSM5@Cu _{1.3} ZnAl- LDH-Na ₂ CO ₃	21.4	6.3	0.3
ZSM5+Cu _{1.3} ZnAl- LDH-Na	20.2	7.0	0.3	ZSM5+Cu _{1.3} ZnAl- LDH-Na ₂ CO ₃	18.9	7.0	0.4
Cu _{1.3} ZnAl-LDH- Na	18.5	6.0	0.3	Cu _{1.3} ZnAl-LDH- Na ₂ CO ₃	17.1	6.9	0.4

^aK = 0.9 in Scherrer's equation

The physical mixtures exhibited D_{003} and D_{110} values comparable to their respective LDH counterparts, consistent with the PXRD results for ZSM5+Cu_{1.3}ZnAl-LDH-TPA and Cu_{1.3}ZnAl-LDH-TPA (see Chapter 2.2.2 for more details).

Ultimately, the results from PXRD analysis shows that the Cu_{1.3}ZnAl-LDH and ZSM-5 phases were present in all core-shells and physical mixtures. The coprecipitation method mostly affected crystallite domain lengths and not the crystal structure of either the LDH or the ZSM-5 phase in the core-shells.

Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis were used to investigate changes to the morphology of the Na- and Na₂CO₃-treated core-shells and physical mixtures.

As shown in Figure 3.4, the LDH platelets and semi-cuboidal ZSM-5 particles (with dimensions from 100 nm to 1 – 2 μ m) are present in all core-shell and physical mixture samples. The LDH platelets appear as thin nanosheets that partially aggregate while also coating around the ZSM-5 particles. Such aggregation is typical of bulk LDHs as a consequence of the high surface charges of the LDH sheets favouring *ab*-face stacking of the LDH platelets.^{44, 54} The size of the ZSM-5 particles determines the overall dimensions of the core-shell structures which tend towards the micrometre scale.

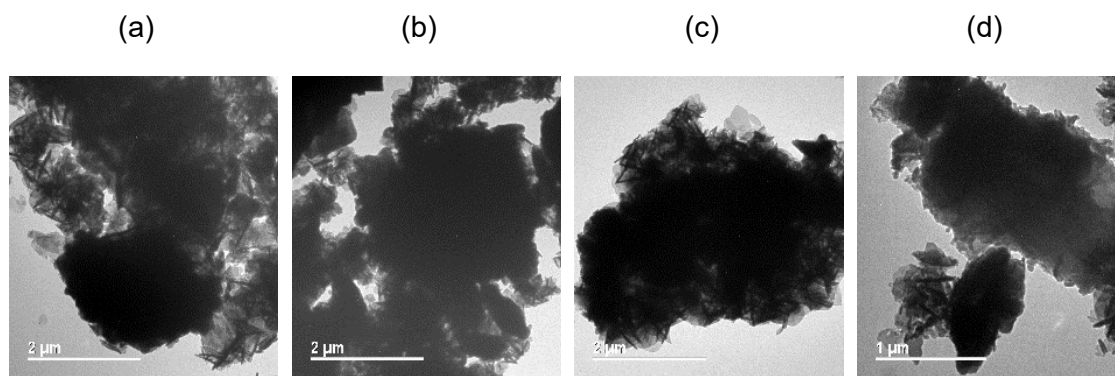


Figure 3.4: TEM images of (a) ZSM5@Cu_{1.3}ZnAl-LDH-Na, (b) ZSM5+Cu_{1.3}ZnAl-LDH-Na, (c) ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃, and (d) ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ catalyst precursors.

TEM imaging in combination with EDX mapping (Figure 3.5) highlights the distribution of Cu/Zn over the zeolites in the core-shell and physical mixture samples. The coverage of the LDHs over the ZSM-5 particles in ZSM5@Cu_{1.3}ZnAl-LDH-Na is not as uniform as the coverage in the ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ core-shell. It also appears that the Na-treated physical mixture has better coverage than the Na₂CO₃-treated physical mixture and is comparable to that observed in ZSM5@Cu_{1.3}ZnAl-LDH-Na. TEM produces 2D projection images of a sample which makes it challenging to distinguish the overlapping features. An alternative technique, SEM, can provide clearer images of the surface topology. This will be discussed in greater detail in the following section based on the images collected from SEM imaging. The crystallite domain lengths of the LDH-phase (estimated using PXRD data) changed depending on the sodium-treatment used which might have impacted the growth of the LDH on the zeolite surface, accounting for the differences in coverage seen between the core-shells. Some coverage is anticipated for the physical mixtures due to the attractive electrostatic forces between the positively charged LDH sheets and the negatively charged ZSM-5 surface.⁵⁵

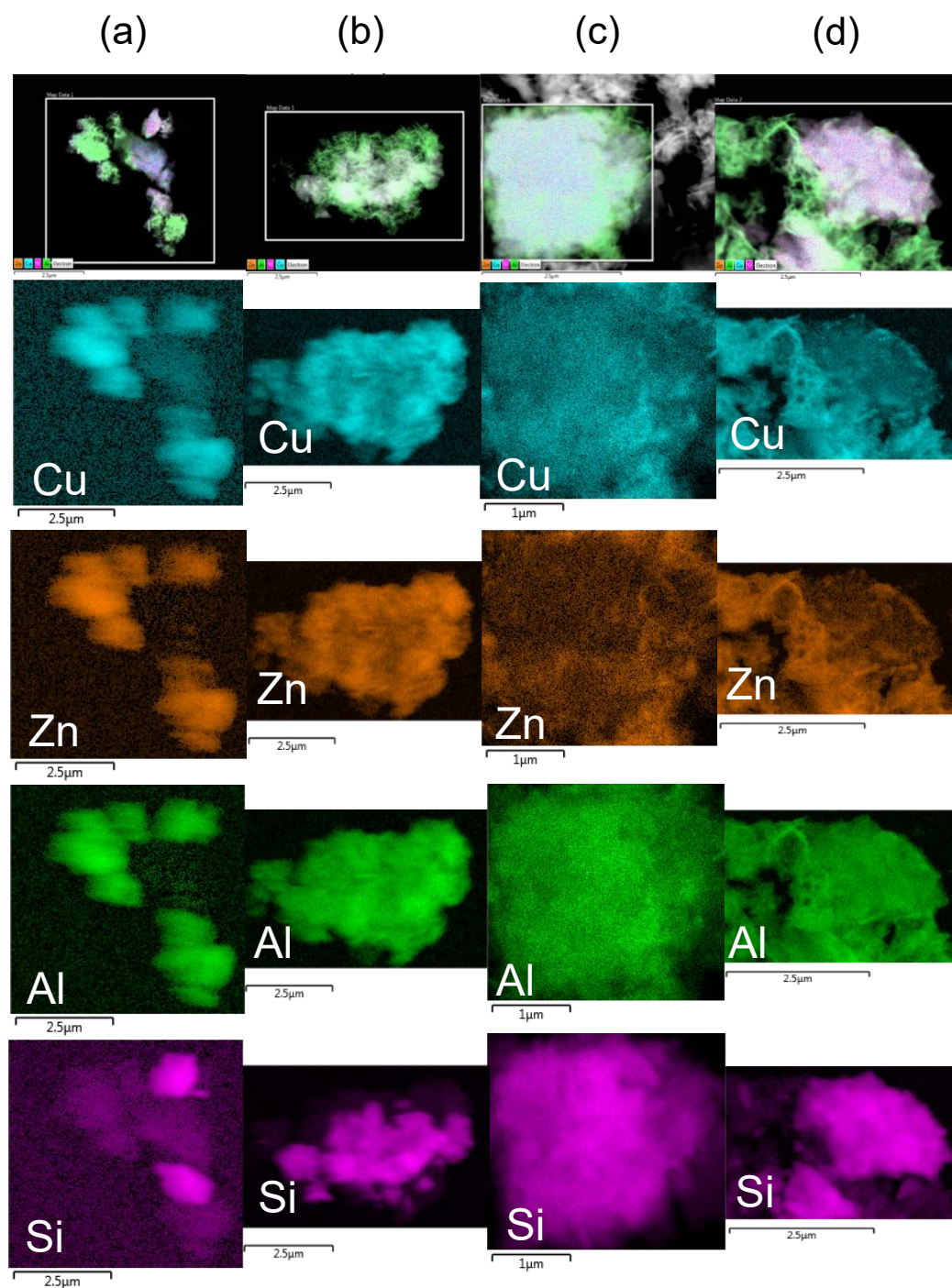


Figure 3.5: STEM/EDX of (a) $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH-Na}$, (b) $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDH-Na}$, (c) $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$, and (d) $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$ catalyst precursors showing the distribution of on Cu (blue), Zn (orange), Al (green) and Si (magenta).

The platelet size distribution of the $\text{Cu}_{1.3}\text{ZnAl-LDH}$ phase for Na- and Na_2CO_3 -treated LDHs, and in the core-shell and physical mixtures were taken from multiple TEM images and are summarised in Figure 3.6. The average platelet size of $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH-Na}$ (15.9 ± 6.4 nm) is thinner than $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$ (27.8 ± 10.0 nm) which is consistent with the D_{003} length calculated from PXRD analysis. Also consistent with the PXRD data are the results for the physical mixture samples which show that the average thickness of the LDH platelets in $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDH-Na}$ (29.7 ± 11.3 nm) is larger than the core-shell counterpart. The platelet thickness in the Na_2CO_3 -treated core-shell is slightly thicker than in the physical mixture (26.3 ± 9.9 nm); however, this difference is considered minimal due to the large standard deviation. This reiterates the earlier observation that the D_{003} values for $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$ and $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$ are similar. Comparing the TEM platelet size distribution of the core-shell and physical mixtures with sodium-free $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH-TPA}$ and $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDH-TPA}$ (see Chapter 2.2.2), it can be said that the size of the LDH sheets is the largest in the Na_2CO_3 -treated core-shell.

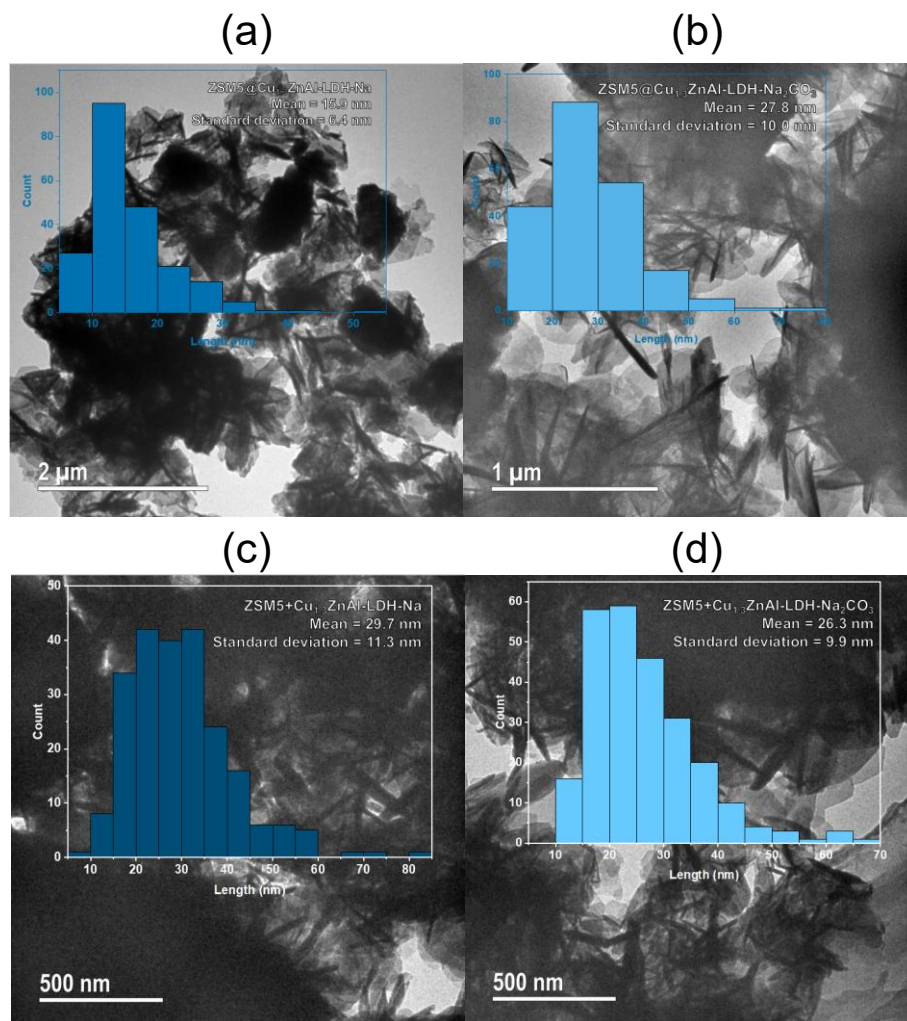


Figure 3.6: $\text{Cu}_{1.3}\text{ZnAl-LDH}$ platelet size distribution in (a) Na-treated and (b) Na_2CO_3 -treated $\text{ZSM5}@Cu_{1.3}\text{ZnAl-LDH}$ core-shells and (c) Na-treated and (d) Na_2CO_3 -treated $\text{ZSM5}+Cu_{1.3}\text{ZnAl-LDH}$ physical mixture.

Taken together, the TEM images shows that the involvement of sodium in the coprecipitation method has a minor effect on the platelet thickness of the $\text{Cu}_{1.3}\text{ZnAl-LDH}$ phase in the core-shell. EDX mapping shows that the coverage is uniform across the zeolite cores in either the Na- or Na_2CO_3 -treated core-shell samples. The major difference appears in the coverage of the ZSM-5 particle in the physical mixtures, whereby the thinner $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}$ appears to have better coverage over the zeolite in $\text{ZSM5}+Cu_{1.3}\text{ZnAl-LDH-Na}$ compared to Na_2CO_3 -treated or TPA-treated physical mixtures. This suggests that while the *in-situ* coprecipitation of $\text{Cu}_{1.3}\text{ZnAl-LDH}$

successfully forms a core-shell, reasonable LDH coverage over the ZSM-5 particle can still occur in the physical mixture, particularly with the thinner $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}$ platelets. In contrast, the thicker $\text{Cu}_{1.3}\text{ZnAl-Na}_2\text{CO}_3$ platelets do not coat the zeolite as well in $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$.

EDX analysis of the micrographs show clear differences in the extent of $\text{Cu}_{1.3}\text{ZnAl-LDH}$ coverage between the core-shells and physical mixtures, confirming that the core-shell morphology can be successfully achieved using all three *in-situ* coprecipitation methods.

SEM in combination with EDX analysis was also used to investigate the distribution of Cu/Zn over the core-shells and physical mixtures. As shown in Figure 3.7, SEM imaging provides a clearer assessment of the extent of LDH coverage over the ZSM-5 surface. EDX mapping of the physical mixtures $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDH-Na}$ and $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$ reveals minimal overlap between the Si (magenta) of the ZSM-5 particles and the Cu (blue) or Zn (orange) from the LDH. This indicates that the LDH coverage on the zeolite is neither uniform nor extensive in these samples. The results suggest inferior LDH dispersion in the physical mixtures compared to the core-shells, consistent with the observations made for sodium-free $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDH-TPA}$ and $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDH-TPA}$. Point analysis of the EDX mapping also demonstrates how the distribution of Cu/Zn over ZSM-5 improved in the core-shells as opposed to the physical mixtures (Table B.5 – Table B.8). The Cu:Zn ratios from the EDX analysis ranges between 1.3 – 1.5 and therefore reflect the 1.3:1 ratio used in the coprecipitation method (also confirmed by ICP-OES).

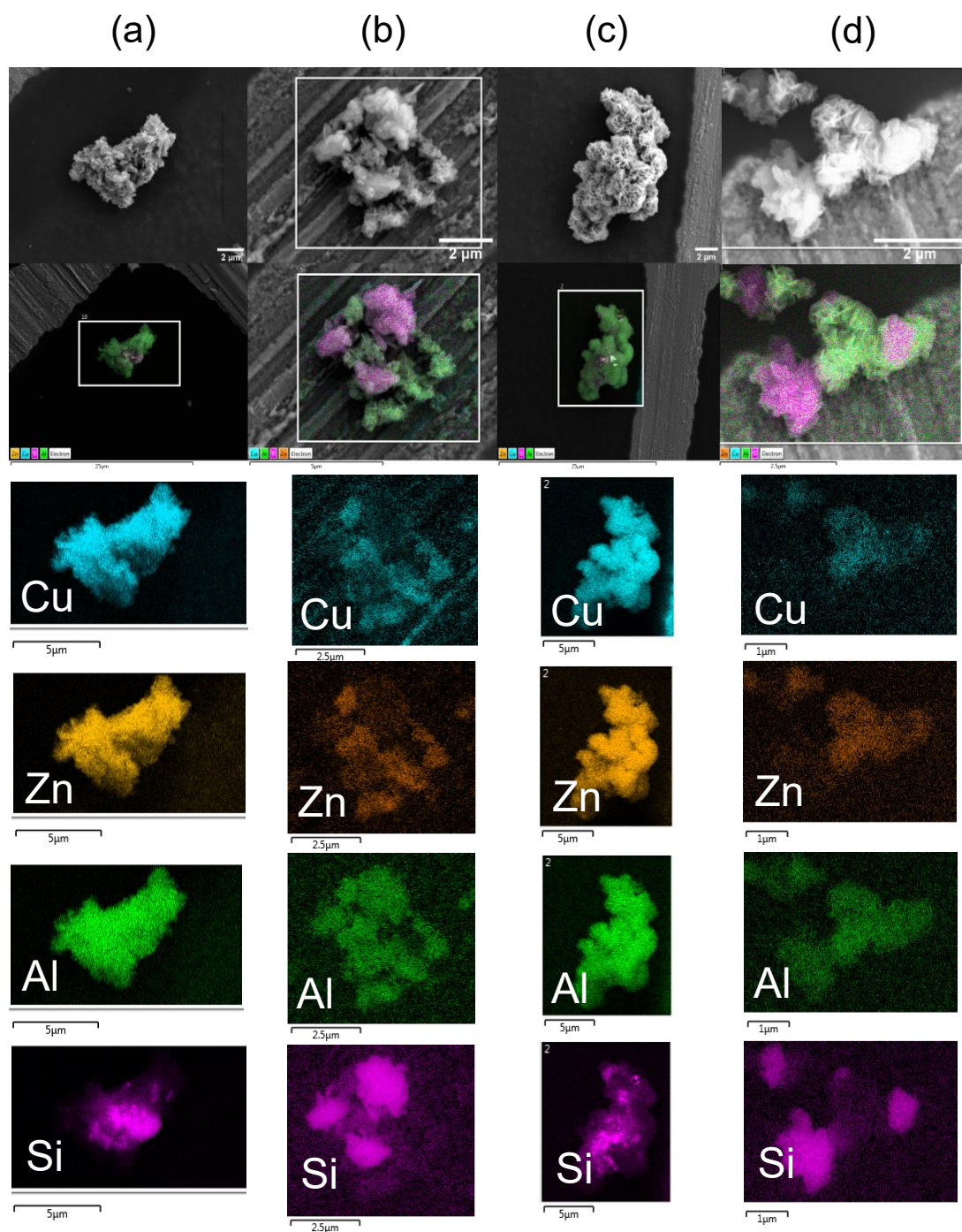


Figure 3.7: SEM/EDX of (a) ZSM5@Cu_{1.3}ZnAl-LDH-Na, (b) ZSM5+Cu_{1.3}ZnAl-LDH-Na, (c) ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ and (d) ZSM5+Cu_{1.3}ZnAl-LDH-Na₂CO₃ catalyst precursors showing the distribution of on Cu (blue), Zn (orange), Al (green) and Si (magenta).

SEM images of the base-treated zeolites showed no discernible differences in surface morphology when compared to one another or to pristine ZSM-5 (Table B.10). This suggests there were no significant structural alterations at the external surface. To confirm if the mesoporosity or surface area had been affected by alkaline treatments, N₂ adsorption (BET) analysis was carried out and are discussed later in this chapter.

SEM/EDX imaging supports the results from STEM/EDX analysis and suggests that the Cu_{1.3}ZnAl-LDH coverage over ZSM-5 is more effective in the core-shell samples than in the physical mixtures. This effect is consistent across all core-shells, irrespective of the coprecipitation method.

FTIR spectra of ZSM5@Cu_{1.3}ZnAl-LDH-TPA, ZSM5@Cu_{1.3}ZnAl-LDH-Na and ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃, shown in Figure 3.8a, display characteristic peaks corresponding to both the LDH and ZSM-5 phases, confirming the presence of both components in all three samples.

The spectra for the pristine ZSM-5 and base-treated ZSM-5 show absorbances at ~1200, 1041 and 788 cm⁻¹ that are characteristic of the SiO₄ tetrahedron units.⁵⁰ As previously described in Chapter 2.2.2, the bands at ~1200 cm⁻¹ and 788 cm⁻¹ are associated with the vibrations of the external linkages between the (Si, Al)O₄ tetrahedra whilst the absorbance band at 1041 cm⁻¹ is associated with the internal (asymmetric) stretching vibrations of the tetrahedra.^{50, 56} The absence of stretching vibrations in the 2980 – 2880 cm⁻¹ region across all zeolite samples indicates a lack of C-H functional groups.⁵⁷ This suggests that neither pristine ZSM-5 nor the base-treated samples contain residual organic linkers, and that treatment with TPAOH does not lead to pore blocking within the zeolite framework. This is expected given the bulky size of TPAOH, which

has the longest dimension of ~ 7.4 Å as simulated in Chem3D (Figure 3.8b), making it unlikely to diffuse through the 10-membered ring openings of ZSM-5 (5.3×5.6 Å and 5.1×5.5 Å, Figure 3.8c). The absorption band at 1450 cm^{-1} is associated with the bending mode of bound ions within the zeolite framework, in this case NH_4^+ .^{58, 59} This NH_4^+ bending peak appears in the profiles of all physical mixtures (see Table B.11 for the FTIR profiles of ZSM5+Cu_{1.3}ZnAl-LDH-Na and ZSM5+Cu_{1.3}ZnAl-LDH-Na₂CO₃) which further suggests that some NH_4^+ ion exchange has occurred during coprecipitation of the core-shells. It is possible that pristine ZSM-5 may undergo ion exchange with the $\text{Cu}^{2+}/\text{Zn}^{2+}/\text{Al}^{3+}/\text{Na}^+$ ions during coprecipitation. For instance, after suspending ZSM-5 in a $\text{Cu}(\text{NO}_3)_2$ solution at room temperature, Kim *et al.* incorporated Cu^{2+} ions into the zeolite, forming Cu-impregnated ZSM-5.⁶⁰

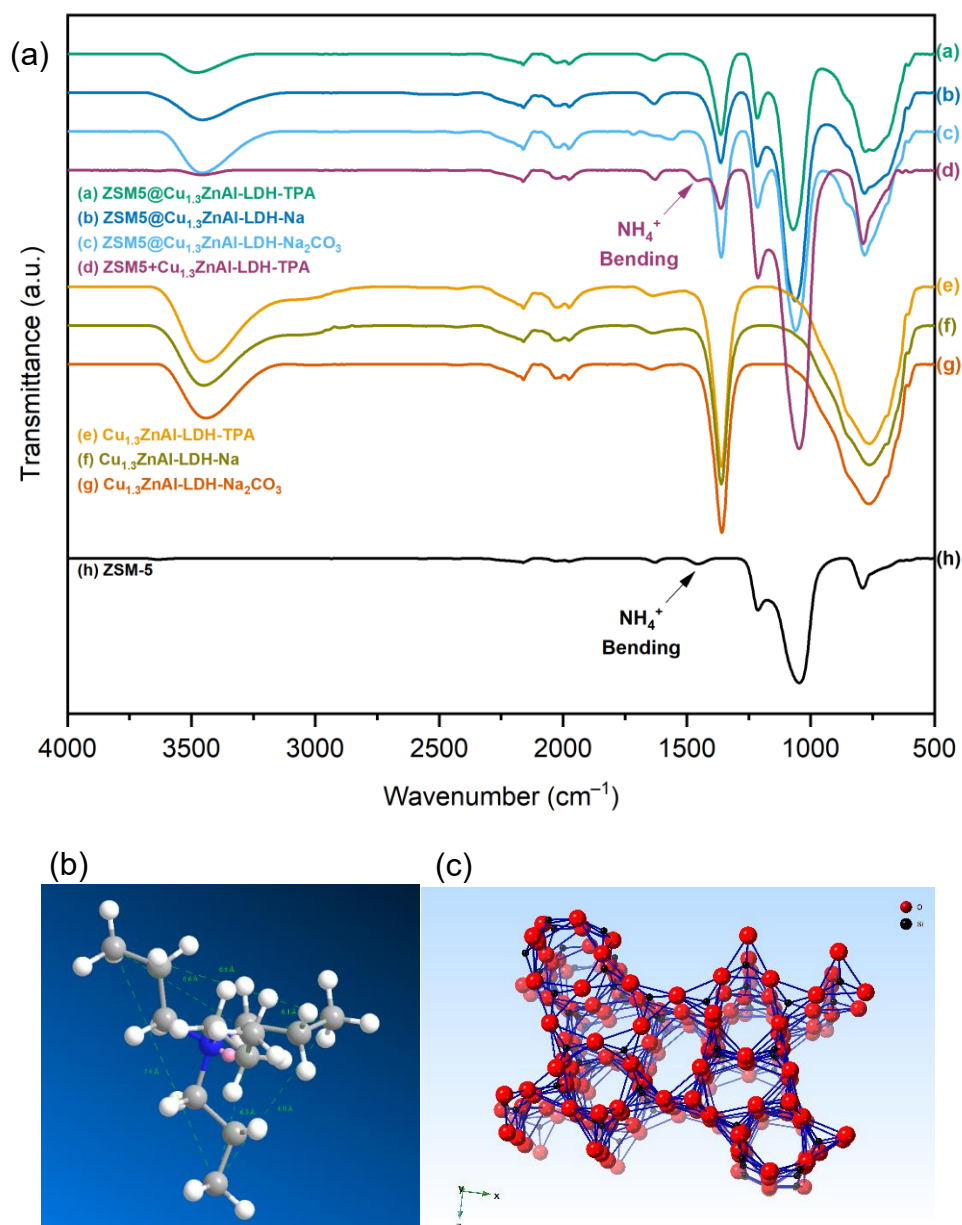


Figure 3.8: (a) FTIR profiles of the core-shells, physical mixtures and ZSM-5 synthesised/treated in different bases, (b) Simulated TPAOH molecule in Chem3D, (c) pore channels simulated from ZSM-5 CIF files (generated from synchrotron data collected at Ill Diamond Light Source).

In the case of the core-shells (and physical mixtures) the 788 cm^{-1} peak is obstructed by the broader, more intense peaks associated with CO_3^{2-} bending mode (1360 cm^{-1}) and lattice vibrations (780 cm^{-1}) in the Cu_{1.3}ZnAl LDH.^{47, 61, 62} Other peaks that are

characteristic of an LDH include the transmittance between $3670 - 2760 \text{ cm}^{-1}$ (O–H stretching of hydroxyl groups), and 1630 cm^{-1} (H_2O bending) (Table B.9).⁶¹

FTIR analysis confirms the presence of both the $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and ZSM-5 phases in the Na- and Na_2CO_3 -treated core-shells (and physical mixtures). The presence of the peak associated with NH_4^+ bending in the profiles of TPA-, Na- and Na_2CO_3 -treated ZSM-5 suggests that the ammonium counter cation in pristine ZSM-5 undergoes partial exchange with Na^+ ions. The absence of this peak in the $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH}$ core-shells suggests that the ZSM-5 core may have undergone ion exchange with $\text{Cu}^{2+}/\text{Zn}^{2+}/\text{Al}^{3+}/\text{Na}^+$ species during the coprecipitation. ICP-OES analysis was also conducted to investigate this further and is discussed in a later section.

To assess the impact of sodium incorporation on the thermal stabilities of Na- and Na_2CO_3 -treated core-shells, physical mixtures and LDHs, TGA was conducted on the samples and compared against the sodium-free counterparts.

The TGA profiles for $\text{ZSM5@Cu}_{1.3}\text{nAl-LDH}$ core-shells (Figure 3.9a) support previous characterisations, indicating the presence of both LDH and ZSM-5 phases in the sample (likewise for the physical mixtures). For full summaries of the TGA data consult Table B.10). The first WLR in the TGA/dTGA profiles of the core-shells occurs between $30 - 200 \text{ }^\circ\text{C}$ and is associated with the loss of surface-adsorbed water as well as water within the pores of ZSM-5.⁶³⁻⁶⁵ This is reflected in the TGA/dTGA profiles of the TPA-, Na- and Na_2CO_3 -treated LDHs (weight loss between $17.3 - 18.2\%$) and ZSM-5 (weight loss between $7.8 - 8.3\%$).

Pristine ZSM-5 and the base-treated ZSM-5 samples show a small weight loss ($1.7 - 2.9\%$) between $200 - 400 \text{ }^\circ\text{C}$, which is attributed to the decomposition of

ammonium.⁶⁶ Thus, the second WLR in the core-shells (5.9 – 9.8%) and physical mixtures (6.3 – 6.8%) is primarily attributed to dehydroxylation of the metal hydroxide lattice and partial decarbonylation of the interlayer carbonates in the $\text{Cu}_{1.3}\text{ZnAl-LDH}$.⁶⁴

⁶⁷ The final WLR between 500 – 800 °C for the zeolites is minimal (~0.4%), hence the loss observed within this region of the TGA/dTGA profiles for the core-shells and physical mixtures is due to decarbonylation of strongly held carbonates in the LDH.⁶⁸

Differences in the relative intensities of the two peaks in this region are likely due to $\text{M}^{2+}\text{M}^{3+}\text{O}_y(\text{CO}_3)_2$ oxycarbonate groups with different thermal stabilities.^{69, 70}

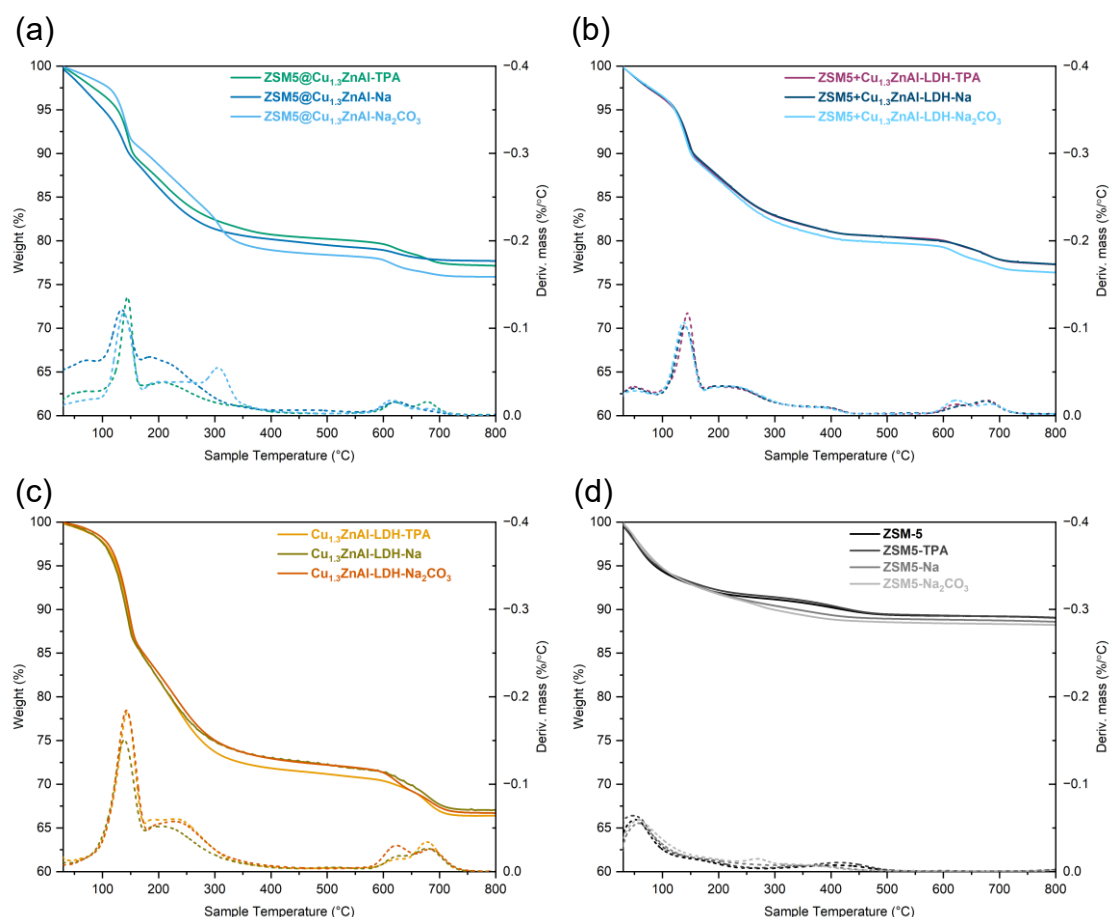


Figure 3.9: TGA/dTGA profiles for TPA-, Na-, Na_2CO_3 -treated (a) core-shells, (b) physical mixtures, (c) LDHs and (d) ZSM-5 zeolites.

The sodium-treatment does not have a significant impact on the thermal properties of the core-shells or the physical mixtures. All hybrid samples possess an ZSM-5:LDH ratio of $\sim 1:1$ which matches the anticipated amount based on the synthesis method. The TGA also confirms the presence of both LDH and ZSM-5 phases within all hybrid samples.

ICP-OES/CHN elemental analysis was used to determine the Cu:Zn ratio in the LDH phase and the total Na content across the various core-shells, physical mixtures, LDHs and ZSM-5 samples. Results of the elemental analysis are summarised in Table 3.3 where the Na, Cu, Zn, Al wt% in the Na- and Na_2CO_3 -treated samples have been compared against the sodium-free counterparts.

For all LDH-containing samples, the Cu:Zn ratio ranged between 1.3 – 1.52 which matches the ratios used in the synthesis method. The Al content was lower than anticipated which suggests that the zeolite had not digested in the preparation method, reflecting the ICP-OES results discussed in Chapter 2.2.2.

ZSM5@Cu_{1.3}ZnAl-LDH-Na (1.51 wt%) and ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ (1.06 wt%) contain higher sodium content than ZSM5@Cu_{1.3}ZnAl-LDH-TPA (0.22 wt%) generated in the sodium-free coprecipitation method. The presence of Na in ZSM5@Cu_{1.3}ZnAl-LDH-TPA was previously attributed to contamination in the water used during the coprecipitation (see Chapter 2.2.2 for more details). Cu_{1.3}ZnAl-LDH-Na (0.32 wt%) and Cu_{1.3}ZnAl-LDH-Na₂CO₃ (0.23 wt%) show similar sodium contents to their corresponding physical mixtures, ZSM5+Cu_{1.3}ZnAl-LDH-Na (0.31 wt%) and ZSM5+Cu_{1.3}ZnAl-LDH-Na₂CO₃ (0.27 wt%). In contrast, the sodium content in the core-shell samples is greater than the physical mixture and LDH counterparts, suggesting that the increased amount of sodium arises from Na⁺ being retained within the zeolite core.

CHN analysis shows lower nitrogen content in the core-shells compared to the physical mixtures. The nitrogen detected is attributed to the NH_4^+ in ZSM-5 and is present in all zeolite samples. Among the zeolites, ZSM-5 contained the largest amount of nitrogen (1.49 wt%), followed closely by TPA-treated ZSM-5 (1.44 wt%). In contrast, ZSM5- Na_2CO_3 showed considerably higher carbon content (2.20 wt%) and the lowest amount of nitrogen level (0.47 wt%) suggesting that carbonate species may have been trapped within the zeolite during base treatment. These results suggest partial ion-exchange between NH_4^+ in pristine ZSM-5 and Na^+ species, consistent with the FTIR analysis showing the NH_4^+ peak present in all base-treated ZSM-5 samples.

Table 3.3: ICP-OES/CHN elemental analysis of the TPA-, Na- and Na₂CO₃-treated core-shells, physical mixtures, LDHs and zeolites treated with different bases.

Sample	Na (wt%)	Cu (wt%)	Zn (wt%)	Al (wt%)	Cu:Zn:Al	C (wt%)	H (wt%)	N (wt%)
ZSM5@Cu _{1.3} ZnAl-LDH-TPA	0.22	14.11	10.02	4.43	1.45:1:1.07	2.34	1.89	0.47
ZSM5@Cu _{1.3} ZnAl-LDH-Na	1.51	13.10	9.49	3.95	1.42:1:1.01	0.94	1.76	0.11
ZSM5@Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	1.06	14.77	10.09	4.66	1.51:1:1.12	1.80	1.61	0
ZSM5+Cu _{1.3} ZnAl-LDH-TPA	0	12.73	10.08	4.20	1.30:1:1.01	1.71	1.97	0.95
ZSM5+Cu _{1.3} ZnAl-LDH-Na	0.31	13.35	9.01	4.31	1.52:1:1.16	1.01	1.83	0.90
ZSM5+Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	0.27	9.38	6.82	3.34	1.41:1:1.19	1.26	1.76	0.88
^a Cu _{1.3} ZnAl-LDH-TPA	0.26	26.17	19.00	7.45	1.42:1:0.95	2.02	2.59	0

Sample	Na (wt%)	Cu (wt%)	Zn (wt%)	Al (wt%)	Cu:Zn:Al	C (wt%)	H (wt%)	N (wt%)
Cu _{1.3} ZnAl-LDH-Na	0.32	28.29	19.81	7.99	1.47:1:0.98	1.79	2.42	0.26
Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	0.23	24.86	18.46	6.92	1.39:1:0.91	1.98	2.37	0
^a ZSM-5	0.04	-	-	-	-	0.10	0.11	1.49
ZSM5-TPA	0.26	-	-	-	-	0.60	1.05	1.44
ZSM5-Na	1.60	-	-	-	-	0.18	1.07	0.81
ZSM5-Na ₂ CO ₃	0.24	-	-	-	-	2.20	1.11	0.47

ICP-OES results of Na- and Na₂CO₃-treated samples suggest that the incorporation of sodium does not affect the Cu:Zn:Al ratio of the Cu_{1.3}ZnAl-LDH phase in the core-shell samples. Considering the detected amounts of sodium, carbon and nitrogen, it can be said that partial ion-exchange occurs within the pores of the ZSM-5 core during the *in-situ* coprecipitation of the core-shells. It is likely that the M²⁺/M³⁺ cations, CO₃²⁻ or Na⁺ ions from the reaction mixture become trapped in the ZSM-5 cores of the core-shell samples, displacing some NH₄⁺ in the process.

Zeolites are shape-selective catalysts due to their molecular dimensions, however, their microporous nature can restrict diffusion, leading to deactivation by coking in the presence of carbon-containing reactants.²⁷ Introducing mesopores (2 – 50 nm) through controlled desilication can improve the accessibility and catalytic performance.^{26, 27} N₂ BET analysis was conducted to assess how the choice of base during coprecipitation affects the textural properties of the ZSM-5 and core-shell samples.

The t-plots for N₂ adsorption at 77 K were used to estimate the BET specific surface areas (S_{BET}) and micropore volumes (V_{Micro}) which are summarised in Figure 3.10. For the full breakdown of the N₂ BET surface areas and micropore volumes consult Table B.11. All ZSM-5 samples exhibited high overall surface areas, with the majority of the contribution attributed to the internal micropore surface area (S_{Micro}), as expected of the microporous nature of ZSM-5 zeolites. The changes in the external surface areas (S_{External}) of the samples are minimal and have an average of $46 \pm 2.5 \text{ m}^2/\text{g}$. Although the S_{Micro} ($334 \text{ m}^2/\text{g}$) and V_{Micro} ($0.129 \text{ cm}^3/\text{g}$) values for ZSM5-TPA are slightly lower than for ZSM-5, they fall within the error expected with BET measurements and thus the difference is considered to be negligible. Na-treated ZSM-5 exhibited the largest increase in S_{Micro} by 6.2%, whereas the S_{Micro} for Na₂CO₃-treated ZSM-5 decreased by approximately 4%.

Hence, the surface areas of the zeolites remain largely unchanged following base treatment under conditions that are representative of the coprecipitation process, indicating that any structural changes observed in the zeolite core of the *in-situ* coprecipitated core-shell samples are unlikely to result from desilication.

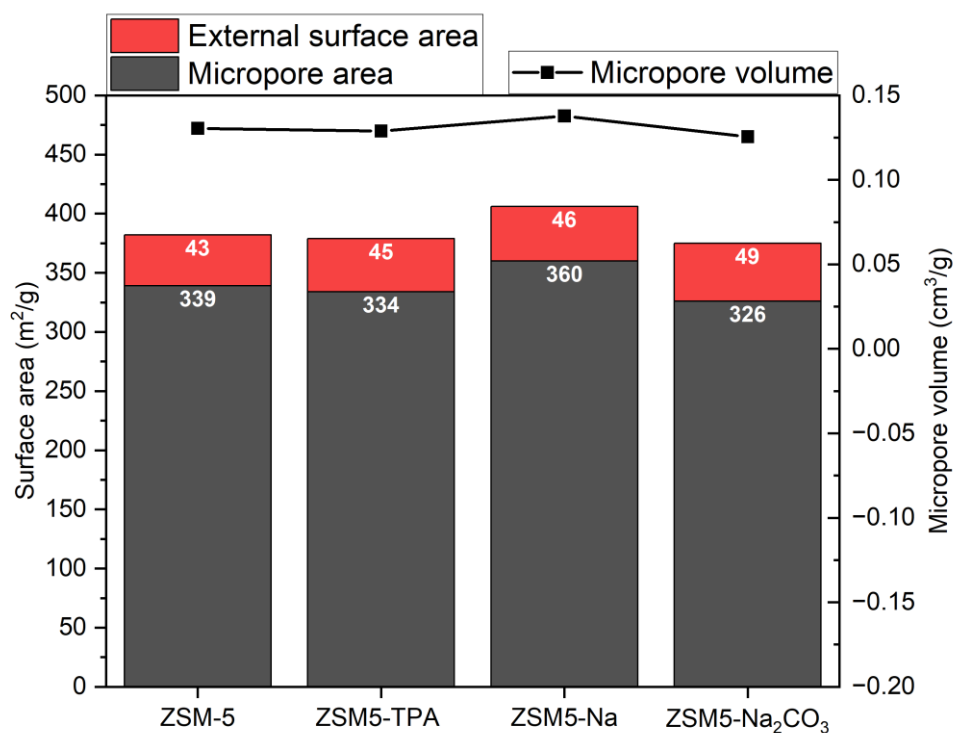


Figure 3.10: N₂ BET surface areas and micropore volumes of the ZSM-5 and base-treated ZSM-5 zeolites. The grey and red bars show the estimated micropore surface area and external surface area respectively, whilst the line plot shows the estimated micropore volume of the samples.

N₂ adsorption-desorption isotherms of the zeolites are summarised in Figure 3.11a and show that all the zeolites examined possess the same profiles with similar N₂ capacities. From the isotherms it is possible to describe the porosity type of the materials according to IUPAC definitions.⁷¹ At low relative pressure $\{< 0.3 (p/p^0)\}$ the zeolites demonstrate a classic type I isotherm with high N₂-uptake indicative of microporous materials.^{71, 72} The profile plateaus as the relative pressure increases. The base-treated zeolites show a

similar profile to pristine ZSM-5 at high relative pressures $\{> 0.5 (p/p^0)\}$ where a small type IV hysteresis loop is observed, suggesting there are mesoporous interstitial spaces between the zeolite crystals.⁷¹ The Barrett-Joyner-Haleda (BJH) model was applied to the adsorption branch of the N₂ isotherms (Figure 3.11b) and confirm the presence of some mesopores and macropores (> 50 nm) in the zeolites although the majority are clearly microporous. The similarities in the profiles for the mesopore and macropore range suggests there were no major desilication events that could lead to the formation of new mesopores in the base-treated samples. It should be noted however that N₂ uptake at ~ 200 nm is higher in ZSM5-Na₂CO₃; the macroporosity in ZSM-5 can be attributed to the interstitial spaces between single crystal agglomerates which may have occurred to a greater extent in the Na₂CO₃-treated ZSM-5 sample. Figure 3.11c summarises the micropore size distribution of the zeolites and was obtained using the DFT model on the adsorption branch of the N₂ isotherm. 0.4 nm micropores appear to be the dominant size in all ZSM-5 samples. The abundance of these micropores decreases along the series ZSM5-Na $>$ ZSM-5 $>$ ZSM5-TPA $>$ ZSM5-Na₂CO₃ which correlates with the S_{Micro} data previously described. Some variations in micropore sizes are observed between 0.6 – 0.7 nm and 1.1 – 1.4 nm, however the 0.4 nm pore is always present and is the dominant micropore size. It is difficult to say if the differences are due to legitimate

changes in the micropore structure of ZSM-5 in response to the base treatment, because of the limited accuracy associated with N₂ adsorption at low relative pressures.^{73, 74}

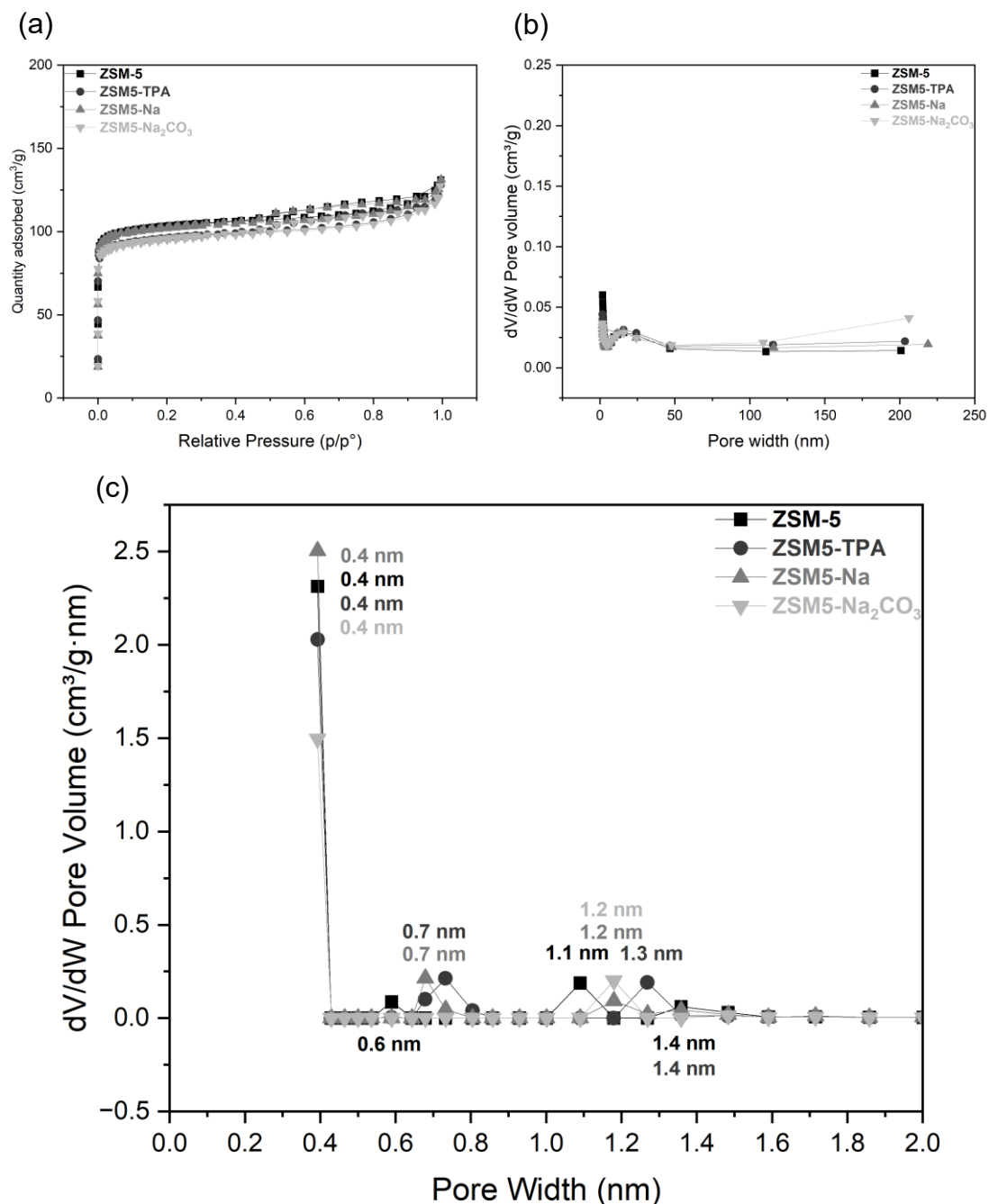


Figure 3.11: (a) N₂ adsorption isotherms, (b) BJH pore size distribution, (c) DFT micropore size distribution of ZSM-5, ZSM5-TPA, ZSM5-Na and ZSM5-Na₂CO₃.

Thus, it can be said that the porosity of ZSM-5 remains largely unchanged after being exposed to the alkaline conditions of the coprecipitation method. Changes in the micropore region of the zeolite are minimal suggesting ion-exchange with $\text{Na}^+/\text{CO}_3^{2-}$ ions in the zeolite (as determined from previous characterisations) does not result in major pore blockage in the zeolite structure.

The surface areas of the TPA-, Na- and Na_2CO_3 - treated ZSM5@ $\text{Cu}_{1.3}\text{ZnAl-LDH}$ core-shells were also investigated by N_2 BET analysis. Summarised in Figure 3.12, the results were compared against the ZSM-5 samples and the physical mixture and LDH counterparts.

The $\text{Cu}_{1.3}\text{ZnAl-LDH}$ samples exhibit similar overall surface areas, with $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$ ($66 \text{ m}^2/\text{g}$) and $\text{Cu}_{1.3}\text{ZnAl-LDH-TPA}$ ($62 \text{ m}^2/\text{g}$) showing slightly higher specific surface areas than $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}$ ($56 \text{ m}^2/\text{g}$). Minimal microporosity is observed in the Na- and Na_2CO_3 -treated samples, whereas $\text{Cu}_{1.3}\text{ZnAl-LDH-TPA}$ has a small microporous surface area ($18 \text{ m}^2/\text{g}$). This suggests that the addition of sodium in the coprecipitation enhances the external surface area at the expense of microporosity. Although $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}$ has a higher S_{External} ($55 \text{ m}^2/\text{g}$) than $\text{Cu}_{1.3}\text{ZnAl-LDH-TPA}$ ($44 \text{ m}^2/\text{g}$), the absence of micropores results in a lower overall surface area. These results suggests that the sodium-free coprecipitation method may reduce platelet aggregation in the $\text{Cu}_{1.3}\text{ZnAl-LDH}$, whereas NaOH treatment leads to a decrease in the overall surface area. These variations are relatively minor, suggesting that the choice of base has a limited impact on the overall structural and textural properties of the $\text{Cu}_{1.3}\text{ZnAl-LDH}$.

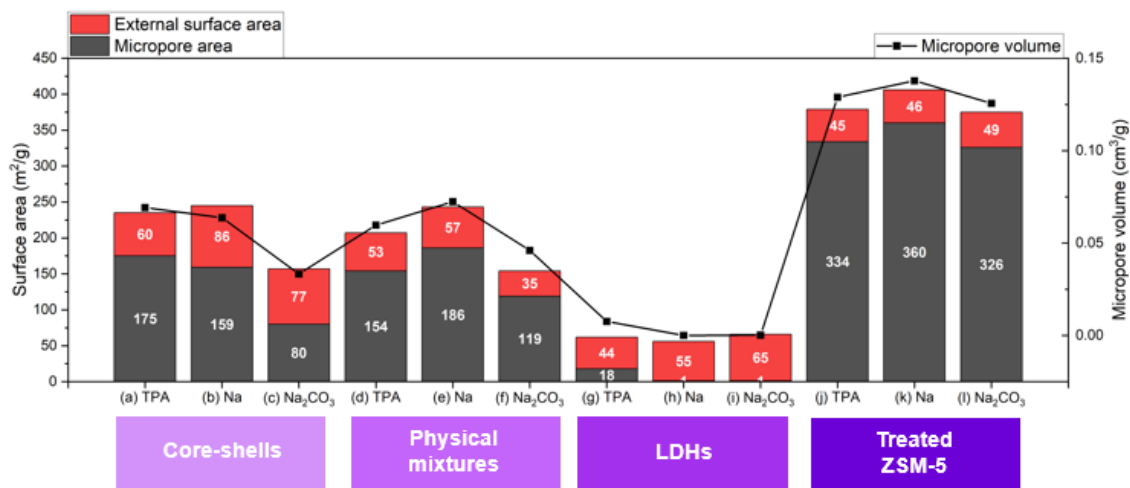


Figure 3.12: N_2 BET surface areas and micropore volumes of the Na- and Na_2CO_3 -treated core-shells, physical mixtures, LDHs and zeolites. (a) $ZSM5@Cu_{1.3}ZnAl-LDH-TPA$, (b) $ZSM5@Cu_{1.3}ZnAl-LDH-Na$, (c) $ZSM5@Cu_{1.3}ZnAl-LDH-Na_2CO_3$, (d) $ZSM5+Cu_{1.3}ZnAl-LDH-TPA$, (e) $ZSM5+Cu_{1.3}ZnAl-LDH-Na$, (f) $ZSM5+Cu_{1.3}ZnAl-LDH-Na_2CO_3$, (g) $Cu_{1.3}ZnAl-LDH-TPA$, (h) $Cu_{1.3}ZnAl-LDH-Na$, (i) $Cu_{1.3}ZnAl-LDH-Na_2CO_3$, (j) $ZSM5-TPA$, (b) $ZSM5-Na$, (c) $ZSM5-Na_2CO_3$. The grey and red bars show the estimated micropore surface area and external surface area respectively, while the line plot shows the estimated micropore volume of the samples.

Between the core-shells, $ZSM5@Cu_{1.3}ZnAl-LDH-Na_2CO_3$ had the lowest S_{BET} ($157 m^2/g$), which was 35% lower compared to $ZSM5@Cu_{1.3}ZnAl-LDH-TPA$ ($235 m^2/g$). Although $ZSM5@Cu_{1.3}ZnAl-LDH-TPA$ and $ZSM5@Cu_{1.3}ZnAl-LDH-Na$ had similar S_{BET} values, the distribution between $S_{External}$ and S_{Micro} was different. Compared to $ZSM5@Cu_{1.3}ZnAl-LDH-TPA$, the external surface area was enhanced at the expense of the microporosity in $ZSM5@Cu_{1.3}ZnAl-LDH-Na$. Specifically, $S_{External}$ accounted for 35% of the total surface area in $ZSM5@Cu_{1.3}ZnAl-LDH-Na$ compared to 26% in $ZSM5@Cu_{1.3}ZnAl-LDH-TPA$. $ZSM5@Cu_{1.3}ZnAl-LDH-Na_2CO_3$ showed considerable changes in both external and internal surface areas, as well as in the micropore volume. While $S_{External}$ ($77 m^2/g$) was greater than that of the TPA-treated core-

shell, a considerable reduction in the S_{Micro} was observed. Here, S_{External} makes up almost 50% of the overall surface area of the Na_2CO_3 -treated core-shell.

In Chapter 2.2.2, the surface area of the $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDH-TPA}$ core-shell was compared to its physical mixture counterpart $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDH-TPA}$. The core-shell exhibited higher external surface areas than expected based on calculated (S_{External} , S_{Micro} and V_{Micro}) values for a theoretical 1:1 mixture of ZSM-5:LDH, while the physical mixture showed reduced microporosity, attributed to increased platelet aggregation. In contrast, the specific surface areas of the $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDH-Na}$ ($245 \text{ m}^2/\text{g}$) and $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$ ($157 \text{ m}^2/\text{g}$) core-shells are comparable to their respective physical mixtures ($243 \text{ m}^2/\text{g}$ and $154 \text{ m}^2/\text{g}$), although both show a redistribution between microporous and external surface areas (see Table B.12 for more details). Specifically, the Na-treated core-shells and physical mixtures have higher-than-expected surface areas, whereas the Na_2CO_3 -treated samples showed lower surface areas than anticipated. Additionally, the physical mixtures had larger micropore surface areas than the core-shells, contributing around 77% of the total S_{BET} . Among the physical mixtures, $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDH-Na}$ exhibited the highest overall surface area, which correlates with the TEM observations showing more extensive coverage of the $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}$ over ZSM-5 particles compared to $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDH-TPA}$ and $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$. The lower surface areas observed in $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$ may result from increased platelet aggregation of $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$ on account of the thicker platelets identified by PXRD analysis.

The results suggest that the coprecipitation method influences the textural properties of the core-shells with the NaOH and NaOH/ Na_2CO_3 treatments increasing the external

surface area at the expense of microporosity, particularly in the Na_2CO_3 -treated sample. Overall, $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDH-TPA}$ and $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDH-Na}$ exhibited the highest total surface areas.

N_2 adsorption-desorption isotherms of the core-shells, physical mixtures and LDHs are summarised in Figure 3.13. All LDHs demonstrate the same pattern of a type II isotherm with a H3 hysteresis loop at high relative pressure $\{> 0.5 (p/p^0)\}$. In combination with the lack of N_2 uptake at low relative pressures, this confirms that the LDHs are macroporous with poorly defined pore shapes and sizes.⁷¹ LDHs are often cited as having slit-like mesopores/macropores which is also true for the different base-treated $\text{Cu}_{1.3}\text{ZnAl-LDHs}$.^{54, 75, 76} The profile patterns for the core-shell and physical mixtures are similar and exhibit characteristics which indicate the presence of both the zeolite and LDH phase. The type I isotherm associated with the microporous zeolite is observed at low relative pressure $\{< 0.3 (p/p^0)\}$ whilst the type II isotherm with H3 hysteresis loop associated with the mesoporous/macroporous LDH is observed at higher relative pressures.⁷⁵

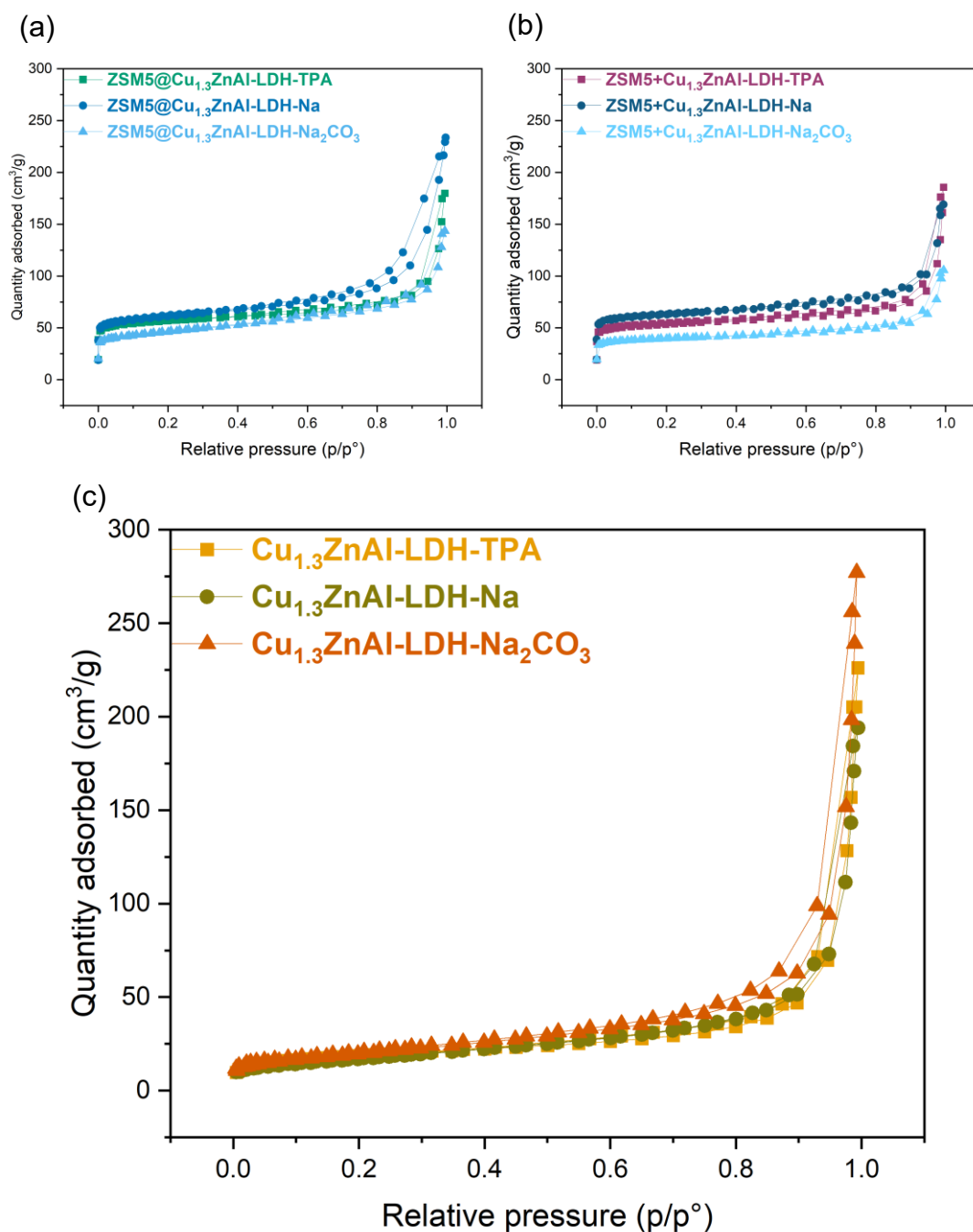


Figure 3.13: N_2 adsorption isotherms of the different base treated (a) core-shells, (b) physical mixtures and (c) LDHs.

To investigate the mesopore distribution of the samples, the Barrett-Joyner-Haleda (BJH) model was applied to the adsorption branch of the N_2 isotherm. The TPA-, Na- and

Na_2CO_3 -treated $\text{Cu}_{1.3}\text{ZnAl}$ -LDHs show similarly broad distribution profiles with high uptake in the macropore range (> 50 nm) (Figure 3.14a). LDHs often suffer from platelet aggregation on account of their high surface charges which leads to the characteristically broad distribution profile with no maxima (indicating the pores are non-uniform).^{44, 45, 54, 77} Although the LDHs are largely macroporous, adsorption within the 2 – 50 nm indicates the presence of mesoporosity, likely due to interparticle voids formed between stacked nanoplatelets.

The core-shell and physical mixture samples (Figure 3.14b and Figure 3.14c respectively) all show N_2 uptake in the micropore (< 2 nm), mesopore and macropore regions as expected due to the combined presence of both LDH and zeolite phases. The BJH pore size distribution reveals that the core-shell samples exhibit nitrogen uptake at multiple distinct pore widths in the mesopore range, whereas the physical mixtures show uptake at fewer mesopore widths. This suggests a more diverse mesopore structure in the core-shells, likely arising from greater interaction between the LDH shell and the ZSM-5 core.

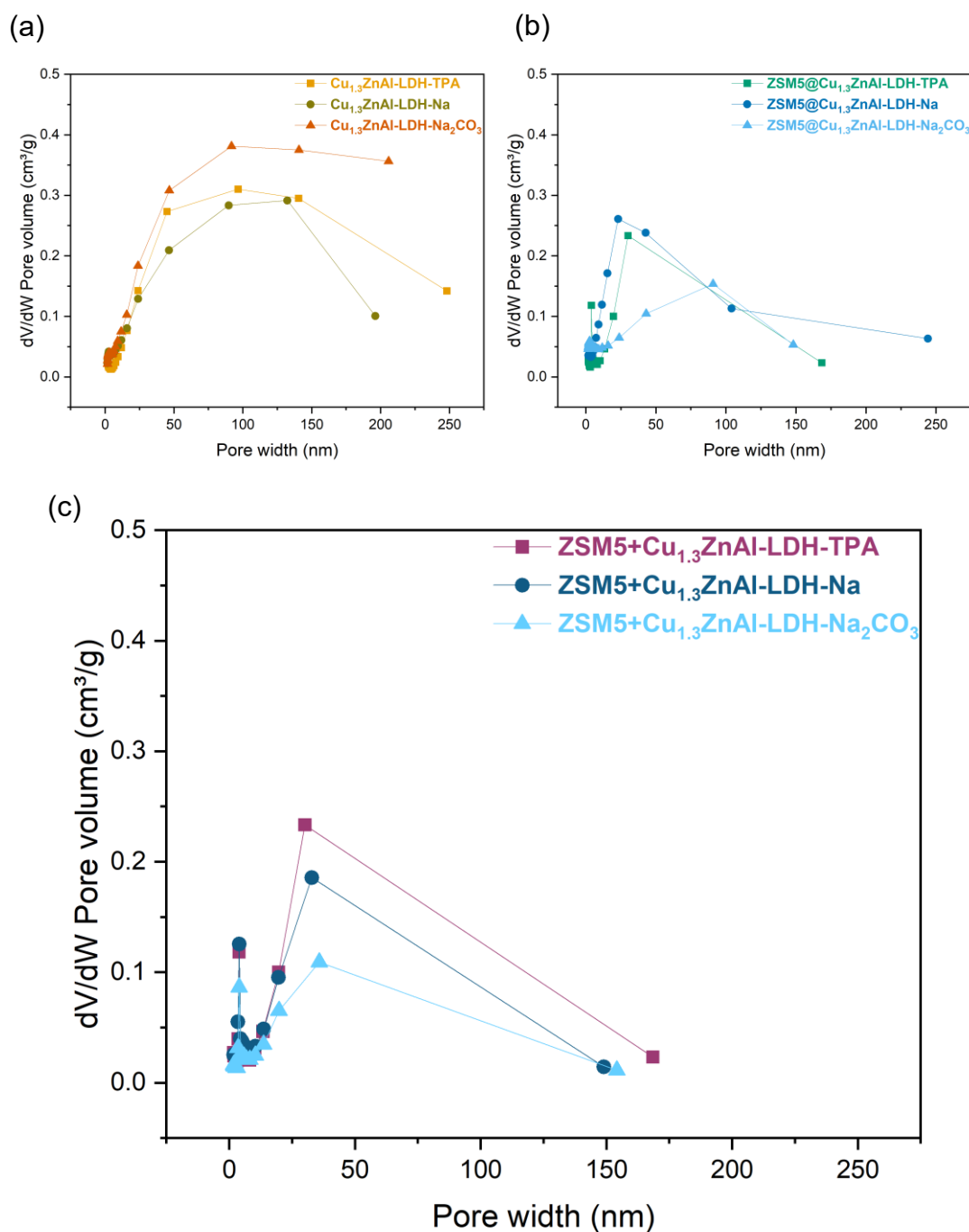


Figure 3.14: BJH pore size distribution of the different base treated (a) LDHs, (b) core-shells and (c) physical mixtures.

The micropore size distribution of the core-shells and physical mixtures were determined by applying the DFT model on the adsorption branch of the isotherms and are

summarised in Figure 3.15. All hybrid samples showed an average micropore diameter of 0.4 nm arising from the micropores in ZSM-5. Variations in the micropore size distributions were observed among the base-treated ZSM-5 within the 0.6 – 0.7 nm and 1.1 – 1.4 nm ranges. Although all samples showed a consistent peak at 1.3 nm, the differences emerged in the 0.7 – 0.9 nm range. These observations highlight the limitations of using N₂ as the adsorbate for micropore analysis.^{73, 78} Using an inert gas like Ar may offer some improved sensitivity.⁷⁸

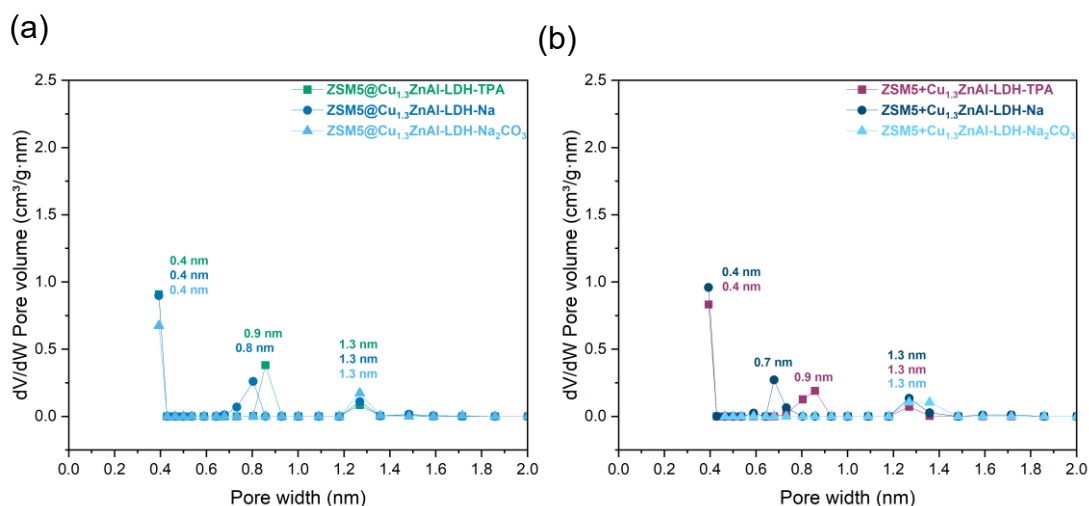


Figure 3.15: DFT micropore size distribution of the different base treated (a) core-shells and (b) physical mixtures.

TEM/SEM imaging revealed distinct differences in the morphology of the LDH platelets across the TPA-, Na- and Na₂CO₃-treated core-shell samples. This, in combination with the N₂ BET analysis, suggests that the choice of coprecipitation method influences the extent of LDH platelet aggregation, which in turn affects the textural properties of the core-shell materials. The lower S_{BET} observed for ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ is likely due to the thicker Cu_{1.3}ZnAl-LDH platelets (identified by TEM and PXRD analysis). The thicker platelets may have led to poorer LDH deposition on the zeolite due

to increased competition on the surface, resulting in more LDH aggregation. This may account for the smaller mesopore size distribution and smaller micropore surface area in ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃.

Characterisation of the ZSM5@Cu_{1.3}ZnAl-LDH core-shell catalyst precursors indicate that, although the inclusion of sodium in the coprecipitation method has a minor effect on the thickness of the Cu_{1.3}ZnAl-LDH platelets, there is a considerable effect on their dispersion and interaction with the ZSM-5 cores. Additionally, partial ion-exchange of NH₄⁺ within the ZSM-5 framework occurs during the coprecipitation, likely involving Cu²⁺/Zn²⁺/Al³⁺.

Following the characterisation of the LDH-based catalyst precursors, CO₂ hydrogenation tests were conducted. The first series of reactions investigates the performance of the Cu_{1.3}ZnAl catalyst in CTM conversion to determine if the structural changes to the LDH phase influenced the activity of the catalyst. This was followed by an investigation of the activated core-shell catalysts to identify differences in their CTD performance.

3.3: CO₂ hydrogenation performance and discussion

3.3.1: CO₂ hydrogenation results of the CTM catalysts

The function of the CZA catalyst is to activate the CO₂ molecule and convert the CO₂ to methanol. Previous studies have suggested that Na-incorporation into CZA catalysts negatively impact the activity of the catalyst.^{12, 13, 35} Characterisation of the TPA-, Na-, Na₂CO₃-treated Cu_{1.3}ZnAl-LDHs suggested there were no major changes to the structure/textural properties of the precursor CTM catalysts. Nevertheless, before

evaluating the core-shell catalysts, it was essential to assess how the coprecipitation method might influence the performance of the CTM phase.

The non-hybrid, LDH-based CTM catalysts were activated from the TPA-, Na- and Na_2CO_3 -treated $\text{Cu}_{1.3}\text{ZnAl-LDH}$ precursors as per the method described in Chapter 6.3.11. The activation method used in this chapter is based on the results found from the optimisation study in Chapter 2.4.1.1. Hence, $\text{Cu}_{1.3}\text{ZnAl-LDH-TPA}$, $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}$ and $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$ were *ex-situ* calcined in O_2 (forming dark green LDO powders) and reduced *in-situ* under H_2 to form the CTM catalysts $\text{Cu}_{1.3}\text{ZnAl-TPA}$, $\text{Cu}_{1.3}\text{ZnAl-Na}$ and $\text{Cu}_{1.3}\text{ZnAl-Na}_2\text{CO}_3$. The CTM catalysts were black in colour and approximately 0.1 g was loaded in a pressurised fixed-bed reactor, then reacted under $\text{CO}_2:\text{H}_2:\text{N}_2$ (24:72:4) flow with a weight hourly space velocity (*WHSV*) of 18,000 $\text{mL/g}_{\text{cat}}\cdot\text{h}$, with temperature points between 260 – 340 °C. The products of the CO_2 hydrogenation were analysed by GC and the results are summarised in Figure 3.16 and Table 3.4. Catalysts are described without the LDH suffix, e.g., the catalyst generated from the Na-treated precursor is named “ $\text{Cu}_{1.3}\text{ZnAl-Na}$ ”. For full details of the testing method see Chapter 6.5.

All three CZA catalysts produced a mixture of methanol and CO, with the highest space time yields (summarised in Figure 3.17) occurring at 260 °C (calculated using the formula in S2.27). The catalysts exhibited similar trends with increasing X_{CO_2} and S_{CO} as the reaction temperature increases. CO_2 conversion is expected to increase with temperature between this temperature range (based on the thermodynamics of CO_2 to methanol conversion) as the increase in temperature allows a greater proportion of reactant molecules to overcome the high energy barrier of CO_2 activation. Concurrently, CO becomes the dominant product due to the thermodynamics associated with the CTM

and the competing RWGS reaction.⁷⁹ The biggest differences in STY_{CH_3OH} between the catalysts occurs at 260 °C where $Cu_{1.3}ZnAl-Na_2CO_3$ demonstrates the highest methanol productivity ($0.33 \text{ g}_{CH_3OH}/\text{g}_{cat}\cdot\text{h}$). This aligns well with the methanol productivity of the same $Cu_{1.3}ZnAl$ catalyst ($0.34 \text{ g}_{CH_3OH}/\text{g}_{cat}\cdot\text{h}$) reported in previous work conducted by the group where S_{CH_3OH} was 43% and X_{CO_2} was 13%.⁴⁵ In comparison to the $Cu_{1.3}ZnAl-TPA$ catalyst, $Cu_{1.3}ZnAl-Na$ exhibits a 6.7% increase in methanol productivity, while the productivity of $Cu_{1.3}ZnAl-Na_2CO_3$ increased by a considerable 15.6%. The methanol selectivities between the catalysts are similar, for instance at 260 °C, the S_{CH_3OH} of the catalysts (~41%) are within 0.09% of each other, and at 280 °C S_{CH_3OH} (~27%) are within 0.14% of each other. The differences in STY_{CH_3OH} are largely due to the differences in X_{CO_2} where $Cu_{1.3}ZnAl-Na_2CO_3$ converts the most CO_2 (~14.12%) of the three CTM catalysts at 260 °C.

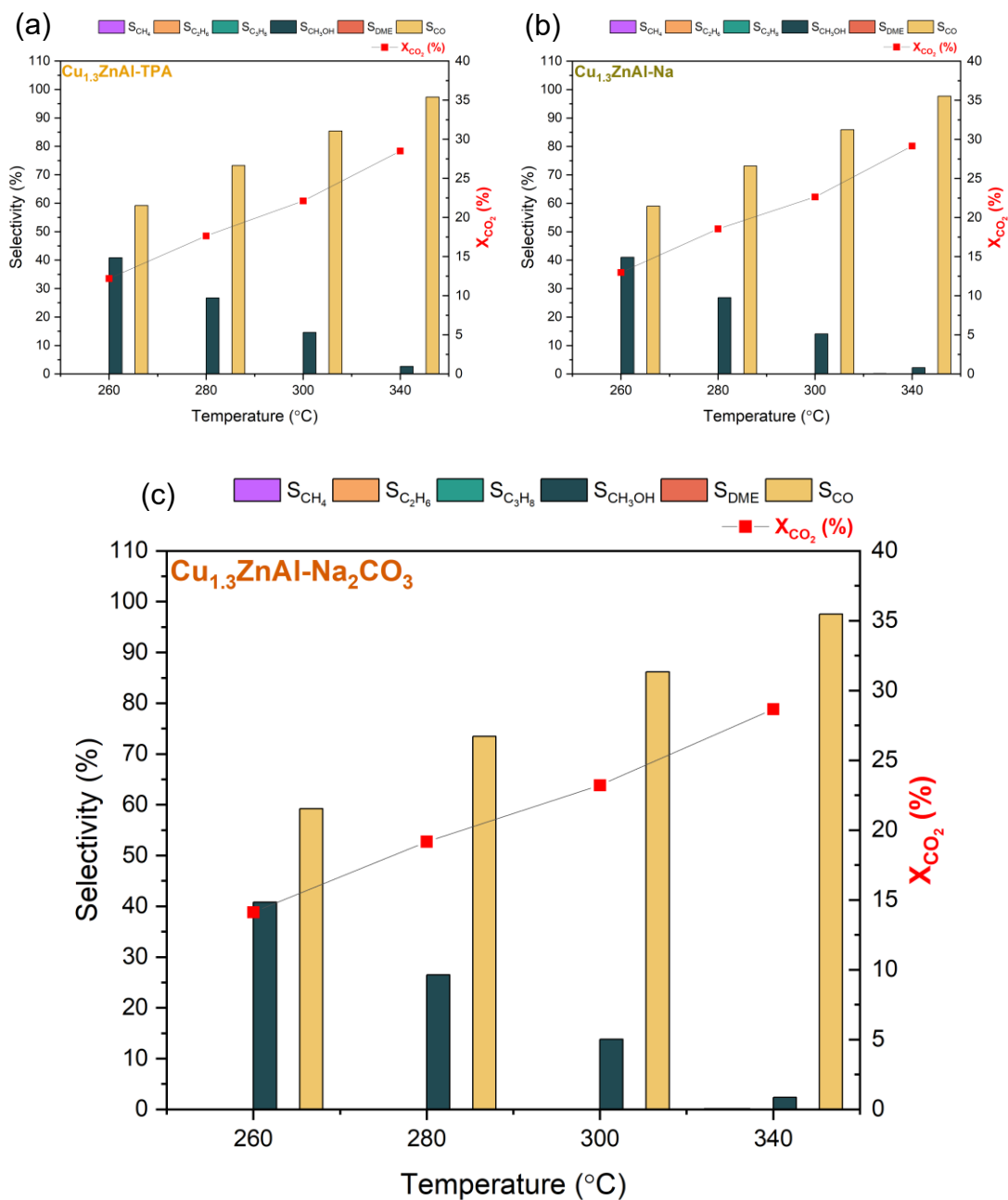


Figure 3.16: Product distribution of CO₂ hydrogenation reaction over core-shell (a) Cu_{1.3}ZnAl-TPA, (b) Cu_{1.3}ZnAl-Na and (c) Cu_{1.3}ZnAl-Na₂CO₃ as a function of temperature (260 – 340 °C). Reaction conditions: $P = 3.0$ MPa; $\text{CO}_2:\text{H}_2:\text{N}_2 = 24:72:4$; $WHSV = 18,000$ mL/g_{cat}·h, carbon balance 97.92 – 101.04%.

Table 3.4: CO₂ hydrogenation performance for the LDH-based CTM catalysts.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)		Yield (%) $Y_{\text{CH}_3\text{OH}}$	$STY_{\text{CH}_3\text{OH}}$ (g _{CH₃OH} /g _{cat} ·h)
			$S_{\text{CH}_3\text{OH}}$	S_{CO}		
Cu_{1.3}ZnAl-TPA	260	12.2	40.81	59.18	4.98	0.28
	280	17.64	26.71	73.25	4.71	0.27
	300	22.11	14.58	85.37	3.22	0.18
	340	28.5	2.61	97.3	0.74	0.04
Cu_{1.3}ZnAl-Na	260	12.98	41.00	59.00	5.32	0.30
	280	18.55	26.86	73.11	4.98	0.28
	300	22.64	14.08	85.85	3.19	0.18
	340	29.15	2.2	97.67	0.64	0.04
Cu_{1.3}ZnAl-Na₂CO₃	260	14.12	40.79	59.20	5.76	0.33
	280	19.17	26.52	73.44	5.08	0.29
	300	23.21	13.79	86.14	3.20	0.18
	340	28.67	2.35	97.53	0.67	0.04

^aReaction conditions: $P = 3.0$ MPa, CO₂/H₂/N₂ = 24:72:4, and $WHSV = 18,000$ mL/g_{cat}·h.

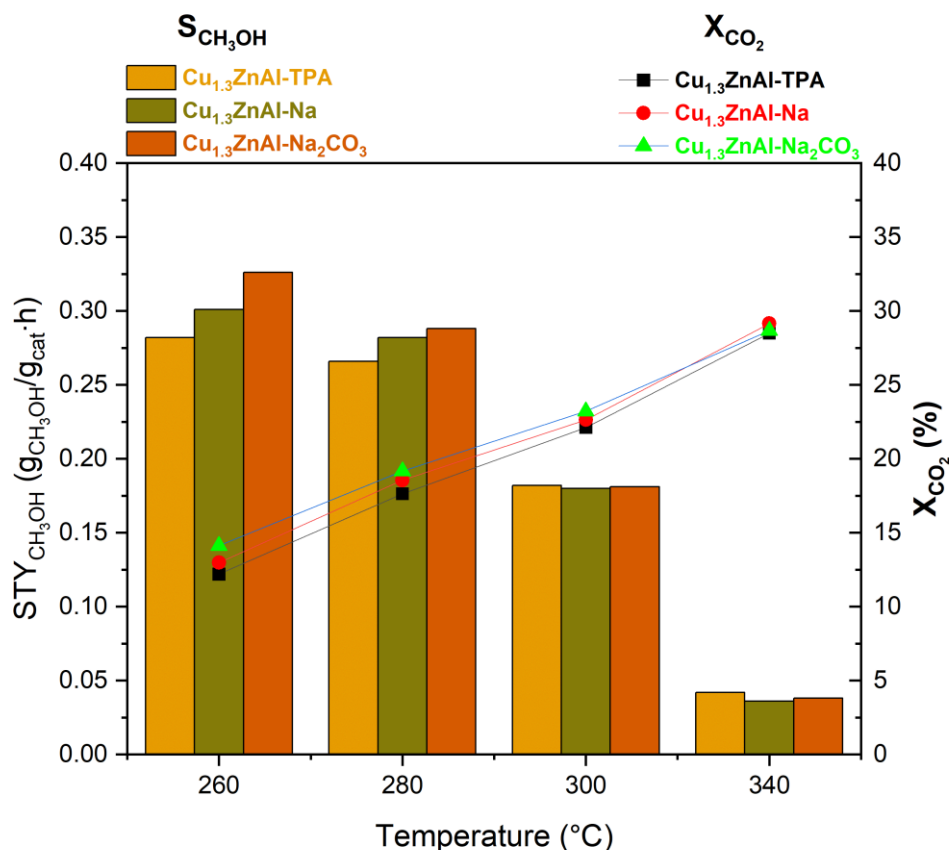


Figure 3.17: STY_{CH_3OH} and CO_2 conversions for $Cu_{1.3}ZnAl-TPA$, $Cu_{1.3}ZnAl-Na$ and $Cu_{1.3}ZnAl-Na_2CO_3$.

Reaction conditions: $P = 3.0$ MPa; $CO_2:H_2:N_2 = 24:72:4$; $WHSV = 18,000$ mL/g_{cat}·h, carbon balance 97.92 – 101.04%.

Based on the CO_2 hydrogenation results, it can be said that the $Cu_{1.3}ZnAl-Na_2CO_3$ CTM catalyst demonstrates the best methanol productivity at 260 °C due to the improvement in CO_2 conversion. All catalysts demonstrated similar selectivity towards methanol at all temperatures, with CO as the only other by-product from the RWGS reaction. The methanol productivities out-performed a commercial CTM catalyst (0.15 g_{CH₃OH}/g_{cat}·h).⁸⁰ The results reflect those found in other papers of CTM catalysts where lower temperatures lead to greater methanol selectivity and thus higher methanol STY s.^{45, 81, 82} The improved performance of the $Cu_{1.3}ZnAl-Na_2CO_3$ catalyst in comparison to $Cu_{1.3}ZnAl-Na_2CO_3$ and $Cu_{1.3}ZnAl-Na_2CO_3$ may be due to the improved

surface area of the $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$ precursor catalyst determined by N_2 BET analysis. Minimal amounts of sodium were detected in the $\text{Cu}_{1.3}\text{ZnAl-LDH}$ precursors. The Na wt% of $\text{Cu}_{1.3}\text{ZnAl-TPA}$ (0.26%), which should be sodium-free based on the preparation method, was similar to the amount detected in $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$ (0.23%). Hence the differences in performance are unlikely to be due to any residual Na within the CTM catalysts. The D_{003} length of $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$ was found to be smallest of the LDHs, which corresponds with the higher S_{BET} values determined in the previous section. With thinner LDH platelets and a higher surface area, the active sites on the $\text{Cu}_{1.3}\text{ZnAl-Na}_2\text{CO}_3$ catalyst may be more exposed which may explain the improvement in CO_2 conversion. To confirm this, BET analysis needs to be conducted on the catalyst samples. It would also be beneficial to investigate the amount of exposed Cu on the catalysts by performing an N_2O decomposition experiment. N_2O is used to selectively oxidise surface Cu^0 atoms to Cu_2O without penetrating into the bulk catalyst, the amount of H_2 used to re-reduce the surface copper species is then used to quantify the amount of Cu^0 on the surface of the catalyst.

CO_2 hydrogenation results from Chapter 2.4.2. suggested that $280\text{ }^\circ\text{C}$ was the optimal temperature for DME formation at high $WHSV$. At $280\text{ }^\circ\text{C}$ the $STY_{\text{CH}_3\text{OH}}$ of the ex-LDH CTM catalysts are similar ($0.27 - 0.29\text{ g}_{\text{CH}_3\text{OH}}/\text{g}_{\text{cat}}\cdot\text{h}$). Thus, it was necessary to test each combination of base-treated core-shell and physical mixtures for the direct CTD reaction to ascertain which hybrid catalyst has the best performance.

3.3.2: CO_2 hydrogenation results of the CTD catalysts

Characterisation of TPA-, Na and Na_2CO_3 -treated $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH}$ core-shell precursor catalysts in Section 3.2.2 showed differences in the sizes of the $\text{Cu}_{1.3}\text{ZnAl-LDH}$

crystallite phase as well as differences in the overall surface areas and mesoporosity size distribution. Thus, physical properties of the core-shell precursor catalysts were affected by the coprecipitation method. To investigate how the activity or selectivity of the core-shell catalysts might be affected by the coprecipitation method, Na- and Na₂CO₃-treated core-shell precursors were activated and tested for their CO₂ hydrogenation performance. The physical mixture counterparts were also tested and compared against the core-shell samples. The preparation of the catalysts from the ZSM5@Cu_{1.3}ZnAl-LDH and ZSM5+Cu_{1.3}ZnAl-LDH precursors is summarised in Chapter 6.2.5. Catalysts are described without the LDH suffix, e.g., the catalyst generated from the Na-treated core-shell and physical mixture precursors are named “ZSM5@Cu_{1.3}ZnAl-Na” and “ZSM5+Cu_{1.3}ZnAl-Na” respectively. For full details of the testing method see Chapter 6.5.

Results from CO₂ hydrogenation over the hybrid catalysts are summarised in Figure 3.18 and Table 3.5. All hybrid catalysts produced a combination of DME, methanol and CO where S_{DME} and $S_{\text{CH}_3\text{OH}}$ are observed to decrease with increasing temperature whilst S_{CO} increases with temperature. This is expected due to the thermodynamics associated with the initial conversion of CO₂ to methanol which is in competition with the RWGS reaction.⁸³ Due to the exothermicity of the CTM reaction and the endothermicity of the RWGS, CO (and water) as the product of the RWGS reaction becomes favourable at higher temperatures.^{79, 83} X_{CO_2} increases with temperature as the kinetics improves, with more CO₂ molecules able to overcome the large energy barrier of CO₂ activation. These results reflect the trends seen in similar catalysts including the hybrid ZSM5@Cu_{1.3}ZnAl-TPA and ZSM5+Cu_{1.3}ZnAl-TPA catalysts in Chapter 2.3.^{37, 38, 84, 85} As was the case for ZSM5@Cu_{1.3}ZnAl-TPA, the highest DME productivities for the Na-

and Na_2CO_3 -treated core-shells/physical mixtures were observed at 280 °C where the CO_2 conversion-DME selectivity relationship is maximised (Figure 3.19).

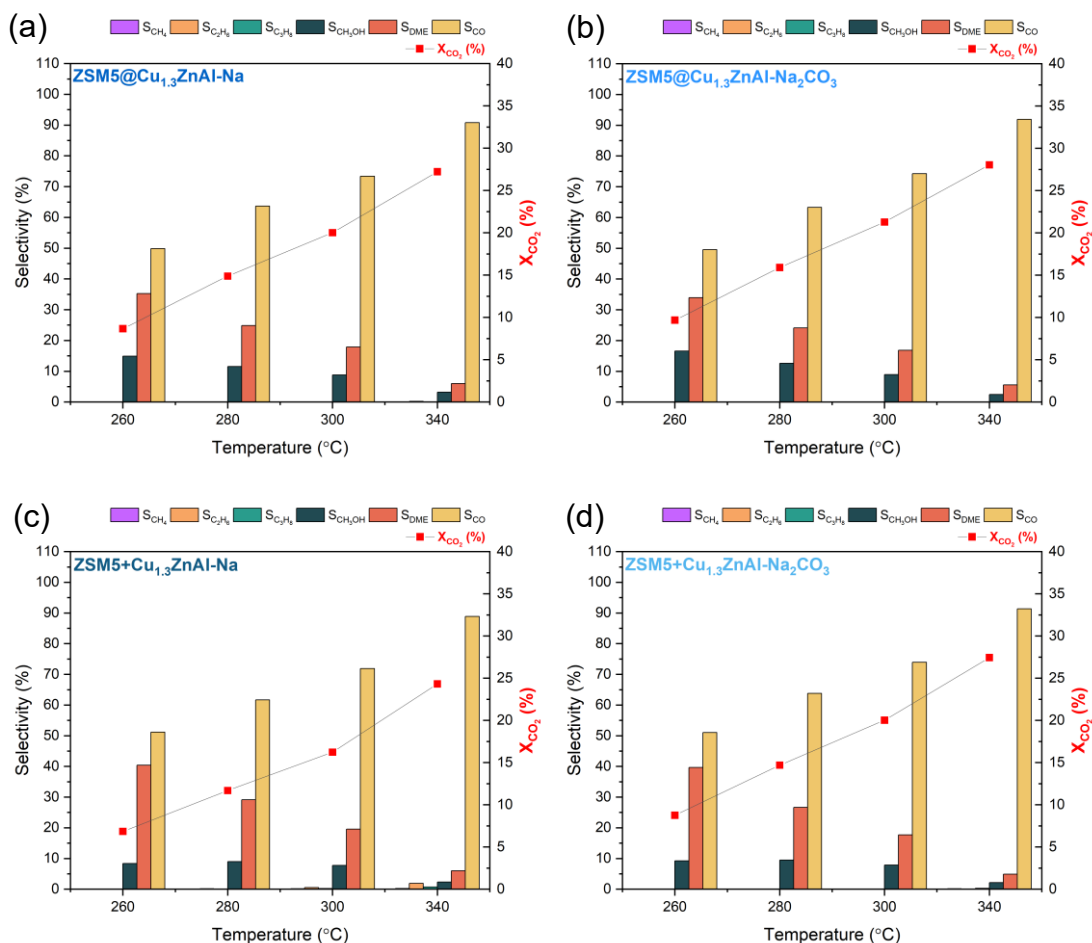


Figure 3.18: CO_2 hydrogenations performance for the core-shells (a) ZSM5@Cu_{1.3}ZnAl-Na and (b) ZSM5@Cu_{1.3}ZnAl-Na₂CO₃ and the physical mixtures (c) ZSM5+Cu_{1.3}ZnAl-Na and (d) ZSM5+Cu_{1.3}ZnAl-Na₂CO₃ as a function of temperature (260 – 340 °C). Reaction conditions: $P = 3.0$ MPa; $\text{CO}_2:\text{H}_2:\text{N}_2 = 24:72:4$; $WHSV = 18,000$ mL/g_{cat}·h, carbon balance 99.34 – 101.32%.

The core-shell catalysts exhibit very similar performances when tested between 280 – 340 °C, with the highest STY_{DME} of 0.30 g_{DME}/g_{cat}·h and 0.31 g_{DME}/g_{cat}·h for ZSM5@Cu_{1.3}ZnAl-Na and ZSM5@Cu_{1.3}ZnAl-Na₂CO₃ respectively (Table 3.5). Based on the error found in Chapter 2.3, the differences in S_{DME} between the Na- and Na₂CO₃-treated core-shell are considered minimal. In comparison to ZSM5@Cu_{1.3}ZnAl-TPA

(0.38 g_{DME}/g_{cat}·h, see Chapter 2.4.1.1 for the O₂-calcined core-shell results), the Na- and Na₂CO₃-treated core-shell catalysts have lower DME productivities. The difference in the maximum STY_{DME} between ZSM5+Cu_{1.3}ZnAl-Na₂CO₃ (0.32 g_{DME}/g_{cat}·h) and ZSM5+Cu_{1.3}ZnAl-Na (0.28 g_{DME}/g_{cat}·h) is more notable. ZSM5+Cu_{1.3}ZnAl-Na₂CO₃ also performs better than the Na-treated physical mixture catalyst between 260 – 300 °C. This suggests that the Na₂CO₃ coprecipitation method produces precursors that, upon activation, exhibit enhanced DME production. Comparing the core-shell catalysts with the physical mixture catalysts, X_{CO_2} is generally lower in the physical mixture counterparts. At 280 °C, the order of DME yield increases from ZSM5+Cu_{1.3}ZnAl-Na (3.4%) > ZSM5@Cu_{1.3}ZnAl-Na (3.7%) > ZSM5@Cu_{1.3}ZnAl-Na₂CO₃ (3.8%) > ZSM5+Cu_{1.3}ZnAl-Na₂CO₃ (3.9%). In Chapter 2.3, the maximum STY_{DME} was observed for the ZSM5+Cu_{1.3}ZnAl-TPA physical mixture catalyst although the error was found to be much larger compared to that of the core-shell catalyst. Due to time constraints, repeat tests were not conducted. Therefore, it is a minimum error of 10% is assumed for all reported STY values.

ZSM5@Cu_{1.3}ZnAl-Na and ZSM5@Cu_{1.3}ZnAl-Na₂CO₃ demonstrate slightly higher S_{CH_3OH} in comparison to the TPA-treated core-shell catalyst. This is more clearly seen at 260 °C where S_{CH_3OH} is greater than 14% for the Na- and Na₂CO₃-treated core-shell catalysts (whereas S_{CH_3OH} of ZSM5@Cu_{1.3}ZnAl-TPA stayed below 10% at all reaction temperatures). This observation is not reflected in the physical mixture catalysts, which also demonstrate S_{CH_3OH} values under 10%. At 280 °C, S_{CO} for ZSM5@Cu_{1.3}ZnAl-Na (63.6%) and ZSM5@Cu_{1.3}ZnAl-Na₂CO₃ (63.3%) are slightly lower than for ZSM5@Cu_{1.3}ZnAl-TPA (65.24%). In combination with the higher selectivity towards methanol, the results suggests that the Na- and Na₂CO₃-treated core-shell catalysts were

less able to convert the methanol generated by the CZA phase into DME. As previously discussed, the base used in the coprecipitation method had little effect on the $S_{\text{CH}_3\text{OH}}$ of the $\text{Cu}_{1.3}\text{ZnAl}$ catalysts. This explains why the $S_{\text{CH}_3\text{OH}}$ trend for the physically mixed $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-Na}$ and $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-Na}_2\text{CO}_3$ catalysts are similar.

Table 3.5: CO₂ hydrogenation results for the Na- and Na₂CO₃-treated core-shell and physical mixture CTD catalysts.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)			Yield (%) Y_{DME}	STY_{DME} (g _{DME} /g _{cat} ·h)
			S_{DME}	S_{CH_3OH}	S_{CO}		
ZSM5@Cu_{1.3}ZnAl-Na	260	8.7	35.2	14.9	49.9	3.1	0.25
	280	14.9	24.8	11.5	63.6	3.7	0.30
	300	20.0	17.9	8.8	73.4	3.6	0.29
	340	27.2	6.0	3.2	90.8	1.6	0.13
ZSM5@Cu_{1.3}ZnAl-Na₂CO₃	260	9.7	33.9	16.5	49.5	3.3	0.27
	280	15.9	24.1	12.6	63.3	3.8	0.31
	300	21.3	16.8	8.9	74.2	3.6	0.29
	340	28.0	5.6	2.5	91.9	1.6	0.13
ZSM5+Cu_{1.3}ZnAl-Na	260	6.8	40.4	8.4	51.2	2.8	0.23
	280	11.7	29.1	9.0	61.7	3.4	0.28
	300	16.2	19.6	7.7	71.9	3.2	0.26
	340	24.3	6.0	2.3	88.9	1.5	0.12
ZSM5+Cu_{1.3}ZnAl-Na₂CO₃	260	8.8	39.7	9.3	51.0	3.5	0.28
	280	14.7	26.7	9.5	63.8	3.9	0.32
	300	20.0	17.7	7.9	73.9	3.5	0.29
	340	27.4	4.9	2.1	91.3	1.3	0.11

^aReaction conditions: $P = 3.0$ MPa, CO₂/H₂/N₂ = 24:72:4, and $WHSV = 18,000$ mL/g_{cat}·h.

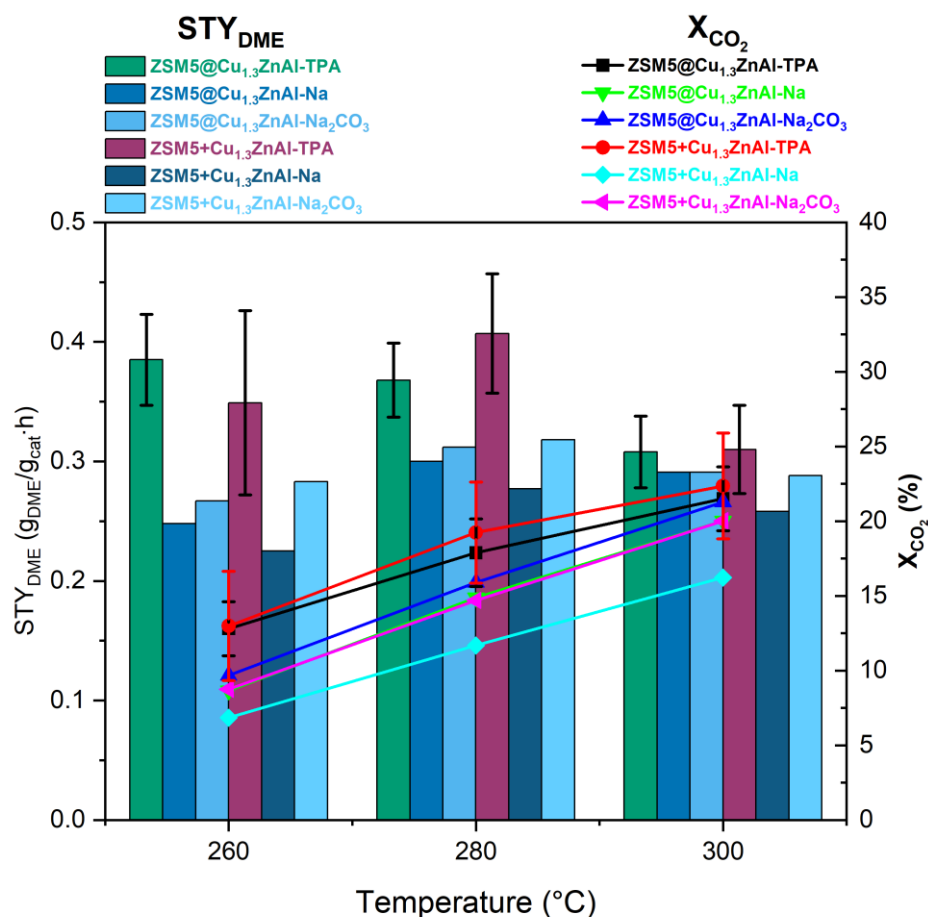


Figure 3.19: STY_{DME} and X_{CO_2} of the TPA-, Na- and Na_2CO_3 -treated core-shell and physical mixture CTD catalysts.

Between the Na- and Na_2CO_3 -treated core-shell catalyst, the highest DME space time is observed at 280 °C for $ZSM5@Cu_{1.3}ZnAl-Na_2CO_3$. In comparison to $ZSM5@Cu_{1.3}ZnAl-TPA$ (0.38 g_{DME}/g_{cat}·h) and considering the error associated with the CO_2 hydrogenation results, Na- and Na_2CO_3 -treatment in the coprecipitation of the catalyst precursors has a negative impact on the CTD performance of the hybrid catalyst.

The difference in performance between the core-shell catalysts suggests that the nature of the basic treatment influences the MTD activity of the zeolite phase. To investigate this further, pristine ZSM-5 and $ZSM5-TPA/Na/Na_2CO_3$ could be reacted under methanol flow under the same reacting conditions ($P = 3.0$ MPa,

$WHSV = 18,000 \text{ mL/g}_{\text{cat}} \cdot \text{h}$); in doing so the impact of the sodium treatment on the zeolite can be studied in isolation.

Differences in the activity of the catalysts may also be due to the interactions between the CZA and ZSM-5 phase rather than the ZSM-5 phase being affected by the presence of sodium. To confirm this, characterisation of the catalyst materials should be conducted including HR-TEM (to provide more information on the Cu nanoparticle distribution, the nature of the Cu-ZnO interactions and the exposed facets of the catalyst), PXRD (to identify the copper phases present in the catalysts), N_2O decomposition (to quantify the number of exposed active Cu sites and normalise the space time yields against the Cu surface area), and BET analysis (to normalise the space time yields against the overall surface area of the activated samples). It would also be beneficial to run a series of a TPD studies to identify changes to the acid/base strength of the hybrid materials.

3.4: Synthesis and characterisation of $(\text{ZSM5})_x@(\text{Cu}_{1.3}\text{ZnAl})_y$ precursors and catalysts

For the direct synthesis of DME from CO_2 and hydrogen, both CZA and ZSM-5 catalysts play a crucial role. As previously described, the overall CTD reaction proceeds by two sequential steps: CO_2 hydrogenation to methanol over the CZA phase followed by methanol dehydration to DME on the acid sites in ZSM-5. The $\text{ZSM5}@(\text{Cu}_{1.3}\text{ZnAl})$ core-shell catalyst was designed to maximise the functions of the CZA and ZSM-5 component by facilitating uniform and well dispersed Cu^0 over the ZSM-5 core. The sensitivity of the core-shell catalyst towards Na^+ ions was determined in the previous section, and it was found that the catalyst generated from the sodium-free $\text{ZSM5}@(\text{Cu}_{1.3}\text{ZnAl})\text{-LDH}$

precursor had the highest DME productivity at 280 °C. In terms of performance optimisation, it is also necessary to investigate how the relative proportions of the CZA (basic) and ZSM-5 (acidic) phases might affect the conversion and selectivity of the core-shell catalyst. For instance, a higher ZSM-5:CZA ratio may lead to increased methanol production due to a larger number of active sites with potentially higher CO₂ conversion. However, with less ZSM-5 present, there may be insufficient acid sites for the complete methanol dehydration to DME. Previous studies used a variety of metal to acid catalyst ratios for direct CTD conversion with no clear correlation between the relative proportions of the hybrid catalysts and the performance. Hence, to optimise DME productivity, the impact of varying the ZSM-5:CZA ratio on CTD performance was investigated.

3.4.1: Preparation of the (ZSM5)_x@(Cu_{1.3}ZnAl)_y-LDH catalyst precursors

To understand how the phase composition of CZA and ZSM-5 might affect the activity of the core-shell catalyst towards the direct CTD conversion, core-shells with a 1:2 and 2:1 (by weight) ZSM-5:LDH ratio were synthesised. The method used to synthesise the core-shell precursors is outlined in Chapter 6.3.9 and was free from Na-containing reagents. To achieve the right ratios, the amount of ZSM-5 was altered and the concentration of metal salts was kept the same. ICP-OES results confirmed that the Cu:Zn:Al ratios of the core-shells are in agreement with the molar ratios used in the synthesis (Table B.12). The core-shell precursor catalysts containing the 2:1 (ZSM-5:LDH) ratio is named as (ZSM5)₂@Cu_{1.3}ZnAl-LDH-TPA and the 1:2 ratio is defined as ZSM5@Cu_{1.3}ZnAl₂-LDH-TPA.

3.4.1: Characterisation of the $(\text{ZSM5})_x@(\text{Cu}_{1.3}\text{ZnAl})_y\text{-LDH}$ catalyst precursors

Two-phase Rietveld refinement of the PXRD data confirmed the presence of both LDH and zeolite phases within the core-shell samples (Table B.13 and Table B.14). As demonstrated in Figure 3.20, Bragg reflections characteristic of crystalline $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and ZSM-5 are observable in the PXRD pattern for $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2\text{-LDH}$ and $(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl-LDH}$ (see Chapter 2.2.2 for the detailed analysis of the LDH and zeolite PXRD diffraction patterns).^{47, 86, 87} No significant changes were observed in the crystallinity of the ZSM-5 core in either of the two core-shells and no other phases were identified in the PXRD pattern.

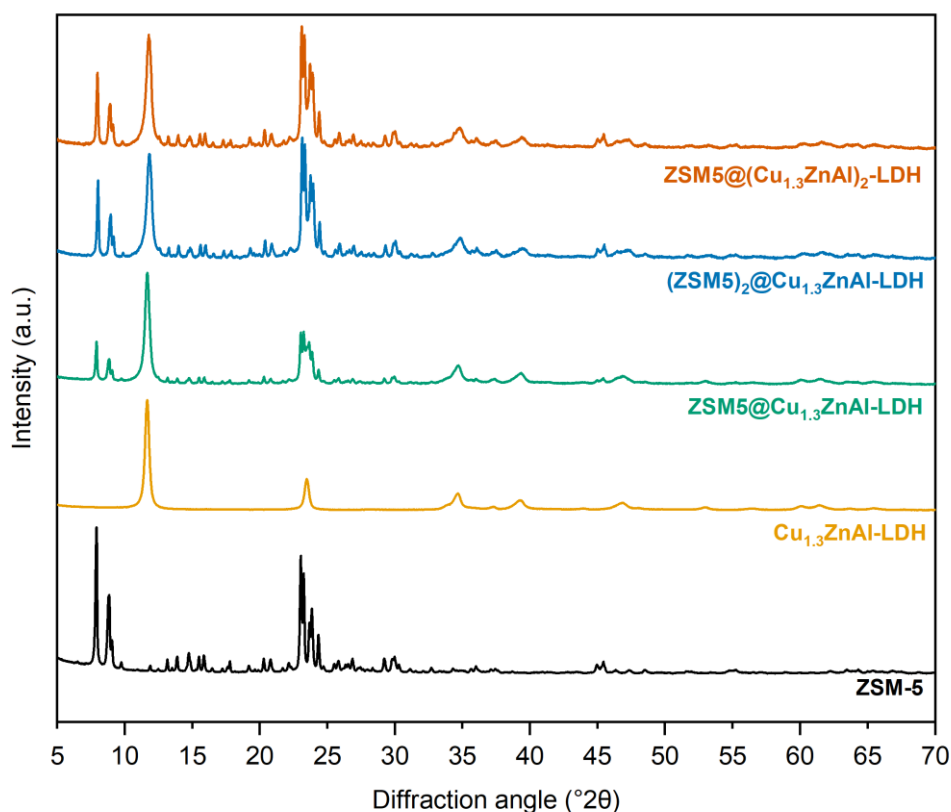


Figure 3.20: PXRD profiles of the ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$)₂-LDH and (ZSM5)₂@ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH core-shell catalyst precursors.

ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$)₂-LDH and (ZSM5)₂@ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH exhibit similar lattice parameters (summarised in Table 3.6), corresponding to d_{003} and d_{110} values of approximately 7.570 Å and 1.540 Å (for full details of the refinements and structural parameters refer to Table B.13). The d_{003} value corresponds to those reported for carbonate-intercalated LDHs and is similar to the value previously reported for the 1:1 ZSM-5:LDH ratio core-shell, ZSM5@ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH (7.559 Å).^{47, 52} Both core-shells exhibit similar domain lengths ($D_{003} \approx 16.3$ nm, $D_{110} \approx 5.8$ nm) and anisotropy (full Scherrer parameters are summarised in Table B.14). Compared to ZSM5@ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH, ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$)₂-LDH and (ZSM5)₂@ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH

are more anisotropic, suggesting that although the crystal structure of the $\text{Cu}_{1.3}\text{ZnAl-LDH}$ shell is unchanged, crystal growth is affected by the ratios used in the coprecipitation.

Table 3.6: d-spacing and domain lengths of $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2\text{-LDH}$ and $(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl-LDH}$ core-shell catalyst precursors from two-phase Rietveld refinement.

Sample	d_{003} (Å)	d_{110} (Å)	D_{003}^a (nm)	D_{110}^a (nm)	Crystalline anisotropy (D_{110}/D_{003})
$\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2\text{-LDH}$	7.559	1.537	16.1	6.0	0.4
$(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl-LDH}$	7.572	1.534	16.4	5.6	0.3
$\text{ZSM5} @ \text{Cu}_{1.3}\text{ZnAl-LDH}$	7.580	1.538	18.4	12.4	0.7

^aK = 0.9 in Scherrer's equation.

PXRD analysis confirms that the carbonate-intercalated $\text{Cu}_{1.3}\text{ZnAl-LDH}$ phase was grown in the presence of ZSM-5. Altering the ZSM-5:LDH ratio in the synthesis leads to the formation of core-shells with smaller LDH domain lengths compared to the 1:1 $\text{ZSM5} @ \text{Cu}_{1.3}\text{ZnAl-LDH}$ core-shell.

It was determined that for the sodium-free coprecipitation method, in-situ coprecipitation of the LDH in the presence of ZSM-5 facilitated thinner LDH platelets. By altering the ratio of ZSM-5 to metal salts in the coprecipitation mixture, the LDH platelets in the $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2\text{-LDH}$ and $(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl-LDH}$ core-shell samples are also thinner than the 1:1 core-shell. TEM analysis of the $\text{ZSM5} @ \text{Cu}_{1.3}\text{ZnAl-LDH}$ core-shell in Chapter 2.2.2 revealed the presence of some free LDH particles. This could suggest that as the available surface area of ZSM-5 decreases, less LDH is able to nucleate and

grow on the zeolite, leading to an increase in free LDH formation. Consequently, the LDH crystal size in such cases is expected to approach values similar to those observed in the physical mixture. For ZSM5+Cu_{1.3}ZnAl-LDH, the D_{003} length (19.7 nm larger than the ZSM5@Cu_{1.3}ZnAl-LDH core-shell and was more similar to the D_{003} length of Cu_{1.3}ZnAl-LDH (20.2 nm). In the case of (ZSM5)₂@Cu_{1.3}ZnAl-LDH, increasing the amount of ZSM-5 in the coprecipitation, thereby increasing the available surface area for LDH nucleation, may result in fewer free LDH species. The thinner platelets observed in (ZSM5)₂@Cu_{1.3}ZnAl-LDH may indicate that more LDH has nucleated on the surface of the zeolite. As the lattice parameters from the PXRD are an average of the whole sample, this would account for the smaller D_{003} value in (ZSM5)₂@Cu_{1.3}ZnAl-LDH.

STEM/EDX analysis was used to determine how the coverage of Cu_{1.3}ZnAl-LDH over the ZSM-5 particles were affected by the different ZSM-5:LDH ratios used in the coprecipitation method.

TEM images of ZSM5@(Cu_{1.3}ZnAl)₂-LDH and (ZSM5)₂@Cu_{1.3}ZnAl-LDH core-shells are shown in Figure 3.21. The micrographs clearly reveal a greater presence of free LDH in the 1:2 ZSM-5:LDH ratio core-shell, which was expected based on the presence of free LDH in the 1:1 ZSM5@Cu_{1.3}ZnAl-LDH core-shell previously described in Chapter 2.2.2. Some free LDH is also present in the (ZSM5)₂@Cu_{1.3}ZnAl-LDH sample.

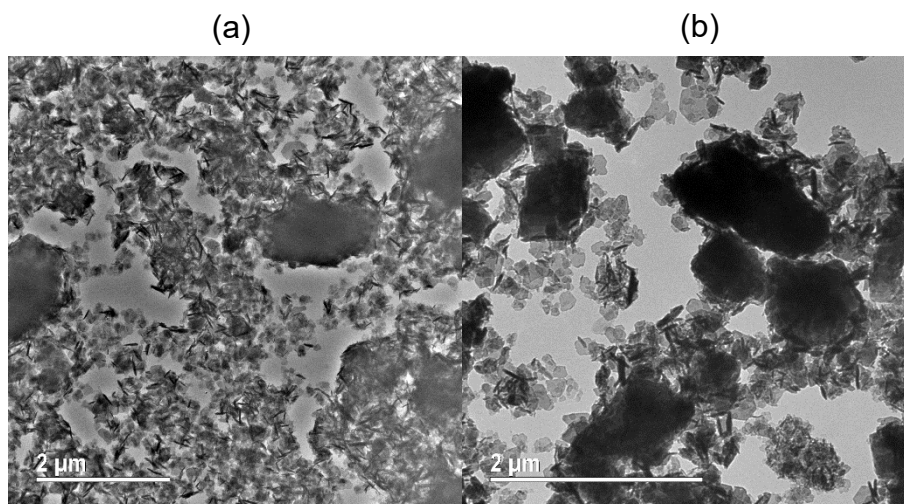


Figure 3.21: TEM images of (a) ZSM5@ $(\text{Cu}_{1.3}\text{ZnAl})_2$ -LDH and (b) $(\text{ZSM5})_2$ @ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH catalyst precursors.

EDX mapping in Figure 3.22 shows a uniform distribution of Cu (blue) and Zn (orange) from the $\text{Cu}_{1.3}\text{ZnAl}$ -LDH across both core-shells. This suggests that, after the ZSM-5 core is coated with LDHs, the remaining metal salts form $\text{Cu}_{1.3}\text{ZnAl}$ -LDH as a separate phase. The presence of free LDH in $(\text{ZSM5})_2$ @ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH suggests that a higher ZSM-5 content could be introduced into the coprecipitation method. Results from the CO_2 hydrogenation of the hybrid ZSM5@ $\text{Cu}_{1.3}\text{ZnAl}$ core-shell catalyst (Chapter 2.3) highlight the importance of strong interaction between the CZA and ZSM-5 phases for achieving high DME productivity. Hence, altering the ZSM-5:LDH ratios to minimise the amount of free LDH could be beneficial for the performance of the catalyst.

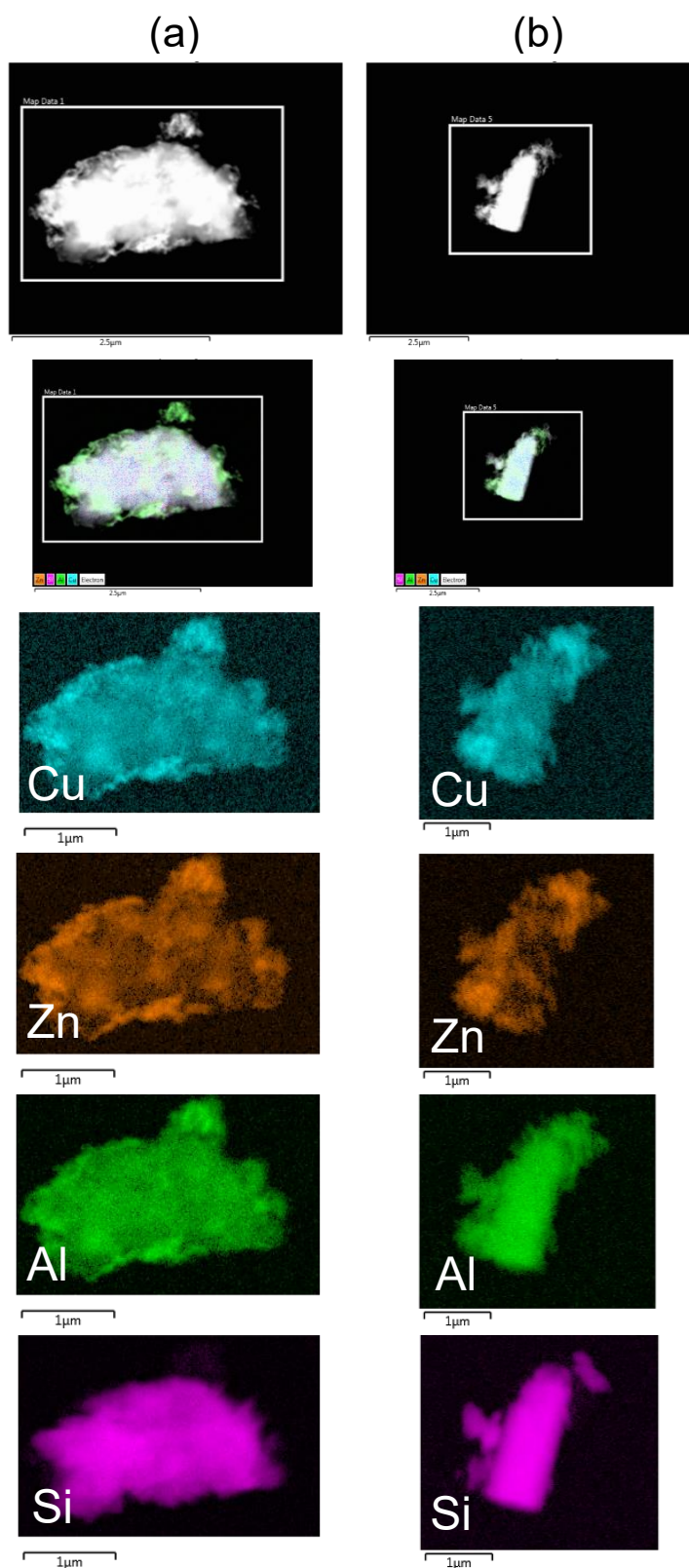


Figure 3.22: STEM/EDX of (a) ZSM5@Cu_{1.3}ZnAl-LDH and (b) (ZSM5)₂@Cu_{1.3}ZnAl-LDH catalyst precursors showing the distribution of on Cu (blue), Zn (orange), Al (green) and Si (magenta).

The sizes of the ZSM-5 particles used in the coprecipitation are not uniform, making control of LDH growth over the zeolite challenging. It would be beneficial to conduct an investigation on the synthesis of the core-shell using ZSM-5 particles of uniform sizes.

$(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl-LDH}$ does not appear to have less coverage in comparison to the original 1:1 ratio core-shell based on SEM/EDX imaging (Figure 3.23). Meanwhile, $\text{ZSM5}@\text{(Cu}_{1.3}\text{ZnAl)}_2\text{-LDH}$ appears to have greater amounts of free LDH which aligns with the results from the TEM analysis. Both $\text{ZSM5}@\text{(Cu}_{1.3}\text{ZnAl)}_2\text{-LDH}$ and $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl-LDH}$ precursor catalysts exhibit a uniform coating of Cu (blue) and Zn (orange) over the ZSM-5 aluminosilicate (identified by the Si (magenta)).

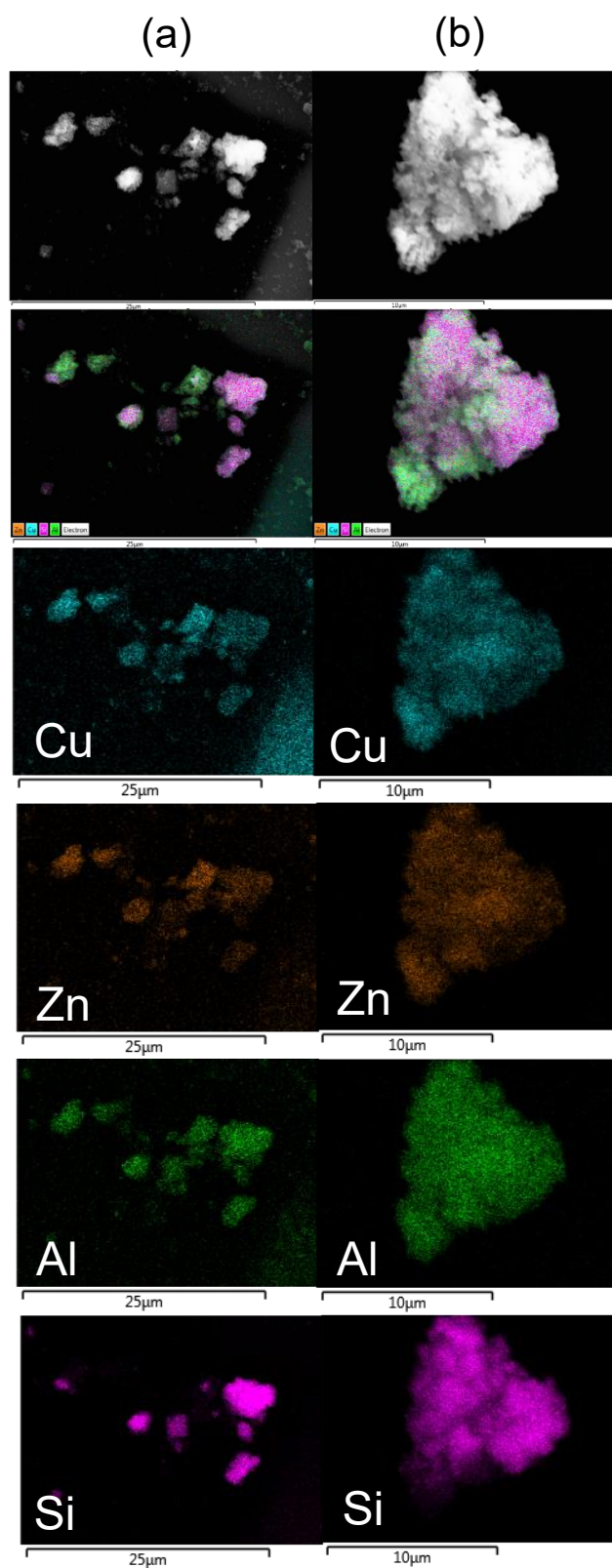


Figure 3.23: SEM/EDX images of (a) ZSM5@((Cu_{1.3}ZnAl)₂-LDH and (b) (ZSM5)₂@Cu_{1.3}ZnAl-LDH catalyst precursors showing the distribution of on Cu (blue), Zn (orange), Al (green) and Si (magenta).

Thus, SEM/EDX analysis reflects the results from STEM/EDX imaging. Namely that there is an abundance of free $\text{Cu}_{1.3}\text{ZnAl-LDH}$ in the 1:2 ZSM-5:LDH ratio core-shell ($\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2\text{-LDH}$) and the coverage of the LDH shell over the ZSM-5 core is uniform in both 1:2 and 2:1 core-shell samples.

FTIR profiles of $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2\text{-LDH}$ and $(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl-LDH}$ in Figure 3.24 shows absorbances characteristic of both LDH and ZSM-5 phases (see Chapter 2.2.2 for full breakdown of FTIR peaks in $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and ZSM-5).

Consistent with the FTIR results of other core-shells explored in this work, the NH_4^+ bending peak in the pristine ZSM-5 (1450 cm^{-1}) is not present in the core-shell samples.⁵⁸

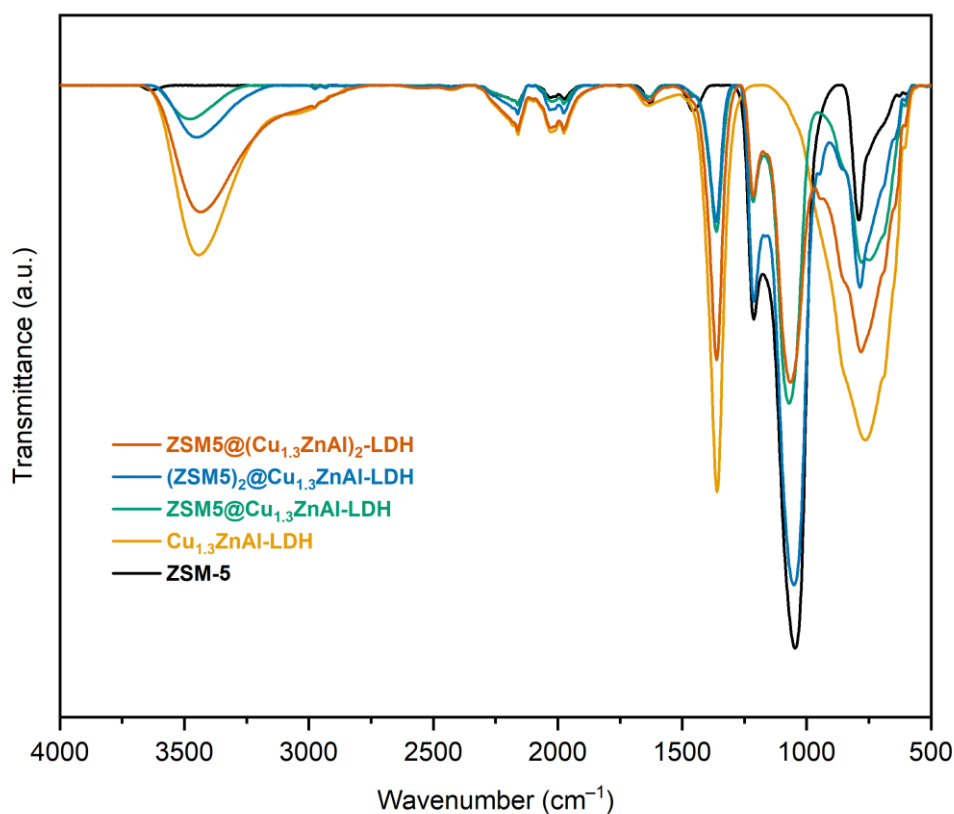


Figure 3.24: FTIR profiles of the core-shell catalyst precursors, $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2\text{-LDH}$ and $(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl-LDH}$, against $\text{ZSM5} @ \text{Cu}_{1.3}\text{ZnAl-LDH}$, $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and ZSM-5.

The FTIR profiles of $\text{ZSM5}@\text{(Cu}_{1.3}\text{ZnAl)}_2\text{-LDH}$ and $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl-LDH}$ confirm that both the carbonate-intercalated (1360 cm^{-1} and 780 cm^{-1}) $\text{Cu}_{1.3}\text{ZnAl-LDH}$ shell and ZSM-5 core is present in the core-shell samples. The profiles also suggest that NH_4^+ within the ZSM-5 is displaced following coprecipitation, which was anticipated based on previous core-shell characterisations conducted in this work. Based on ICP-OES/CHN analysis (Table B.12) the extent of NH_4^+ displacement is minimised in $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl-LDH}$ compared to the $\text{ZSM5}@\text{(Cu}_{1.3}\text{ZnAl)}_2\text{-LDH}$. The exchange of NH_4^+ in the core-shell precursor catalysts synthesised in Section 3.2.2 was considered to be partial, and is likely due to ion exchange with $\text{Cu}^{2+}/\text{Zn}^{2+}/\text{Al}^{3+}$ present in the coprecipitation mixture. This may be why the nitrogen wt% detected in the core-shells increases in order of increasing ZSM-5 content ($\text{ZSM5}@\text{(Cu}_{1.3}\text{ZnAl)}_2\text{-LDH}$ (0.35%) > $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDH}$ (0.47%, see Chapter 2.2.2) > $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl-LDH}$ (0.84%)).

The thermal stabilities of the 1:2 and 2:1 ZSM-5:LDH core-shells are summarised in Figure 3.25 and Table 3.7. Both $\text{ZSM5}@\text{(Cu}_{1.3}\text{ZnAl)}_2\text{-LDH}$ and $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl-LDH}$ core-shell precursor catalysts demonstrate three major WLRs (more easily seen in the dTGA profiles). Weight loss within these regions can be ascribed to losses in both the $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and ZSM-5 phases, and can be summarised as regions between $30 - 200\text{ }^\circ\text{C}$, $200 - 400\text{ }^\circ\text{C}$ and $500 - 800\text{ }^\circ\text{C}$. The thermal decomposition events that occur within these regions are the same in both core-shells, however, the extent of decomposition is dependent on the sample composition (i.e. the ZSM-5:LDH ratio).

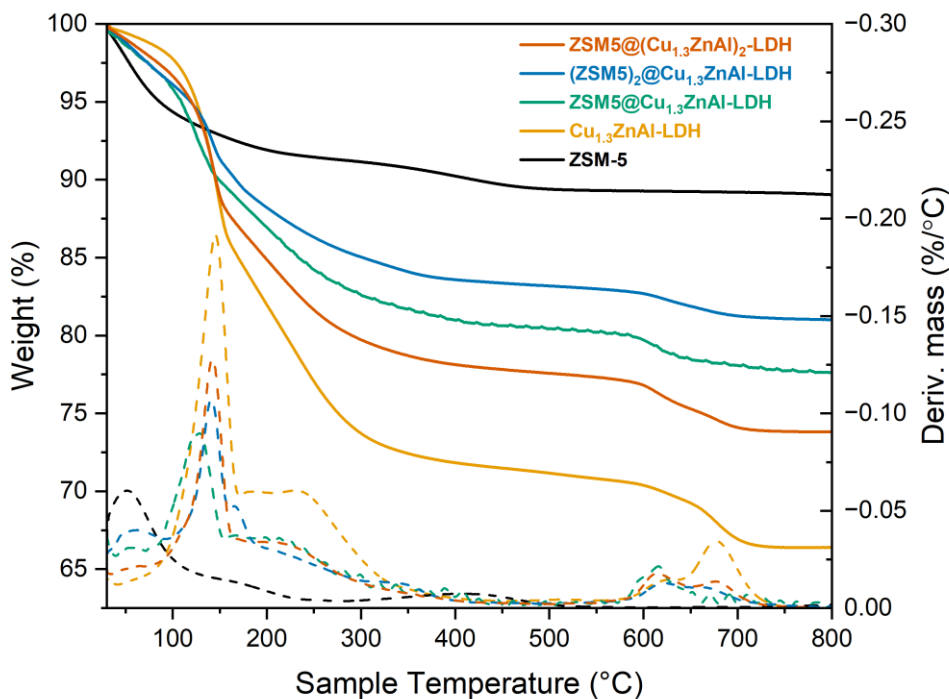


Figure 3.25: TGA and dTGA curves of the core-shell catalyst precursors, ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$)₂-LDH and (ZSM5)₂@ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH, in comparison to ZSM5@ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH, $\text{Cu}_{1.3}\text{ZnAl}$ -LDH, and ZSM-5.

For instance, the first WLR in ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$)₂-LDH has a loss of 15.1% whilst (ZSM5)₂@ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH has a weight loss of 11.8%. This region corresponds to the loss of surface-adsorbed water in the $\text{Cu}_{1.3}\text{ZnAl}$ -LDH shell and ZSM-5 core, as well as the decomposition of water within the interlayers of the LDH and water within the ZSM-5 pores.⁶³⁻⁶⁵ For previous core-shell samples, the major contribution to the second WLR had been ascribed to the decomposition of the $\text{Cu}_{1.3}\text{ZnAl}$ -LDH. As shown in the dTGA profiles of ZSM-5, weight loss in this region is minimal (1.7%) and is associated with the decomposition of ammonium.⁶⁶ For the $\text{Cu}_{1.3}\text{ZnAl}$ -LDH shell, lattice dehydroxylation and partial decomposition of the interlayer carbonate anions occurs between 200 – 400 °C.^{64, 67} At these temperatures, the LDH transforms into the LDO and by 400 °C, 2:1 and 1:2 ZSM-5:LDH core-shells respectively lose 6.7% and 4.6% of weight.⁶⁸ The final thermal event is ascribed to the full decarbonation of the LDO with

the two peaks indicative of $M^{2+}M^{3+}O_y(CO_3)_2$ oxycarbonates with different thermal stabilities.^{69, 70} At 800 °C, ZSM5@($Cu_{1.3}ZnAl$)₂-LDH demonstrates a higher residual weight (81.0%) than (ZSM5)₂@ $Cu_{1.3}ZnAl$ -LDH (73.8%). Weight loss in all three regions is greater for ZSM5@($Cu_{1.3}ZnAl$)₂-LDH than (ZSM5)₂@ $Cu_{1.3}ZnAl$ -LDH which is expected based on the thermal decomposition events exhibited by $Cu_{1.3}ZnAl$ -LDH and ZSM-5. Calculated from the residual weights, ZSM-5:LDH ZSM5@($Cu_{1.3}ZnAl$)₂-LDH has a ZSM-5:LDH ratio of 38:62 (~1:2) and (ZSM5)₂@ $Cu_{1.3}ZnAl$ -LDH has a ratio of 67:33 (~2:1), which correlates well with the weights used in the reaction synthesis.

Table 3.7: Summary of data from TGA of ZSM5@($Cu_{1.3}ZnAl$)₂-LDH and (ZSM5)₂@ $Cu_{1.3}ZnAl$ -LDH, including the weight loss percentages for the major weight loss regions (WLRs), the residual weights of the samples and the LDH:ZSM5 ratio.

Sample	WLR (%)			Residual weight (%)	LDH:ZSM-5
	30 – 200 °C	200 – 400 °C	500 – 800 °C		
ZSM5@($Cu_{1.3}ZnAl$) ₂ -LDH	15.1	6.7	3.8	73.8	38:62
(ZSM5) ₂ @ $Cu_{1.3}ZnAl$ -LDH	11.8	4.6	2.2	81.0	67:33

The difference in the weight loss percentages in the three major WLRs of the core-shells reflect the different thermal stabilities in the LDH and ZSM-5 phases. Using the residual weights of the samples, the ZSM-5:LDH ratio was determined for the core-shells and was found to correlate with the weight ratios used in the synthesis method.

The characterisation of the core-shell precursors confirmed the successful synthesis of the materials. The Cu:Zn:Al ratio within the LDH phase matched the target composition, and the crystallinity of both the $\text{Cu}_{1.3}\text{ZnAl}$ -LDH and ZSM-5 phases was consistent with expectations. Additionally, the ZSM-5:LDH ratios were in line with the reactant amounts used in the coprecipitation and the thermal stability of the materials corresponded to what was anticipated based on the weight ratio. With this, the precursor core-shells were tested for their CTD performance.

3.5: CO_2 hydrogenation performance of $(\text{ZSM5})_x@(\text{Cu}_{1.3}\text{ZnAl})_y$ catalysts

The activation of the $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$ -LDH than $(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl}$ -LDH core-shells follows the same procedure as described in Section 3.3. Catalysts are described without the LDH suffix, i.e. the core-shell catalyst generated from the 1:2 ZSM-5:LDH precursor is named “ $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$ ” whilst the catalyst generated from the 2:1 ZSM-5:LDH precursor is named “ $(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl}$ ”. The catalysts were then reacted under the same conditions used in Section 3.3. For full details of the catalyst preparation method and testing conditions see Chapter 6.3.11 and Chapter 6.5.

Results from the CO_2 hydrogenation experiments over the $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$ and $(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl}$ core-shell catalysts are summarised in Figure 3.26 and Table 3.8. Both core-shell catalysts produced a combination of DME, methanol and CO. Similar to the other hybrid CZA/ZSM-5 direct CTD catalysts tested in this work, the highest DME productivities occurred at 280 °C. X_{CO_2} increases with temperature whilst the yield of DME (Y_{DME}) decreases as S_{CO} increases, which was anticipated based on the

thermodynamics associated with the CTM and the competing RWGS reaction.^{79, 84} This reflects the results seen in previous CO₂ hydrogenation tests of the hybrid ZSM5/Cu_{1.3}ZnAl catalysts, including those in the 1:1 ZSM5@Cu_{1.3}ZnAl core-shell.

The highest STY_{DME} recorded for ZSM5@(Cu_{1.3}ZnAl)₂ was 0.36 g_{DME}/g_{cat}·h which was similar to the performance of the ZSM5@Cu_{1.3}ZnAl catalyst (0.37 g_{DME}/g_{cat}·h) but considerably higher than the DME productivity of (ZSM5)₂@Cu_{1.3}ZnAl (0.27 g_{DME}/g_{cat}·h). Looking at the CO₂ conversion between the catalysts at 280 °C, X_{CO_2} of ZSM5@(Cu_{1.3}ZnAl)₂ (16.8%) more closely resembles the conversion observed in the 1:1 ratio catalyst (18.3%) and is considerably greater than the conversion over the 2:1 ratio catalyst (11.2%).

Looking at the product selectivities of the core-shell catalysts, compared to (ZSM5)₂@Cu_{1.3}ZnAl (29.9%), ZSM5@(Cu_{1.3}ZnAl)₂ is less selective towards DME (26.6%). In fact, across the temperature range S_{DME} values for ZSM5@(Cu_{1.3}ZnAl)₂ are consistently lower than those for (ZSM5)₂@Cu_{1.3}ZnAl. Both core-shell catalysts have similar methanol selectivities ranging from 3.0 – 10.3% decreasing with temperature. Between 260 – 280 °C, the methanol selectivities approach the thermodynamic equilibrium values suggesting that the catalysts are under kinetic control.^{38, 88, 89} ZSM5@(Cu_{1.3}ZnAl)₂ also demonstrates greater S_{CO} than (ZSM5)₂@Cu_{1.3}ZnAl. Given the small error margins observed in previous CO₂ hydrogenation tests (see Chapter 2.3), the uncertainty in the product selectivity is minimal, and therefore the differences in the selectivities are meaningful. Hence, the 2:1 ratio catalyst with the larger amount of ZSM-5 relative to the CZA phase minimises the formation of CO in comparison to the 1:2 catalyst. For CO₂ conversion, the values for the 1:2 ZSM-5:LDH ratio catalyst falls within the range of error associated with the 1:1 core-shell catalyst. Hence, X_{CO_2} , S_{DME} ,

$S_{\text{CH}_3\text{OH}}$ and S_{CO} values for $\text{ZSM5}@\text{(Cu}_{1.3}\text{ZnAl)}_2$ are similar to $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$. This suggests that increasing the amount of CZA phase relative to ZSM-5 does not improve the conversion or overall performance of the hybrid catalyst. Although $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$ is more selective towards DME, the lower conversion severely impacts the overall DME productivity of the catalyst. To obtain a high DME productivity both the conversion and the selectivity need to be maximised, hence why the DME space time yields of $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$ are lower than the 1:2 and 1:1 core-shell catalyst (see Figure 3.27).

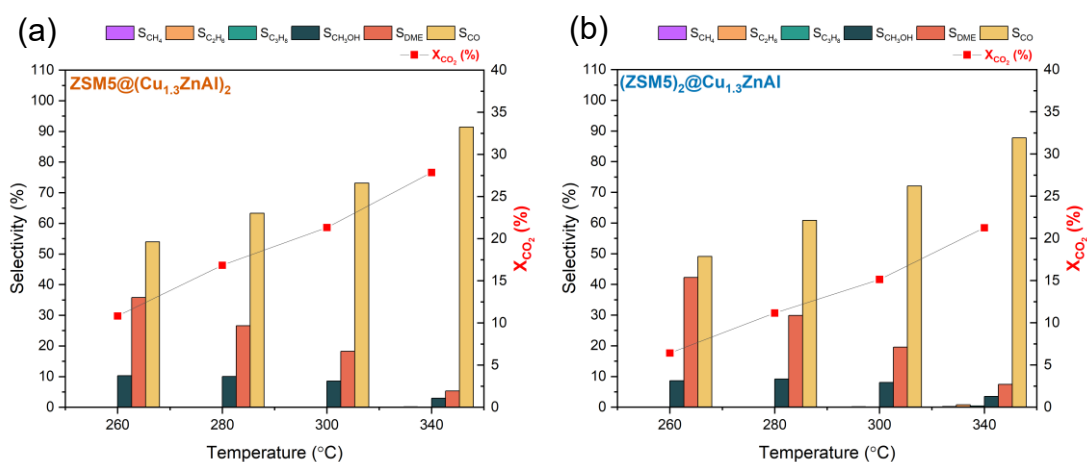


Figure 3.26: Product distribution of CO₂ hydrogenation reaction over (a) $\text{ZSM5}@\text{(Cu}_{1.3}\text{ZnAl)}_2$ and (b) $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$ as a function of temperature (260 – 340 °C). Reaction conditions: $P = 3.0$ MPa; $\text{CO}_2:\text{H}_2:\text{N}_2 = 24:72:4$; $WHSV = 18000$ mL/g_{cat}·h, carbon balance 99.42 – 100.07%.

Table 3.8: CO₂ hydrogenation results for ZSM5@Cu_{1.3}ZnAl and (ZSM5)₂@Cu_{1.3}ZnAl.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)			Yield (%)	<i>STY</i> _{DME} (g _{DME} /g _{cat} ·h)
			<i>S</i> _{DME}	<i>S</i> _{CH₃OH}	<i>S</i> _{CO}		
ZSM5@Cu _{1.3} ZnAl	260	10.8	35.8	10.3	54.0	3.9	0.32
	280	16.8	26.6	10.1	63.3	4.5	0.36
	300	21.3	18.2	8.6	73.1	3.9	0.32
	340	27.9	5.3	3.0	91.4	1.5	0.12
(ZSM5) ₂ @Cu _{1.3} ZnAl	260	6.4	42.2	8.6	45.6	2.7	0.22
	280	11.2	29.9	9.2	59.9	3.3	0.27
	300	15.1	19.6	8.0	70.5	3.0	0.24
	340	21.3	7.5	3.5	88.3	1.6	0.13

^aReaction conditions: $P = 3.0$ MPa, CO₂/H₂/N₂ = 24:72:4, and $WHSV = 18,000$ mL/g_{cat}·h.

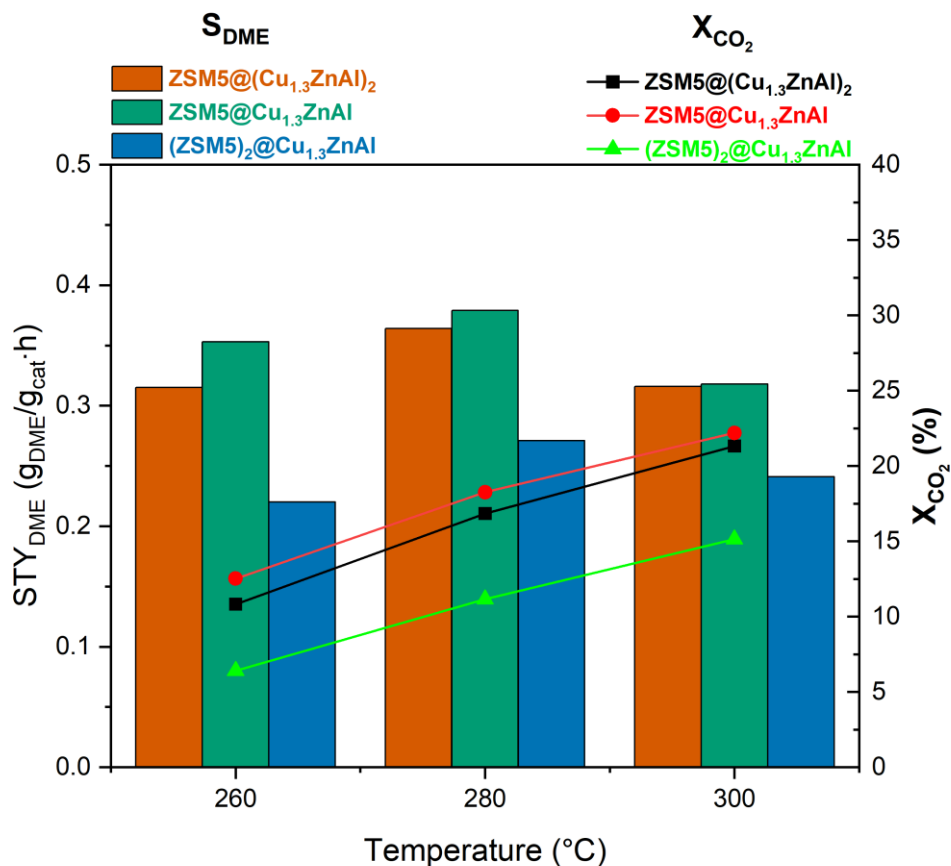


Figure 3.27: STY_{DME} and CO_2 conversions of $ZSM5@Cu_{1.3}ZnAl_2$ and $(ZSM5)_2@Cu_{1.3}ZnAl$ core-shell catalysts against $ZSM5@Cu_{1.3}ZnAl$ (data collected from Chapter 2.4.1). Reaction conditions: $P = 3.0$ MPa; $CO_2:H_2:N_2 = 24:72:4$; $WHSV = 18,000$ mL/g_{cat}·h.

$ZSM5@Cu_{1.3}ZnAl_2$ has a similar performance as the 1:1 core-shell catalyst, $ZSM5@Cu_{1.3}ZnAl$. A key thermodynamic advantage of a single hybrid catalyst is that the conversion of methanol to DME shifts the CO_2 conversion equilibrium toward the products. As the relative amount of CZA phase to ZSM-5 phase is greater in the $ZSM5@Cu_{1.3}ZnAl_2$ core-shell catalyst, an increase in CO_2 conversion was anticipated (due to an increased number of active sites per gram of catalyst). However, with a lower proportion of ZSM-5, the reduced number of acidic sites for methanol dehydration limits the extent of DME formation. As a result, the position of equilibrium of the CTM reaction

lies closer to the reactants, which may promote the RWGS reaction, leading to increased CO selectivity. In the case of the 2:1 ratio core-shell $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$, there are fewer Cu active sites per gram of catalyst than in the 1:2 ratio catalyst. This accounts for the lower CO_2 conversions observed for $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$. For the CO_2 that is converted to methanol, a larger proportion of methanol was transformed by ZSM-5 as there was a greater amount of solid catalyst per gram of catalyst. This corresponds with the higher S_{DME} selectivity seen for $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$. Since methanol is more rapidly converted to DME in this case, the RWGS reaction is minimised, thereby limiting the formation of CO. This behaviour is reflected in the selectivity results, for e.g., at 260 °C $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$ has a S_{CO} value of 54.0% which is similar to the 1:1 core-shell $\text{ZSM5} @ \text{Cu}_{1.3}\text{ZnAl}$ catalyst (55.8%) and the 1:1 physical mixture $\text{ZSM5} + \text{Cu}_{1.3}\text{ZnAl}$ catalyst (57.2%) whilst for $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$ S_{CO} is minimised at 45.6%.

A range of characterisation techniques were used to investigate the textural, acidic and basic properties of the core-shell catalysts to explain the observations made in the CO_2 hydrogenation tests.

N_2 BET analysis was used to investigate the textural properties of the $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$ and $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$ catalysts. BET surface areas and pore volumes are summarised in Figure 3.28 and Table 3.9.

The overall surface area of $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$ ($259 \text{ m}^2/\text{g}$) was considerably higher than the $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$ catalyst ($156 \text{ m}^2/\text{g}$), although the S_{External} were similar ($\sim 56 \text{ m}^2/\text{g}$). Based on N_2 BET analysis of similar materials within this work, the major contribution to the overall surface area in core-shell catalysts (and precursors) is typically due to the microporosity of the ZSM-5 phase. For $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$, the S_{BET} is low

due to the smaller micropore surface area ($88 \text{ m}^2/\text{g}$). Comparing the results to the BET surface areas and V_{Micro} of the 1:1 ZSM5@Cu_{1.3}ZnAl catalyst (see Figure B.15) when the amount of LDH is doubled in relation to ZSM-5, the micropore surface area decreases by ~52%. As described in Chapter 2.2.3, the S_{External} and S_{Micro} was facilitated in ZSM5@Cu_{1.3}ZnAl (and the physical mixture ZSM5+Cu_{1.3}ZnAl) and was greater than the anticipated values (calculated using the S_{External} values for Cu_{1.3}ZnAl and H-ZSM-5). S_{External} for (ZSM5)₂@Cu_{1.3}ZnAl ($55 \text{ m}^2/\text{g}$) matches the theoretical combination of the CZA/ZSM-5 catalyst with a 2:1 ratio ($55 \text{ m}^2/\text{g}$). Meanwhile the external surface area for the 1:2 ZSM-5:LDH core-shell catalyst is lower than the theoretical S_{External} ($67 \text{ m}^2/\text{g}$). S_{Micro} for (ZSM5)₂@Cu_{1.3}ZnAl also matches the anticipated value, whilst the micropore internal surface area of ZSM5@(Cu_{1.3}ZnAl)₂ is, again, less than expected ($105 \text{ m}^2/\text{g}$).

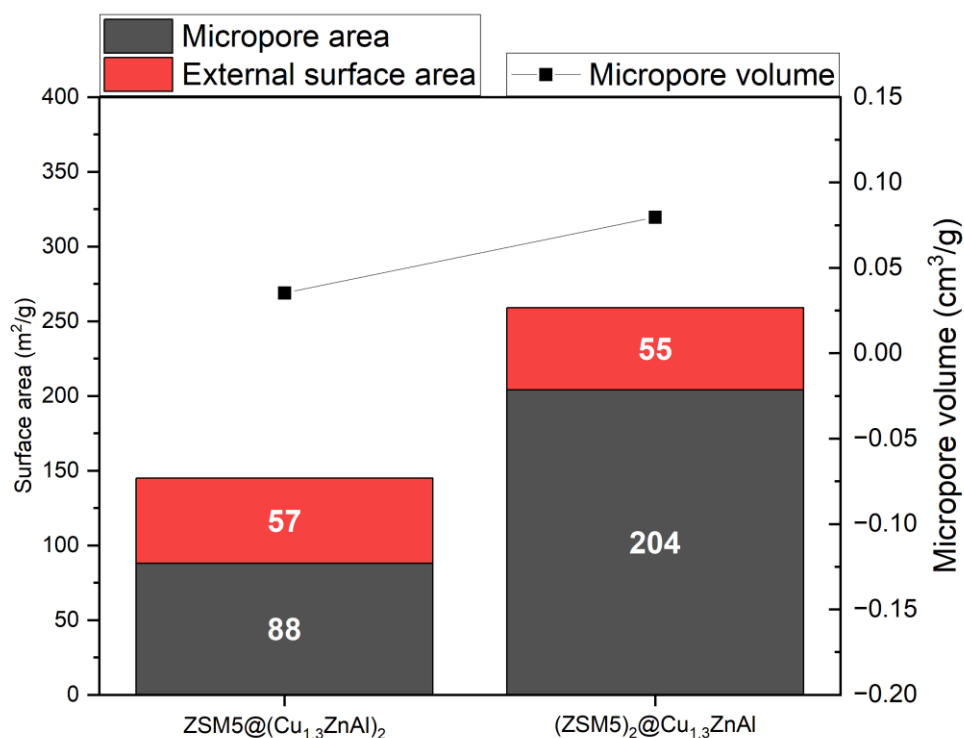


Figure 3.28: N₂ BET surface areas of ZSM5@Cu_{1.3}ZnAl₂ and (ZSM5)₂@Cu_{1.3}ZnAl core-shell catalysts.

The grey and red bars show the estimated micropore surface area and external surface area respectively, whilst the line plot shows the estimated micropore volume of the samples.

Table 3.9: Textural properties of activated ZSM5@Cu_{1.3}ZnAl₂ and (ZSM5)₂@Cu_{1.3}ZnAl core-shell catalysts.

Sample	S_{External} (m ² /g)	S_{Micro} (m ² /g)	S_{BET} (m ² /g)	V_{Micro} (cm ³ /g)
ZSM5@Cu _{1.3} ZnAl ₂	57	88	145	0.035
(ZSM5) ₂ @Cu _{1.3} ZnAl	55	204	259	0.080

Although the surface areas of (ZSM5)₂@Cu_{1.3}ZnAl align with the theoretical values, ZSM5@Cu_{1.3}ZnAl₂ possess a lower external and internal micropore surface area than

anticipated. S_{External} is not improved by the introduction of more LDH and pore blocking within the micropores of the zeolite cores is considerable. In spite of this, the catalyst behaves similarly to $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$. For $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$, although the surface areas are comparable to $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$, its CO_2 conversion was lower, leading to a reduced DME productivity.

N_2 adsorption isotherms for $\text{ZSM5}@(\text{Cu}_{1.3}\text{ZnAl})_2$ and $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$ show patterns that are indicative of the microporous zeolite phase and the meso/macroporous CZA phase (Figure 3.29a). Looking at the isotherm for $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$, high N_2 uptake at low relative pressures ($p/p^0 < 0.3$) is indicative of microporosity (< 2 nm) within the sample. It is a type I isotherm that plateaus at medium relative pressures, a pattern which is commonly seen in zeolites. Uptake at high relative pressures ($p/p^0 > 0.5$) stems from the mesoporosity (2 – 50 nm) and macroporosity (> 50 nm) from the CZA phase. The CZA catalyst analysed by N_2 BET in Chapter 2.4.1.2 demonstrated a similar type II isotherm with a H3 hysteresis. High N_2 uptake at high relative pressures is indicative of the mesopores/macropores in the CZA phase and is associated with pore formation between stacked nanoplatelets. This is also observed in the isotherms of the $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$ catalyst (Chapter 2.4.1.2). For $\text{ZSM5}@(\text{Cu}_{1.3}\text{ZnAl})_2$, the isotherm pattern more closely resembles that of the $\text{Cu}_{1.3}\text{ZnAl}$ catalyst where there is a much higher N_2 uptake when $p/p^0 > 0.5$ compared to $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$ although some microporosity from the ZSM-5 core is still observed. This is expected based on the relative amounts of CZA/ZSM-5 within the core-shell catalysts, thus, $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$ has a higher proportion of micropores than mesopores/macropores. This is also evident in the micropore size distribution. The density functional theory (DFT) model was used to determine the micropore size distribution and was applied to

the adsorption branch of the isotherms. The distribution, summarised in Figure 3.29b, highlights the difference in microporosity between $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$ and $(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl}$. The 0.4 nm, 0.6 nm and 1.3 nm micropores stem from the ZSM-5 core whereas $\text{Cu}_{1.3}\text{ZnAl}$ does not possess micropores (see Chapter 2.4.1.2). The 1:2 ratio core-shell $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$ exhibits only one micropore at 1.4 nm. Notably, $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$ does not possess any of the smaller micropores that are present in $(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl}$ or $\text{ZSM5} @ \text{Cu}_{1.3}\text{ZnAl}$. The absence is not representative of a reduction in micropore quantity as this would be reflected by some uptake at 0.4 nm and 0.6 nm pore widths. Hence, the data suggests more substantial micropore blocking occurred in $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$. In contrast, the 1:1 core-shell catalyst $\text{ZSM5} @ \text{Cu}_{1.3}\text{ZnAl}$ does possess 0.4 nm and 1.2 nm micropores although the performance of $\text{ZSM5} @ \text{Cu}_{1.3}\text{ZnAl}$ and $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$ are similar. This suggests that the 1.4 nm micropore is capable of converting methanol to DME. Micropore blocking may be due to the increased amount of $\text{Cu}^{2+}/\text{Zn}^{2+}/\text{Al}^{3+}$ relative to ZSM-5 within the reactant mixture during coprecipitation.

The mesopore and macropore size distribution was determined using the Barrett-Joyner-Haleda (BJH) model applied to the adsorption branch of the N_2 isotherms. The resulting distribution (Figure 3.29c) clearly shows that $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$ has a larger number of mesopores and macropores compared to $(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl}$ which was anticipated based on the larger amount of CZA relative to ZSM-5 (see Figure B.16 for BJH comparison).

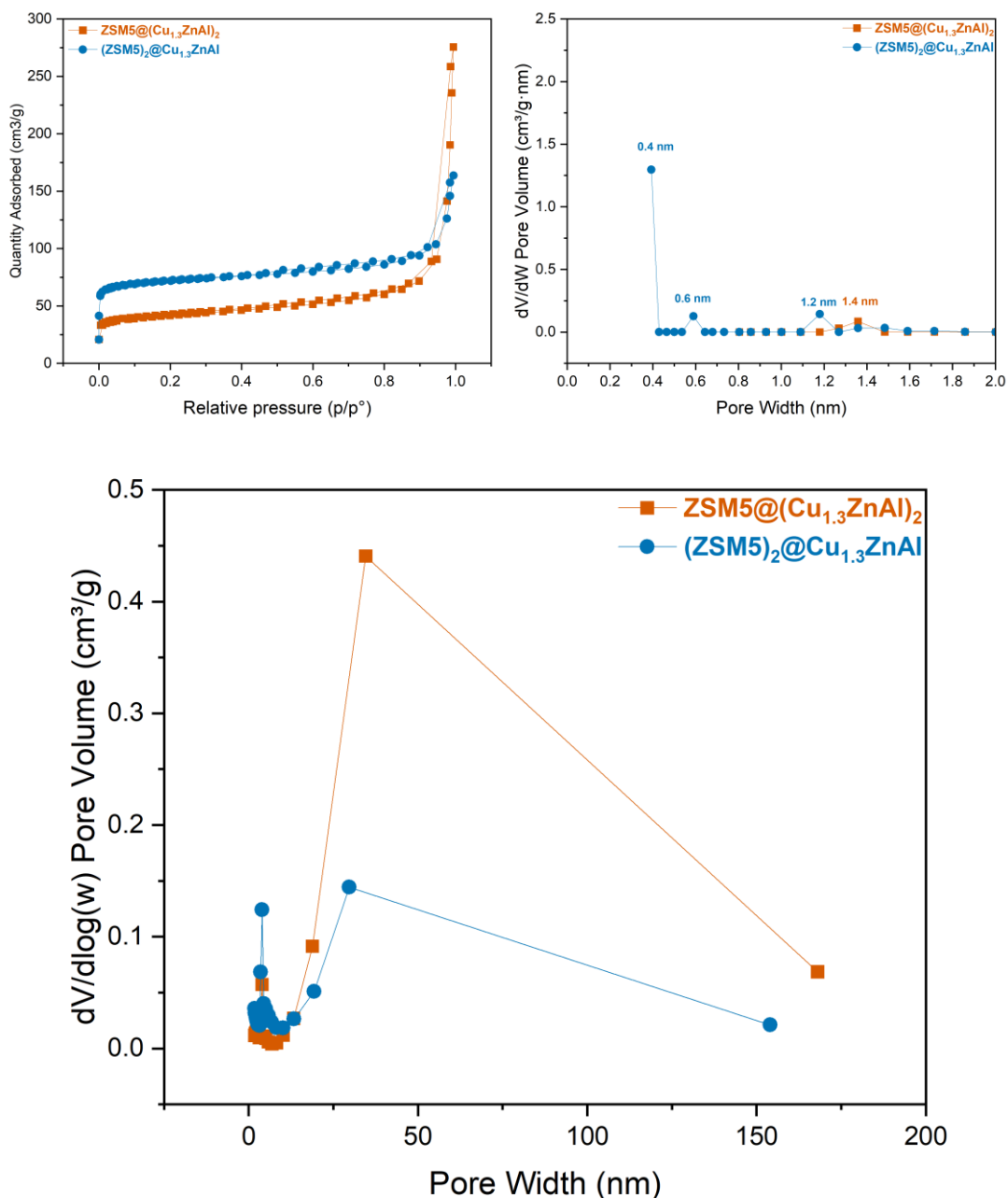


Figure 3.29: (a) N_2 adsorption isotherms, (b) DFT size distributions, and (c) BJH pore size distributions of activated $\text{ZSM5}@(\text{Cu}_{1.3}\text{ZnAl})_2$ and $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$ core-shell catalysts.

N_2 BET surface analysis of the $\text{ZSM5}@(\text{Cu}_{1.3}\text{ZnAl})_2$ and $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl}$ core-shell catalysts demonstrate that the ratio of ZSM-5:LDH used in the synthesis of the catalyst precursors has an impact on the textural properties of the activated catalysts. When the amount of LDH used in the coprecipitation is doubled micropore blocking

occurs in the ZSM-5 core and appears to affect pore widths of 0.4 nm and 0.6 nm. However, the lower external and micropore surface areas does not significantly impact the performance of the core-shell catalyst towards the direct conversion of CO₂ to DME. The surface areas of the (ZSM5)₂@Cu_{1.3}ZnAl catalyst closely aligns with the theoretical values expected for a 2:1 ZSM-5:LDH mixture, indicating that, unlike ZSM5@Cu_{1.3}ZnAl, no enhancement in external surface area is observed. The results suggests that the differences observed in the catalytic performance of the 2:1, 1:1 and 1:2 core-shell catalysts are unlikely to be due to differences in surface areas.

CO₂-TPD analysis was conducted on the ZSM5@Cu_{1.3}ZnAl and (ZSM5)₂@Cu_{1.3}ZnAl core-shell catalysts to investigate changes to the basicity of the CZA phase. Figure 3.30 summarises the CO₂ desorption profiles of the catalysts and includes the profiles for ZSM5@Cu_{1.3}ZnAl, Cu_{1.3}ZnAl and H-ZSM-5. The quantitative data calculated from the deconvoluted spectra (Figure B.17) can be found in Table 3.10.

ZSM5@Cu_{1.3}ZnAl and (ZSM5)₂@Cu_{1.3}ZnAl exhibit different CO₂-TPD profile patterns suggesting there are considerable differences in the basicity of the CZA phase. ZSM5@Cu_{1.3}ZnAl, with a larger amount of the CZA phase, has a profile that resembles that of the 1:1 core-shell catalyst, ZSM5@Cu_{1.3}ZnAl. ZSM5@Cu_{1.3}ZnAl exhibits CO₂ desorption in three major regions and possesses weak (desorption below 260 °C), medium (desorption between 260 °C and 440 °C) and strong (desorption above 440 °C) basic sites. The temperatures of maximum CO₂ desorption demonstrated by ZSM5@Cu_{1.3}ZnAl within these three regions (T_{1,CO_2} , T_{2,CO_2} , T_{3,CO_2}) occur at similar temperatures as ZSM5@Cu_{1.3}ZnAl. Thus, it can be said that the strength of the weak, medium and strong basic sites are unchanged between the 1:2 and 1:1 ZSM-5:LDH core-shell catalysts. In CZA catalysts, the weak basic sites are associated with Brønsted basic

OH groups (which reside even after thermal treatment of the LDH), the medium basic sites with moderate metal-oxide (Zn-O, Al-O) pairs, and the strong basic sites with unsaturated O^{2-} ions.⁹⁰⁻⁹³ For $ZSM5@(\text{Cu}_{1.3}\text{ZnAl})_2$, CO_2 uptake at the strong basic sites is notably more intense than in $ZSM5@Cu_{1.3}ZnAl$ which suggests there is a larger number of strong basic sites in the 1:2 core-shell catalyst. The T_{3,CO_2} peak in the CO_2 -TPD profile of $\text{Cu}_{1.3}\text{ZnAl}$ has a similar intensity to the $ZSM5@Cu_{1.3}ZnAl$ core-shell catalyst, hence an abundance of the CZA phase in relation to the ZSM-5 core generates a larger number of strong acid sites. $ZSM5@(\text{Cu}_{1.3}\text{ZnAl})_2$ also has a larger number of medium strength acid sites. Hence, the total CO_2 uptake for $ZSM5@(\text{Cu}_{1.3}\text{ZnAl})_2$ ($291 \text{ cm}^3/\text{g}$) is almost 50% larger than for $ZSM5@Cu_{1.3}ZnAl$. This however, did not improve the CO_2 hydrogenation performance of the $ZSM5@(\text{Cu}_{1.3}\text{ZnAl})_2$ catalyst compared to $ZSM5@Cu_{1.3}ZnAl$.

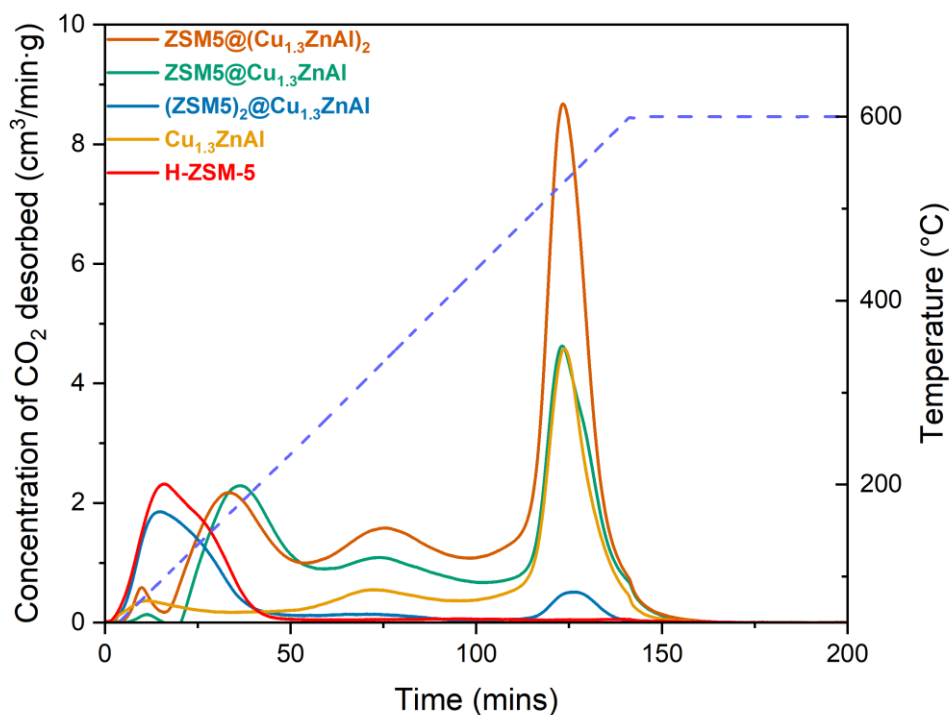


Figure 3.30: CO₂-TPD of the ZSM5@Cu_{1.3}ZnAl₂ and (ZSM5)₂@Cu_{1.3}ZnAl core-shell catalysts against ZSM5@Cu_{1.3}ZnAl, Cu_{1.3}ZnAl and H-ZSM-5.

The CO₂-TPD profile for (ZSM5)₂@Cu_{1.3}ZnAl is more closely resembles the profile for H-ZSM-5 although some desorption occurs between 260 °C and 440 °C and above 440 °C which suggests the core-shell has mostly weak and strong basic sites with barely any medium strength sites. The peak at T_{1,CO_2} (90 °C) is associated with the weak Lewis-basic type sites in the ZSM-5 core of the catalyst (i.e. negatively charged lattice oxygen atoms within the zeolite framework).²⁶ The weak basic sites in the 1:2 and 1:1 core-shell catalysts also arise from the ZSM-5 core, however, these occur at higher temperatures (where T_{1,CO_2} = 160 °C and 180 °C respectively) than in the 2:1 core-shell catalyst. Desorption at higher temperatures suggests that these sites are stronger in ZSM5@Cu_{1.3}ZnAl₂ and ZSM5@Cu_{1.3}ZnAl and that the improvement is dependent on the amount of CZA present in the hybrid catalyst.

Table 3.10: Quantitative data of CO₂ chemisorption measurements for ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$)₂, ZSM5@ $\text{Cu}_{1.3}\text{ZnAl}$, (ZSM5)₂@ $\text{Cu}_{1.3}\text{ZnAl}$, $\text{Cu}_{1.3}\text{ZnAl}$ and H-ZSM-5.

Sample	CO ₂ uptake (cm ³ /g)	T_{1,CO_2} ^a (°C)	T_{2,CO_2} ^b (°C)	T_{3,CO_2} ^c (°C)
ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$)₂	291	164	328	532
ZSM5@$\text{Cu}_{1.3}\text{ZnAl}$	199	180	329	526
(ZSM5)₂@$\text{Cu}_{1.3}\text{ZnAl}$	58	90	333	527
$\text{Cu}_{1.3}\text{ZnAl}$	113	71	318	530
H-ZSM-5	51	91	-	-

^a T_{1,CO_2} , temperature of maximum CO₂ desorption below 260 °C. ^b T_{2,CO_2} , temperature of maximum CO₂ desorption between 260 °C and 440 °C. ^c T_{3,CO_2} , temperature of maximum CO₂ desorption above 440 °C.

The overall CO₂ uptake of (ZSM5)₂@ $\text{Cu}_{1.3}\text{ZnAl}$ (58 cm³/g) is much lower than in ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$)₂ or ZSM5@ $\text{Cu}_{1.3}\text{ZnAl}$. This correlates with the poorer CO₂ conversion seen in the CO₂ hydrogenation tests of the core-shell catalysts. The small amounts of medium and strong basic sites observed in (ZSM5)₂@ $\text{Cu}_{1.3}\text{ZnAl}$ is due to the lower proportion of CZA in the hybrid catalyst. Although the number of basic sites is reduced, the core-shell catalyst still demonstrates CO₂ hydrogenation activity, albeit less effectively than ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$)₂ or ZSM5@ $\text{Cu}_{1.3}\text{ZnAl}$. This indicates that a minimum amount of CZA relative to ZSM-5 is required to achieve high CO₂ conversion.

3.6: Conclusions and future work

A series of $\text{Cu}_{1.3}\text{ZnAl}$ catalysts were tested for their CTM performance. The catalysts were derived from $\text{Cu}_{1.3}\text{ZnAl}$ -LDHs prepared using different coprecipitation methods to investigate the effect of residual sodium. All CTM catalysts showed similar methanol productivities ($0.27 - 0.29 \text{ g}_{\text{CH}_3\text{OH}}/\text{g}_{\text{cat}}\cdot\text{h}$), indicating that residual sodium does not impact the catalyst performance of the CZA catalyst developed in this work.

In contrast, $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$ core-shell catalysts were tested for direct CTD conversion, where the catalyst prepared using the sodium-free coprecipitation method ($\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$ -TPA) exhibited the highest DME productivity $0.38 \text{ g}_{\text{DME}}/\text{g}_{\text{cat}}\cdot\text{h}$. This suggests that residual sodium in the core-shell catalysts negatively affects CTD performance.

The core-shell catalyst was also made with different ZSM-5:LDH ratios. The performance of the 1:2 core-shell catalyst ($0.36 \text{ g}_{\text{DME}}/\text{g}_{\text{cat}}\cdot\text{h}$) was comparable to 1:1 core-shell ($0.37 \text{ g}_{\text{DME}}/\text{g}_{\text{cat}}\cdot\text{h}$) despite the higher proportion of the active CZA phase. This was attributed to the lower ZSM-5 content, which limited methanol dehydration and shifted the reaction equilibrium away from DME formation, favouring CO production via the RWGS reaction. In contrast, the 2:1 catalyst, with a higher ZSM-5 content, showed lower CO_2 conversion but higher DME selectivity.

Of the catalysts tested for the CTD conversion in this chapter, $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$ -TPA demonstrated the highest performance at 280°C . Its superior DME productivity highlights the importance of minimising residual sodium and optimising the metal to acid ratio in the bifunctional catalyst. These findings suggest that careful control of the synthesis conditions is critical for achieving efficient and selective CTD conversion.

To better understand the impact of sodium on the CTD performance, future work should include testing the base-treated zeolites for their MTD conversion. Additionally, to clarify why the 1:1 core-shell catalyst shows the best performance, further investigations are needed. Specifically, NH_3 -TPD measurements would help assess changes in the acidity of the ZSM-5 component and how these variations relate to the different core-shell ratios and overall catalyst performance. Moreover, evaluating the exposed Cu^0 surface areas through N_2O titration could provide valuable insights into the active metal dispersion and its influence on the CTD performance.

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4

Synthesis, characterisation and catalytic testing of zirconium incorporated, LDH-based catalysts for CO₂ conversion

4.1: Introduction

4.1.1: Overview

This chapter is a continuation of previous efforts in this thesis to optimise a ZSM5@Cu_{1.3}ZnAl core-shell catalyst for the direct conversion of CO₂-to-DME (CTD). The previous chapter examined the effects of sodium incorporation and variations in the ZSM-5:CZA ratios. CO₂ hydrogenation tests revealed that the 1:1 ZSM5@Cu_{1.3}ZnAl core-shell catalyst, synthesised using a sodium-free coprecipitation method, exhibited the highest DME productivity. These results highlight the importance of compositional and structural control to maximise the CTD catalyst performance.

This chapter explores the incorporation of Zr as a promoter in the $\text{Cu}_{1.3}\text{ZnAl}$ phase. Zr has been widely reported to improve CTM activity in CuZnZrAl (CZZA) catalysts due to its ability to increase metal dispersion, modify surface basicity and improving resistance to deactivation by water. The first part of the chapter focuses on the synthesis and characterisation of Zr-incorporated CuZnAl LDHs, with the aim of evaluating the suitability of the sodium-free coprecipitation method (used in Chapter 2 and 3) for preparing CZZA LDHs. A series of Zr-incorporated $\text{Cu}_{1.3}\text{ZnAl}$ -LDH precursors with varying Zr loadings were synthesised and tested for their performance in CO_2 hydrogenation. Based on these results, a $\text{ZSM5}@\text{Cu}_{1.3}\text{Zn}(\text{Al}_{0.25}\text{Zr}_{0.75})$ core-shell catalyst was prepared and tested for CTD conversion, with its performance compared against $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl}$.

4.1.2 Zirconium promoted CZA catalysts

Transforming CO_2 into value-added fuels and chemical feedstocks is essential for a circular economy. More recently, the direct conversion of CO_2 to dimethyl ether (DME), which combines CO_2 hydrogenation to methanol with the subsequent dehydration of methanol to DME, has emerged as a promising route. This approach not only drives CO_2 conversion by continuously removing the intermediate methanol, but also reduces capital expenditure, requiring only a single reactor as opposed to the traditional two-step process.

The first CO_2 to methanol (CTM) step is the most challenging due to the high thermodynamic stability of CO_2 and the presence of the competing reverse water gas shift (RWGS) side reaction.¹ To date, a variety of metal oxide catalysts have been explored for the CTM reaction, yet the $\text{Cu/ZnO/Al}_2\text{O}_3$ (CZA) type catalyst remains one of the most extensively studied and widely used heterogeneous catalysts for the conversion of CO_2

to methanol.²⁻⁹ Their popularity stems from several key advantages: they are composed of earth-abundant metals, they can be synthesized at industrial scale, and they typically exhibit high methanol productivity.¹⁰⁻¹²

Although several studies report promising performance, CZA catalysts typically suffer from limited long-term stability.^{6, 10, 13-16} The deactivation of solid catalysts, i.e. the gradual loss in catalytic activity and/or selectivity over prolonged periods, remains a critical challenge in industrial catalytic processes and can arise from a variety of mechanisms.¹⁷ In the case of CZA catalysts, sintering is widely recognised as the primary cause of deactivation. Sintering occurs by particle migration and coalescence, and Oswald ripening, where metal nanoparticles merge to form larger aggregates.¹⁸ As a result, the active surface area is significantly reduced, leading to a decline in catalytic activity. This effect is exacerbated in the presence of water produced *in-situ* during the CTM reaction, as well as from the competing RWGS reaction (see Chapter 1.4 for more details).¹⁹⁻²¹ In CZA catalysts, water accelerates deactivation through three pathways: promoting particle sintering, blocking active sites and re-oxidation. Excessive water accumulation on the surface has been reported to promote the sintering of Cu⁰ sites which disrupts the strong metal-support interactions (SMSI) beneficial for catalyst activity.^{15, 19-22} Additionally, the formation of surface hydroxyl groups can block active sites, while the reoxidation of Cu⁰ to the less active Cu²⁺ further contributes to the decline in overall catalytic performance.^{23, 24} Prašnikar *et al.* also observed aggregation of Al₂O₃ in a CZA catalyst in the presence of water.²²

The strong interaction with water is often attributed to the hydrophilic nature of the Al₂O₃ phase the CZA catalyst.^{19, 25, 26} Consequently, a substantial amount of research is focused on modifying and improving the performance of CZA catalysts, especially through the

incorporation of promoting metals or metal oxides. Among these, the incorporation of zirconium to form quaternary Cu/ZnO/ZrO₂/Al₂O₃ (CZZA) catalysts has shown promising results with enhanced methanol selectivity and thermal stabilities.^{19, 20, 27-29}

Experimentally, CZZA catalysts often outperform traditional CZA catalysts under CTM conditions.^{10, 19, 29, 30} Numerous studies have investigated the role of Zr (typically as ZrO₂) to understand its impact on the catalyst's physiochemical properties and its interaction with reactant and intermediate species.³¹⁻³⁸ Findings from these investigations indicate that Zr plays a multifaceted role and impacts several key aspects of the catalyst's structure, surface chemistry and reactivity. Based on extensive literature review, Li *et al.* described the introduction of ZrO₂ in CTM catalysts as one that alters: (i) CO₂ adsorption and activation; (ii) H₂ adsorption, dissociation and spillover; (iii) the stability of the active species; (iv) the reaction pathway and binding of key intermediates; (v) metal dispersion and surface area and (vi) defect concentrations.²⁰

ZrO₂ is known for its basic surface properties which are crucial for the adsorption and activation of CO₂.^{20, 29, 39, 40} For instance, Witoon *et al.* incorporated Zr into a CuO/ZnO catalyst which then showed improved reducibility, CO₂ adsorption strength and Cu dispersion.⁴¹ Xaba *et al.* also demonstrated that the ZrO₂ promoted CZA catalyst exhibited higher CO₂ adsorption capacity and higher reducibility (which correlated with a larger number of active sites).⁴² The high CO₂ adsorption strength combined with moderate H₂ adsorption of the CZZA catalyst minimised premature CO₂ desorption whilst simultaneously facilitating H₂ spillover from the Cu active sites to the neighbouring metal oxides.^{42, 43} It is often found that Zr enhances Cu dispersion by preventing the aggregation of CuO and ZnO.^{19, 40, 44-48} Thus ZrO₂ acts as both a promoter and support for CO₂ hydrogenation.

Efforts to improve the performance of CTD hybrid catalysts tend to involve optimisations of both the metallic and acid catalyst components. Thus, the nature of the metal-acid combination plays an important role in determining the activity, selectivity and stability of the overall catalyst. For effective CTD conversion, the design of a high-performance catalyst relies on the integration of active metals with suitable acid supports, ensuring that both CTM and methanol-to-DME (MTD) steps occur efficiently within a single reactor system.^{27, 49} Several studies have investigated the integration of CZZA (or CZZ) catalysts with ZSM-5 to develop bifunctional catalysts for direct CTD conversion.^{14, 27, 43, 50, 51} Compared to traditional CZA/ZSM-5 catalysts, CZZA-based systems demonstrate enhanced DME synthesis activity and long-term stability due to improved resistance to water-induced deactivation.^{14, 19}

In Chapter 2, a ZSM5@Cu_{1.3}ZnAl LDH-based core-shell catalyst demonstrated high CTD performance where the DME productivity was comparable to other CZA-containing hybrid catalysts in the literature. After several optimisation studies, ZSM5@Cu_{1.3}ZnAl, with a 1:1 CZA:ZSM-5 ratio, was found to be the most reliable catalyst that functioned well under industrially relevant CO₂ operating conditions. The high performance of the core-shell catalyst for CTD conversion was attributed to the high CTM activity of the Cu_{1.3}ZnAl shell and the advantageous interaction between the CZA and ZSM-5 phase. The Cu_{1.3}ZnAl-LDH precursor was developed in previous work by the O'Hare group and demonstrated good CTM capabilities.⁵² The work discussed in this chapter aims to optimise the CTM portion of a core-shell catalyst for the direct CTD reaction by incorporating Zr⁴⁺ into the Cu_{1.3}ZnAl LDH structure. The rationale is based on previous reports of enhanced catalytic performance in CZZA and CZZ CTM catalysts. Building on an already effective CZA catalyst (Cu_{1.3}ZnAl), this chapter explores the sequential

incorporation of Zr at increasing loadings to evaluate its impact on catalytic performance in the CTD reaction. Thus, the first section is concerned with the formation of Zr-incorporated LDHs by modifying the coprecipitation method to progressively substitute Al^{3+} with Zr^{4+} , thereby generating a series of $\text{Cu}_{1.3}\text{Zn}(\text{Al}_{1-x}\text{Zr}_x)$ materials with varying Zr content. The crystal structure, morphology and thermal stability of the CZZA-LDHs were examined to assess the impact of Zr incorporation on the physiochemical properties of the catalyst precursors. Following this, the activated CZZA catalysts were tested for their CTM activity under the same operating conditions as those used in Chapter 3, enabling a direct comparison with the $\text{Cu}_{1.3}\text{ZnAl}$ catalyst to identify the optimal Zr loading that enhances methanol productivity.

In the second part of this chapter, the top-performing CZZA catalyst from the CTM tests was used to construct a hybrid CZZA/ZSM-5 core-shell catalyst. This design integrates the methanol synthesis function (shell), with a solid acid function (core), enabling the one-step conversion of CO_2 to DME. The core-shell catalyst strategy is one that directs the growth of the LDH precursor around the support, leading to a homogeneous dispersion of M^{2+} and M^{3+} cations in the activated catalyst that uniformly coats the core material.^{53, 54} The growth of the LDH on a support also prevents the aggregation of the LDH platelets.⁵² This is often observed for non-supported LDHs on account of their high surface charges leading to excessive agglomeration of the LDH sheets and to the formation of dense, stone-like particles with poor surface area.^{52, 55-57} Thus, the core-shell strategy was used to create a bifunctional catalyst with an active acidic core for the direct synthesis of DME from CO_2 . The Zr-incorporated core-shell precursor catalyst was characterised to evaluate the impacts of Zr incorporation on the physiochemical properties of the core-shell compared to $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDH}$. The precursor was

then activated and tested for direct CTD conversion to assess how Zr affects the overall activity and selectivity relative to the ZSM5@Cu_{1.3}ZnAl benchmark.

4.2: CZA-Zr_x catalysts for CO₂ hydrogenation to methanol

4.2.1: Preparation of the CZA-Zr_x catalyst precursors and catalysts

A series of Zr-incorporated Cu_{1.3}ZnAl LDHs were synthesised following a modified coprecipitation method. The sodium-free coprecipitation described in Chapter 2.2.1 was used in which a solution containing Cu²⁺, Zn²⁺, Al³⁺ and Zr⁴⁺ nitrate salts were slowly added to a solution of water, kept at pH 10 by the controlled addition of tetrapropylammonium hydroxide (TPAOH). A 1.3:1:(1−*x*):*x* Cu:Zn:Al:Zr ratio was used where *x* = 0.25, 0.5 and 0.75. This yielded blue powders which are referred to using the CZA-Zr_{*x*} naming convention, where *x* represents the Zr content. For instance, a sample with *x* = 0.25 is labelled as CZA-Zr_{0.25}. The Cu:Zn:Al:Zr ratios were confirmed by ICP-OES elemental analysis and are summarised in Table C.1. For full synthesis conditions consult Chapter 6.4.2.

4.2.3: Characterisation of the CZA-Zr_x catalyst precursors

High-resolution PXRD was carried out at the I11 Diamond Light Source Synchrotron facility to determine the structure of the synthesised CZA-Zr_{*x*} materials. Single-phase Pawley refinements of the PXRD data, performed using the TOPAS software, identified a hydrotalcite-like (htl) phase in all Zr-incorporated samples, as evidenced by the characteristic Bragg reflections in Figure 4.1.^{58, 59} Maxima occurring at $2\theta = \sim 6.2^\circ$ and 12.5° are associated with the (003) and (006) basal plane Bragg reflections that are

typically seen in the PXRD profiles of LDHs.^{60, 61} The Bragg peaks at $2\theta = \sim 17.9^\circ$, $\sim 31.1^\circ$ and $\sim 32.0^\circ$ are attributed to the (101), (110), and (113) reflections respectively. While these features confirm the presence of an LDH material, an increase in Zr content leads to a notable decrease in peak intensity and significant broadening, indicating a progressive loss of crystallinity and increased amorphous character at higher Zr loadings.

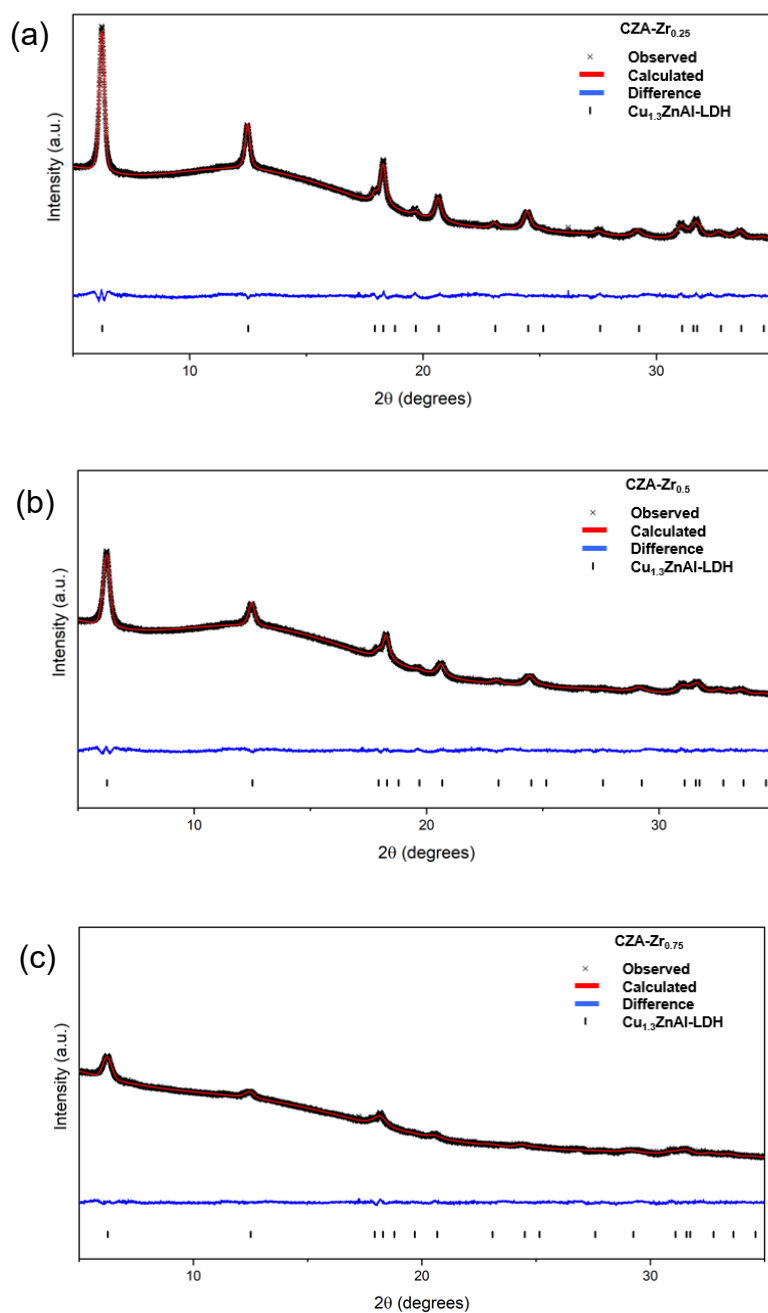


Figure 4.1: Pawley refinement of (a) $\text{Cu}_{1.3}\text{Zn}(\text{Al}_{0.75}\text{Zr}_{0.25})\text{-LDH}$, (b) $\text{Cu}_{1.3}\text{Zn}(\text{Al}_{0.5}\text{Zr}_{0.5})\text{-LDH}$ and (c) $\text{Cu}_{1.3}\text{Zn}(\text{Al}_{0.25}\text{Zr}_{0.75})\text{-LDH}$ against $\text{Cu}_{1.3}\text{ZnAl-LDH}$. PXRD data was collected at I11 Diamond Light Source.

Although Zr^{4+} has a larger ionic radius (0.720 Å) than Al^{3+} (0.534 Å), its higher charge may cause interlayer compression due to stronger electrostatic forces of attraction between the positively charged layers and interlayer anions. Hence, the substitution of Zr^{4+} for Al^{3+} within the metal hydroxide interlayer is unlikely to cause major changes to the interlayer spacing. If Zr^{4+} was incorporated into the metal hydroxide layers, an increase in the d_{110} spacing (which describes the metal-metal distances within the metal hydroxide layer) would be expected due to the larger ionic radius of Zr^{4+} .

Based on the refined a - and c -lattice parameters (Table C.2), the corresponding d_{003} and d_{110} interplanar spacings for the CZA- Zr_x samples are summarised in Table 4.1. The CZA- Zr_x samples exhibited similar d_{003} spacings of ~ 7.61 Å, which corresponds to those reported for carbonate-intercalated LDHs.^{60, 62} Differences in the d_{003} spacings between the htl samples is more complicated to interpret due to a combination of factors, e.g. changes in orientation of the anions or variations in the amount of water in the interlayers. The linear relationship between the a -lattice parameter and Zr content is in good agreement with Vegard's law—where the lattice constant of an alloy varies linearly with its composition—suggesting that the isomorphic substitution of Zr^{4+} with Al^{3+} in the LDH was successful (Figure 4.2).^{63, 64}

The extent of the substitution is unclear. Broadening in the PXRD Bragg peaks suggests reduced crystallinity which could be due to the random incorporation of Zr^{4+} causing local structural distortions. The distortions may have introduced lattice strain and disrupt long-range order, resulting in a more amorphous diffraction pattern. It is also possible that a secondary amorphous phase may have been synthesised during the coprecipitation.

Table 4.1: d-spacing of CZA-Zr_x samples calculated from simple Pawley refinements of PXRD data collected at I11 Diamond Light Source.

Sample	d_{003} (Å)	d_{110} (Å)	D_{003}^a (nm)	D_{110}^a (nm)	Crystalline
					anisotropy (D_{110}/D_{003})
Cu _{1.3} ZnAl-LDH	7.569	1.534	24.6	9.3	0.4
CZA-Zr _{0.25}	7.611	1.542	16.3	9.3	0.6
CZA-Zr _{0.5}	7.622	1.545	12.1	8.7	0.7
CZA-Zr _{0.75}	7.613	1.547	9.4	6.7	0.7

^aK = 0.9 in Scherrer's equation.

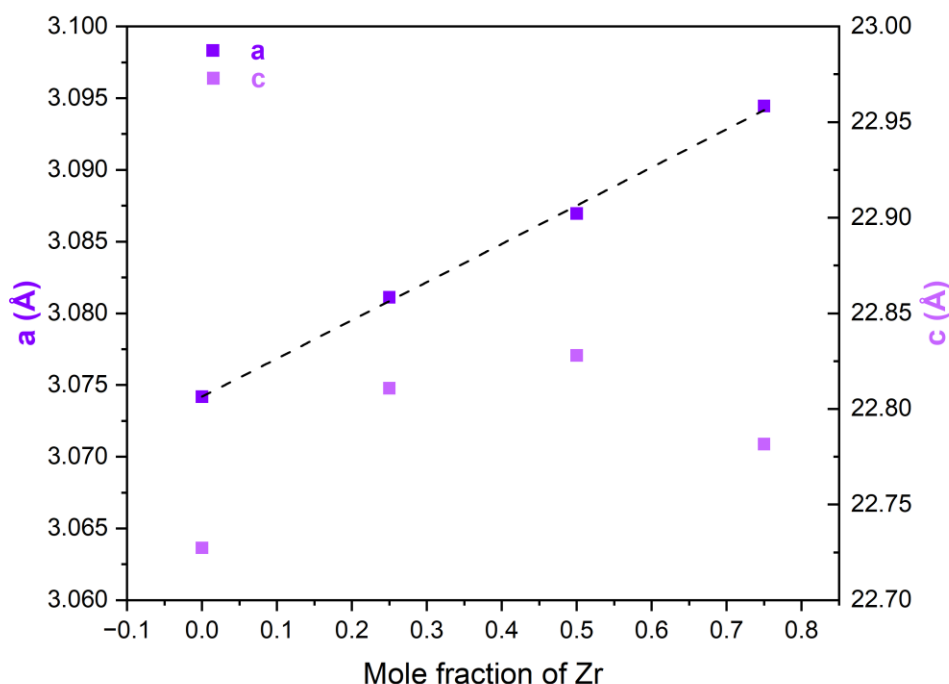


Figure 4.2: Values for the a - and c -lattice parameters, calculated from simple Pawley refinements of PXRD data collected at I11 Diamond Light Source, with various mole fractions of Zr. The dotted line indicates the linear correlation between a and increasing Zr content.

The Scherrer equation was used to estimate the crystallite domain lengths of the LDH phase in the CZA-Zr_{0.25} samples (full Scherrer parameters are summarised in Table C.3). The increasingly broad Bragg reflections of the htl phase in the samples (with Zr content) indicates a disruption of the LDH structure which is reflected in the decreasing crystallite domain lengths. If Al³⁺ was partially removed and not fully replaced by Zr⁴⁺, the htl compound formed in the coprecipitation would be unstable. The lower Al³⁺ content may have led to the collapse of the LDH structure. PXRD patterns taken on a Bruker D8 ECO diffractometer show that peaks in the Zr-loaded samples have a “shark’s fin” shape which is commonly associated with turbostratic structures (see Figure C.1). Turbostraticity refers to a form of structural disorder where the LDH layers are randomly shifted relative to each other, leading to a loss of long-range stacking order.⁶⁵⁻⁶⁷ Consequently, the lateral growth of the LDH in the (003) plane is minimised.

A separate amorphous zirconium species is likely to have also formed during the coprecipitation alongside the CZA LDH. Zirconium oxide is a white, poorly soluble compound, that typically precipitates from zirconium nitrate salts under alkaline conditions, making it a likely secondary phase, although zirconium hydroxide can also be produced by precipitation.⁶⁸⁻⁷¹ If either zirconium hydroxide or zirconium oxide were formed during the coprecipitation, a mixture of compounds would be expected following filtration, potentially resulting in a paler coloured sample (non Zr-incorporated $\text{Cu}_{1.3}\text{ZnAl-LDH}$ is blue in colour). However, as shown in Figure C.2, increasing Zr content leads to progressively deeper blue samples. In the $\text{Cu}_{1.3}\text{ZnAl-LDH}$, the blue colour is associated with Cu^{2+} ions. The colour change suggests that increasing Zr content may have led to changes in the local coordination environment of Cu^{2+} , either from structural disorder or the formation of amorphous Cu-Zr mixed hydroxide/oxide domains, affecting its optical properties and contributing to the deeper blue colour. UV-Vis spectroscopy or X-ray photoelectron spectroscopy (XPS) should be used to identify changes to the local environment of Cu^{2+} within the sample. In addition, variable temperature PXRD analysis should be conducted to monitor the structural evolution of the CZA- Zr_x samples upon heating. This may reveal the crystallisation of the amorphous Zr-containing phases which would be indicated by the emergence of new diffraction peaks in the spectrum. Additionally, a PXRD study on a series of CZA-LDHs with decreasing Al content should be conducted to investigate how the crystal structure and crystallite size changes. These results could provide a reference for identifying the extent of Zr^{4+} substitution in $\text{Cu}_{1.3}\text{Zn}(\text{Al}_{1-x}\text{Zr}_x)$.

Ultimately, PXRD of the CZA-Zr_x samples indicate that a combination of a CZZA htl phase and zirconium-containing amorphous phase is formed following coprecipitation, where, CZA-Zr_{0.25} with the lowest Zr content shows the highest degree of crystallinity.

STEM/EDX analysis was used to investigate how the structure and morphology of the CZA-Zr_x samples changed with increasing Zr content. As shown in Figure 4.3 the micrographs are consistent with the PXRD analysis. With higher Zr loadings, the characteristic LDH platelet morphology becomes progressively less distinct, and the sample exhibits a more amorphous appearance, lacking well-defined structural features. Whilst some platelet-like structures remain in the CZA-Zr_{0.5} sample, they are largely absent in CZA-Zr_{0.75}, which supports the increasingly amorphous characteristics demonstrated in the PXRD patterns.

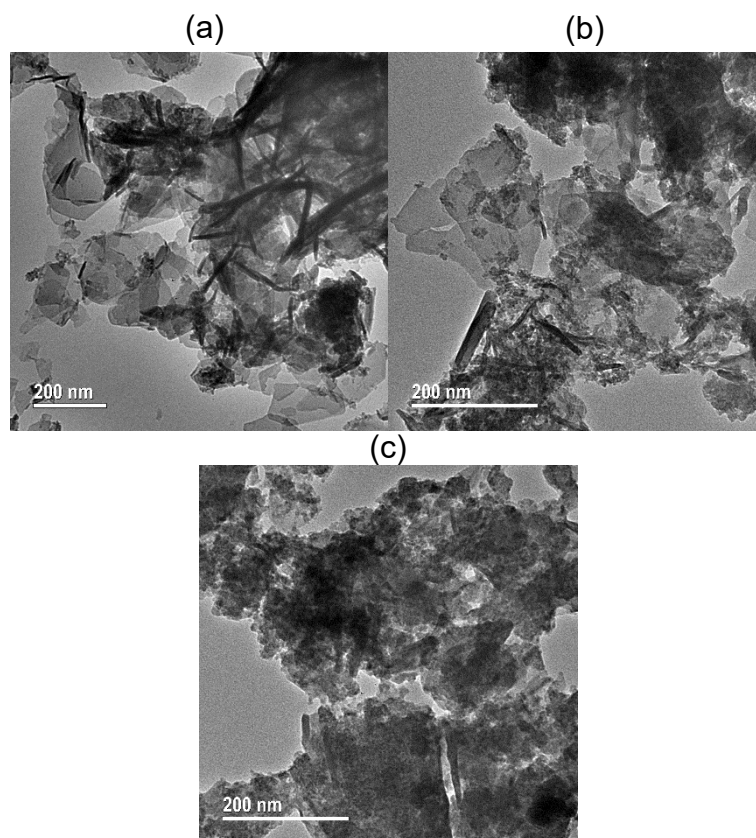


Figure 4.3: TEM images of (a) CZA-Zr_{0.25}, (b) CZA-Zr_{0.5} and (c) CZA-Zr_{0.75} catalyst precursors.

EDX mapping in Figure 4.4 confirms the presence of Cu (blue), Zn (orange), Al (green) and Zr (red) in all samples. Cu, Zn and Al are uniformly distributed across the particles irrespective of the Zr loading. However, in CZA-Zr_{0.25}, Zr is unevenly distributed, forming localised clusters or “pools”. In contrast, Zr is more evenly dispersed in CZA-Zr_{0.5} and CZA-Zr_{0.75}, suggesting that the amorphous zirconium species has greater integration with the htl phase at higher Zr loadings.

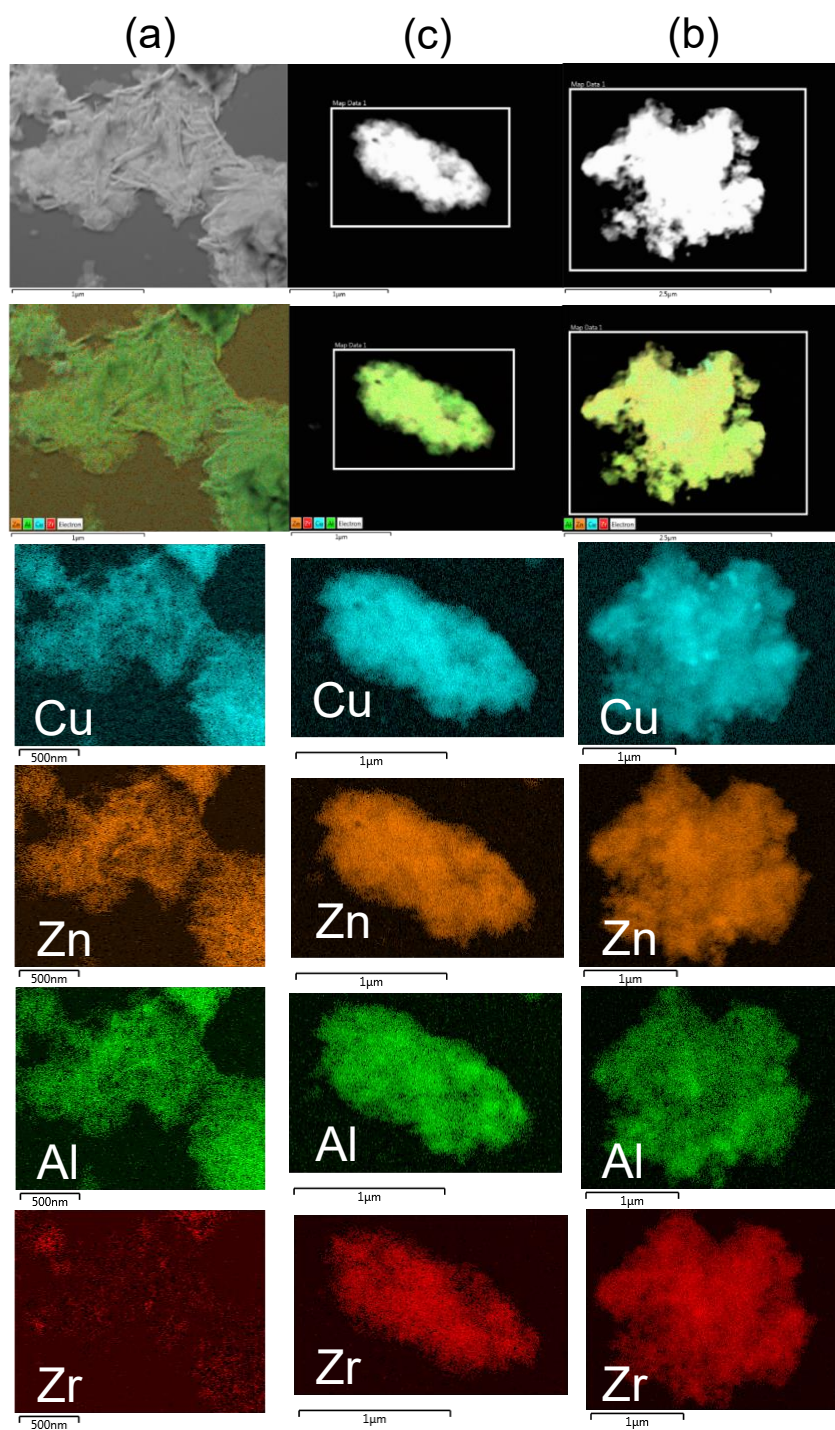


Figure 4.4: STEM/EDX analysis of (a) CZA-Zr_{0.25}, (b) CZA-Zr_{0.5} and (c) CZA-Zr_{0.75} catalyst precursors showing the distribution of on Cu (blue), Zn (orange), Al (green) and Zr (red).

TEM images of the $\text{Cu}_{1.3}\text{Zn}(\text{Al}_{1-x}\text{Zr}_x)\text{-LDHs}$ reveal a clear loss of the characteristic LDH platelet morphology with increasing Zr loading, reflecting the transition toward a more amorphous material.

As TEM provides a 2D projection of the sample, it is difficult to ascertain from these images if the Zr species exists as distinct, separate phase. To gain a clearer understanding of the spatial distribution and localisation of the Zr species, SEM imaging combined with EDX mapping is recommended.

FTIR analysis was conducted on the CZA- Zr_x samples and compared against $\text{Cu}_{1.3}\text{ZnAl-LDH}$ (Figure 4.5). The FTIR profiles for the CZA- Zr_x samples have peaks in regions that overlap with the peaks in the pure $\text{Cu}_{1.3}\text{ZnAl-LDH}$ reflecting the presence of the LDH in the sample. For instance, the broad adsorption bands observed between $3700 - 2700 \text{ cm}^{-1}$ is attributed to the O-H stretching frequency of hydroxyl groups.⁶⁰ Meanwhile, the sharp peaks at 1630 cm^{-1} and 1360 cm^{-1} typically correspond to the bending vibrations of interlayer water molecules and the asymmetric stretching (ν_3) mode of carbonate anions within the interlayer gallery of the LDHs.^{72, 73}

Differences in the FTIR profiles of the CZA- Zr_x samples were observed with increasing Zr content. Notably, the bands around 780 cm^{-1} , typically associated with lattice vibrations in the metal oxide/metal hydroxide layers ($\text{M}^{x+}\text{-O}$, $\text{M}^{x+}\text{-OH}$ and $\text{O-M}^{x+}\text{-O}$), became less broad as the Zr loading increased.⁷⁴ The narrowing of this region suggests a reduction in these bonding environments due to the structural distortions of the LDH, particularly in the CZA- $\text{Zr}_{0.75}$ sample.

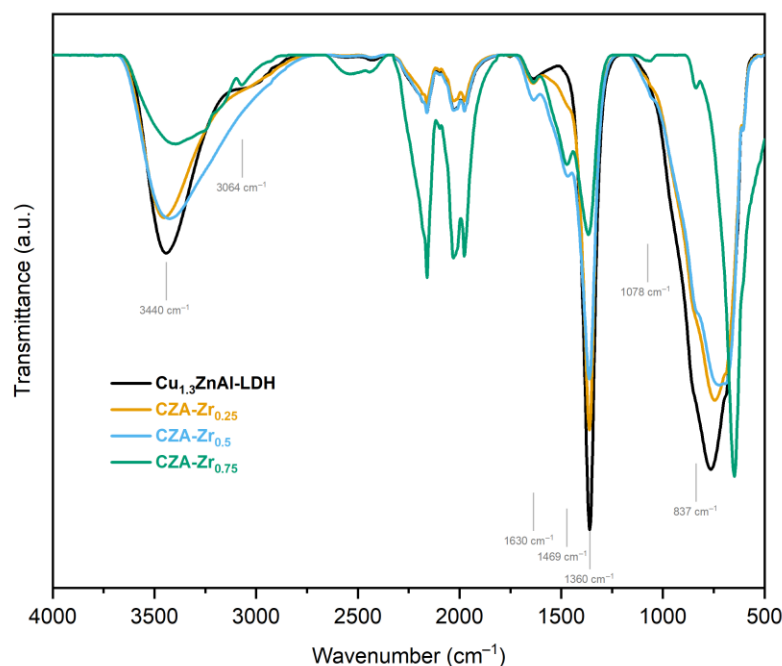


Figure 4.5: FTIR profiles of the CZA-Zr_x samples compared against Cu_{1.3}ZnAl-LDH.

Regarding the identity of the Zr-containing phase, the formation of zirconium carbonate during coprecipitation is a strong possibility. In the literature, zirconium carbonate exhibits bands at 3320 cm^{-1} and 1640 cm^{-1} , corresponding to the asymmetric stretching and bending vibrations of hydroxyl groups.⁷⁵ As Zr content increases in the CZA-Zr_x samples, a shoulder emerges at 1470 cm^{-1} adjacent to the peak at 1360 cm^{-1} . This feature may correspond to the asymmetric stretching vibration of carbonate anions, which is typically observed around 1530 cm^{-1} , but may be shifted due to variations in the environment and coordination of CO_3^{2-} .⁷⁵⁻⁷⁷ Additionally, peaks at 1078 cm^{-1} and 837 cm^{-1} are present in all samples but most clearly in the highest Zr loaded, CZA-Zr_{0.75} sample.^{75, 76} These peaks are attributed to the symmetric stretching mode and out of plane bending vibrations of CO_3^{2-} .^{75, 76}

The FTIR analysis suggests that, although htl features are present in the Zr-containing samples, the integrity of the metal hydroxide lattice becomes increasingly disrupted with

higher Zr content. This is consistent with previous characterisation in this chapter which demonstrated increased amorphous character in the CZA-Zr_x series. The FTIR profiles also suggest the formation of a zirconium carbonate phase during coprecipitation. Supporting this, Pathan *et al.* reported that higher pH favoured the formation of zirconium carbonate species over its hydroxide during precipitation.⁷⁷ Furthermore, zirconium carbonate is amorphous which may account for the broad diffraction patterns observed in the PXRD profiles of the CZA-Zr_x samples.⁷⁵⁻⁷⁷

The thermal degradation behaviour of the Zr-incorporated LDHs was studied with TGA. The TGA/dTGA curves are shown in Figure 4.6 with the major weight loss regions (WLRs) and residual weights summarised in Table 4.2.

The CZA-Zr_x samples show three major weight loss regions (WLRs). The first region between 30 – 200 °C, is associated with the loss of surface-adsorbed water and water of crystallisation.⁷⁷⁻⁷⁹ The second region, between 200 – 400 °C, is attributed to dehydroxylation and partial decomposition of the carbonate anions.^{77, 79, 80} The final region, observed above 500 °C, is associated with full decarbonation following the removal of strongly held carbonate anions.^{60, 61, 77, 78, 81-83} These weight loss events apply to both the CZZA LDH phase and the zirconium carbonate phase. At temperatures greater than 400 °C, LDHs undergo structural collapse and transform into their corresponding layered double oxide (LDO).^{61, 82, 84, 85} LDOs are highly dispersed metal oxides and often exhibit enhanced surface areas, thermal stabilities and catalytic activities.⁸⁶⁻⁹⁰

In the first WLR, the Zr-incorporated samples exhibit a weight loss of ~18%, consistent with that observed for the non-modified Cu_{1.3}ZnAl-LDH. The dTGA profile of CZA-Zr_{0.25} more closely resembles that of Cu_{1.3}ZnAl-LDH, with the highest rate of weight loss

(in the first WLR) occurring at ~ 140 °C. A smaller peak is also observed at ~ 50 °C, corresponding to the loss of weakly adsorbed surface water.^{78, 79} This two-peak pattern is similarly present in the dTGA profiles of CZA-Zr_{0.5} and CZA-Zr_{0.75}; however, in these samples, the second peak shifts to lower temperatures with increasing Zr content.^{78, 79} This shift may indicate a weakening of the hydrogen bonding network within the CZZA LDH phase, facilitating easier desorption of interlayer water. PXRD analysis indicated a reduction in crystallite domain lengths and increasing structural disorder with high Zr loadings. These changes likely disrupted the electrostatic and hydrogen bonding network between the metal hydroxide layers and the interlayer water, resulting in the reduced thermal stability in the first WLR.

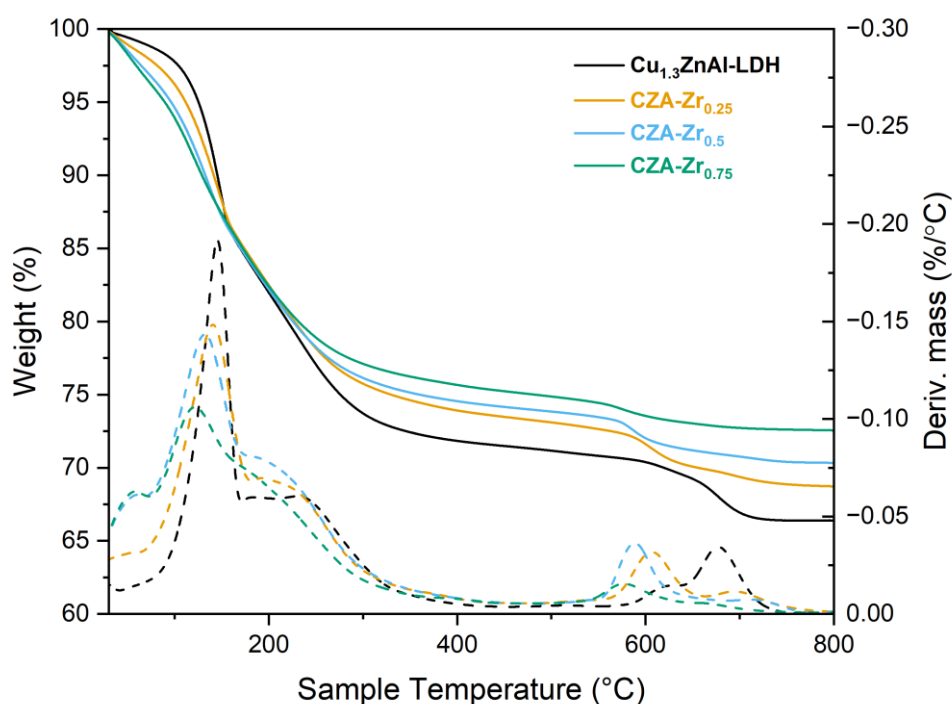


Figure 4.6: TGA and dTGA curves of the CZA-Zr_x samples compared against Cu_{1.3}ZnAl-LDH.

The rate of decomposition in the second WLR, associated with dehydroxylation and partial decarbonation of the LDH structure, is comparable across all CZA-Zr_x samples

and the $\text{Cu}_{1.3}\text{ZnAl-LDH}$ reference. However, the percentage of weight loss in this region decreases along the CZA-Zr_x series, indicating a reduction in the number of hydroxyl groups. This observation is consistent with the diminished htl phase with increasing Zr content. In particular, the $\text{CZA-Zr}_{0.75}$ exhibits the smallest weight loss (6.6%), which likely reflects the weakest interlayer interactions in the CZZA LDH phase among the Zr-incorporated samples.

The dTGA profiles in the final WLR (500 – 800 °C) varies considerably between the samples. For the CZZA LDH phase, thermal decomposition in this region is associated with the full decarbonation of $\text{M}^{2+}\text{M}^{3+}\text{O}_y(\text{CO}_3)_2$ oxycarbonates.^{91, 92} In $\text{Cu}_{1.3}\text{ZnAl-LDH}$, two peaks are observed, corresponding to the decomposition of metal oxycarbonate species with different thermal stabilities. Similar features appear in the Zr-incorporated samples, indicating that similar metal oxycarbonates are present. Upon Zr incorporation, the first peak shifts to lower temperatures (570 – 600 °C) and becomes more prominent, reflecting the reduced thermal stability of the htl phase with increasing Zr loading. Despite comparable carbonate contents across the samples (based on CHN elemental analysis, Table C.1), the CZA-Zr_x samples have higher residual weights at 800 °C, suggesting that some carbonate species are more strongly retained. This points to the presence of the second, more thermally stable, zirconium carbonate species.

Table 4.2: Summary of data from TGA including the weight loss percentages for the major weight loss regions (WLRs) and the residual weights of the Zr incorporated LDHs and Cu_{1.3}ZnAl-LDH.

Sample	Weight loss (%)			Residual weight (%)
	30 – 200 °C	200 – 400 °C	500 – 800 °C	
Cu _{1.3} ZnAl-LDH	18.2	10.1	4.8	66.4
CZA-Zr _{0.25}	17.7	8.4	4.4	68.7
CZA-Zr _{0.5}	17.9	7.6	3.5	70.3
CZA-Zr _{0.75}	17.7	6.6	2.4	72.7

TGA results further corroborate structural changes in the LDH with increasing Zr incorporation. While some htl features are maintained in CZA-Zr_{0.5} and CZA-Zr_{0.75}, the reduction in dehydroxylation and decarbonation, persistence of carbonate at high temperatures, and higher residual masses indicates the presence of a distinct zirconium carbonate phase as well as a CZZA LDH.

Based on the characterisation of the CZA-Zr_x samples, the incorporation of Zr in the coprecipitation method led to the formation of a mixed CZZA-LDH/zirconium carbonate precursor catalyst material. The Zr-incorporated samples were evaluated for their CO₂ hydrogenation performance.

4.2.4: CO₂ hydrogenation performance of CZA-Zr_x catalysts

The Zr-containing samples were activated and tested for their performance in the CTM reaction. The CZA-Zr_x precursor samples were *ex-situ* calcined in O₂ (based on the results from the optimisation study discussed in Chapter 2.4.1), loaded into a pressurised fixed-bed reactor (3 MPa) and reduced *in-situ* under H₂ to form the active CTM catalysts. The catalysts are described with the “C” suffix, for example when $x = 0.25$, the catalyst is described as CZA-Zr_{0.25}-C. For full details consult Chapter 6.4.4. Approximately 0.1 g of catalyst was reacted under CO₂:H₂:N₂ (24:72:4) flow with a weight hourly space velocity (WHSV) of 18,000 mL/g_{cat}·h. Temperatures between 260 – 340 °C were studied. The outlet gas composition was analysed by GC. For full details of the testing method see Chapter 6.5.

The results for the CO₂ hydrogenation over Zr-incorporated CZA-Zr_x-C catalysts are summarised in Figure 4.7 and Table 4.3. All three CZA-Zr_x-C catalysts produced a mixture of methanol and CO, with the highest methanol space time yields occurring at 260 °C, reflecting the CO₂ hydrogenation results for the Cu_{1.3}ZnAl catalyst (see Figure 4.8). For all Zr-incorporated catalysts, selectivity to methanol ($S_{\text{CH}_3\text{OH}}$) decreases whilst selectivity to CO (S_{CO}) increases with temperature. The increased production of CO at higher temperatures is expected due to the thermodynamics associated with the CTM reaction and the competing RWGS reaction.⁹³ Whilst the conversion of CO₂ to methanol is exothermic, the RWGS reaction is endothermic, hence CO formation becomes increasingly favoured at higher temperatures.^{93, 94}

Among the CZA-Zr_x-C catalysts, CZA-Zr_{0.75}-C exhibited the highest methanol space time yield ($STY_{\text{CH}_3\text{OH}}$) at 0.33 g_{CH₃OH}/g_{cat}·h which considerably outperforms the

$\text{Cu}_{1.3}\text{ZnAl}$ catalyst ($0.28 \text{ g}_{\text{CH}_3\text{OH}}/\text{g}_{\text{cat}}\cdot\text{h}$). Based on the CO_2 hydrogenation results in Chapter 3.3.1, $\text{CZA-Zr}_{0.75}\text{-C}$ has comparable performance to the Na_2CO_3 -treated $\text{Cu}_{1.3}\text{ZnAl}$ CTM catalyst ($0.33 \text{ g}_{\text{CH}_3\text{OH}}/\text{g}_{\text{cat}}\cdot\text{h}$). In light of this, it would be beneficial to synthesise a series of CZA-Zr_x using the standard coprecipitation method (an example of the standard coprecipitation method can be found in Chapter 6.3.6) to evaluate their performance as catalysts for CTM conversion. This approach offers more control over carbonate content during the synthesis, potentially promoting the formation of a well-defined htl phase, which could affect the catalyst performance following activation.

Published studies have reported that Zr incorporation influences the selectivity of CTM catalysts towards methanol.⁴⁰ At 260°C , the $S_{\text{CH}_3\text{OH}}$ value for $\text{CZA-Zr}_{0.25}\text{-C}$ (38.7%) is lower than in the non-Zr incorporated $\text{Cu}_{1.3}\text{ZnAl}$ catalyst (40.8%). For the $\text{CZA-Zr}_x\text{-C}$ catalysts where $x = 0.5$ and 0.75 , $S_{\text{CH}_3\text{OH}}$ is comparable to $\text{Cu}_{1.3}\text{ZnAl}$ (40.3%). The increase in $STY_{\text{CH}_3\text{OH}}$ for the higher Zr-loaded catalysts is due to their enhanced CO_2 conversion, where X_{CO_2} is highest for $\text{CZA-Zr}_{0.5}\text{-C}$ (14.2%).

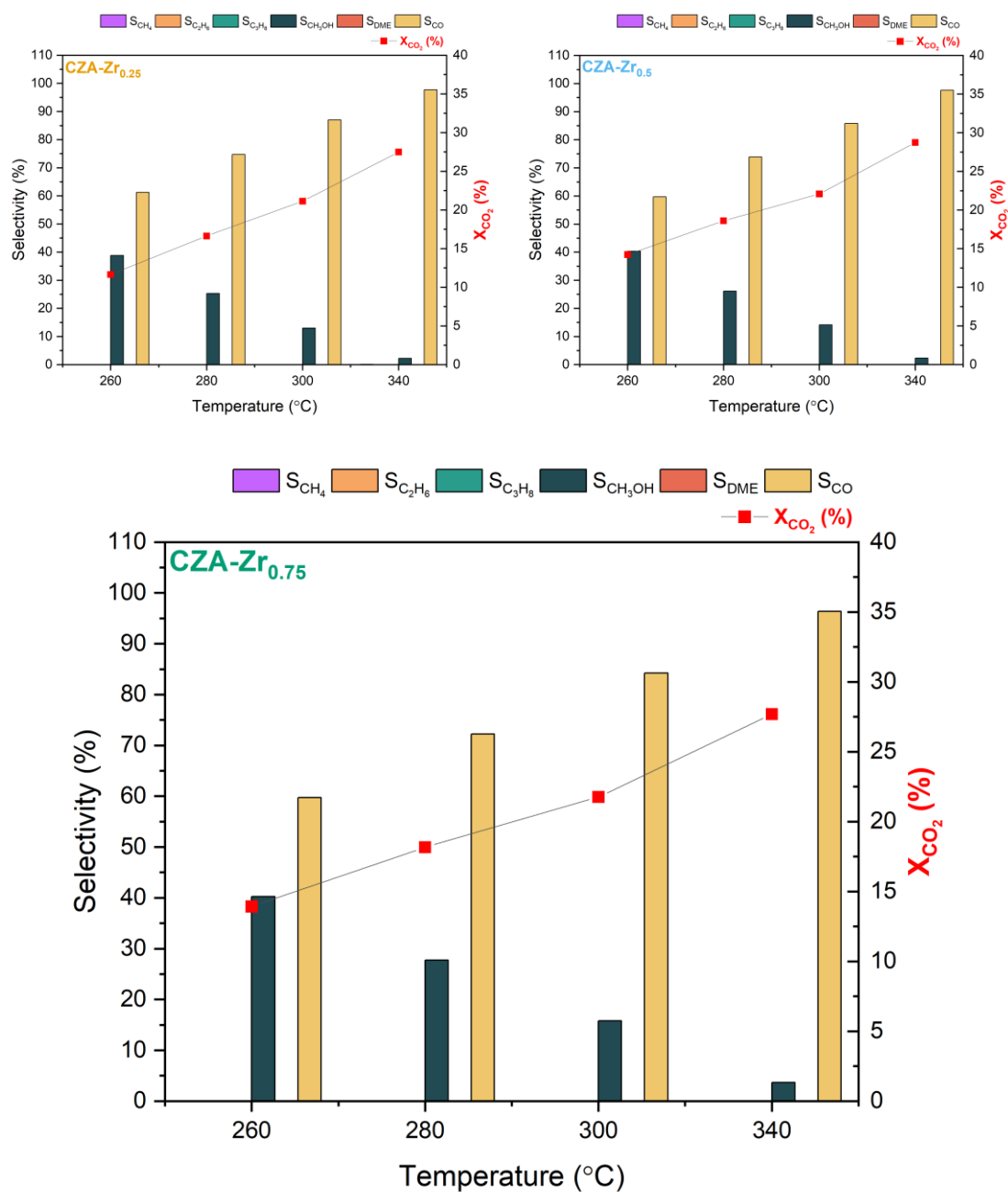


Figure 4.7: Product distribution of CO₂ hydrogenation reaction over (a) CZA-Zr_{0.25}-C (b) CZA-Zr_{0.5}-C and (c) CZA-Zr_{0.75}-C catalysts as a function of temperature (260 – 340 °C); Reaction conditions: $P = 3.0$ MPa; CO₂:H₂:N₂ = 24:72:4; $WHSV = 18,000$ mL/g_{cat}·h, carbon balance 98.60% – 100.62%.

Table 4.3: CO₂ hydrogenation results for CZA-Zr_{0.25}-C, CZA-Zr_{0.5}-C and CZA-Zr_{0.75}-C.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity		Yield	STY_{CH_3OH} (g _{CH₃OH} /g _{cat} ·h)
			(%)		(%)	
			S_{CH_3OH}	S_{CO}	Y_{CH_3OH}	
CZA-Zr _{0.25} -C	260	11.7	38.8	61.2	4.5	0.23
	280	16.6	25.3	74.7	4.2	0.24
	300	21.1	13.0	87.0	2.7	0.16
	340	27.5	2.2	97.7	0.6	0.03
CZA-Zr _{0.5} -C	260	14.2	40.3	59.7	5.7	0.33
	280	18.6	26.1	73.9	4.9	0.28
	300	22.1	14.2	85.8	3.1	0.18
	340	28.7	2.3	97.6	0.7	0.04
CZA-Zr _{0.75} -C	260	13.9	40.3	59.7	5.6	0.32
	280	18.2	27.8	72.2	5.0	0.28
	300	21.8	15.8	84.2	3.4	0.19
	340	27.7	3.6	96.3	1.0	0.06

^aReaction conditions: $P = 3.0$ MPa, CO₂/H₂/N₂ = 24:72:4, and $WHSV = 18,000$ mL/g_{cat}·h.

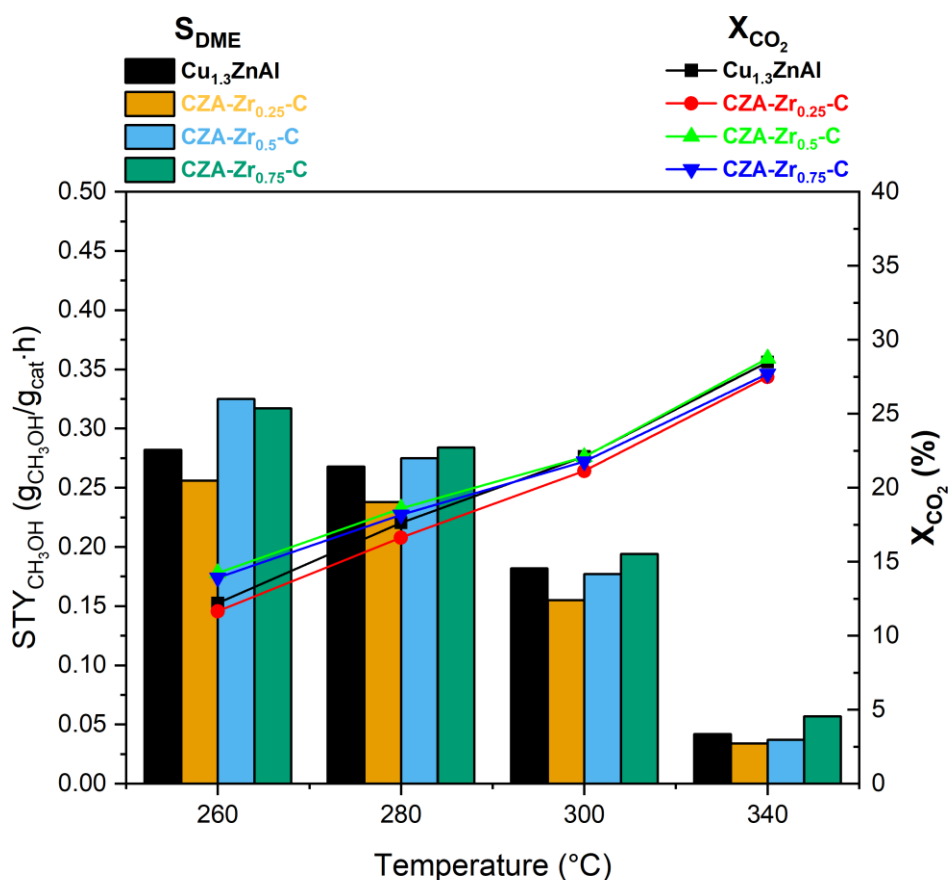


Figure 4.8: S_{CH_3OH} and CO_2 conversions for CZA-Zr_{0.25}-C, CZA-Zr_{0.5}-C and CZA-Zr_{0.75}-C catalysts.

Reaction conditions: $P = 3.0$ MPa; $CO_2:H_2:N_2 = 24:72:4$; $WHSV = 18,000$ mL/g_{cat}·h, carbon balance 98.6% – 100.62%.

Based on the CO_2 conversion results, CZA-Zr_{0.25}-C demonstrates the poorest performance as a consequence of its lower methanol selectivity and CO_2 conversion. In contrast, CZA-Zr_{0.5}-C and CZA-Zr_{0.75}-C exhibited greater methanol productivities than the non-zirconium Cu_{1.3}ZnAl catalyst at all temperature points. The highest methanol productivities were achieved at 260 °C for CZA-Zr_{0.5}-C (0.33 g_{CH₃OH}/g_{cat}·h) and CZA-Zr_{0.75}-C (0.32 g_{CH₃OH}/g_{cat}·h), both surpassing the performance of the un-modified Cu_{1.3}ZnAl catalyst and considerably outperformed a commercial COM catalyst

(0.15 g_{CH₃OH}/g_{cat}·h).⁴⁵ This enhancement is primarily attributed to improved CO₂ conversion rather than increased selectivity towards methanol. The higher CO₂ conversion in these catalysts may indicate that the active copper sites are more accessible, however detailed characterisation of the catalyst materials is required to confirm this. N₂O titration should be conducted to quantify the exposed Cu surface area and investigate how this is affected by the increased Zr loading. HR-TEM can be used to investigate the relative locations between the Cu, Zn and Zr species, providing insight into the structural features that may influence catalytic performance. Additionally, techniques such as X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) can provide information on the oxidation states of Cu, while also probing metal-support interactions. As Zr is known to affect the basicity of CTM catalysts, CO₂-TPD in combination with pyrrole FTIR adsorption studies should be conducted to investigate both the strength and quantity of basic sites. Finally, BET analysis should be carried out to determine if changes in the textural properties contribute to the observed activity trends.

4.3 Core-shell ZSM5@CZA-Zr_{0.75}-C catalysts for direct CO₂ to DME conversion

Given the improved CTM performance observed at higher Zr loadings, the CZA-Zr_{0.75} precursor material was integrated into the core-shell catalyst design by synthesising CZA-Zr_{0.75} in the presence of ZSM-5. This approach aims to improve the overall efficacy of the bifunctional catalyst for the direct CTD reaction. The following sections describe the

synthesis and characterisation of the ZSM5@CZA-Zr_{0.75} core-shell catalyst precursor, as well as the results from the preliminary CO₂ hydrogenation test.

4.3.1: Preparation of ZSM5@CZA-Zr_{0.75} core-shell catalyst precursor

The CZA-Zr_{0.75} catalyst precursor was grown in the presence of ZSM-5 zeolites following the coprecipitation method described in Chapter 6.4.3. A metal salt solution containing Cu²⁺, Zn²⁺, Al³⁺ and Zr⁴⁺ in the ratio 1.3:1:0.25:0.75 was added dropwise to a dispersion of ZSM-5 that was maintained at pH 10 by the addition of TPAOH. The resulting blue powder product is referred to as ZSM5@CZA-Zr_{0.75}. The Cu:Zn:Al:Zr ratios was confirmed by ICP-OES elemental analysis and is summarised in Table C.4.

4.3.2: Characterisation of ZSM5@CZA-Zr_{0.75} catalyst precursor

PXRD was used to analyse the structure of the core-shell. The diffraction patterns for ZSM5@CZA-Zr_{0.75} and CZA-Zr_{0.75} were collected on a Bruker D8 diffractometer and refined using the TOPAS software through a two-phase Pawley refinement (Figure C.3 and Figure C.4) to extract crystallographic details (summarised in Table C.5 and Table C.6).^{58, 59} As shown in Figure 4.9, Bragg reflections associated with the ZSM-5 core occur between $2\theta = 7 - 9^\circ$ and $22 - 25^\circ$, with no significant changes in its crystallinity based on the refined *a*-, *b*- and *c*-lattice parameters.^{59, 95} The broadened peaks at $2\theta = \sim 11.6^\circ$ and $\sim 23.4^\circ$, corresponding to the characteristic (003) and (006) basal plane Bragg reflections of the CZZA LDH, reflect the structural collapse observed in the non-supported CZA-Zr_{0.75} sample.^{60, 61} The presence of the amorphous zirconium carbonate phase may also be observed.

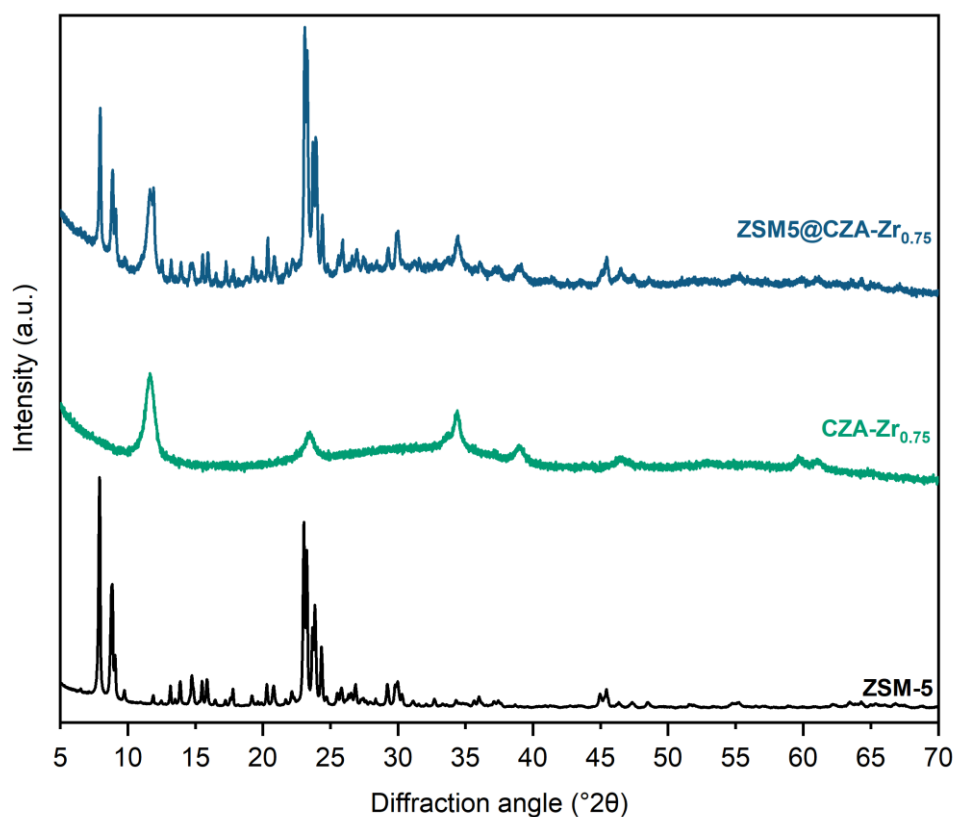


Figure 4.9: PXRD of ZSM5@CZA-Zr_{0.75}, CZA-Zr_{0.75} and ZSM-5. PXRD data was collected on a Bruker D8 ECO diffractometer.

The d-spacings and crystallite domain lengths of the CZZA htl phase in ZSM5@CZA-Zr_{0.75} is presented in Table 4.4 (for full structural parameters see Table C.7). The d_{110} and d_{003} interplanar spacings for both the core-shell and un-supported CZA-Zr_{0.75} sample match with the values refined from PXRD data collected at I11 Diamond Light Source (see Section 4.2.3 for more details). This suggests that coprecipitation of the CZA-Zr_{0.75} sample in the presence of the ZSM-5 core does not have an impact on the structure/crystallinity of the carbonate-intercalated CZA LDH phase.^{60, 62, 92}

Differences were mostly observed in the crystallite domain lengths. Here, the estimated D_{003} length in the core-shell ZSM5@CZA-Zr_{0.75} was thicker (13.4 nm) than in CZA-

Zr_{0.75} (9.3 nm). Given the sensitivity of LDH growth to various parameters during coprecipitation, the change in platelet thickness in the presence of ZSM-5 was expected. This suggests that, in this case, the *in-situ* core-shell coprecipitation facilitates the formation of thicker CZA LDH platelets.

Table 4.4: d-spacing and crystallite domain lengths of ZSM5@CZA-Zr_{0.75} refined from simple Pawley refinement of PXRD data collected on a Bruker D8 ECO diffractometer.

Sample	d_{003} (Å)	d_{110} (Å)	D_{003}^a (nm)	D_{110}^a (nm)	Crystalline anisotropy (D_{110}/D_{003})
ZSM5@CZA-Zr _{0.75}	7.60	1.55	13.4	5.8	0.4
CZA-Zr _{0.75}	7.60	1.55	9.3	5.6	0.6

^aK = 0.9 in Scherrer's equation.

PXRD analysis therefore shows that the CZA-Zr_{0.75}) was successfully grown in the presence of the ZSM-5 core. The coprecipitation in the presence of the zeolite did not affect the crystal structure of the CZA LDH phase, although there were changes to the crystallite domain lengths whereby the LDH platelets were thicker in the core-shell sample.

TEM in combination with EDX analysis was used to examine the morphology of the ZSM5@CZA-Zr_{0.75} core-shell as summarised in Figure 4.10.

The as-purchased ZSM-5 particles are identified in the images by the presence of Si (magenta) and are large with non-uniform sizes. This is consistent with previous TEM characterisation which showed the zeolite sizes ranging from 100 nm to micrometre

dimensions (see Chapter 2.2.2). EDX mapping reveals that Cu (blue) and Zn (orange) are distributed uniformly around the ZSM-5 particles, while Zr (red) exhibits an uneven distribution, forming clusters primarily in regions corresponding to the CZA LDH phase. This contrasts earlier observations in this chapter where, unsupported samples showed uneven Zr dispersion at low Zr loadings (CZA-Zr_{0.25}) and more uniform distribution at higher loadings (CZA-Zr_{0.75}).

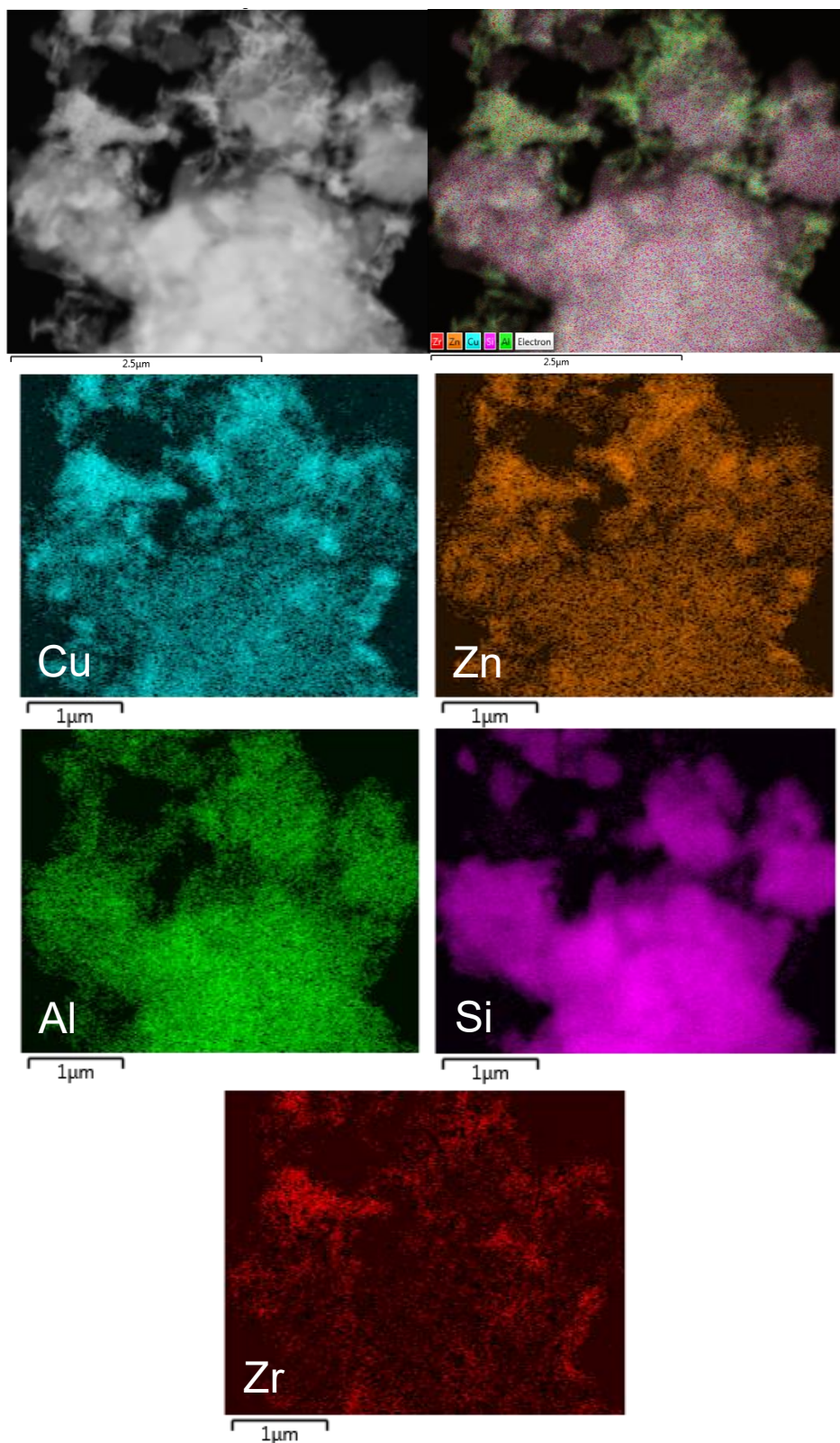


Figure 4.10: STEM/EDX of ZSM5@CZA-Zr_{0.75} catalyst precursor showing the distribution of on Cu (blue), Zn (orange), Al (green), Si (magenta), and Zr (red).

As anticipated based on the TEM results in section 4.2.3, platelet formation in the ZSM5@CZA-Zr_{0.75} is diminished due to the structural disorder of the CZA LDH phase, hence, it was not possible to collect platelet size distribution from the TEM images. The STEM/EDX results confirm that Cu/Zn of the htl phase forms a coating around the ZSM-5 particles, creating a core-shell morphology. It also confirms that Zr is mostly located in/around the LDH phase and is distributed less homogeneously around the ZSM-5 core compared to Cu and Zn.

The FTIR profile of the core-shell shows peaks associated with both ZSM-5 and the CZA-Zr_{0.75} sample (Figure 4.11) as expected. The adsorption bands at $\sim 1210\text{ cm}^{-1}$ and 790 cm^{-1} are associated with the external Si–O asymmetric stretching and symmetric T–O (where T=Si/Al) stretching vibrations of the of the ZSM-5 lattice, whilst the peak at 1047 cm^{-1} is attributed to the internal asymmetric Si–O–T stretches.^{96, 97} These peaks are typically observed in the FTIR profiles of the ZSM-5 zeolites and correspond to the values determined in this work and in the literature.

The FTIR profile of the core-shell exhibits peaks associated with the CZA-Zr_{0.75} sample, appearing at positions consistent with those identified in section 4.2.3. This includes the broad band between $3700 - 2700\text{ cm}^{-1}$ and the sharp peaks at 1630 cm^{-1} and 1360 cm^{-1} attributed to the O–H stretching of hydroxyl groups, the bending vibrations of the interlayer water molecules (in the CZA LDH phase) and carbonate anions ($\nu_3\text{-CO}_3^{2-}$ stretching) respectively.^{60, 72} This aligns with the d_{003} spacing calculated from the PXRD analysis, confirming that the htl-like material present in the core-shell sample is carbonate intercalated. The bands around 780 cm^{-1} which are typically associated with $\text{M}^{x+}\text{--O}$, $\text{M}^{x+}\text{--OH}$ and $\text{O--M}^{x+}\text{--O}$ lattice vibrations are slightly more broad in the case of the ZSM5@CZA-Zr_{0.75} core-shell compared to CZA-Zr_{0.75}.^{72, 73} The thickness of the CZA-

$\text{Zr}_{0.75}$ platelets in $\text{ZSM5@CZA-Zr}_{0.75}$ was larger than in $\text{CZA-Zr}_{0.75}$, suggesting that the LDH structure may be less distorted when grown in the presence of the ZSM-5 core. One of the reasons ZSM-5 was chosen as the core was its potential to act as a nucleation site, with aluminium sites in the zeolite framework facilitating the nucleation and growth of the Al-containing LDH. As previously discussed in Section 4.2.3, the high Zr loaded $\text{CZA-Zr}_{0.75}$ sample exhibited significant layer distortion, likely due to the reduced availability of Al^{3+} during coprecipitation, which underscores the importance of aluminium in maintaining the structural integrity of the LDH. Ultimately, The FTIR profiles of the $\text{ZSM5@CZA-Zr}_{0.75}$ core-shell suggests that the ZSM-5, CZA-LDH and zirconium carbonate phases are present in the core-shell sample.

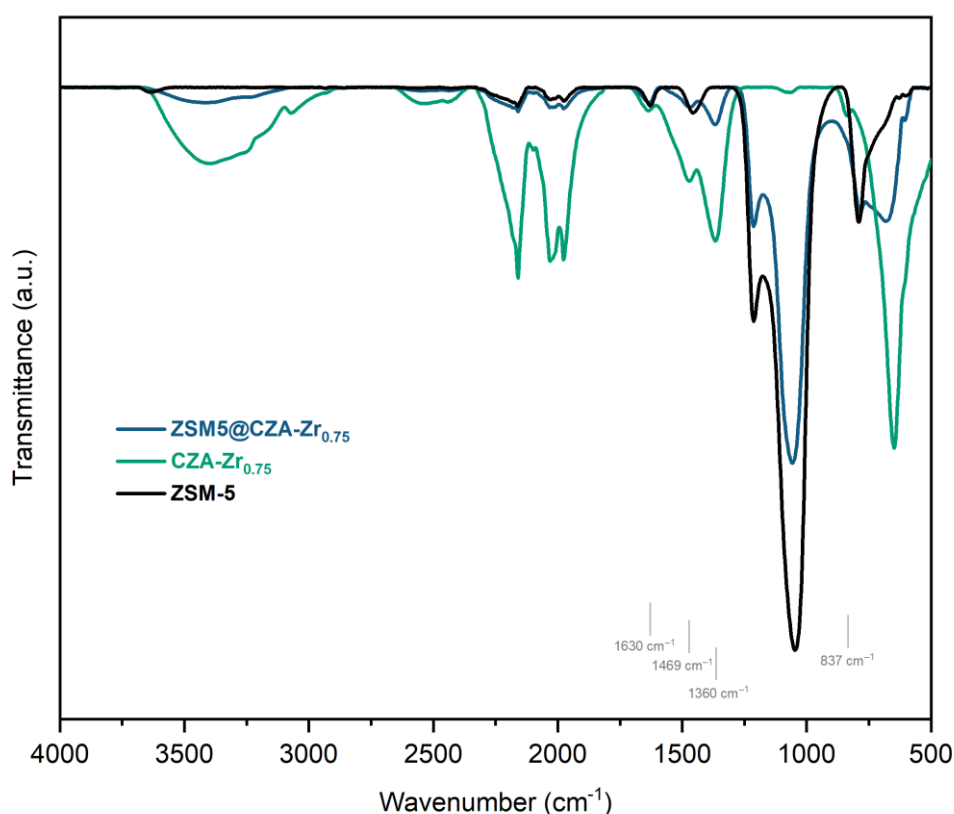


Figure 4.11: FTIR of $\text{ZSM5@CZA-Zr}_{0.75}$, $\text{CZA-Zr}_{0.75}$ and ZSM-5.

The thermal stability of the ZSM5@CZA-Zr_{0.75} precursor catalyst was compared against CZA-Zr_{0.75} and ZSM-5. The TGA data is summarised in Figure 4.12 and Table 4.5.

The core-shell demonstrates three major WLRs between 30 – 200 °C, 200 – 400 °C, and between 500 – 800 °C. The core-shell exhibits an 18.2% weight loss in the first WLR, which is attributed to the loss of surface adsorbed water, interlayer water within the CZA LDH phase and water in the pores of the ZSM-5 core.^{78, 79, 98} In this region, two peaks appear in the dTGA profile of the core-shell at ~50 °C and ~120 °C. These peaks were previously identified in the analysis of CZA-Zr_{0.75} and attributed to the loss of surface adsorbed water (~50 °C) and the dehydration of the LDH interlayers (~120 °C).^{78, 79}

Based on previous thermal stability studies of core-shells conducted in this thesis, the second WLR is primarily attributed to the decomposition of the CZA LDH phase. A small contribution (1.7%) is expected from the ZSM-5 core which is associated with the decomposition of NH₄⁺.⁹⁹ As described in Section 4.2.3, the htl-like material undergoes dehydroxylation and partial decomposition of the interlayer carbonates at these temperatures.^{82, 83} The weight loss for ZSM5@CZA-Zr_{0.75} (10.1%) is notably higher than in CZA-Zr_{0.75} (6.6%). Furthermore, the last WLR, associated with the full decarbonisation of the LDH phase, also shows a greater percentage of mass loss in the core-shell catalyst precursor (4.8%) compared to CZA-Zr_{0.75} (2.4%). These results suggest that the carbonate species in the ZSM5@CZA-Zr_{0.75} core-shell are less thermally stable and more readily decomposed which is expected as the CZA LDH phase is more well-formed than in CZA-Zr_{0.75}. Supporting PXRD analyses indicates that the CZA-Zr_{0.75} phase formed in the presence of ZSM-5 possesses thicker CZA LDH platelets, suggesting improved crystallization. This enhancement was attributed to ZSM-5 acting as an additional source of Al³⁺ during coprecipitation, facilitating the nucleation and (more

effective) growth of the LDH phase. Hence, a greater amount of carbonate is released upon decomposition, and the residual mass is lower, consistent with an increased proportion of the CZA LDH phase in the sample.

The residual weights of the core-shell (66.4%) and CZA-Zr_{0.75} (72.7%) indicate a ZSM-5:LDH ratio of approximately 1.4:1, which reflects the reduced formation CZA LDH on account of the simultaneous formation of the zirconium carbonate species.

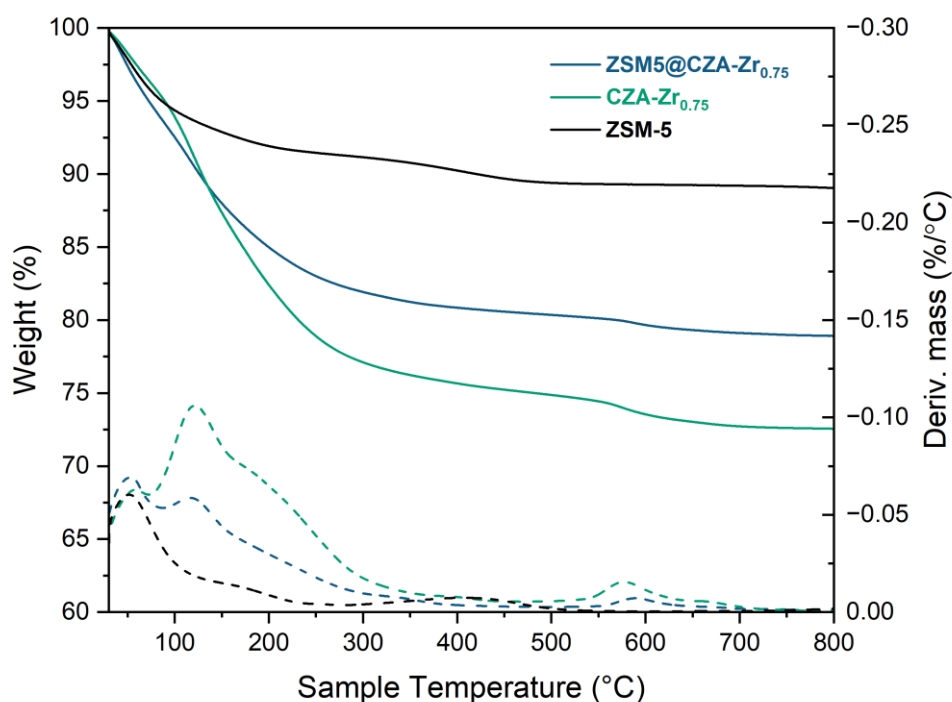


Figure 4.12: TGA and dTGA curves of ZSM5@CZA-Zr_{0.75}, CZA-Zr_{0.75} and ZSM-5.

Table 4.5: Summary of data from TGA including the weight loss percentages for the major weight loss regions (WLRs) and the residual weights of ZSM5@CZA-Zr_{0.75}, CZA-Zr_{0.75} and ZSM-5.

Sample	Weight loss (%)			Residual weight (%)
	30 – 200 °C	200 – 400 °C	500 – 800 °C	
ZSM5@CZA-Zr _{0.75}	18.2	10.1	4.8	66.4
CZA-Zr _{0.75}	17.7	6.6	2.4	72.7
ZSM-5	8.1	1.7	0.4	89.1

Characterisation of the ZSM5@CZA-Zr_{0.75} core-shell, designed as a precursor catalyst for the direct conversion of CO₂ to DME, confirms the following: (a) the CZA-Zr_{0.75} CTM precursor material synthesised in Section 4.2.3. was successfully incorporated as a shell around the ZSM-5 core; (b) Cu and Zn are homogenously distributed around the zeolite core, whereas Zr dispersion is uneven, localising within the CZA LDH regions; and (c) the CZA LDH phase in the core-shell has thicker and more well-defined platelets than in the un-supported CZA-Zr_{0.75} sample. Following this, ZSM5@CZA-Zr_{0.75} was activated and tested for its catalytic performance as a direct CTD catalyst.

4.3.2: CO₂ hydrogenation performance of ZSM5@CZA-Zr_{0.75}-C catalyst

The ZSM5@CZA-Zr_{0.75}-C precursor was activated following the same method used in section 4.2.4.1, whereby the precursor was calcined *ex-situ* in O₂, loaded into a pressured fixed-bed reactor and reduced *in-situ* under H₂. For full details regarding the activation

of the catalyst see Chapter 6.4.4. The core-shell catalyst is referred to as ZSM5@CZA-Zr_{0.75}-C. Approximately 0.1 g of ZSM5@CZA-Zr_{0.75}-C was reacted under CO₂:H₂:N₂ (24:72:4) flow, with a *WHSV* of 18,000 mL/g_{cat}·h and tested between 260 – 240 °C. The outlet gas composition was analysed by GC. For full details of the testing method see Chapter 6.5.

Results from the CO₂ hydrogenation experiment over the ZSM5@CZA-Zr_{0.75}-C catalyst are summarised in Figure 4.13 and Table 4.6. The core-shell catalyst produces a mixture of DME, methanol and CO suggesting that both the CTM and MTD reactions are occurring simultaneously with the competing RWGS reaction. The presence of CO as a side product is commonly seen due to the thermodynamics associated with the initial CTM conversion and the RWGS reaction.^{100, 101} Thus, with increasing temperature, the *S*_{DME} decreases while the *S*_{CO} increases. In terms of the *S*_{CH₃OH}, ZSM5@CZA-Zr_{0.75}-C approaches the thermodynamic equilibrium values which suggests that under these reaction conditions the catalyst is operating under kinetic control.¹⁰²⁻¹⁰⁴

The highest DME productivity occurs at 280 °C where ZSM5@CZA-Zr_{0.75}-C has a *STY*_{DME} value of 0.31 g_{DME}/g_{cat}·h. This is consistent with the optimum temperature for direct CTD conversion seen in other hybrid catalysts tested in this thesis and also lies in the optimum temperature range described in the literature.¹⁰⁵⁻¹⁰⁷ Compared to the non-Zr incorporated ZSM5@Cu_{1.3}ZnAl catalyst (0.37 g_{DME}/g_{cat}·h) and physical mixture ZSM5+Cu_{1.3}ZnAl catalyst (0.407 g_{DME}/g_{cat}·h), ZSM5@CZA-Zr_{0.75}-C has a lower DME productivity (see Figure 4.14, for full details consult Table C.8). In ZSM5@CZA-Zr_{0.75}, the *S*_{DME} is observed to be consistently higher than the non-Zr hybrid CTD catalysts across the same temperature range (260 – 300 °C), however, *X*_{CO₂} is considerably lower which impacts its overall DME productivity.

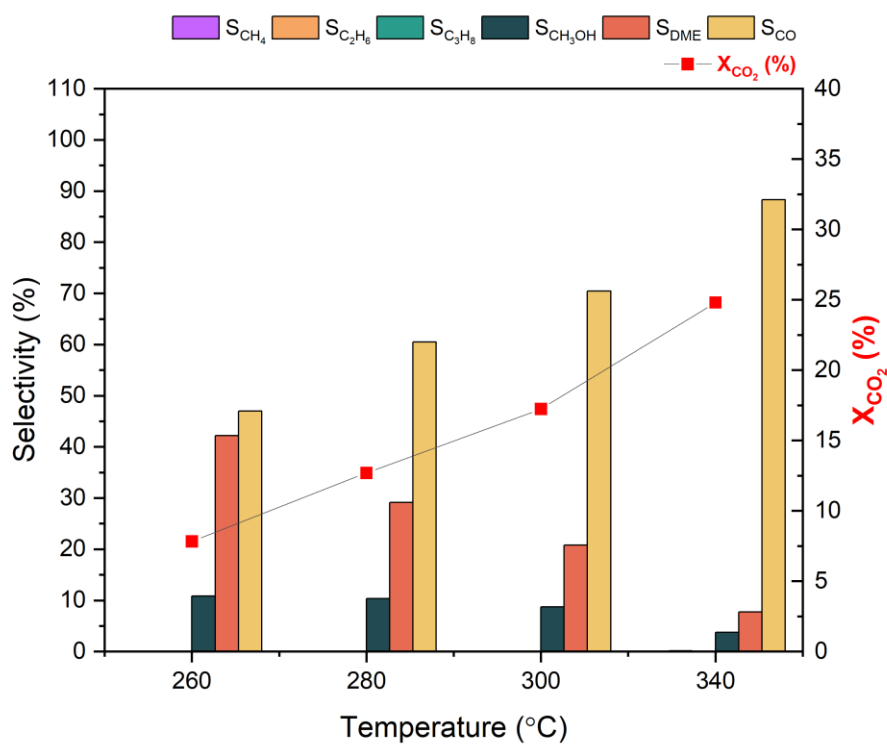


Figure 4.13: Product distribution of CO_2 hydrogenation reaction over ZSM5@CZA- $Zr_{0.75}$ -C catalysts as a function of temperature (260 – 340 °C); Reaction conditions: $P = 3.0$ MPa; $CO_2:H_2:N_2 = 24:72:4$; $WHSV = 18000$ mL/ $g_{cat} \cdot h$, carbon balance 101.13% – 101.51%.

Table 4.6: CO₂ hydrogenation results for ZSM5@CZA-Zr_{0.25}-C.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)			Yield (%)	STY_{DME} (g _{DME} /g·h)
			S_{DME}	S_{CH_3OH}	S_{CO}	Y_{DME}	
ZSM5@CZA-Zr _{0.75} -C	260	7.8	42.2	10.8	47.0	3.3	0.28
	280	12.7	29.1	10.4	60.5	3.7	0.31
	300	17.2	20.8	8.7	70.4	3.6	0.30
	340	24.8	7.7	3.7	88.3	1.9	0.16

^aReaction conditions: $P = 3.0$ MPa, CO₂/H₂/N₂ = 24:72:4, and $WHSV = 18,000$ mL/g_{cat}·h.

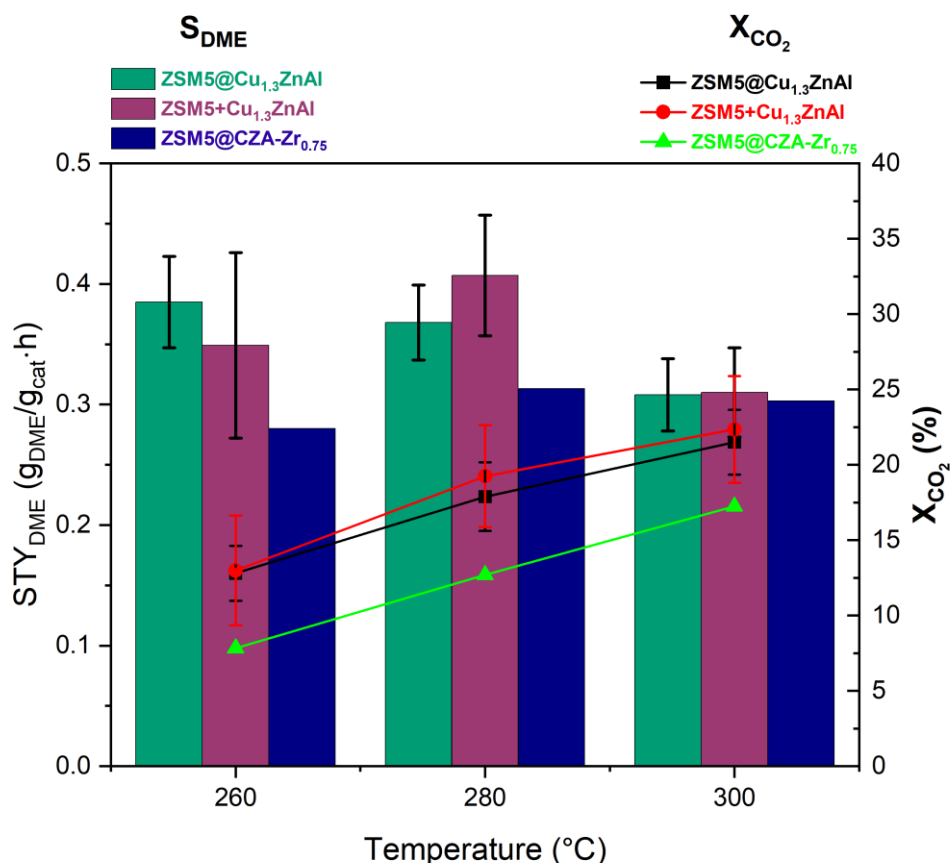


Figure 4.14: S_{DME} and CO_2 conversions for ZSM5@CZA-Zr_{0.75}-C catalysts. Reaction conditions: $P = 3.0$ MPa; $\text{CO}_2:\text{H}_2:\text{N}_2 = 24:72:4$; $WHSV = 18,000$ mL/g_{cat}·h, carbon balance 101.13% – 101.51%.

The lower DME productivity for ZSM5@CZA-Zr_{0.75}-C relative to the non-Zr containing ZSM5@Cu_{1.3}ZnAl core-shell catalyst, is likely due to a combination of structural and compositional effects arising from the incorporation of Zr. As demonstrated in Section 4.2.4, the CZA-Zr_{0.75}-C catalyst exhibited good methanol productivity (0.32 g_{CH₃OH}/g_{cat}·h, 260 °C) during CO₂ hydrogenation to methanol, which was expected to enhance DME formation in the hybrid catalyst. However, this was not reflected in the CTD performance of the Zr-incorporated core-shell as the CO₂ conversion was lower.

A possible explanation may be a reduction in available active hydrogenation sites, however a quantitative assessment of the exposed Cu²⁺ surface area through N₂O titration

would be needed to confirm this. The zirconium carbonate phase was less well dispersed in the presence of the zeolite as indicated by STEM/EDX analysis. While Zr is generally recognised as a structural promoter enhancing Cu dispersion, its localisation into distinct domains in the core-shell sample may limit these benefits. The Cu-Zr interface plays a role in CO₂ activation and hydrogenation.^{6, 30} Therefore, the poorly dispersed Zr in ZSM5@CZA-Zr_{0.75}-C may have led to fewer beneficial interfacial sites, reducing CO₂ conversion and consequently DME productivity. XPS analysis should be used to investigate the oxidation states and local environments of Cu and Zr. Such data would provide insight into the structural and electronic effects induced by Zr incorporation and the role of zeolite in influencing active site availability and distribution.

4.4 Conclusions and future work

The highest methanol productivities were observed for the CZA-Zr_{0.5}-C (0.33 g_{CH₃OH}/g_{cat}·h) and CZA-Zr_{0.75}-C (0.31 g_{CH₃OH}/g_{cat}·h) catalysts at 260 °C, both of which outperformed the corresponding unmodified Cu_{1.3}ZnAl catalyst synthesised via the sodium-free coprecipitation route. However, their performance was comparable to that of the Na₂CO₃-treated CZA catalyst discussed in Chapter 3 which also achieved a productivity of 0.33 g_{CH₃OH}/g_{cat}·h. These findings indicate that Zr incorporation may enhance methanol productivity, though the basis for this requires further investigation.

A more detailed structural characterisation of the catalyst precursors and active catalysts is necessary to understand the role of Zr and the different phases present in the samples. Temperature-dependent PXRD analysis can be used to monitor structural changes in the samples to help identify additional amorphous phases that crystallise at elevated

temperatures. PXRD of the activated catalysts should also be conducted to determine the nature of the Cu species (e.g. CuO vs Cu₂O) present after reduction. Furthermore, HR-TEM could be used to identify lattice fringes and provide insight into the distribution and interaction of the Cu, ZnO, Al₂O₃ and ZrO₂ phases in the active catalysts.

The ZSM5@CZA-Zr_{0.75}-C core-shell catalyst designed for direct CTD conversion demonstrated lower performance (0.31 g_{DME}/g_{cat}·h) than the unmodified ZSM5@Cu_{1.3}ZnAl core-shell (0.37 g_{DME}/g_{cat}·h). Despite the enhanced methanol productivity observed for the unsupported CZA-Zr_{0.75}-C catalyst, the improvement did not translate into superior CTD performance once the catalyst was integrated with the zeolite core. To better understand the effects happening in the Zr-containing core-shell, future work should focus on comparative analysis between the supported and unsupported CZA-Zr_{0.75}-C catalysts. HR-TEM could be used to assess Cu dispersion, while N₂O titration can determine the amount of accessible Cu active sites on the catalyst surface. In previous chapters, the *in-situ* coprecipitation method used to synthesise the core-shells can result in ion exchange within the pores of the zeolite support. It is possible that Zr⁴⁺ ions also participated in this exchange process, potentially influencing catalytic performance. To investigate this further, BET surface area analysis of the activated catalysts is required to assess changes in the textural properties of the core-shell resulting from Zr incorporation and ion exchange. A combination of these characterisation techniques would provide a deeper understanding of how the support and Zr incorporation influences active site availability and catalytic behaviour in the CTM and CTD processes.

4.4 References

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5

Conclusions

The objective for this thesis was to develop an efficient bifunctional catalyst for the direct conversion of CTD, contributing to the broader goal of utilising CO₂ as a chemical feedstock in support of a circular and defossilised chemical industry. A core-shell design was used for the bifunctional CTD catalyst, comprising of a ZSM-5 core and a CZA ex-LDH shell, prepared via a facile *in-situ* coprecipitation method. The ZSM5@Cu_{1.3}ZnAl catalyst (with a 1:1 ZSM-5:LDH weight ratio) was tested for CO₂ hydrogenation ($P = 3$ MPa; $T = 280$ °C; CO₂:H₂:N₂ = 24:72:4; $WHSV = 44,000$ mL/g_{cat}·h), achieving a DME space time yield of 0.72 g_{DME}/g_{cat}·h. This outperformed several CTD catalysts in the literature and was comparable to those operating at higher pressure. ZSM5@Cu_{1.3}ZnAl demonstrates good performance as a high throughput catalyst for direct CTD conversion. Its high productivity reflects the synergy between the Cu_{1.3}ZnAl methanol synthesis phase, derived from the LDH precursor, and the highly acidic ZSM-5 core.

In Chapter 2, comparative testing against a physical mixture of the CZA and ZSM-5 catalyst components (ZSM5+Cu_{1.3}ZnAl) revealed that the core-shell catalyst had a more consistent CO₂ hydrogenation performance. Furthermore, the activation method of the catalyst was critical: only calcination under oxidising conditions led to the high activity of ZSM5@Cu_{1.3}ZnAl. There is limited discussion on how the calcination environment of CTD catalysts influences performance, making this a novel aspect of the work in this thesis.

Chapter 3 explored the effects of sodium incorporation in the coprecipitation method and ZSM-5:LDH ratios on the performance of the subsequent core-shell catalyst. Three coprecipitation methods were compared: a sodium-free method, an NaOH-based method, and a conventional coprecipitation method using both NaOH and Na₂CO₃. Whilst the methods had little effect on the performance of the Cu_{1.3}ZnAl catalyst, DME productivity in the core-shell catalysts decreased with higher levels of residual sodium. Additionally, increasing zeolite content in the ZSM-5:LDH ratio improved DME selectivity but reduced CO₂ conversion, illustrating the trade-off between methanol dehydration and methanol synthesis rates and the critical role of the ZSM-5 phase.

Lastly, Chapter 4 evaluated the impact of Al³⁺ substitution with Zr⁴⁺ incorporation into the Cu_{1.3}ZnAl phase. While high Zr-loading improved methanol productivity in the unsupported CTM catalysts (up to 0.33 g_{CH₃OH}/g_{cat}·h), these gains did not lead to an enhancement in the CTD conversion performance of the corresponding Zr-incorporated core-shell catalyst (ZSM5@CZA-Zr_{0.75}-C), which had lower DME space time yields than the Zr-free counterpart. It suggests that the coprecipitation method needs to be further optimised to access the promoting effects of Zr.

Looking forward, several routes are proposed to investigate and develop the core-shell catalyst for direct CTD conversion:

Catalyst stability and deactivation mechanisms

Given that the ZSM5@Cu_{1.3}ZnAl catalysts achieved CO₂ conversions and DME selectivities approaching the thermodynamic equilibrium limit, it would be pertinent to investigate their long-term stability. Understanding the rate and mechanism of deactivation is essential for assessing its viability as a catalyst for industrial application. CZA-based catalysts are known to suffer from deactivation, primarily due to sintering of the Cu sites. Furthermore, non-mesoporous, highly acidic zeolites (like the 23:1 Si:Al ratio ZSM-5 used in this work) are prone to deactivation from coke deposition. A systematic time-on-steam study is therefore required to evaluate the durability of ZSM5@Cu_{1.3}ZnAl.

Improving core-shell uniformity and coverage

TEM/SEM analysis revealed that the commercial ZSM-5 used in this study has a broad particle size distribution, translating into a considerable variation in the sizes of the core-shells. Using nano-sized ZSM-5, which has demonstrated superior catalytic performance in the literature, could enable better control over LDH nucleation and growth due to its higher surface area and more uniform particle size. This may help suppress the formation of free LDH platelets and increase the ZSM-5/Cu_{1.3}ZnAl interactions.

Optimising the solid acid component

While ZSM-5 was chosen due to its established reputation as a high surface area and effective catalyst for the methanol to DME conversion, alternative zeolites should be investigated to assess whether improved performance can be achieved. In particular, the

FER zeolite is frequently reported in the literature as a more favourable acid component for CTD catalysts. Future efforts should include the synthesis of core-shell catalysts with alternative zeolite cores (FER, SAPO-18 etc.), to investigate how variations in pore structure and zeolite topology influences overall CTD performance.

In conclusion, this work establishes ZSM5@Cu_{1.3}ZnAl as a promising, low-cost catalyst for the direct conversion of CO₂ to DME under industrially relevant conditions. The findings in this thesis provide a foundation for the continued development of LDH-based catalysts in CO₂ utilisation.

6

Experimental details

6.1: Analytical techniques

6.1.1: PXRD

Standard powder X-ray diffraction (PXRD) analysis was carried out on a Bruker D8 Advance Eco Diffractometer in scanning mode using Cu K_{α} radiation (40 kV, 25 mA, $\lambda_{\alpha,1} = 1.54057 \text{ \AA}$, $\lambda_{\alpha,2} = 1.54433 \text{ \AA}$). The sample was compressed into PMMA sample holders with 2mm recession, resulting in peaks at 43.5, 44.3, and 50.5° which did not interfere with the analysis. Signals between $2\theta = 3 - 70^{\circ}$ were gathered with a step size of 0.0298°. Air sensitive samples were loaded in a glove box and sealed within a similar sample holder for measurement. High resolution synchrotron X-ray powder diffraction data were collected at the Diamond Light Source Synchrotron Facility on the I11 beamline ($\lambda = 0.825276 \text{ \AA}$). Samples were loaded into 0.5 mm quartz capillaries for measurement.

Rietveld refinements were performed using TOPAS-Academic V6. The crystallite domain lengths were calculated using the Scherrer equation on the appropriate Bragg reflections.

6.1.2: TEM

Transmission electron microscopy (TEM) images and energy dispersive x-ray spectroscopy (EDX) was obtained from a JEOL-2100 electron microscope with an accelerating voltage of 200 kV using a standard single tilt specimen holder at the David Cockayne Centre for Electron Microscopy (DCCEM) within the Department of Materials, University of Oxford. Some samples in Chapter 2 were analysed using a beryllium holder to minimise spurious signals from copper present in the standard tilt holder. Unless stated, all other samples were measured using the standard tilt holder. Non-catalyst samples were suspended in water and sonicated for 30 minutes before dropping $\sim 7.2 \mu\text{l}$ onto 200 mesh Nickel TEM grids with lacey carbon film. For active catalysts the samples were suspended in ethanol, sonicated for 10 minutes before dropping $\sim 7.2 \mu\text{l}$ onto 200 mesh Gold TEM grids with lacey carbon film.

6.1.3: SEM

SEM images and EDX was obtained from a Zeiss Merlin FEG-SEM at an accelerating voltage of 5 kV at the DCCEM. Samples were suspended in water and sonicated for 30 minutes before dropping $\sim 7.2 \mu\text{l}$ onto a Ni wafer. The wafers were dried overnight and then mounted onto 12.5 mm aluminium stubs using adhesive carbon tape. Due to the

poor conductivity of LDHs, the samples were sputter-coated with 4 nm layer of platinum using a Leica EM AC600 sputter Coater.

6.1.4: ssNMR

Solid-state nuclear magnetic resonance (ssNMR) spectra (cross-polarization magic angle spinning (CPMAS) ^{29}Si and direct-polarization magic angle spinning (DPMAS) ^{27}Al) were obtained on a Bruker Advance IIIHD spectrometer in 4.0 mm O.D zirconia rotors (air-sensitive samples were packed with 3.2 mm O.D zirconia rotors) by Dr Nick Rees, University of Oxford.

The ^{29}Si NMR spectroscopy was gathered at 79.4 MHz at 10 kHz spinning. A one-pulse sequence and spinal 64 proton decoupling was applied to get the quantitative MAS spectra. Typically, 2619 transients were acquired with a 30 second delay. All ^{29}Si chemical shifts are referenced to kaolinite with chemical shift $\delta = -91.7$ ppm on a scale where δ (Tetramethylsilane) = 0 ppm as a secondary reference. The ^{27}Al NMR spectroscopy was collected at 104.2 MHz (9.4 T). ZSM5@Cu_{1.3}ZnAl-LDH and Cu_{1.3}ZnAl-LDH were measured with a MAS rate of 13 kHz whilst ZSM5+Cu_{1.3}ZnAl-LDH was scanned at 20 kHz. A single pulse excitation was applied adopting a short pulse width (0.23 μs) to get the quantitative MAS spectra. Typically, 16725 scans were acquired with a 0.1 second delay. All ^{27}Al chemical shifts in the spectroscopy are referenced to an aqueous solution of Al(NO₃)₃ (0 ppm).

6.1.5: ICP-OES/CHN

Analysis was conducted by Dr Nigel Howard at Microanalysis, University of Cambridge. Samples were dissolved in HNO_3 and diluted to ~ 1 ppm. The solutions were then nebulized and then fed into a high-temperature plasma causing excitation of the ions. The emission wavelengths were separated by a spectrometer and measured by a detector. Quantification was achieved through external calibration with multi-element standards.

CHN analysis was conducted by the Elemental Analysis services team at the London Metropolitan University using a Thermo Scientific ThermoFlash 2000 analyser. Samples were placed in a tin capsule which was melted in a combustion chamber. The sample was then oxidised within an oxygen/helium stream. The reaction gases were passed over a catalyst to ensure complete combustion and a Cu catalyst to reduce NO_x to N_2 , removing excess oxygen. The gases were then separated and analysed by gas chromatography equipped with a thermal conductivity detector (TCD).

6.1.6: FTIR

FTIR measurements were recorded on a Bruker VERTEX 80 FTIR spectrometer fitted with a DuraSamplIR Diamond ATR. Before the sample scans, 128 scans were taken as a background. Transmittance was recorded between $600 - 4000 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} .

6.1.7: TGA

Thermogravimetric analysis (TGA) was carried out with the PerkinElmer TGA 8000 under a N₂ atmosphere. The weight change between 30 – 800 °C was collected with a 2 °C/min ramp rate.

6.1.8: N₂-BET

Pore structures were investigated by N₂ adsorption/desorption isotherms that were collected on a Micrometric 3Flex at 77 K. All samples (~100 mg) were *ex-situ* degassed on a Micromeritics VacPrep at 150 °C overnight prior to loading on the 3Flex. The samples were then *in-situ* degassed at 150 °C for 1 hour with a ramp rate of 10 °C/min. Adsorption measurements were collected at regular intervals in a liquid N₂ bath (–196 °C). Specific surface area was estimated using the Brunauer-Emmett-Teller method. Micropore size distribution was calculated by applying a slit-pore DFT kernel to the adsorption isotherm. Macropore size distribution was determined with the Barrett-Joyner-Halenda (BJH) method.

6.1.8: CO₂-TPD

CO₂-TPD experiments were conducted using a Micromeritics Autochem II system. Following *ex-situ* calcination in a tube-furnace, approximately 20 mg of sample was loaded into a quartz U-tube reactor. The samples were then heated from room temperature to 150 °C at a rate of 10 °C/min in He (50 cm³/min) and held for 1 hour to remove surface adsorbed water. After cooling to 40 °C, the gas stream was swapped to 10% H₂/N₂

(50 cm³/min) and heated to 260 °C (2 °C/min), holding for 2 hours to reflect the H₂ reduction in the catalyst activation method. Following the *in-situ* reduction, the sample was cooled back to 40 °C. The gas was then switched to CO₂ (50 cm³/min) and held for 1 hour. To clear the excess CO₂ from the sample tube and system, the gas was switched to He CO₂ (50 cm³/min) and held for another hour. Finally, the catalyst was heated to 600 °C at a rate of 4 °C/min for 1 hour with He as a carrier gas. Measurements were taken once every second on an online thermal conductivity detector (TCD).

6.1.9: NH₃-TPD

NH₃-TPD experiments were conducted using a Micromeritics Autochem II system and carried out in a quartz U-tube reactor with 20 mg of sample used for each measurement. The pre-treatment step (to remove surface adsorbed water) and *in-situ* reduction method use to prepare the samples are the same as those discussed in Section 6.1.8 for the CO₂-TPD experiments. For NH₃-TPD, an NH₃ gas stream (50 cm³/min) was used and held for 1 hour. To clear the excess NH₃ from the sample tube and system, the gas was switched to He CO₂ (50 cm³/min) and held for another hour. Finally, the catalyst was heated to 600 °C at a rate of 4 °C/min for 1 hour with He as a carrier gas. Measurements were taken once every second on an online TCD.

6.1.10: H₂-TPR

H₂-TPR measurements were conducted using a Micromeritics Autochem II system and carried out in a quartz U-tube reactor with 20 mg of sample used for each measurement. The pre-treatment step (to remove surface adsorbed water) follows the same method used

in Sections 6.1.8 and 6.1.9. The gas was switched to He ($50 \text{ cm}^3/\text{min}$) whilst a cold trap of liquid N_2 and isopropyl alcohol was set up. Once the baseline had stabilised, the gas was switched to $10\% \text{H}_2/\text{N}_2$ ($50 \text{ cm}^3/\text{min}$) and heated to $400 \text{ }^\circ\text{C}$ at a rate of $2 \text{ }^\circ\text{C}/\text{min}$, holding for 30 minutes at the end. H_2 consumption was continuously monitored by a TCD and measurements were taken once every second.

6.2: Experimental details for Chapter 2

6.2.1: Materials

Basic copper(II) carbonate ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and 70% nitric acid (HNO_3) were purchased from Sigma Aldrich. Zeolite NH_4 -ZSM-5 aluminium 23:1 mole ratio (ZSM-5) was bought from Alfa Aesar and 25 wt% tetrapropylammonium hydroxide ($\text{C}_{12}\text{H}_{29}\text{NO}$) in water was purchased from Acros Organics. All chemicals and materials were used without further purification. All references to water/ H_2O refers to deionised water (DI).

6.2.2: Sodium-free coprecipitation of the ZSM5@Cu_{1.3}ZnAl-LDH core-shell

$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (0.57 g, 2.6 mmol), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.1 g, 3.8 mmol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.4 g, 3.8 mmol) were dissolved in 256 mL of water with 70% nitric acid (0.82 mL) to assist in dissolving basic copper carbonate. NH_4 -ZSM-5 (1.2 g; 23:1 Si:Al, ZSM-5) was dispersed in 240 mL de-ionised (DI) water sonicated for 30 minutes.

The pH of the ZSM-5 dispersion was adjusted to 10 with 25wt% TPAOH solution. The metal salt solution was then added to the zeolite dispersion at a rate of 152 mL/hour. The pH of the reaction mixture was kept at 10 using 25wt% TPAOH. After metal addition was completed, the reaction mixture was aged for 1 hour under stirring at 500 rpm. The wet cake obtained by Buchner filtration was washed with water until the pH of the filtrate was neutral. After drying under vacuum at 30 °C overnight, 2.4 g of blue powder was collected. The product is called ZSM@Cu_{1.3}ZnAl-LDH-TPA.

6.2.3: Sodium-free coprecipitation of bulk Cu_{1.3}ZnAl-LDH

CuCO₃·Cu(OH)₂ (0.57 g, 2.6 mmol), Zn(NO₃)₂·6H₂O (1.1 g, 3.8 mmol) and Al(NO₃)₃·9H₂O (1.4 g, 3.8 mmol) were dissolved in 256 mL of water with 70% nitric acid (0.82 mL) to assist in dissolving basic copper carbonate. A separate beaker of 240 mL de-ionised (DI) water was adjusted to pH 10 with 25wt% TPAOH solution. The metal salt solution was then added to the second beaker at a rate of 152 mL/hour. The pH of the reaction mixture was kept at 10 using the 25wt% TPAOH solution. After metal addition was completed, the reaction mixture was aged for 1 hour under stirring at 500 rpm. The wet cake obtained by Buchner filtration was washed with water until the pH of the filtrate was neutral. After drying under vacuum at 30 °C overnight, 1.2 g of blue powder was collected. The product is called Cu_{1.3}ZnAl-LDH-TPA.

6.2.4: Synthesis of the ZSM5+Cu_{1.3}ZnAl-LDH physical mixture

The physical mixture was made by mechanically mixing the Cu_{1.3}ZnAl-LDH powders with ZSM-5 powders in a 1:1 ZSM-5:LDH weight ratio until homogeneity. 2.4 g of blue powder was collected and the product is referred to as ZSM5+Cu_{1.3}ZnAl-LDH.

6.2.5: Catalyst activation method

Precursor catalyst materials were *ex-situ* calcined at 500 °C in a tube furnace for 3 hours at a ramp rate 5 °C/min under constant gas flow (50 mL/min). Unless stated, compressed air was used to calcine the samples. For the O₂- and N₂-calcined samples, high purity N₂ (99.999%, 3 ppm moisture) and O₂ gas (≥99.7%, 5 ppm moisture) was used. Approximately 0.1 g of calcined sample was then loaded into a tubular fixed-bed reactor and *in-situ* reduced at 260 °C for 2 hours (2 °C/min) under constant H₂ flow (50 mL/min). Both calcination and reduction were conducted at 1 bar pressure.

6.3: Experimental details for Chapter 3

6.3.1: Materials

Basic copper(II) carbonate (CuCO₃·Cu(OH)₂), copper nitrate trihydrate Cu(NO₃)₂·3H₂O, zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O), and 70% nitric acid (HNO₃) were purchased from Sigma Aldrich. Zeolite NH₄-ZSM-5 aluminium 23:1 mole ratio (ZSM-5) was bought from Alfa Aesar and 25 wt% tetrapropylammonium hydroxide (C₁₂H₂₉NO) in water was purchased from

Acros Organics. All chemicals and materials were used without further purification. All references to water/H₂O refers to deionised water (DI).

6.3.2: Sodium-free coprecipitation of ZSM5@Cu_{1.3}ZnAl-LDH-TPA

The *in-situ* coprecipitation method for the sodium-free ZSM5@Cu_{1.3}ZnAl-LDH precursor material uses the method described in Section 6.2.2. Here the precursor material is described using the “TPA” suffix (i.e. ZSM5@Cu_{1.3}ZnAl-LDH-TPA) to distinguish it from the core-shells synthesised using different coprecipitation methods in this chapter.

6.3.3: Sodium-free coprecipitation of Cu_{1.3}ZnAl-LDH-TPA

The synthesis method for the sodium-free Cu_{1.3}ZnAl-LDH precursor material uses the method described in Section 6.2.3. Here the precursor material is described using the “TPA” suffix (i.e. Cu_{1.3}ZnAl-LDH-TPA) to distinguish it from the LDHs synthesised different coprecipitation methods in this chapter.

6.3.4: NaOH coprecipitation of ZSM5@Cu_{1.3}ZnAl-LDH-Na

CuCO₃·Cu(OH)₂ (0.57 g, 2.6 mmol), Zn(NO₃)₂·6H₂O (1.1 g, 3.8 mmol) and Al(NO₃)₃·9H₂O (1.4 g, 3.8 mmol) were dissolved in 256 mL water with 70% nitric acid (0.82 mL) to assist in dissolving basic copper carbonate. ZSM-5 (1.2 g; 23:1 Si:Al) was dispersed in 240 mL DI water followed by 30 minutes of sonication; the ZSM-5 dispersion was adjusted to pH 10 with 4M NaOH. The metal salt solution was then added dropwise to the zeolite dispersion at a rate of 152 mL/h whilst the pH of the reaction

mixture was kept at 10 using 4M NaOH. After the metal addition was completed, the reaction mixture was aged for 1 hour under stirring at 500 rpm. The wet cake obtained by Buchner filtration was washed with water until the filtrate was neutral. After drying under vacuum at 30 °C overnight, 2.2 g of blue powder was collected. The product is called ZSM5@Cu_{1.3}ZnAl-LDH-Na.

6.3.5: NaOH coprecipitation of Cu_{1.3}ZnAl-LDH-Na

CuCO₃·Cu(OH)₂ (0.57 g, 2.6 mmol), Zn(NO₃)₂·6H₂O (1.1 g, 3.8 mmol) and Al(NO₃)₃·9H₂O (1.4 g, 3.8 mmol) were dissolved in 256 mL water with 70% nitric acid (0.82 mL) to assist in dissolving basic copper carbonate. A separate beaker of 240 mL de-ionised (DI) water was adjusted to pH = 10 with 4M NaOH solution. The metal salt solution was then added to the second beaker at a rate of 152 mL/hour. The pH of the reaction mixture was kept at 10 using the 4M NaOH solution. After metal addition was completed, the reaction mixture was aged for 1 hour under stirring at 500 rpm. The wet cake obtained by Buchner filtration was washed with water until the pH of the filtrate was neutral. After drying under vacuum at 30 °C overnight, 1.2 g of blue powder was collected. The product is called Cu_{1.3}ZnAl-LDH-Na.

6.3.6: Standard coprecipitation of ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃

Cu(NO₃)₂·3H₂O (1.2 g, 5.0 mmol), Zn(NO₃)₂·6H₂O (1.1 g, 3.7 mmol) and Al(NO₃)₃·9H₂O (1.4 g, 3.7 mmol) were dissolved in 256 mL water. ZSM-5 (1.2 g; 23:1 Si:Al) was added to a dispersion of Na₂CO₃ (0.3 g, carbonate source) in 240 mL DI water and sonicated for 30 minutes. The ZSM-5 dispersion was then adjusted to pH 10 with 4M

NaOH. The metal salt solution was added dropwise to the ZSM-5/ Na_2CO_3 dispersion at a rate of 152 mL/h whilst the pH of the reaction mixture was kept at 10 using 4M NaOH. After the metal addition was completed, the reaction mixture was aged for 1 hour under stirring at 500 rpm. The wet cake obtained by Buchner filtration was washed with water until the filtrate was neutral. After drying under vacuum at 30 °C overnight, 2.2 g of blue powder was collected. The product is called ZSM5@ $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$.

6.3.7: Standard coprecipitation of $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$

$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (1.2 g, 5.0 mmol), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.1 g, 3.7 mmol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.4 g, 3.7 mmol) were dissolved in 256 mL water with 70% nitric acid (0.82 mL) to assist in dissolving basic copper carbonate. A separate beaker with a dispersion of Na_2CO_3 (0.3 g, carbonate source) in 240 mL de-ionised (DI) water was adjusted to pH = 10 with 4M NaOH solution. The metal salt solution was then added to the second beaker at a rate of 152 mL/hour. The pH of the reaction mixture was kept at 10 using the 4M NaOH solution. After metal addition was completed, the reaction mixture was aged for 1 hour under stirring at 500 rpm. The wet cake obtained by Buchner filtration was washed with water until the pH of the filtrate was neutral. After drying under vacuum at 30 °C overnight, 1.2 g of blue powder was collected. The product is called $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$.

6.3.8: Physical mixture samples

Physical mixtures were made by mechanically mixing the $\text{Cu}_{1.3}\text{ZnAl-LDH}$ powders with ZSM-5 powders in a 1:1 ZSM-5:LDH weight ratio to homogeneity.

6.3.9: Alkaline treatment of ZSM-5

ZSM-5 (1.2 g; 23:1 mole ratio $\text{SiO}_2\text{:Al}_2\text{O}_3$) was dispersed in 240 mL DI water and sonicated for 30 minutes. The pH of the dispersion was then adjusted to 10 with either 25 wt% TPAOH or NaOH. The mixture was then stirred at 500 rpm for 2.7 hours (reflecting the total amount of time ZSM-5 is exposed to the base during the standard coprecipitation). The pH was monitored throughout and maintained at 10 by adding more base if required. The dispersion was then filtered and washed with water until pH 7 before drying under vacuum at 30 °C overnight. ZSM-5 dispersed in TPAOH is labelled ZSM5-TPA whilst ZSM-5 dispersed in NaOH is labelled ZSM5-Na.

For the Na_2CO_3 treatment, ZSM-5 was added to a dispersion of Na_2CO_3 (0.3 g) in 240 mL DI water and sonicated for 30 minutes. The pH of the dispersion was then adjusted to 10 using NaOH. Subsequent steps were carried out as described for ZSM5-TPA and ZSM5-Na.

6.3.10: Sodium-free synthesis of $(\text{ZSM5})_x@(\text{Cu}_{1.3}\text{ZnAl})_y\text{-LDH}$

The *in-situ* coprecipitation method for the sodium-free $(\text{ZSM5})_x@(\text{Cu}_{1.3}\text{ZnAl})_y\text{-LDH}$ precursor material uses the method described in Section 6.2.2. For the 2:1 ZSM-5:LDH ratio, the $\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$ (0.57 g, 2.6 mmol), $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (1.1 g, 3.8 mmol) and $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (1.4 g, 3.8 mmol) metal salt solution was added to the ZSM-5 dispersion with 2.6 g of zeolite. For the 1:2 ZSM-5:LDH ratio, 0.6 g of ZSM-5 was used.

6.3.11: Catalyst activation method

Precursor catalyst materials were *ex-situ* calcined at 500 °C in a tube furnace for 3 hours at a rate 5 °C/min under constant O_2 gas flow (50 mL/min, $\geq 99.7\%$, 5 ppm moisture).

Approximately 0.1 g of calcined sample was then loaded into a tubular fixed-bed reactor and *in-situ* reduced at 260 °C for 2 hours (2 °C/min) under constant H₂ flow (50 mL/min). Both calcination and reduction were conducted at 1 bar pressure.

6.4: Experimental details for Chapter 4

6.4.1: Materials

Basic copper(II) carbonate ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$), zinc nitrate hexahydrate ($\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminium nitrate nonahydrate ($\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$), zirconium nitrate pentahydrate ($\text{Zr(NO}_3)_4 \cdot 5\text{H}_2\text{O}$) and 70% nitric acid (HNO_3) were purchased from Sigma Aldrich. Zeolite NH₄-ZSM-5 aluminium 23:1 mole ratio (ZSM-5) was bought from Alfa Aesar and 25 wt% tetrapropylammonium hydroxide ($\text{C}_{12}\text{H}_{29}\text{NO}$) in water was purchased from Acros Organics. All chemicals and materials were used without further purification. All references to water/H₂O refers to deionised water (DI).

6.4.2: Synthesis of bulk CZA-Zr_x materials

A series of Zr-incorporated Cu_{1.3}ZnAl LDHs were synthesised following a similar method to those described for bulk Cu_{1.3}ZnAl-LDH. $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$, $\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Zr(NO}_3)_4 \cdot 5\text{H}_2\text{O}$ were dissolved in 256 mL of water with 70% nitric acid (0.82 mL) to assist in dissolving basic copper carbonate. The weight and molar ratios used to generate the CZA-Zr_x series is summarised in Table 6.1. A separate beaker of 240 mL de-ionised (DI) water was adjusted to pH = 10 with 25wt% TPAOH solution. The metal salt solution was then added to the second beaker at a rate of 152 mL/hour.

The pH of the reaction mixture was kept at 10 using the 25wt% TPAOH solution. After metal addition was completed, the reaction mixture was aged for 1 hour under stirring at 500 rpm. The wet cake obtained by Buchner filtration was washed with water until the pH of the filtrate was neutral. After drying under vacuum at 30 °C overnight, the blue powder products were collected.

Table 6.1: Cu/Zn/Al/Zr content in the CZA-Zr_x precursor catalyst series.

Cu/Zn/Al/Zr content		CZA-Zr _{0.25}	CZA-Zr _{0.5}	CZA-Zr _{0.75}
Cu:Zn:Al:Zr		1.3:1:0.75:0.25	1.3:1:0.5:0.5	1.3:1:0.25:0.75
Cu	g	0.57	0.57	0.57
	mmol	2.6	2.6	2.6
Zn	g	1.1	1.1	1.1
	mmol	3.7	3.7	3.7
Al	g	1.0	0.7	0.3
	mmol	2.8	1.9	0.9
Zr	g	0.4	0.8	1.2
	mmol	0.9	1.9	2.8

6.4.3: Synthesis of ZSM5@CZA-Zr_x

CuCO₃·Cu(OH)₂ (0.57 g, 2.6 mmol), Zn(NO₃)₂·6H₂O (1.1 g, 3.8 mmol), Al(NO₃)₃·9H₂O (0.3 g, 0.9 mmol) and Zr(NO₃)₄·5H₂O (1.2 g, 2.8 mmol) were dissolved in 256 mL of water with 70% nitric acid (0.82 mL) to assist in dissolving basic copper carbonate. NH₄-ZSM-5 (1.2 g; 23:1 Si:Al, ZSM-5) was dispersed in 240 mL de-ionised (DI) water followed by 30 minutes of sonication. The pH value of ZSM-5 dispersion was

adjusted to 10 with 25wt% TPAOH solution. The metal salt solution was then added to zeolite dispersion at a rate of 152 mL/hour. The pH of the reaction mixture was kept at 10 using the 25wt% TPAOH solution. After metal addition was completed, the reaction mixture was aged for 1 hour under stirring at 500 rpm. The wet cake obtained by Buchner filtration was washed with water until the pH of the filtrate was neutral. After drying under vacuum at 30 °C overnight, 2.5 g of blue powder was collected. The product is called ZSM5@CZA-Zr_{0.75}.

6.4.4: Catalyst activation method

Precursor catalysts were *ex-situ* calcined at 500 °C in a tube furnace for 3 hours at a rate 5 °C/min under constant O₂ gas flow (50 mL/min, ≥99.7%, 5 ppm moisture). Approximately 0.1 g of calcined sample was then loaded into a tubular fixed-bed reactor and *in-situ* reduced at 260 °C for 2 hours (2 °C/min) under constant H₂ flow (50 mL/min). Both calcination and reduction were conducted at 1 bar pressure.

6.5: CO₂ hydrogenation method

CO₂ hydrogenation was carried out in a pressurised, continuous flow, tubular fixed-bed reactor, mass flow controllers, a back pressure valve and online gas chromatographs. Following the catalyst activation method described in Section 6.2.8, the reactor was then pressured using the reactant gas comprised of CO₂/H₂/N₂ (24:72:4 molar ratio) to 3 MPa. Unless stated, the weight hourly space velocity (WHSV) was 18,000 mL/g_{cat}·h. The activity of the catalysts was determined with a constant flow of the reactant gas mixture through the catalyst bed at the desired temperature range for at least 2 hours time on steam for catalyst stabilisation at each temperature point. The effluent stream was sampled four

times per temperature point and was quantitatively analysed by a SHIMADZU GC-2030 gas chromatograph equipped with two calibrated thermal conductivity detectors (TCD) and one calibrated flame ionisation detector (FID). CO₂, CO, CH₃OH and DME were detected by GC-2030 equipped with the TCD and three packed column (P-N, P-Q and MS-13X), C₁-C₄ hydrocarbons were detected by GC-2030 equipped with an FID and HP-PLOT Al/S capillary column. The activity was calculated using the internal standard method, with inert N₂ serving as the internal standard. The carbon balance ranged from 95% to 105%, indicating that the majority of compounds were successfully detected and that the calibration for the gas compounds is reliable.

CO₂ conversion (X_{CO_2}), product selectivity ($S_{Product}$), and product yield ($Y_{Product}$), and space time yield (STY) were calculated by the following equations:

$$X_{CO_2} = \frac{[CO_2]_{in} * [N_2]_{out} - [CO_2]_{out} * [N_2]_{in}}{[CO_2]_{in} * [N_2]_{out}} \times 100 \quad (6.1)$$

$$S_{Product} = \frac{n * [Product]_{i,out}}{\sum_{i=1}^{\infty} n * [Product]_{i,out}} \times 100 \quad (6.2)$$

$$Y_{Product} = X_{CO_2} \times S_{Product} \quad (6.3)$$

$$STY_{Product} = \frac{(WHSV \times [CO_2 \text{ fraction}] \times Y_{Product})}{V_m} \times M_{Product} \quad (6.4)$$

where $[CO_2]_{in}$ and $[CO_2]_{out}$ are the CO₂ inlet and outlet concentrations, $[N_2]_{in}$ and $[N_2]_{out}$ are the N₂ inlet and outlet concentrations, $[Product]_{i,out}$ is the concentration of product i in the effluent stream and n refers to the carbon number of the product i (e.g. n for CO and CH₃OH is 1, while n for DME is 2) in the effluent stream, $[CO_2 \text{ fraction}]$ is the ratio of CO₂ in the reactant gas stream (e.g. for CO₂:H₂:N₂ = 24:72:4, $[CO_2 \text{ fraction}] = 0.24$), V_m is the molar volume of gas under normal temperature and pressure, and $M_{Product}$ is the molar mass of the product (g/mol).

A

Appendix for Chapter 2

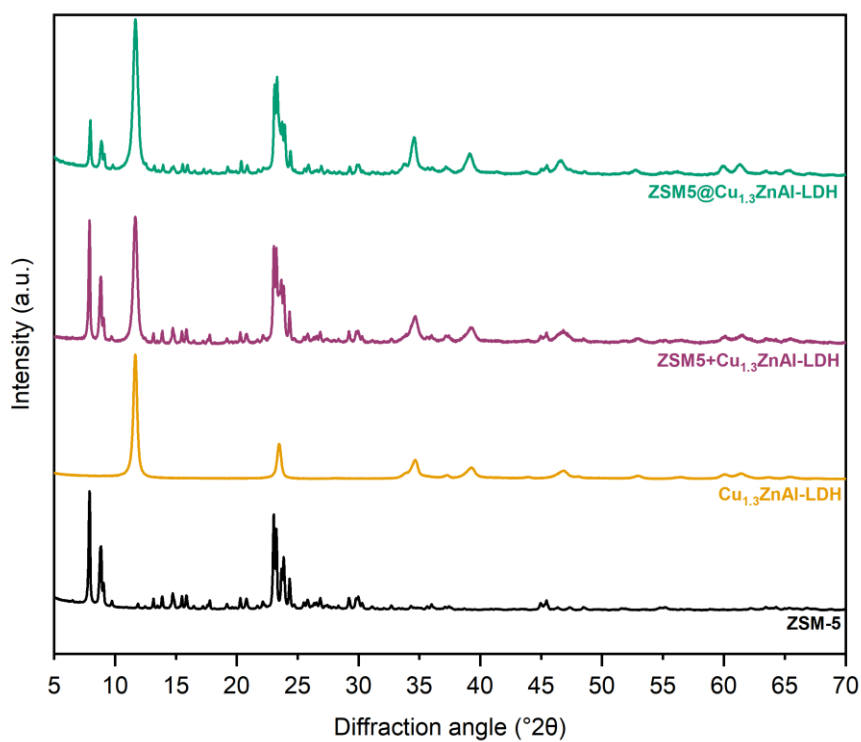


Figure A.1: PXRD of the ZSM5@Cu_{1.3}ZnAl-LDH core-shell, ZSM5+Cu_{1.3}ZnAl-LDH physical mixture, Cu_{1.3}ZnAl-LDH and ZSM-5. PXRD data was collected on a Bruker D8 ECO diffractometer.

Table A.1: Details of the Rietveld refinement and structural parameters for ZSM5@Cu_{1.3}ZnAl-LDH, ZSM5+Cu_{1.3}ZnAl-LDH, Cu_{1.3}ZnAl-LDH, and ZSM-5.

Sample	ZSM5@Cu _{1.3} ZnAl-LDH		ZSM5+Cu _{1.3} ZnAl-LDH		Cu _{1.3} ZnAl-LDH	ZSM-5
Phase component	LDH	Zeolite	LDH	Zeolite	LDH	Zeolite
Space group	R-3m	Pnma	R-3m	Pnma	R-3m	Pnma
R _{wp} (%)	1.12		3.32		1.82	1.63
GOF (%)	3.35		7.16		5.45	4.85
a (Å)	3.081242(3)	20.114915(1)	3.074758(4)	20.157083(7)	3.068740(3)	20.101010(4)
b (Å)	3.081242(3)	19.915277(2)	3.074758(4)	19.952853(1)	3.068740(3)	19.903951(4)
c (Å)	22.779866(2)	13.419283(1)	22.729622(2)	13.452744(1)	22.70765(3)	13.420631(4)

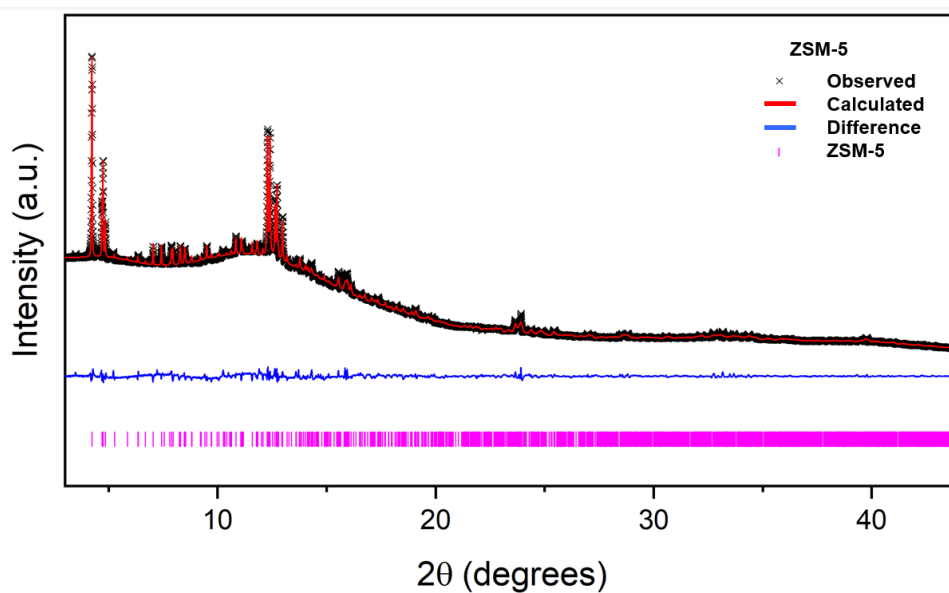


Figure A.2: Single-phase Rietveld refinement of as-purchased ZSM-5. PXRD data was collected at I11 Diamond Light Source.

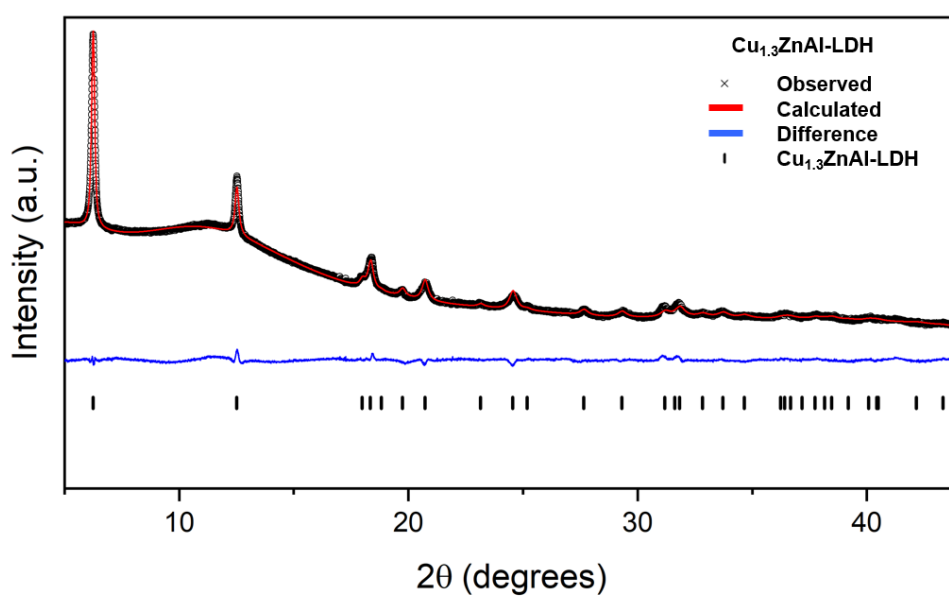


Figure A.3: Single-phase Rietveld refinement of $\text{Cu}_{1.3}\text{ZnAl-LDH}$. PXRD data was collected at I11 Diamond Light Source.

Table A.2: Scherrer parameters for the calculation of the LDH crystal size in the core-shell, physical mixture and LDH samples.

Sample	2θ (°)	Reflection planes	FWHM (radians)	Crystallite
				domain length (nm)
ZSM5@Cu _{1.3} ZnAl- LDH	6.23	(003)	0.00403	18.4
	12.47	(006)	0.00463	15.9
	31.06	(110)	0.00578	12.4
ZSM5+Cu _{1.3} ZnAl- LDH	6.23	(003)	0.00346	21.4
	12.50	(006)	0.00454	16.3
	31.14	(110)	0.007449	9.6
Cu _{1.3} ZnAl-LDH	6.25	(003)	0.00301	24.6
	12.53	(006)	0.00301	21.7
	31.20	(110)	0.00765	9.3

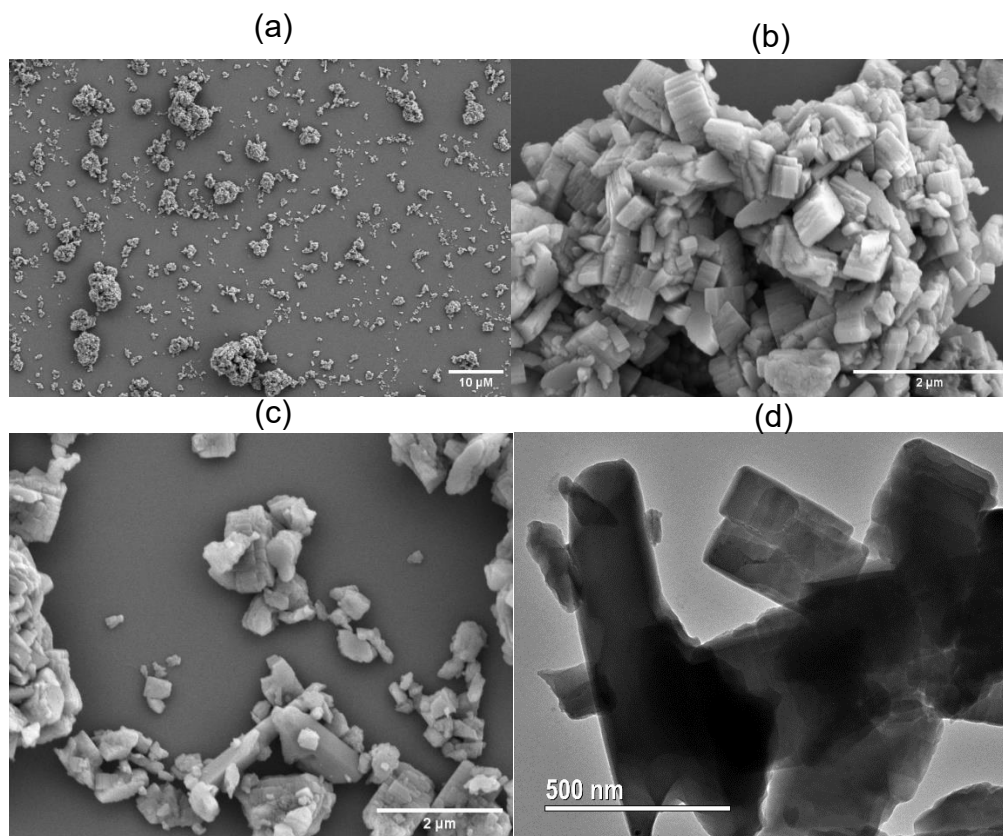


Figure A.4: (a-c) SEM and (d) TEM images of the morphology and sizes of as-purchased (NH₄-ZSM-5) crystals.

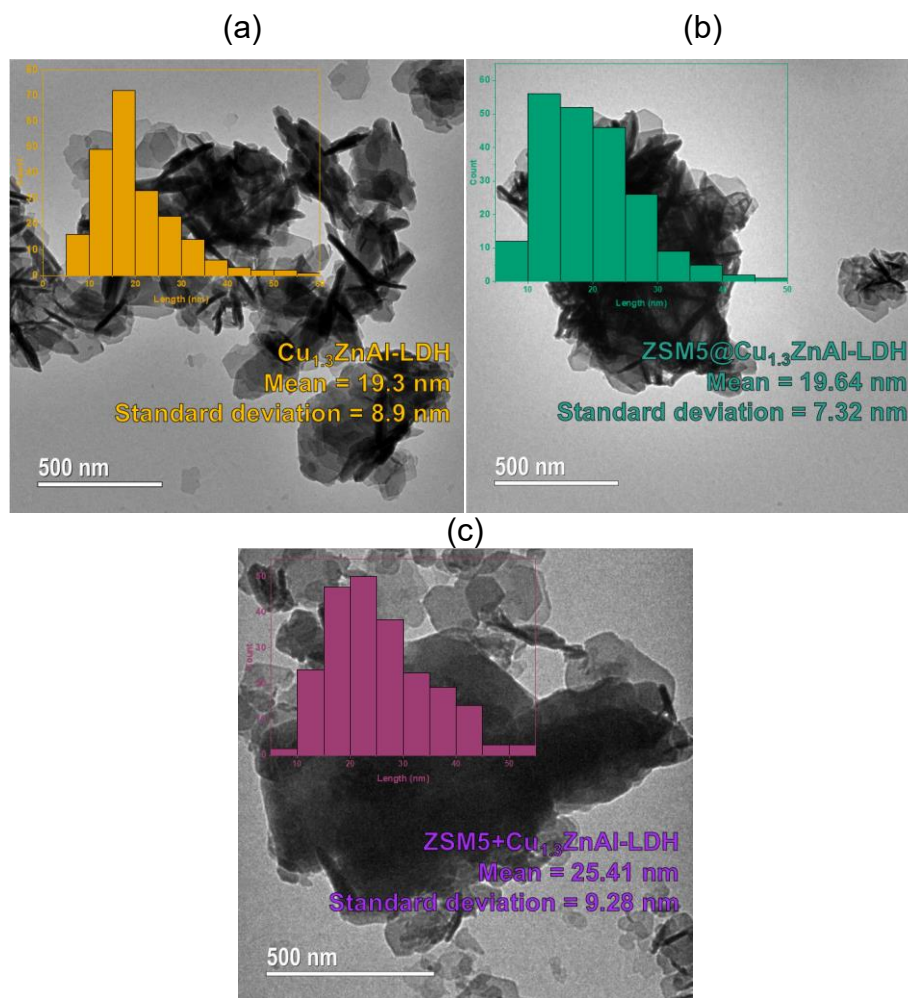


Figure A.5: TEM platelet size distribution of (a) $\text{Cu}_{1.3}\text{ZnAl-LDH}$, (b) $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH}$, and (c) $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDH}$.

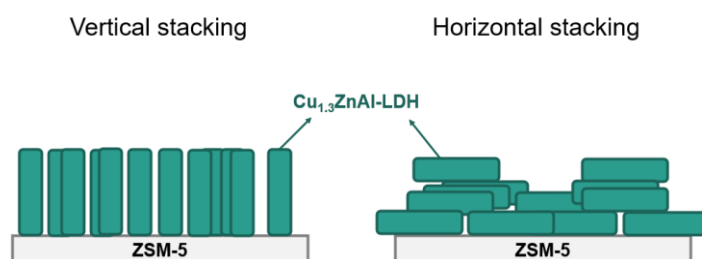


Figure A.6: Illustration of vertically stacked vs horizontally stacked $\text{Cu}_{1.3}\text{ZnAl-LDH}$ platelets covering the ZSM-5 core. The illustrations are representative of two possible core-shell morphologies depending on the growth direction of the LDH.

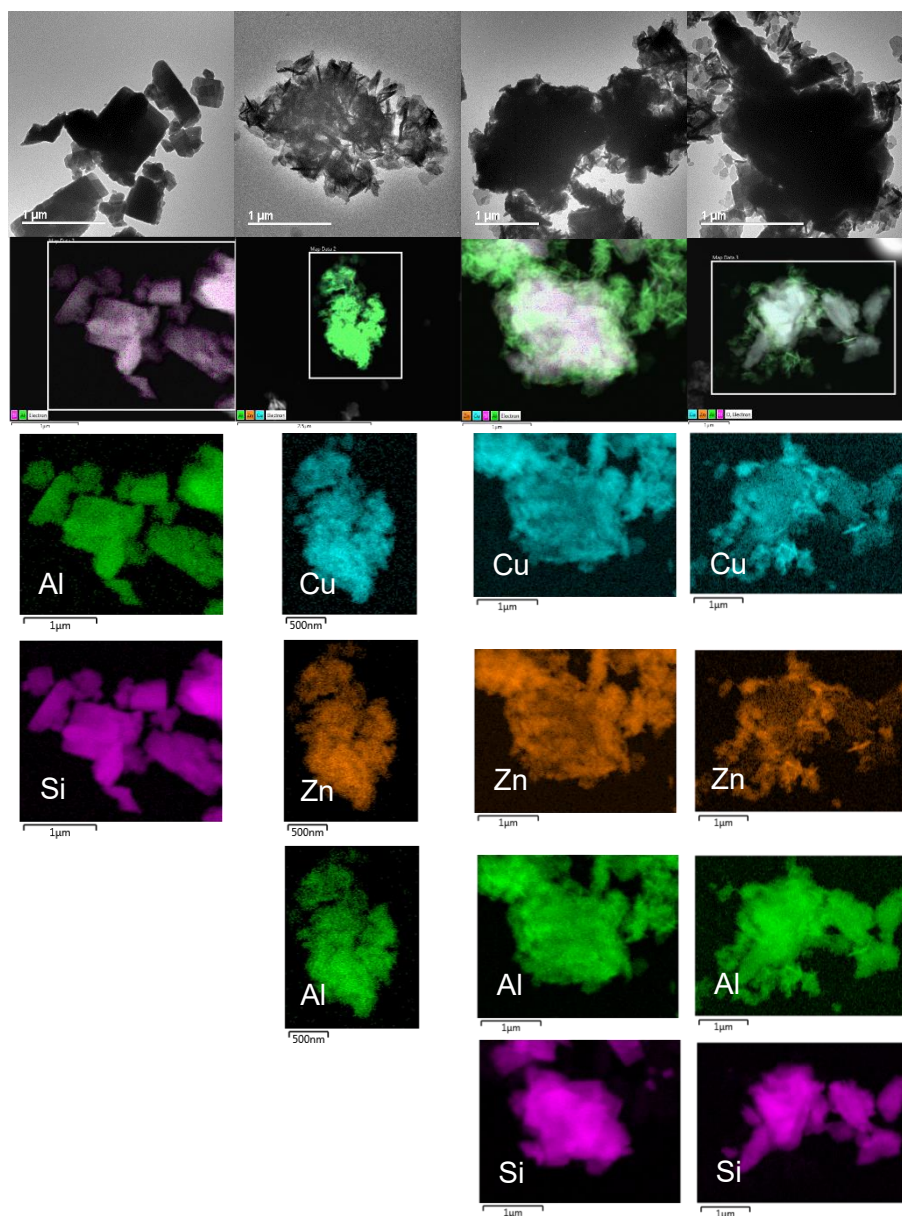


Figure A.7: STEM/EDX images of (a) ZSM-5, (b) $\text{Cu}_{1.3}\text{ZnAl-LDH}$, (c) $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH}$ and (d) $\text{ZSM5+Cu}_{1.3}\text{ZnAl-LDH}$ catalyst precursors showing the distribution of Cu (blue), Zn (orange), Al (green) and Si (magenta). Samples were loaded onto JEOL2100 using a standard single-tilt holder.

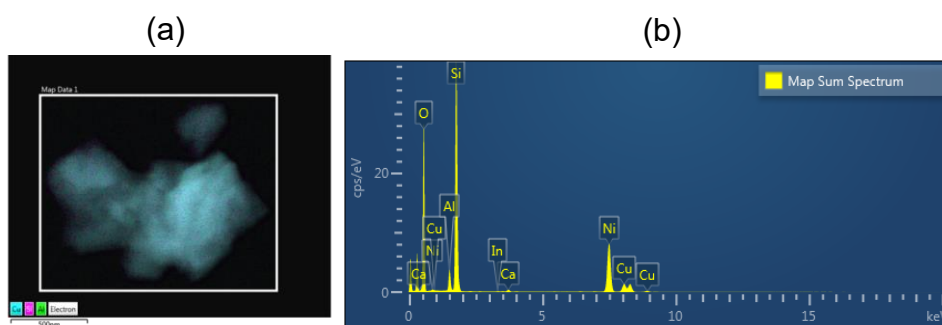


Figure A.8: (a) STEM/EDX elemental mapping of as-purchased ($\text{NH}_4\text{-ZSM-5}$) crystals showing the distribution of Si (magenta) and Al (green) from the zeolite and Cu (blue) from spurious x-rays, and (b) the elemental map sum spectrum of the particle.

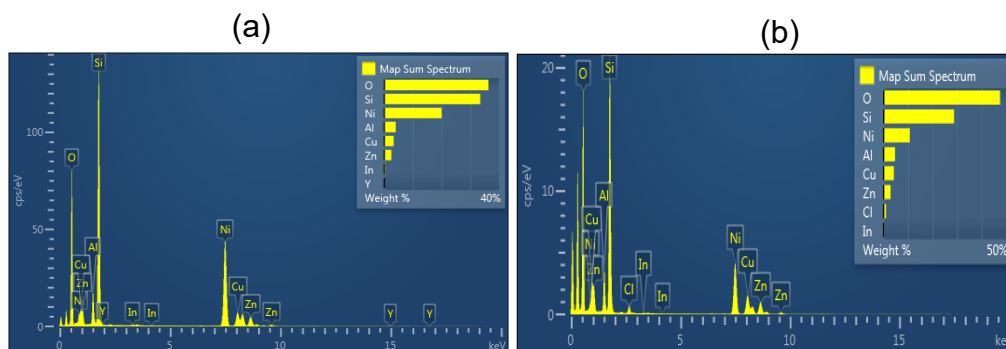


Figure A.9: EDX map sum spectra of (a) ZSM5@Cu_{1.3}ZnAl-LDH and (b) ZSM5+Cu_{1.3}ZnAl-LDH.

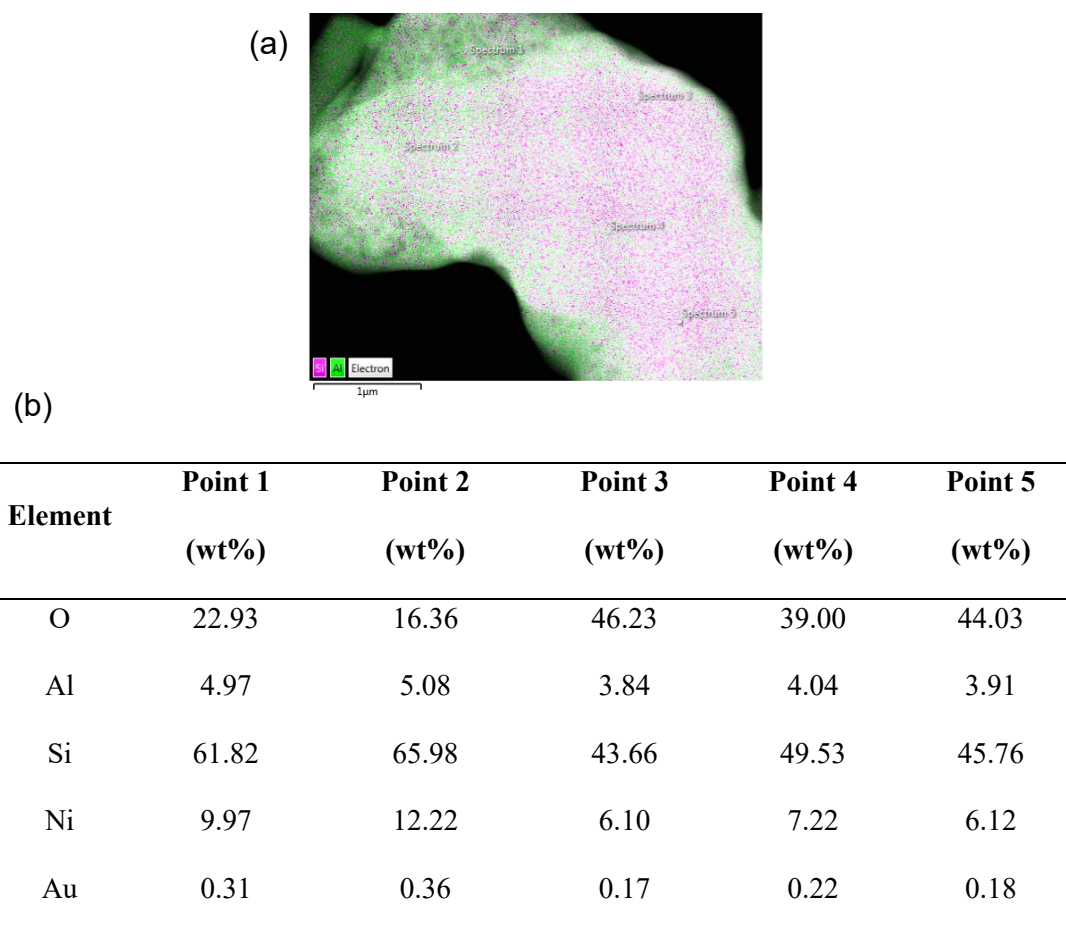


Figure A.10: (a) STEM/EDX with (b) point analysis for ZSM-5 using a Be holder.

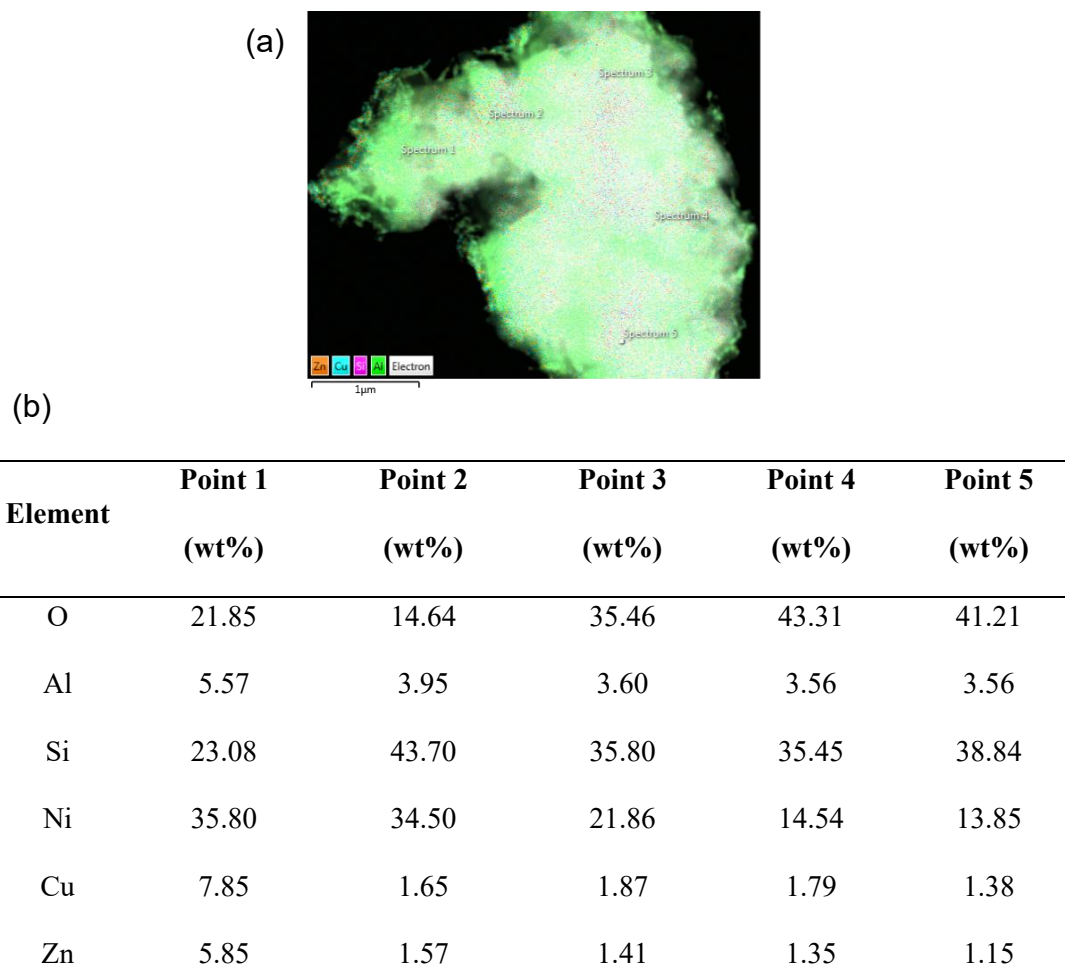


Figure A.11: (a) STEM/EDX with (b) point analysis for ZSM5@Cu_{1.3}ZnAl-LDH using a Be holder.

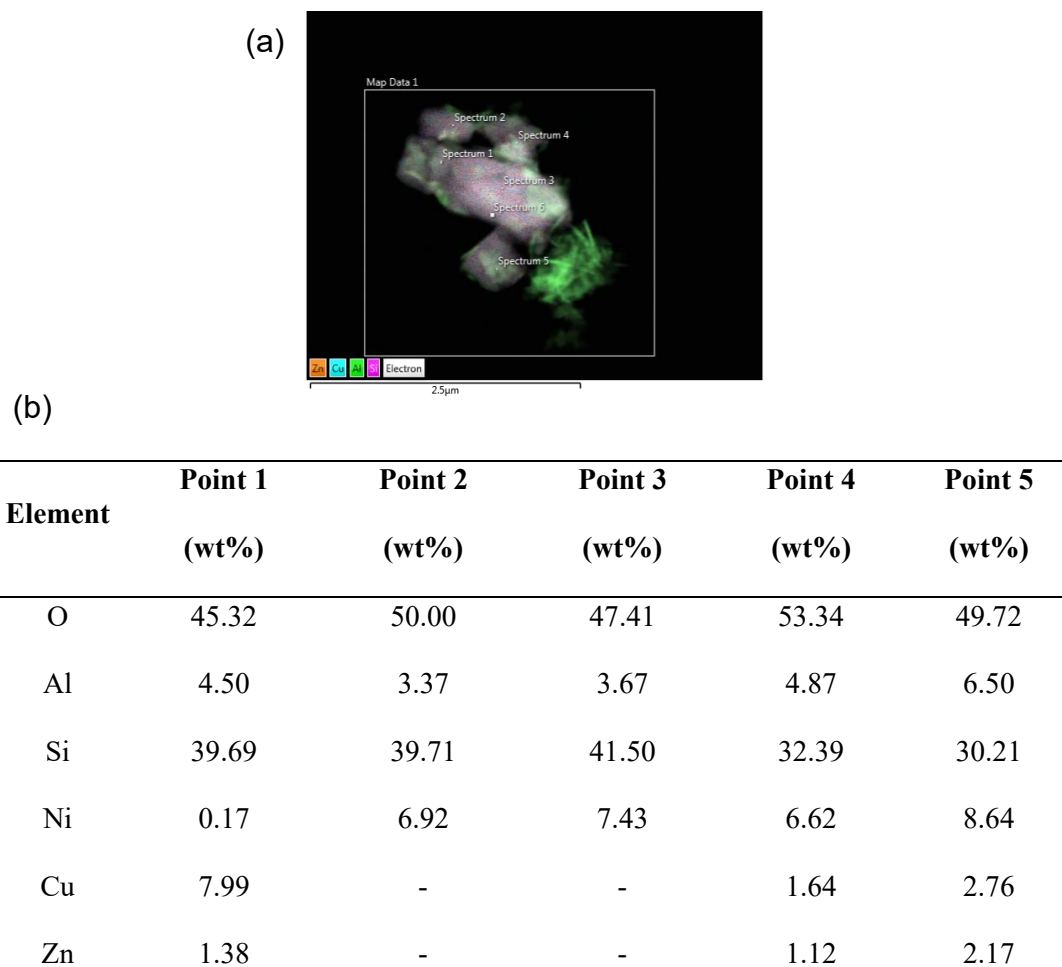


Figure A.12: (a) STEM/EDX with (b) point analysis for ZSM5+Cu_{1.3}ZnAl-LDH using a Be holder.

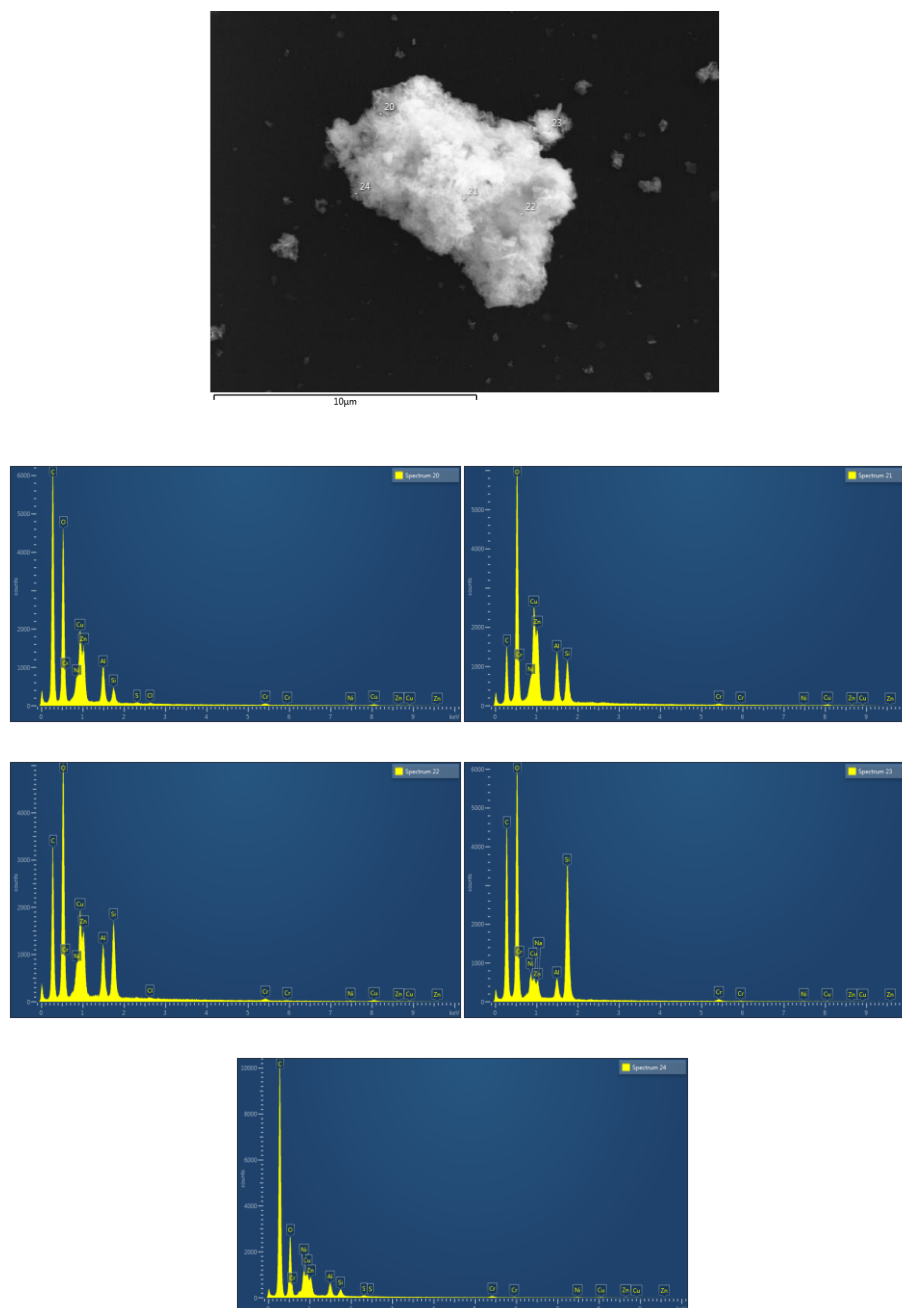


Figure A.13: (a) Electron image and (b-f) EDX elemental spectrum from point analysis ZSM5@Cu_{1.3}ZnAl-LDH SEM image.

Table A.3: Table of elemental weight percentage from point and ID of ZSM5@Cu_{1.3}ZnAl-LDH SEM image.

Element	Specimen 20 (wt%)	Specimen 21 (wt%)	Specimen 22 (wt%)	Specimen 23 (wt%)	Specimen 24 (wt%)
C	37.92	15.01	27.15	32.45	53.12
O	20.09	26.66	23.14	26.70	13.98
Al	3.18	5.48	4.05	0.22	1.81
Si	1.36	4.69	6.29	1.66	0.99
Cr	12.11	11.40	0.16	12.23	0.21
Ni	4.14	3.47	11.27	15.20	9.84
Cu	12.20	18.74	5.34	5.47	8.61
Zn	8.77	14.55	13.07	3.59	6.63

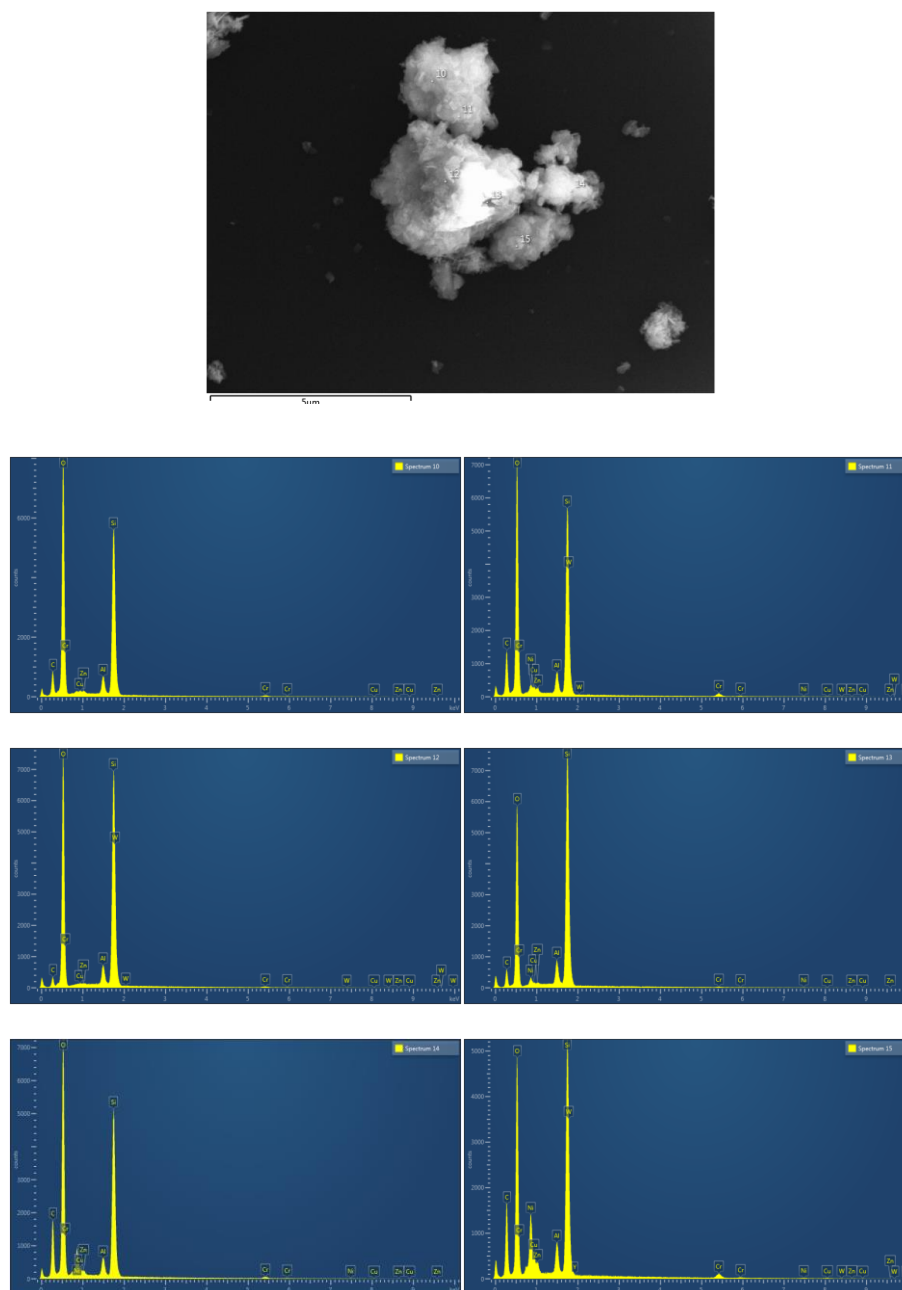


Figure A.14: Electron image and EDX elemental analysis spectrum from point and ID of ZSM5+Cu_{1.3}ZnAl-LDH SEM image.

Table A.4: Table of elemental weight percentage from point and ID of ZSM5+Cu_{1.3}ZnAl-LDH SEM image.

Element	Specimen 20 (wt%)	Specimen 21 (wt%)	Specimen 22 (wt%)	Specimen 23 (wt%)	Specimen 24 (wt%)
C	10.12	14.88	4.80	10.02	17.70
O	36.68	31.47	36.10	33.21	31.50
Al	2.36	2.35	2.50	3.16	2.00
Si	24.75	22.65	31.02	35.61	19.84
Cr	25.28	21.90	23.39	13.42	17.73
Cu	0.33	1.58	0.17	0.71	1.63
Zn	0.47	1.14	0.17	0.45	0.97

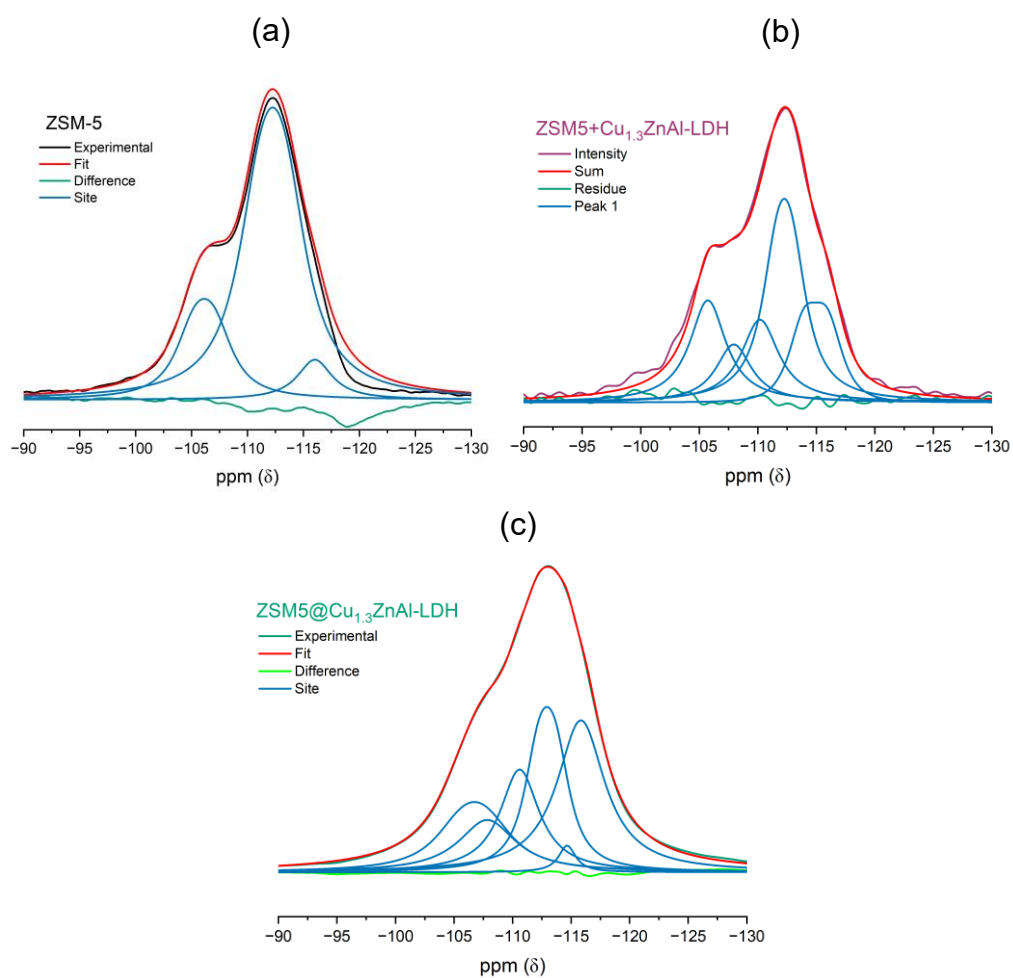


Figure A.15: ^{29}Si CPMAS NMR spectrum of (a) ZSM-5, (b) ZSM5+Cu_{1.3}ZnAl-LDH and (c) ZSM5@Cu_{1.3}ZnAl-LDH with peak deconvolution. Peak fittings were performed in Origin using a Pseudo-Voigt model.

Table A.5: ppm positions, relative areas and assignments of the different Si environments from the deconvoluted ^{29}Si CPMAS NMR spectra.

Sample	ppm position	Relative area (%)	Tentative assignment
ZSM-5	-106.1	20.3	Si(OSi) ₃ (OAl)
	-112.3	72.9	
	-116.0	6.8	Si(OSi) ₄
ZSM5+Cu _{1.3} ZnAl-LDH	-105.7	19.5	Si(OSi) ₃ (OAl)
	-108.0	10.8	
	-110.2	16.4	
	-112.3	36.4	Si(OSi) ₄
	-114.9	16.9	
ZSM5@Cu _{1.3} ZnAl-LDH	-106.7	2.01	Si(OSi) ₃ (OAl)
	-107.8	14.54	
	-110.6	19.56	
	-112.9	26.27	Si(OSi) ₄
	-114.7	2.21	
	-115.8	35.40	

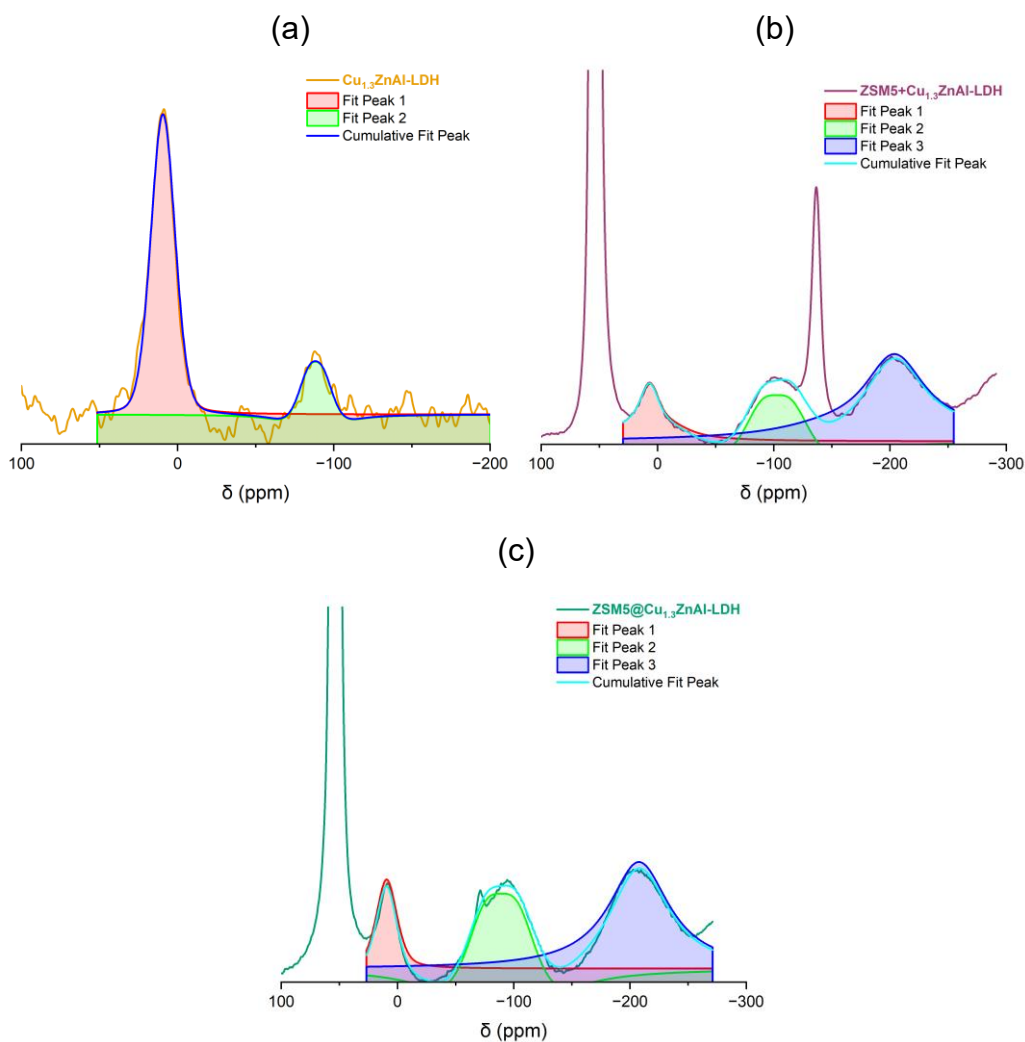


Figure A.16: ^{27}Al solid-state DPMAS NMR spectra of (a) $\text{Cu}_{1.3}\text{ZnAl-LDH}$, (b) $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDH}$ and (c) $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDH}$ with highlighted peak deconvolution. Peak fittings were performed in Origin using a Pseudo-Voigt model. (a) was not scanned out to -300 ppm, hence the peak at -200 ppm associated with AlO_4 is not present in the spectrum. (a) and (c) were scanned at 13 kHz whilst (b) was scanned at 20 kHz.

Table A.6: ppm positions, relative areas and assignments of the different Al environments from the deconvoluted ^{27}Al DPMAS NMR spectra.

Sample	ppm position	Relative area (%)	Tentative assignment
$\text{Cu}_{1.3}\text{ZnAl-LDH}$	9.4	90.5	AlO_6
	-88.3	9.5	
$\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDH}$	6.9	20.8	AlO_6
	-102.7	0.1	AlO_4
	-203.9	79.1	
$\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDH}$	9.3	18.7	AlO_6
	-89.3	0.1	AlO_4
	-207.8	81.2	

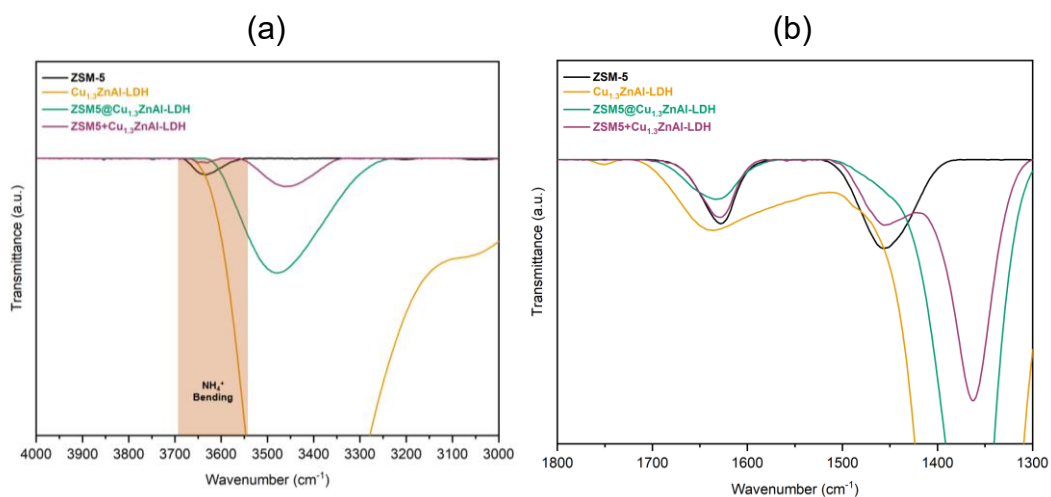


Figure A.17: Enlarged regions of the FTIR profiles of $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDH}$, $\text{ZSM5}+\text{Cu}_{1.3}\text{ZnAl-LDH}$, $\text{Cu}_{1.3}\text{ZnAl-LDH}$ and ZSM-5 between (a) 4000 – 3000 cm⁻¹ and (b) 1800 – 1300 cm⁻¹.

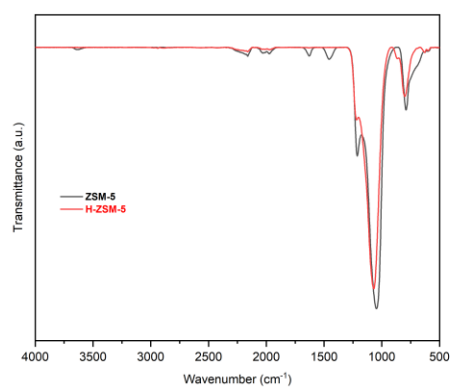


Figure A.18: FTIR profiles of as-purchased ZSM-5 (ammonium form) and synthesised H-ZSM-5.

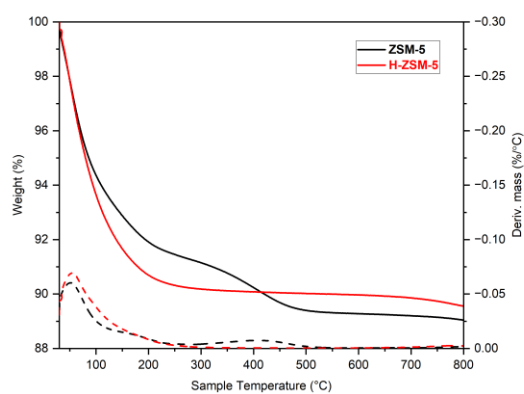


Figure A.19: TGA/dTGA of ZSM-5 and synthesised H-ZSM-5.

Table A.7: Summary of data from TGA including the weight loss percentages for the major weight loss regions (WLRs), the residual weights of the samples and the LDH:ZSM5 ratio.

Sample	WLR (%)			Residual	
	30 – 200 °C	200 – 400 °C	500 – 800 °C	weight (%)	LDH:ZSM5
ZSM5@Cu _{1.3} ZnAl-LDH	12.9	6.4	3.1	77.2	52:48
ZSM5+Cu _{1.3} ZnAl-LDH	12.7	6.8	3.2	77.3	52:48
Cu _{1.3} ZnAl-LDH	18.2	10.1	4.8	66.4	-
ZSM-5	8.1	1.7	0.4	89.1	-

Table A.8: BET surface areas and pore volumes of core, shell and core-shell samples in Section 2.2.2.

Sample	S_{External} (m ² /g)	S_{Micro} (m ² /g)	S_{BET} (m ² /g)	V_{Micro} (cm ³ /g)
ZSM-5	43	339	382	0.131
ZSM5-TPA	45	334	379	0.129
Cu _{1.3} ZnAl-LDH	44	18	63	0.008
Theoretical	44	179	223	0.069
ZSM5@Cu _{1.3} ZnAl-LDH	60	175	235	0.069
ZSM5+Cu _{1.3} ZnAl-LDH	60	175	235	0.059

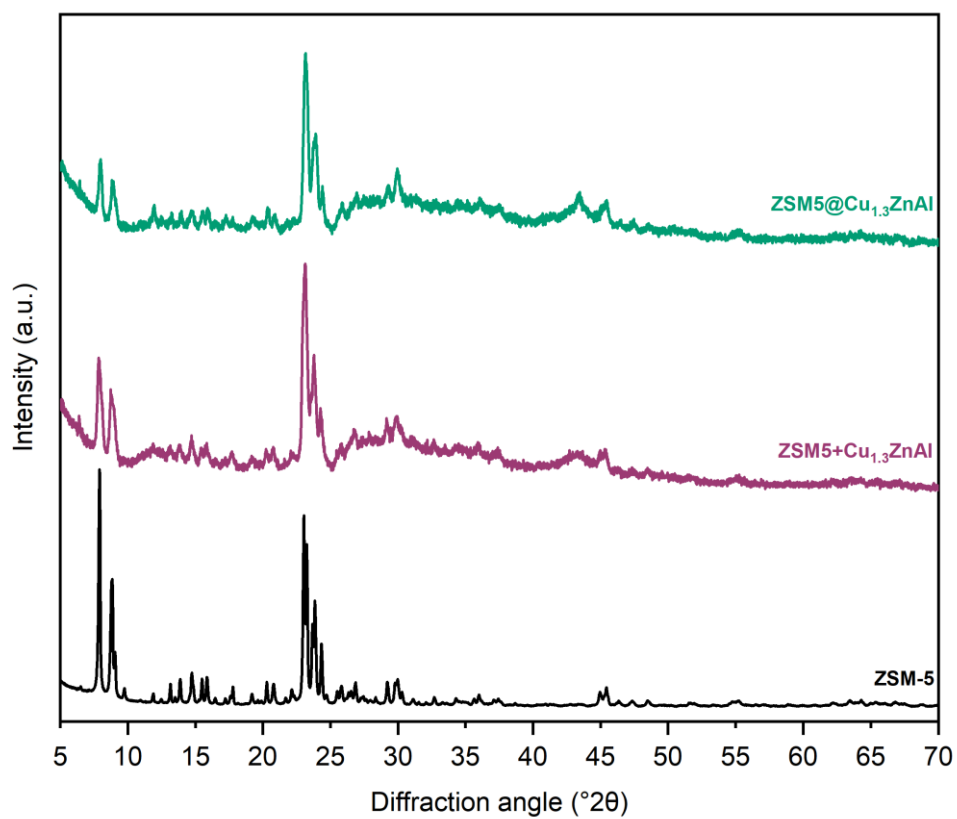


Figure A.20: PXRD profile of the ZSM5@Cu_{1.3}ZnAl, ZSM5+Cu_{1.3}ZnAl and Cu_{1.3}ZnAl catalysts against a ZSM-5.

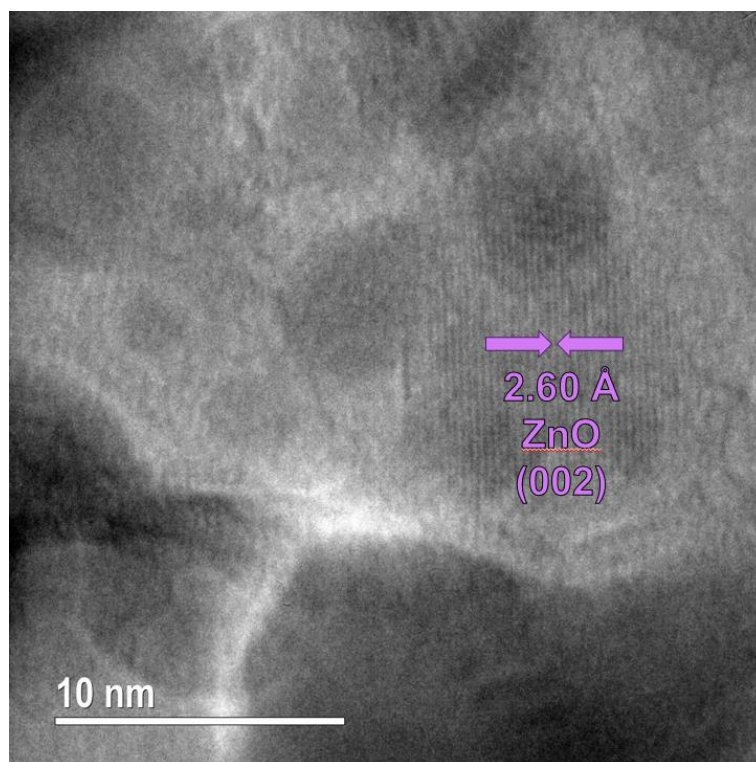


Figure A.21: TEM image of the $\text{Cu}_{1.3}\text{ZnAl}$ catalyst.

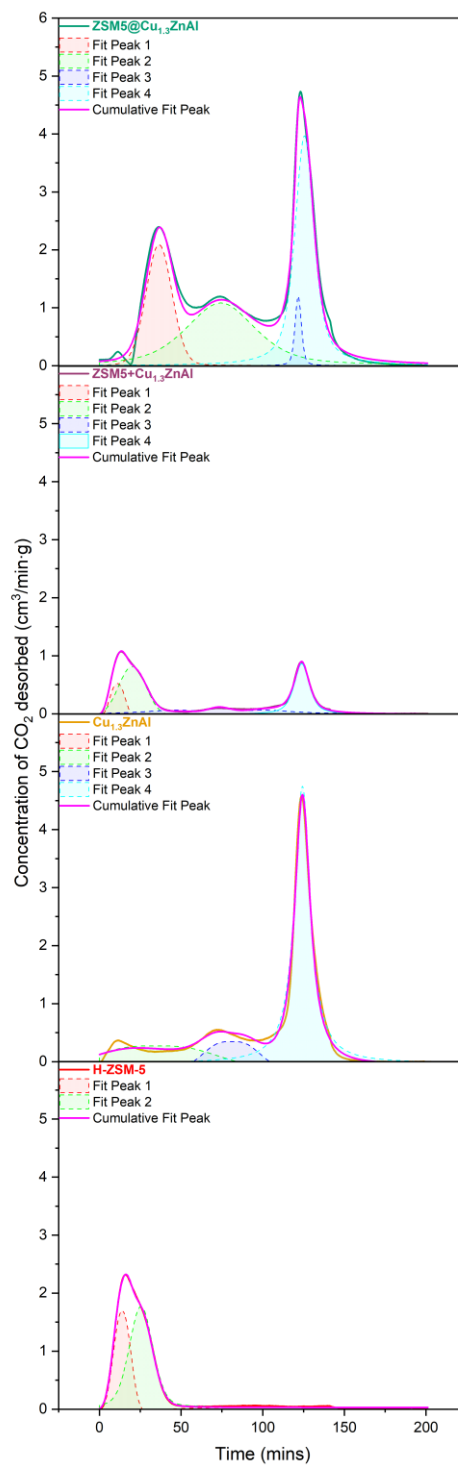


Figure A.22: CO₂-TPD of (a) ZSM5@Cu_{1.3}ZnAl, (b) ZSM5+Cu_{1.3}ZnAl, (c) Cu_{1.3}ZnAl and (d) H-ZSM-5 with highlighted peak deconvolution. Peak fittings were performed in Origin using a Pseudo-Voigt model.

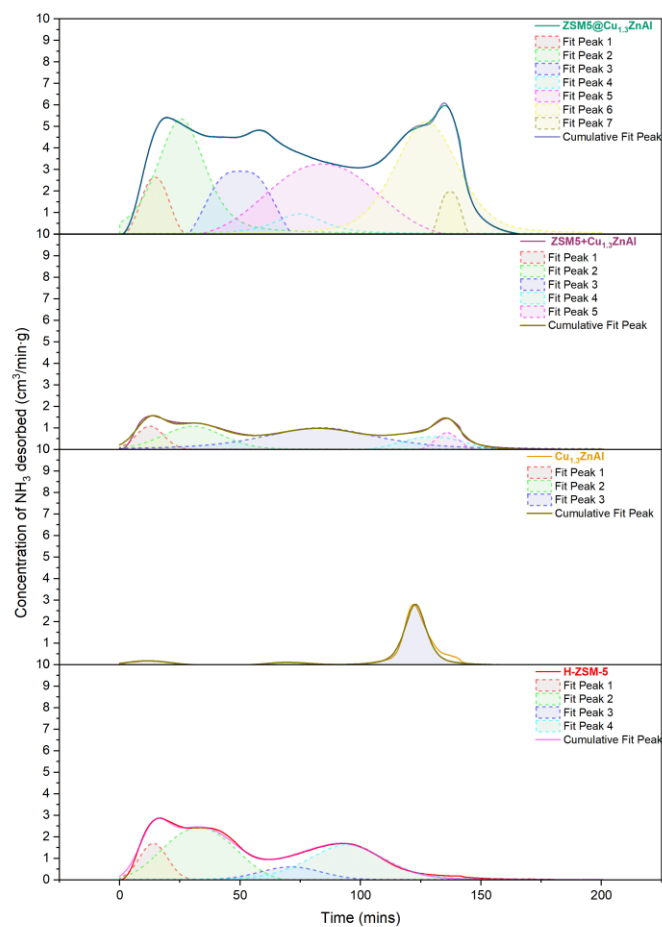


Figure A.23: NH_3 -TPD of (a) ZSM5@Cu_{1.3}ZnAl, (b) ZSM5+Cu_{1.3}ZnAl, (c) Cu_{1.3}ZnAl and (d) H-ZSM-5 with highlighted peak deconvolution. Peak fittings were performed in Origin using a Pseudo-Voigt model.

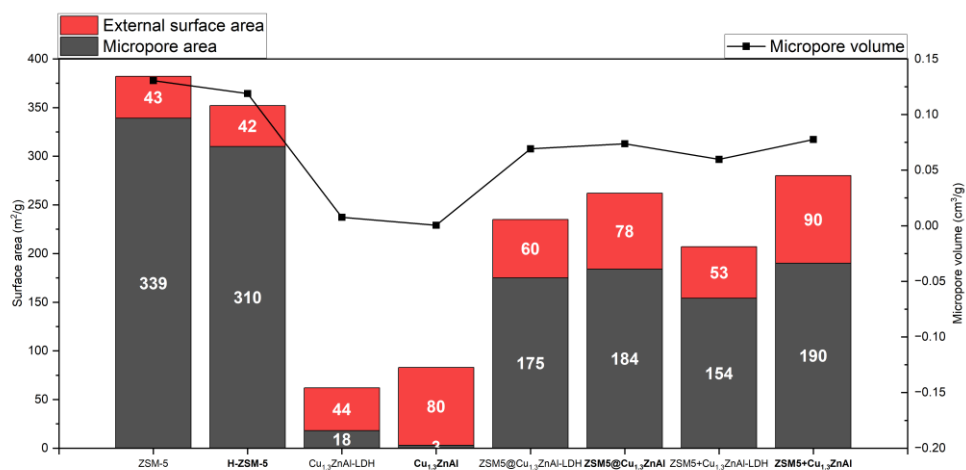


Figure A.24: N₂ BET surface areas of the activated ZSM5@Cu_{1.3}ZnAl, ZSM5+Cu_{1.3}ZnAl, Cu_{1.3}ZnAl and H-ZSM-5 catalysts (labels bolded for emphasis) compared against the precursor counterparts. The grey and red bars show the estimated micropore surface area and external surface area respectively, whilst the line plot shows the estimated micropore volume of the samples.

Table A.9: CO₂ hydrogenation results of N₂-, O₂- and air-treated ZSM5@Cu_{1.3}ZnAl.

Calcination environment	Temperature (°C)	Conversion (%)	Selectivity (%)			Yield (%)	STY _{DME} (g _{DME} /g _{cat} ·h)
			<i>S</i> _{DME}	<i>S</i> _{CH₃OH}	<i>S</i> _{CO}		
N ₂	260	0.8	0	0	99.6	0	0
	280	1.0	0	0	99.5	0	0
	300	2.1	23.2	0	76.2	1.6	0.13
	340	4.5	19.0	0	79.9	3.6	0.29
O ₂	260	12.5	34.7	9.5	55.8	4.3	0.35
	280	18.3	25.5	9.3	65.1	4.7	0.38
	300	22.2	17.6	7.8	74.3	3.9	0.32
	340	27.2	5.9	2.5	90.6	1.6	0.13
Air	220	3.9	64.0	8.9	27.1	2.5	0.20
	260	12.8	34.6	9.5	55.8	4.4	0.36
	280	17.9	25.4	9.3	65.2	4.5	0.37
	300	21.5	17.6	7.6	74.4	3.8	0.31

^aReaction conditions: $P = 3.0$ MPa, CO₂/H₂/N₂ = 24:72:4, and $WHSV = 18,000$ mL/g_{cat}·h.

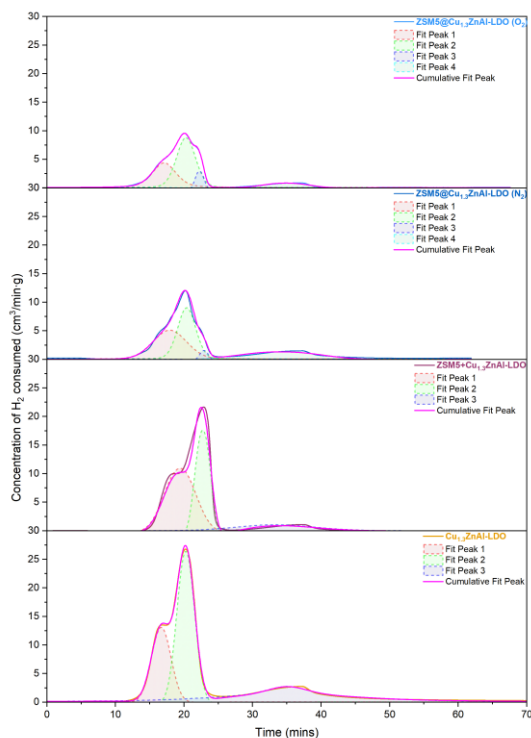


Figure A.25: Deconvoluted H₂-TPR profiles of the O₂ and N₂-calcined ZSM5@Cu_{1.3}ZnAl-LDO, ZSM5+Cu_{1.3}ZnAl-LDO and Cu_{1.3}ZnAl-LDO catalysts with highlighted peak deconvolution. Peak fittings were performed in Origin using a Pseudo-Voigt model.

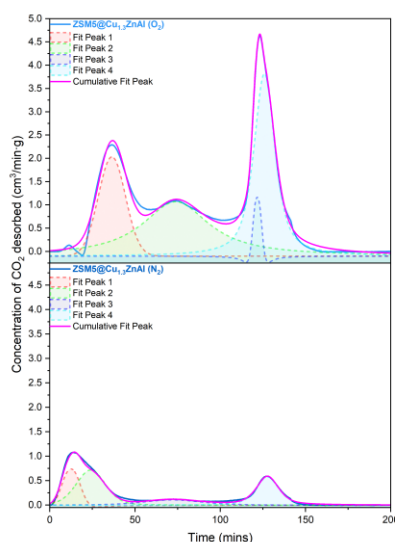


Figure A.26: CO₂-TPD of (a) O₂-calcined ZSM5@Cu_{1.3}ZnAl and (b) N₂-calcined ZSM5+Cu_{1.3}ZnAl with highlighted peak deconvolution. Peak fittings were performed in Origin using a Pseudo-Voigt model.

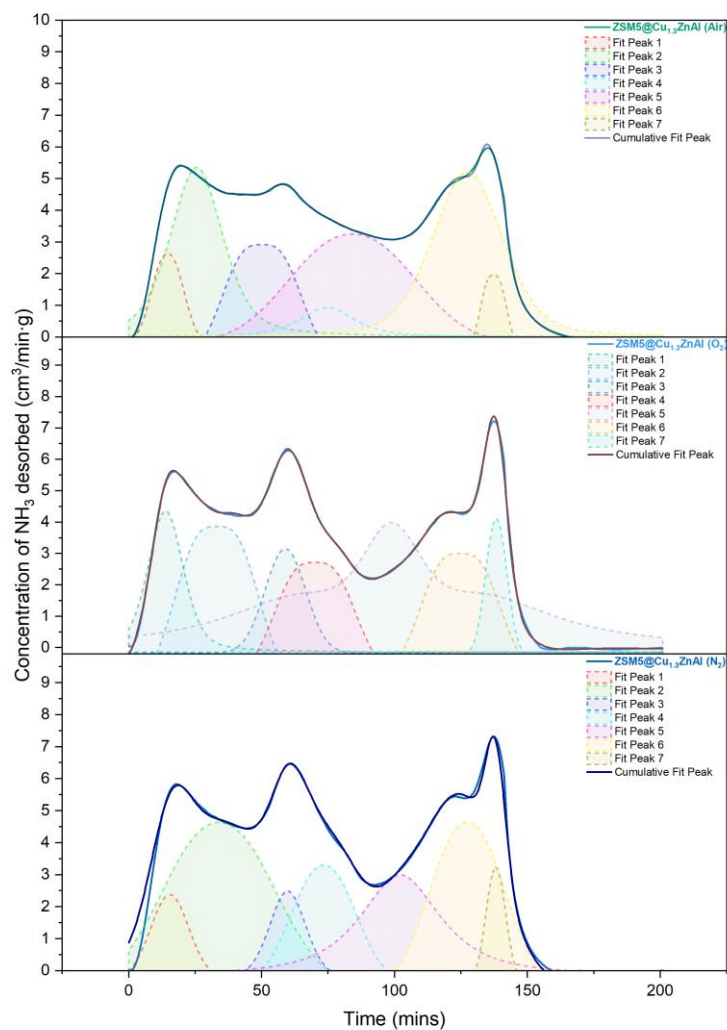


Figure A.27: NH_3 -TPD of ZSM5@Cu_{1.3}ZnAl calcined in (a) air, (b) O_2 and (c) N_2 with highlighted peak deconvolution. Peak fittings were performed in Origin using a Pseudo-Voigt model.

B

Appendix for Chapter 3

Table B.1: Details of the Rietveld refinement and structural parameters for ZSM5@Cu_{1.3}ZnAl-LDH-TPA, ZSM5@Cu_{1.3}ZnAl-LDH-Na, and ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ against Cu_{1.3}ZnAl-LDH-TPA and ZSM-5. Refinements were performed on PXRD data from Ill Diamond.

Sample	Phase component	Space group	R _{wp} (%)	GOF (%)	a (Å)	b (Å)	c (Å)
ZSM5@Cu _{1.3} ZnAl-LDH-TPA	LDH	R-3m	1.12	3.35	3.081242(3)	3.081242(3)	22.779866(2)
	Zeolite	Pnma			20.114915(1)	19.915277(2)	13.419283(1)
ZSM5@Cu _{1.3} ZnAl-LDH-Na	LDH	R-3m	2.34	5.98	3.068038(8)	3.068038(8)	22.792180(3)
	Zeolite	Pnma			20.140917(4)	19.938102(5)	13.430808(6)
ZSM5@Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	LDH	R-3m	2.29	5.76	3.074375(2)	3.074375(2)	22.706101(2)
	Zeolite	Pnma			20.193872(5)	19.992011(8)	13.484601(7)
ZSM5+Cu _{1.3} ZnAl-LDH-TPA	LDH	R-3m	3.32	7.16	3.074758(4)	3.074758(4)	22.729622(2)
	Zeolite	Pnma			20.157083(7)	19.952853(1)	13.452744(1)

Table B.2: Scherrer parameters for the calculation of the LDH domain length in the TPA-, Na- and Na_2CO_3 -treated $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH}$ core-shells. Values calculated from data collected on I11 Diamond Light Source.

Sample	2θ ($^\circ$)	Reflection planes	FWHM (radians)	Domain length (nm)
ZSM5@Cu _{1.3} ZnAl-LDH-TPA	6.23	(003)	0.00403	18.4
	12.47	(006)	0.00463	15.9
	31.06	(110)	0.00578	12.4
ZSM5@Cu _{1.3} ZnAl-LDH-Na	6.23	(003)	0.00591	12.5
	12.47	(006)	0.00856	8.6
	29.23	(110)	0.01488	4.8
ZSM5@Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	6.25	(003)	0.00298	24.9
	12.52	(006)	0.00432	17.1
	31.13	(110)	0.00807	8.9

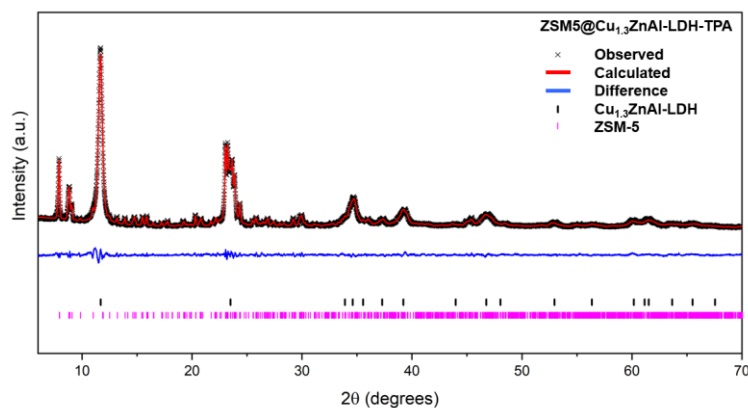


Figure B.1: Two-phase Rietveld refinement of $\text{ZSM5@Cu}_{1.3}\text{ZnAl-LDH-TPA}$ against ZSM-5 and $\text{Cu}_{1.3}\text{ZnAl-LDH}$. PXRD data was collected from a Bruker D8 ECO diffractometer.

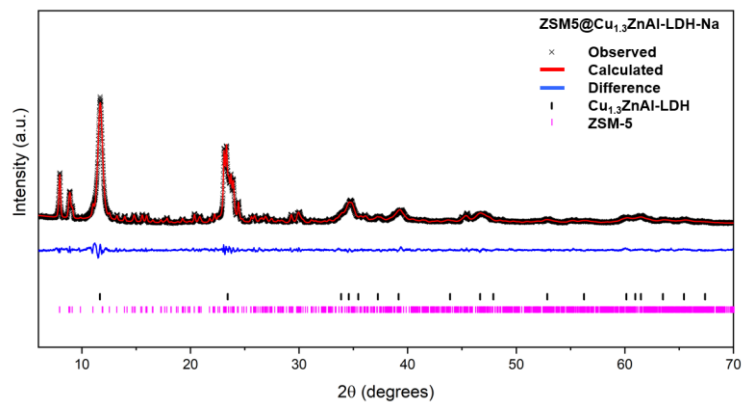


Figure B.2: Two-phase Rietveld refinement of ZSM5@Cu_{1.3}ZnAl-LDH-Na against ZSM-5 and Cu_{1.3}ZnAl-LDH. PXRD data was collected from a Bruker D8 ECO diffractometer.

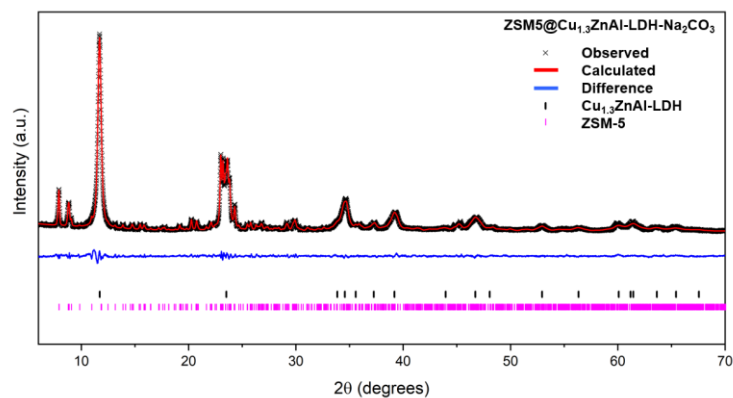


Figure B.3: Two-phase Rietveld refinement of ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃ against ZSM-5 and Cu_{1.3}ZnAl-LDH. PXRD data was collected from a Bruker D8 ECO diffractometer.

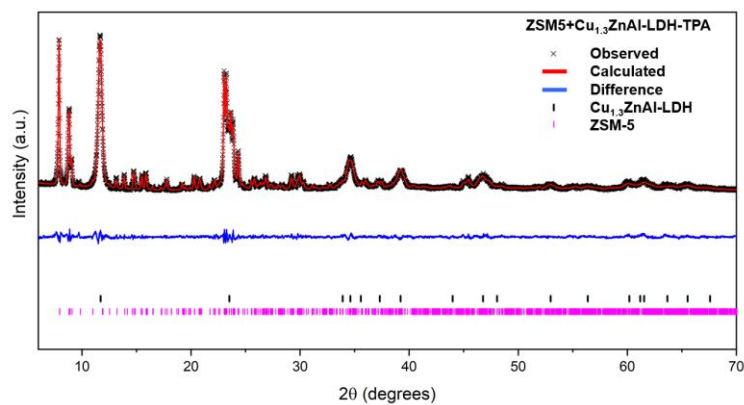


Figure B.4: Two-phase Rietveld refinement of ZSM5+Cu_{1.3}ZnAl-LDH-TPA against ZSM-5 and Cu_{1.3}ZnAl-LDH. PXRD data was collected from a Bruker D8 ECO diffractometer.

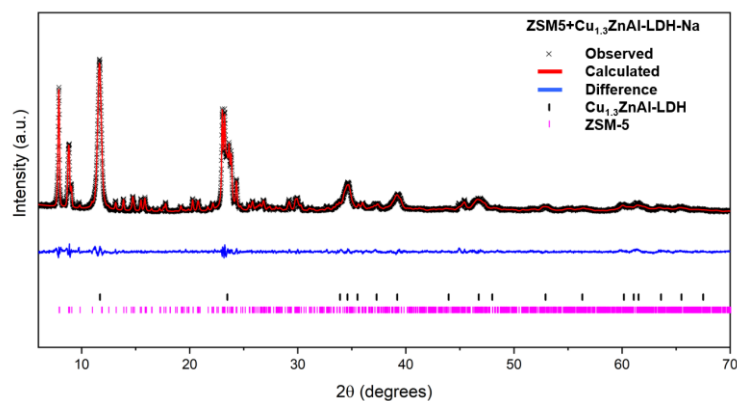


Figure B.5: Two-phase Rietveld refinement of ZSM5+Cu_{1.3}ZnAl-LDH-Na against ZSM-5 and Cu_{1.3}ZnAl-LDH. PXRD data was collected from a Bruker D8 ECO diffractometer.

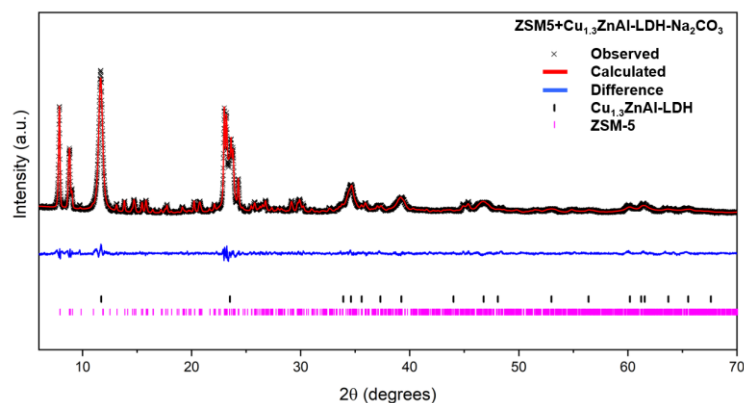


Figure B.6: Two-phase Rietveld refinement of ZSM5+Cu_{1.3}ZnAl-LDH-Na₂CO₃ against ZSM-5 and Cu_{1.3}ZnAl-LDH. PXRD data was collected from a Bruker D8 ECO diffractometer.

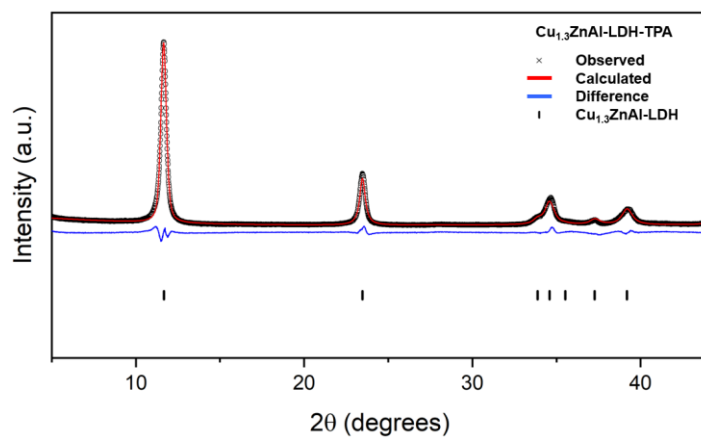


Figure B.7: Single-phase Rietveld refinement of $\text{Cu}_{1.3}\text{ZnAl-LDH-TPA}$. PXRD data was collected from a Bruker D8 ECO diffractometer.

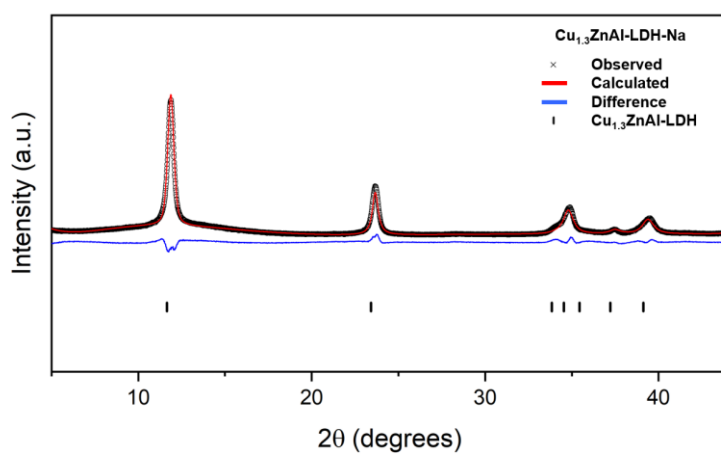


Figure B.8: Single-phase Rietveld refinement of $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}$. PXRD data was collected from a Bruker D8 ECO diffractometer.

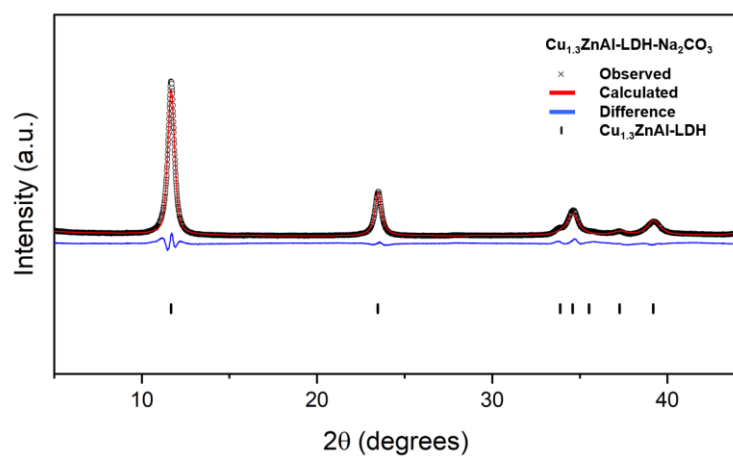


Figure B.9: Single-phase Rietveld refinement of $\text{Cu}_{1.3}\text{ZnAl-LDH-Na}_2\text{CO}_3$. PXRD data was collected from a Bruker D8 ECO diffractometer.

Table B.3: Details of the Rietveld refinement and structural parameters for the core-shell, physical mixtures, LDHs and ZSM-5 zeolites treated in different bases.

Refinements were performed on PXRD data from a Bruker D8 ECO diffractometer.

Sample	Phase component	Space group	R_{wp} (%)	GOF (%)	a (Å)	b (Å)	c (Å)
ZSM5@Cu _{1.3} ZnAl-LDH-TPA	LDH	R-3m	3.83	1.97	3.076630(4)	3.076630(4)	22.739607(2)
	Zeolite	Pnma			20.157519(1)	19.959282(1)	13.437835(8)
ZSM5@Cu _{1.3} ZnAl-LDH-Na	LDH	R-3m	3.77	1.87	3.078624(5)	3.078624(5)	22.804461(2)
	Zeolite	Pnma			20.155658(1)	19.947700(1)	13.438191(1)
ZSM5@Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	LDH	R-3m	4.06	2.12	3.080703(4)	3.080703(4)	22.731570(3)
	Zeolite	Pnma			20.203954(1)	20.008978(2)	13.485988(1)
ZSM5+Cu _{1.3} ZnAl-LDH-TPA	LDH	R-3m	5.46	1.67	3.076024(4)	3.076024(4)	22.731855(2)
	Zeolite	Pnma			20.144482(8)	19.952001(9)	13.450443(8)
ZSM5+Cu _{1.3} ZnAl-LDH-Na	LDH	R-3m	5.58	1.74	3.076493(4)	3.076493(4)	22.714095(2)
	Zeolite	Pnma			20.120993(1)	19.934205(1)	13.443882(9)

Sample	Phase component	Space group	R_{wp} (%)	GOF (%)	a (Å)	b (Å)	c (Å)
ZSM5+Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	LDH	R-3m	5.43	1.69	3.076119(5)	3.076119(5)	22.719997(2)
	Zeolite	Pnma			20.167556(7)	19.976171(1)	13.482275(9)
Cu _{1.3} ZnAl-LDH-TPA	LDH	R-3m	6.47	3.87	3.074188(2)	3.074188(2)	22.727345(3)
Cu _{1.3} ZnAl-LDH-Na	LDH	R-3m	6.93	4.18	3.077289(3)	3.077289(3)	22.777359(3)
Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	LDH	R-3m	6.80	3.99	3.074921(3)	3.074921(3)	22.731865(3)
ZSM-5	Zeolite	Pnma	9.86	3.62	20.151350(6)	19.948898(6)	13.450295(6)
ZSM5-TPA	Zeolite	Pnma	11.7	2.57	20.154740(5)	19.950457(7)	13.449252(6)
ZSM5-Na	Zeolite	Pnma	10.5	3.56	20.166898(6)	19.975395(7)	13.447469(7)
ZSM5-Na ₂ CO ₃	Zeolite	Pnma	10.7	4.55	20.182772(6)	19.974915(7)	13.458887(6)

Table B.4: Scherrer parameters for the calculation of the LDH crystal size in the core-shells, physical mixtures and LDH samples treated in different bases. Estimations were calculated from data collected from a Bruker D8 ECO diffractometer.

Sample	2 θ (°)	Reflection planes	FWHM (radians)	Domain length (nm)
ZSM5@Cu _{1.3} ZnAl- LDH-TPA	11.6635	(003)	0.00742	18.6
	23.4628	(006)	0.01003	13.6
	60.2771	(110)	0.01634	7.4
ZSM5@Cu _{1.3} ZnAl- LDH-Na	11.6891	(003)	0.00866	17.0
	23.4622	(006)	0.01269	10.7
	60.4767	(110)	0.02227	5.4
ZSM5@Cu _{1.3} ZnAl- LDH-Na ₂ CO ₃	11.6909	(003)	0.00646	21.4
	23.5046	(006)	0.00936	14.5
	60.0717	(110)	0.01913	6.3
ZSM5+Cu _{1.3} ZnAl- LDH-TPA	11.6555	(003)	0.00703	19.7
	23.4713	(006)	0.00960	14.2
	60.1932	(110)	0.01674	7.2
ZSM5+Cu _{1.3} ZnAl- LDH-Na	11.6461	(003)	0.00686	20.2
	23.4442	(006)	0.00947	14.4
	60.1346	(110)	0.01710	7.0
ZSM5+Cu _{1.3} ZnAl- LDH-Na ₂ CO ₃	11.6551	(003)	0.00734	18.9
	23.4782	(006)	0.01108	12.3
	60.1402	(110)	0.01708	7.0
Sample	2 θ (°)	Reflection planes	FWHM (radians)	Domain length (nm)

Cu _{1.3} ZnAl-LDH-TPA	11.6528	(003)	0.00685	20.2
	23.4705	(006)	0.00722	18.8
	60.1769	(110)	0.01807	6.7
Cu _{1.3} ZnAl-LDH-Na	11.8770	(003)	0.00748	18.5
	23.6685	(006)	0.00711	19.1
	60.3929	(110)	0.02004	6.0
Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	11.6778	(003)	0.00811	17.1
	23.4943	(006)	0.00792	17.2
	60.2348	(110)	1.00033	6.9

Table B.5: Point analysis information from the SEM/EDX of ZSM5@Cu_{1.3}ZnAl-LDH-Na.

Element	Point 2	Point 3	Point 4	Point 5	Point 6
	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)
C	44.21	32.63	34.66	46.67	51.14
O	25.19	40.18	28.10	30.93	24.62
Al	3.54	2.13	3.63	0.31	2.40
Si	4.30	19.15	10.13	1.51	2.68
Cl	1.56	-	0.89	11.86	0.81
Cr	1.36	1.98	4.82	0.14	3.00
Ni	0.00	0.98	0.79	4.17	0.56
Cu	11.51	1.29	9.71	0.97	8.37
Zn	8.33	1.66	7.27	1.79	6.15

Table B.6: SEM/EDX with point *analysis* information for ZSM5+Cu_{1.3}ZnAl-LDH-Na.

Element	Point 4 (wt%)	Point 8 (wt%)
C	13.33	15.67
O	40.73	18.82
Al	2.68	4.58
Cl	-	2.46
Si	27.67	2.65
Ni	11.64	25.14
Cu	2.28	17.81
Zn	1.67	12.88

Table B.7: SEM/EDX with point and ID information for ZSM5@Cu_{1.3}ZnAl-LDH-Na₂CO₃.

Element	Point 2 (wt%)	Point 3 (wt%)	Point 4 (wt%)	Point 5 (wt%)	Point 6 (wt%)
C	30.71	27.01	26.90	26.61	32.37
O	26.25	25.98	21.97	22.14	19.49
Al	5.54	5.68	5.12	6.67	4.79
Si	2.79	3.01	2.80	13.22	1.65
Cl	1.85	2.16	1.69	2.03	0.13
Cr	0.00	0.00	0.00	0.00	2.47
Ni		1.24	10.34	3.84	0.00
Cu	19.11	20.44	17.70	15.51	10.23
Zn	13.76	14.47	13.48	9.96	15.64

Table B.8: SEM/EDX with point and ID information for ZSM5+Cu_{1.3}ZnAl-LDH-Na₂CO₃.

Element	Point 1 (wt%)	Point 2 (wt%)	Point 4 (wt%)	Point 5 (wt%)
C	32.06	31.36	18.78	21.22
O	23.29	17.02	21.05	25.00
Al	1.64	3.05	4.60	2.28
Si	9.92	1.13	1.88	11.87
Cl	-	1.34	-	-
Ni	28.13	24.80	21.64	28.52
Cu	2.79	12.31	18.40	6.36
Zn	2.16	9.00	13.65	4.75

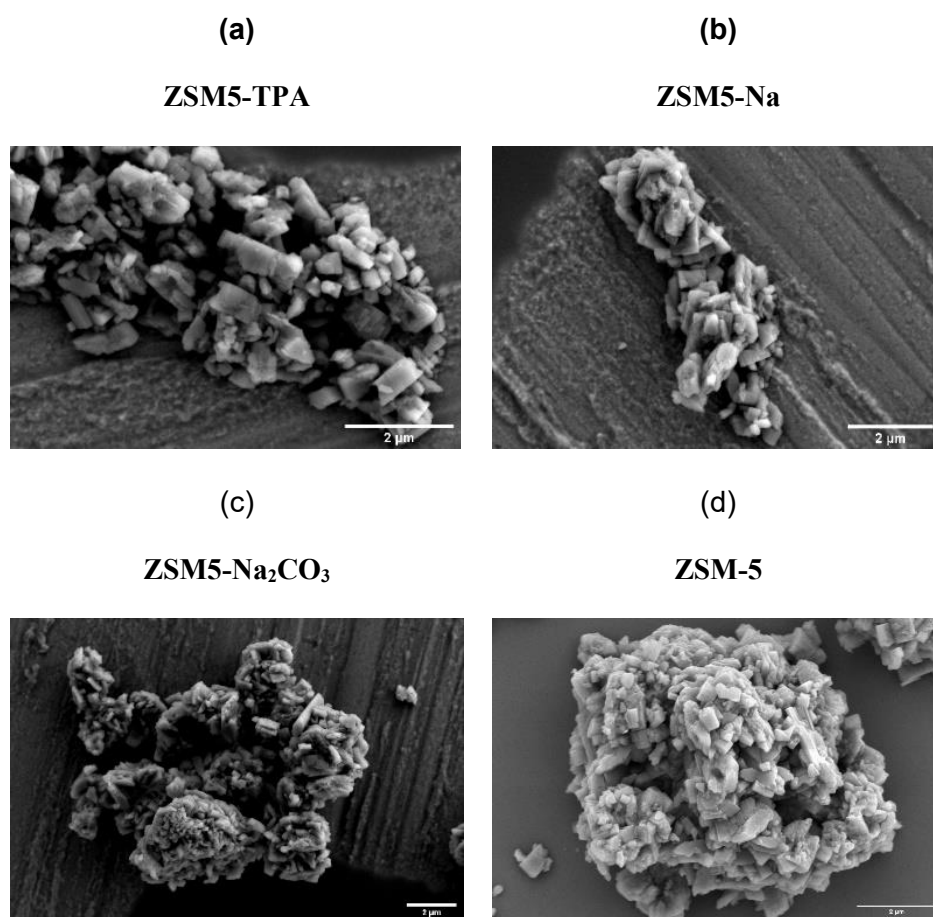


Figure B.10: SEM images of (a) ZSM5-TPA, (b) ZSM5-Na, and (c) ZSM5-Na₂CO₃ and (d) pristine ZSM-5.

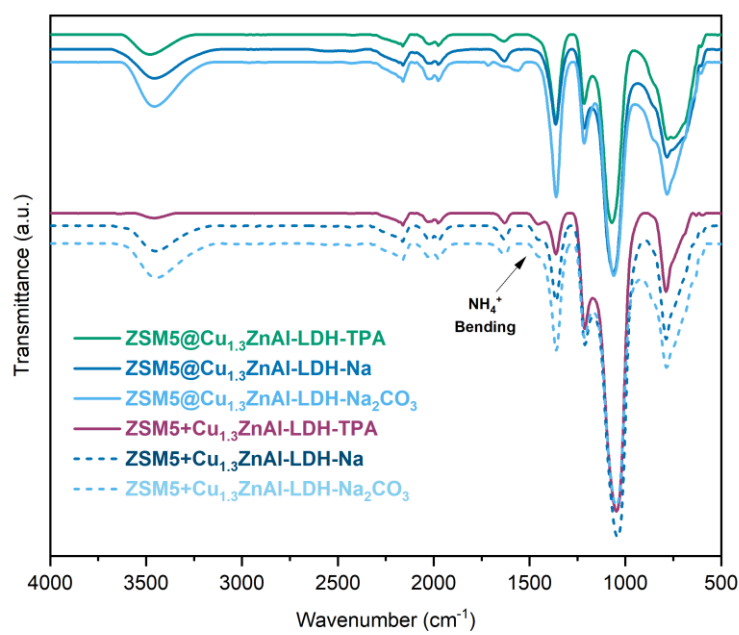


Figure B.11: FTIR absorbance spectra of TPA-, Na- and Na_2CO_3 -treated core-shells and physical mixtures.

Table B.9: Table of FTIR absorbance frequencies and associated functional groups for the core-shells, physical mixtures and zeolites treated with different bases.

Sample	Frequency (cm ⁻¹)	Functional group
	3670 – 2760	O–H stretching
	1630	H ₂ O bending
ZSM5@Cu _{1.3} ZnAl-LDH-TPA, ZSM5@Cu _{1.3} ZnAl-LDH-Na,	1360	ν_3 -CO ₃ ²⁻ stretching
	~1210	SiO ₄ tetrahedron units
ZSM5@Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	1041	Si–O–T (T = Si or Al)
		CO ₃ ²⁻ bending mode, M ^{x+} –O,
	780	M ^{x+} –OH and O–M ^{x+} –O lattice vibrations

Sample	Frequency (cm ⁻¹)	Functional group
	3670 – 2760	O-H stretching
	1630	H ₂ O bending
	~1450	NH ₄ ⁺ bending
ZSM5+Cu _{1.3} ZnAl-LDH-TPA, ZSM5+Cu _{1.3} ZnAl-LDH-Na, ZSM5+Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	1360	ν_3 -CO ₃ ²⁻ stretching
	~1210	SiO ₄ tetrahedron units
	1041	Si-O-T (T = Si or Al)
	780	CO ₃ ²⁻ bending mode, M ^{x+} -O, M ^{x+} -OH and O-M ^{x+} -O lattice vibrations

Sample	Frequency (cm ⁻¹)	Functional group
ZSM-5, ZSM5-TPA, ZSM5-Na, ZSM5-Na ₂ CO ₃	1630	O-H stretching band
	~1450	NH ₄ ⁺ bending
	~1210	Asymmetric stretching vibration
	1041	Internal asymmetric stretching vibration of Si–O–T (T = Si/Al)
	788	Symmetric stretching of the T–O in external linkages
	1630	O-H stretching band

Table B.10: Summary of data from TGA including the weight loss percentages for the major weight loss regions (WLRs), the residual weights of the samples and the LDH:ZSM5 ratio of the Na- and Na₂CO₃-treated core-shells and physical mixtures.

Sample	WLR			Residual weight (%)	LDH:ZSM-5
	30 – 200 °C	200 – 400 °C	500 – 800 °C		
ZSM5@Cu _{1.3} ZnAl-LDH-TPA	12.9	6.4	3.1	77.2	52:48
ZSM5@Cu _{1.3} ZnAl-LDH-Na	13.1	5.9	1.8	77.7	50:50
ZSM5@Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	11.3	9.8	2.5	75.9	57:43
ZSM5+Cu _{1.3} ZnAl-LDH-TPA	12.7	6.8	3.2	77.3	52:48
ZSM5+Cu _{1.3} ZnAl-LDH-Na	12.6	6.3	3.1	77.3	53:47
ZSM5+Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	13.0	6.6	3.4	76.4	57:43
Cu _{1.3} ZnAl-LDH-TPA	18.2	10.1	4.8	66.4	-

Sample	WLR			Residual weight (%)	LDH:ZSM-5
	30 – 200 °C	200 – 400 °C	500 – 800 °C		
Cu _{1.3} ZnAl-LDH-Na	18.1	9.0	5.3	67.0	-
Cu _{1.3} ZnAl-LDH-Na ₂ CO ₃	17.3	9.7	5.5	66.7	-
ZSM-5	8.1	1.7	0.4	89.1	-
ZSM5-TPA	7.8	1.8	0.4	89.1	-
ZSM5-Na	8.2	2.5	0.4	88.6	-
ZSM5-Na ₂ CO ₃	8.3	2.9	0.3	88.2	-

Table B.11: Summary of the textural properties of the core-shells, physical mixtures and zeolites treated with different bases. Also included are the theoretical surface areas of the hybrid core-shell based on the experimentally determined surface areas of the separate LDH and ZSM-5 phase.

Sample	$S_{\text{External}} \text{ (m}^2\text{/g)}$	$S_{\text{Micropore}} \text{ (m}^2\text{/g)}$	$S_{\text{BET}} \text{ (m}^2\text{/g)}$	$V_{\text{Micro}} \text{ (cm}^3\text{/g)}$
ZSM-5	43	339	382	0.131
ZSM5-TPA	45	334	379	0.129
ZSM5-Na	46	360	405	0.138
ZSM5-Na ₂ CO ₃	49	326	375	0.126
Cu _{1.3} ZnAl-TPA	44	18	62	0.008
Cu _{1.3} ZnAl-Na	55	1	56	0
Cu _{1.3} ZnAl-Na ₂ CO ₃	65	1	66	0
Theoretical	44	179	223	0.069
ZSM5@Cu _{1.3} ZnAl-TPA				
Theoretical	51	72	236	0.069
ZSM5@Cu _{1.3} ZnAl-Na				

Sample	S_{External} (m^2/g)	$S_{\text{Micropore}}$ (m^2/g)	S_{BET} (m^2/g)	V_{Micro} (cm^3/g)
Theoretical	57	164	221	0.063
ZSM5@Cu _{1.3} ZnAl- Na ₂ CO ₃				
ZSM5@Cu _{1.3} ZnAl- TPA	60	175	235	0.069
ZSM5@Cu _{1.3} ZnAl- Na	86	159	245	0.064
ZSM5@Cu _{1.3} ZnAl- Na ₂ CO ₃	77	80	156	0.033
ZSM5+Cu _{1.3} ZnAl- TPA	53	154	207	0.060
ZSM5+Cu _{1.3} ZnAl- Na	57	186	243	0.072
ZSM5+Cu _{1.3} ZnAl- Na ₂ CO ₃	34	119	153	0.046

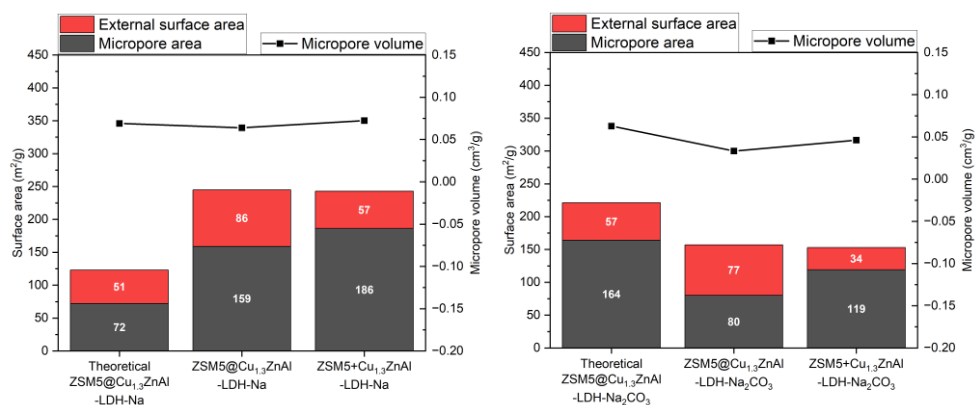


Figure B.12: N₂ BET surface areas of (a) Na-treated and (b) Na₂CO₃-treated core-shells and physical mixtures compared against the theoretical hybrid surface areas (calculated from experimental data). The grey and red bars show the estimated micropore surface area and external surface area respectively, while the line plot shows the estimated micropore volume of the samples.

Table B.12: ICP-MS/CHN elemental analysis of the ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$)₂-LDH and (ZSM5)₂@ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH core-shell precursor catalysts.

Sample	Cu (wt%)	Zn (wt%)	Al (wt%)	Cu:Zn:Al	C (wt%)	H (wt%)	N (wt%)
ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$) ₂ -LDH	18.35	12.84	5.46	1.39:1.00:1.01	1.80	1.97	0.35
(ZSM5) ₂ @ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH	9.89	6.36	3.56	1.47:1.00:1.24	0.80	1.56	0.84

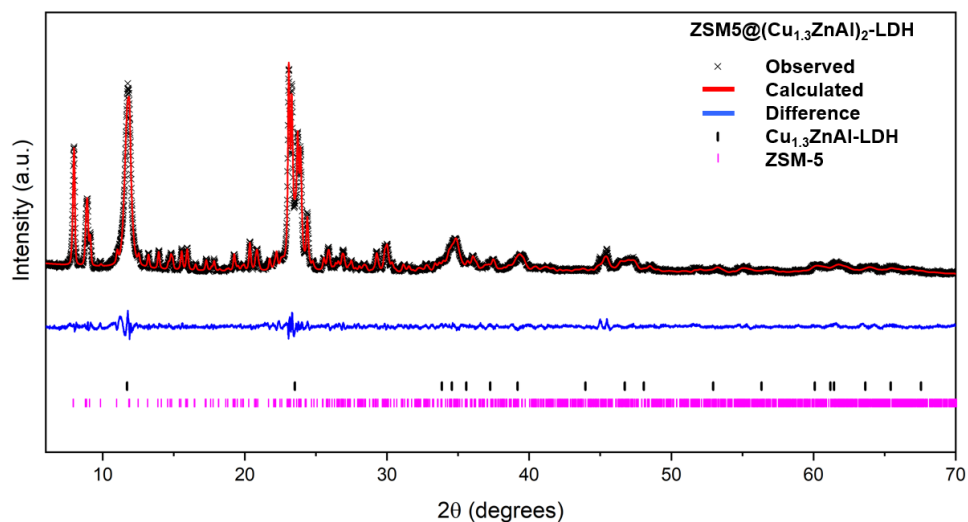


Figure B.13: Two-phase Rietveld refinement of $\text{ZSM5}@\text{Cu}_{1.3}\text{ZnAl-LDH}$ against ZSM-5 and $\text{Cu}_{1.3}\text{ZnAl-LDH}$. PXRD data was collected from a Bruker D8 ECO diffractometer.

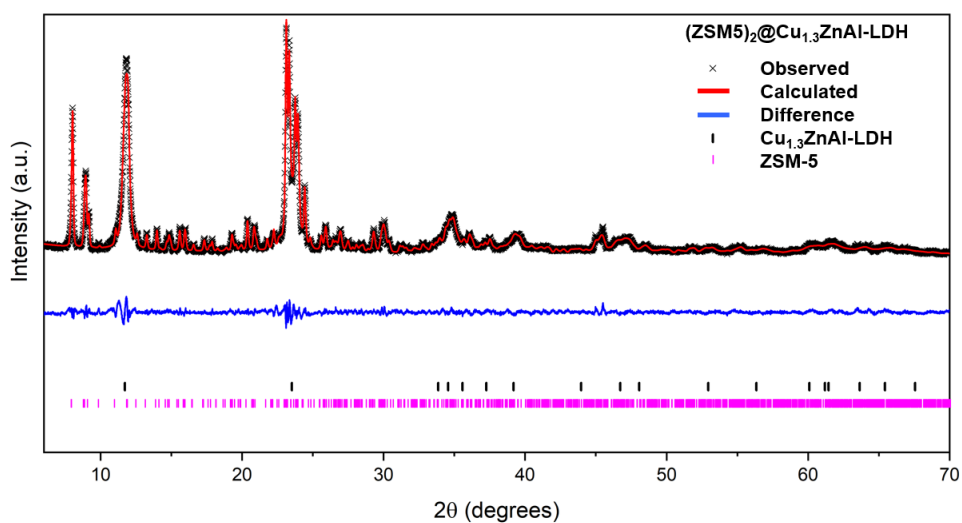


Figure B.14: Two-phase Rietveld refinement of $(\text{ZSM5})_2@\text{Cu}_{1.3}\text{ZnAl-LDH}$ against ZSM-5 and $\text{Cu}_{1.3}\text{ZnAl-LDH}$. PXRD data was collected from a Bruker D8 ECO diffractometer.

Table B.13: Details of the Rietveld refinement and structural parameters for ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$)₂-LDH and (ZSM5)₂@ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH core-shell precursor catalysts.

Refinements were performed on PXRD data from a Bruker D8 ECO diffractometer.

Sample	Phase component	Space group	R_{wp} (%)	GOF (%)	a (Å)	b (Å)	c (Å)
ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$) ₂ -LDH	LDH	R-3m	4.09	1.90	3.073637(7)	3.073637(7)	22.676662(3)
	Zeolite	Pnma			20.160155(5)	19.963104(9)	13.457305(8)
(ZSM5) ₂ @ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH	LDH	R-3m	3.28	2.01	3.068375(9)	3.068375(9)	22.715982(3)
	Zeolite	Pnma			20.175076(6)	19.977310(9)	13.468669(8)

Table B.14: Scherrer parameters for the calculation of the LDH crystal domain lengths in the ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$)₂-LDH and (ZSM5)₂@ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH precursor catalysts. Estimations were calculated from data collected from a Bruker D8 ECO diffractometer.

Sample	2 θ (°)	Reflection planes	FWHM (radians)	Domain length (nm)
ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$) ₂ -LDH	11.7622	(003)	0.08564	16.1
	23.6061	(006)	0.00886	15.3
	60.2742	(110)	0.01996	6.0
(ZSM5) ₂ @ $\text{Cu}_{1.3}\text{ZnAl}$ -LDH	11.7954	(003)	0.008438	16.4
	23.6197	(006)	0.013417	10.1
	60.4445	(110)	0.021586	5.6

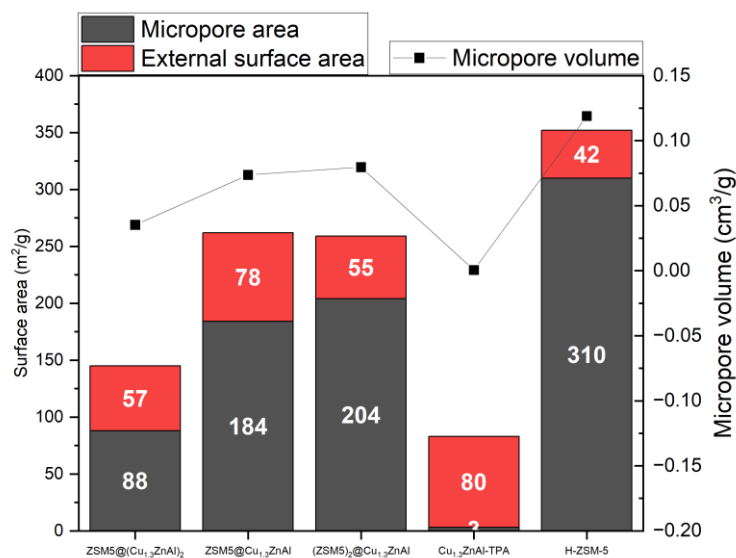


Figure B.15: N₂ BET surface areas of ZSM5@($\text{Cu}_{1.3}\text{ZnAl}$)₂ and (ZSM5)₂@ $\text{Cu}_{1.3}\text{ZnAl}$ core-shell catalysts compared against ZSM5@ $\text{Cu}_{1.3}\text{ZnAl}$, $\text{Cu}_{1.3}\text{ZnAl}$ and H-ZSM-5.

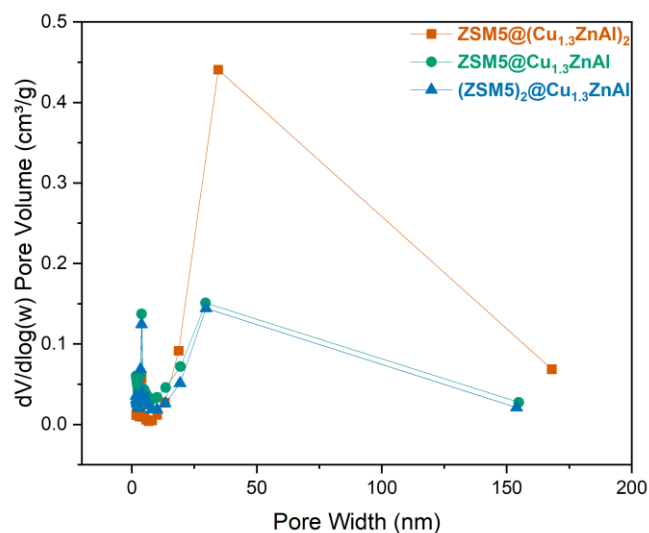


Figure B.16: BJH pore size distributions of activated $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$ and $(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl}$ core-shell catalysts compared against $\text{ZSM5} @ \text{Cu}_{1.3}\text{ZnAl}$.

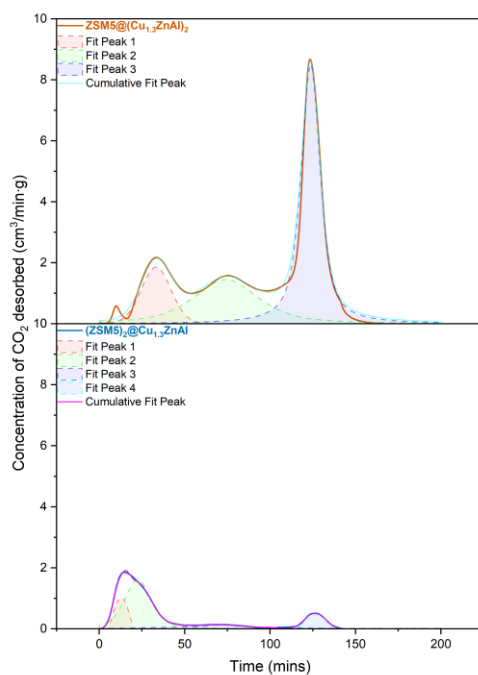


Figure B.17: CO_2 -TPD of (a) $\text{ZSM5} @ (\text{Cu}_{1.3}\text{ZnAl})_2$ and (b) $(\text{ZSM5})_2 @ \text{Cu}_{1.3}\text{ZnAl}$ with highlighted peak deconvolution. Peak fittings were performed in Origin using a Pseudo-Voigt model.

C

Appendix for Chapter 4

Table C.1: ICP-OES/CHN elemental analysis of the Zr-intercalated LDHs compared against Cu_{1.3}ZnAl-LDH.

Sample	Cu (wt%)	Zn (wt%)	Al (wt%)	Zr (wt%)	Cu:Zn:Al:Zr	C (wt%)	H (wt%)	N (wt%)
Cu _{1.3} ZnAl-LDH	26.17	19.00	7.45	-	1.4:1.0:0.1:-	2.02	2.59	0
CZA-Zr _{0.25}	24.43	17.21	5.89	6.31	1.5:1:0.8:0.3	1.75	2.38	0.17
CZA-Zr _{0.5}	22.74	15.83	3.76	11.84	1.5:1:0.6:0.5	1.92	2.16	0
CZA-Zr _{0.75}	22.41	15.57	1.85	17.5	1.5:1:0.3:0.8	1.99	1.83	0

Table C.2: Details of the Pawley refinement and structural parameters for CZA-Zr_{0.25}, CZA-Zr_{0.5} and CZA-Zr_{0.75}. Refinements were performed on PXRD data from Ill Diamond Light Source.

Sample	CZA-Zr _{0.25}	CZA-Zr _{0.5}	CZA-Zr _{0.75}
Phase component	LDH	LDH	LDH
Space group	R-3m	R-3m	R-3m
R_{wp} (%)	1.47	1.28	1.36
GOF (%)	4.30	3.71	3.69
a (Å)	3.083212(2)	3.090893(3)	3.094750(2)
b (Å)	3.083212(2)	3.090893(3)	3.094750 (2)
c (Å)	22.832906(3)	22.866631(4)	22.841347(2)

Table C.3: Scherrer parameters for the calculation of the LDH crystallite domain lengths in the Zr incorporated LDH samples compared to the Cu_{1.3}ZnAl-LDH.

Sample	2θ (°)	Reflection planes	FWHM (radians)	Domain length (nm)
Cu _{1.3} ZnAl-LDH	6.25	(003)	0.00301	24.6
	12.53	(006)	0.00301	21.7
	31.20	(110)	0.00765	9.3
CZA-Zr _{0.25}	6.56	(003)	0.26085	16.3
	12.80	(006)	0.25032	16.9
	31.38	(110)	0.44036	9.3
CZA-Zr _{0.5}	6.23	(003)	0.35074	12.1
	12.47	(006)	0.32665	12.9
	31.03	(110)	0.46985	8.7
CZA-Zr _{0.75}	6.23	(003)	0.44950	9.4
	12.45	(006)	0.49719	8.5
	30.96	(110)	0.61520	6.7

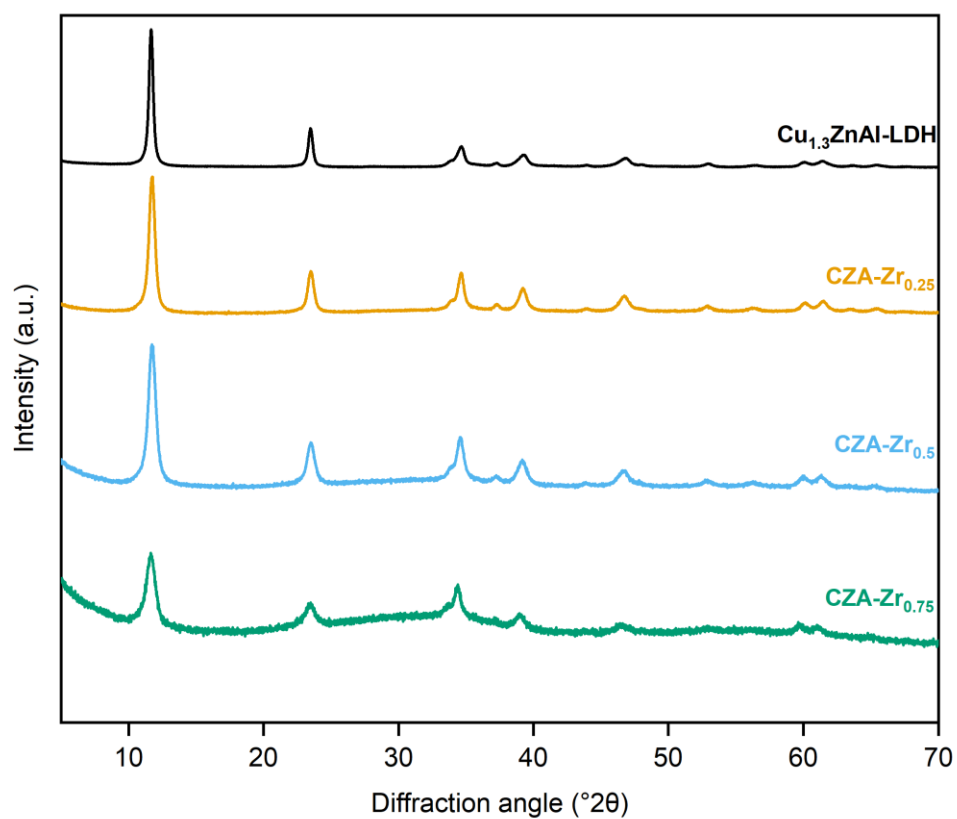


Figure C.1: PXRD of the CZA- Zr_x precursor catalysts collected on a Bruker D8 ECO diffractometer.

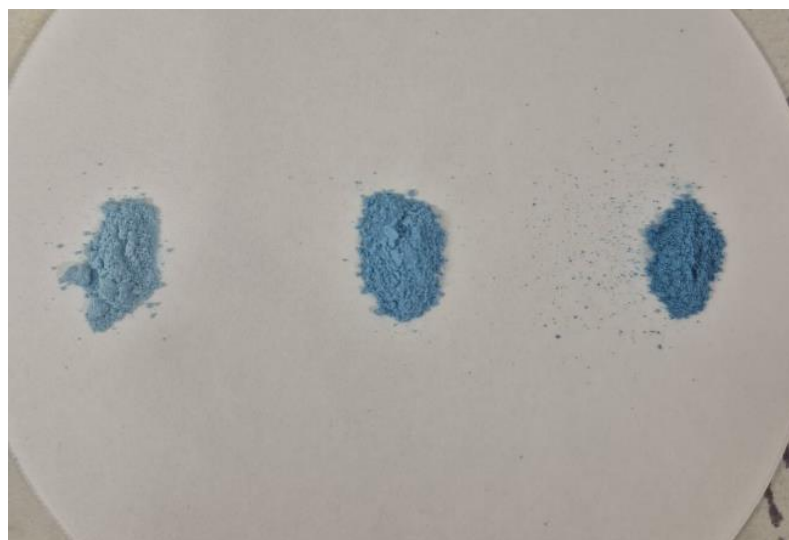


Figure C.2: Samples of (a) CZA- $\text{Zr}_{0.25}$, (b) CZA- $\text{Zr}_{0.5}$ and (c) CZA- $\text{Zr}_{0.75}$.

Table C.4: ICP-OES/CHN elemental analysis of ZSM5@CZA-Zr_{0.25}.

Sample	Cu (wt%)	Zn (wt%)	Al (wt%)	Zr (wt%)	Cu:Zn:Al:Zr	C (wt%)	H (wt%)	N (wt%)
ZSM5@CZA-Zr _{0.75}	11.94	7.95	-	9.52	1.5:1:-:0.9	1.27	1.23	0.42

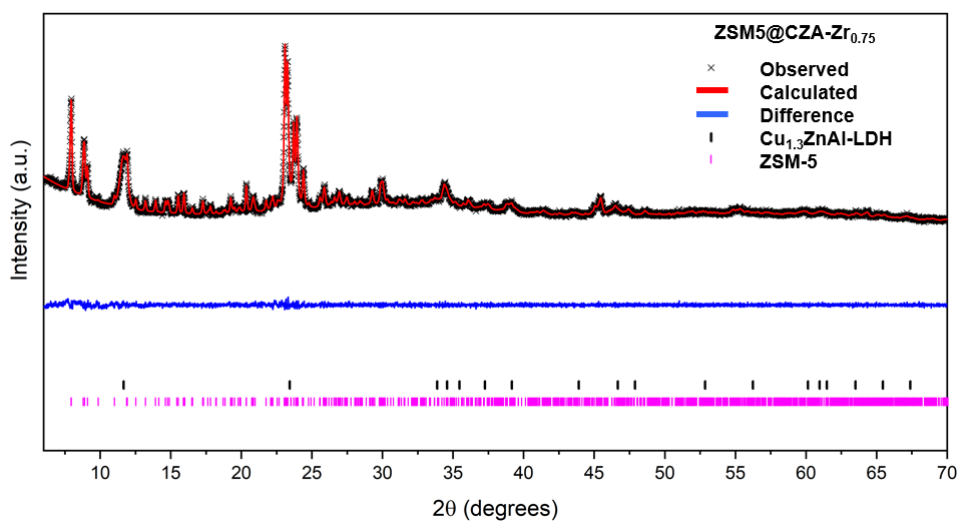


Figure C.3: Two-phase Pawley refinement of ZSM5@CZA-Zr_{0.75} against ZSM-5 and Cu_{1.3}ZnAl-LDH. PXRD data was collected on a Bruker D8 ECO diffractometer.

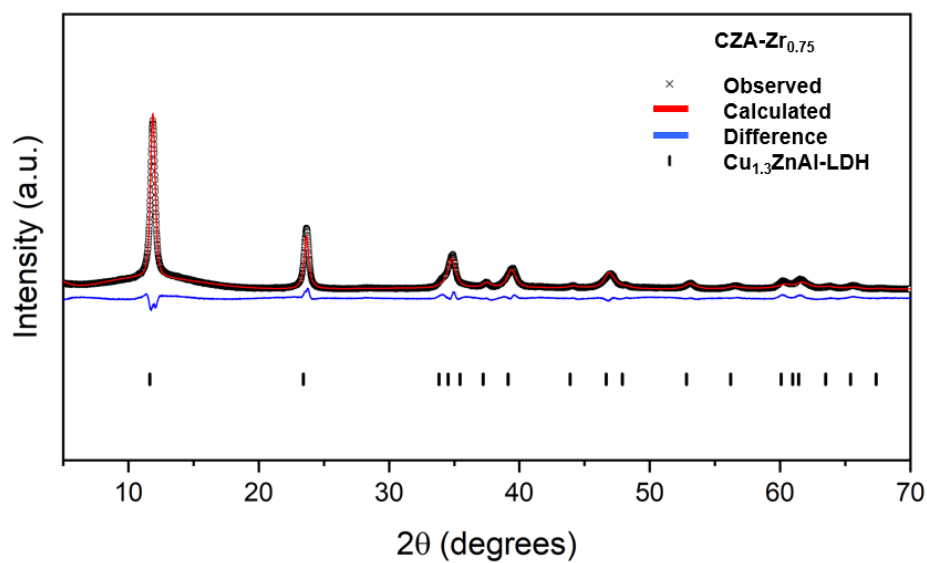


Figure C.4: Single-phase Pawley refinement of CZA-Zr_{0.75} against Cu_{1.3}ZnAl-LDH. PXRD data was collected on a Bruker D8 ECO diffractometer.

Table C.5: Details of the Pawley refinement and structural parameters for ZSM5@CZA-Zr_{0.75}. PXRD data was collected on a Bruker D8 ECO diffractometer.

Sample	ZSM5@CZA-Zr _{0.75}		ZSM-5
Phase component	LDH	Zeolite	Zeolite
Space group	R-3m	Pnma	Pnma
R_{wp} (%)		2.35	1.63
GOF (%)		1.23	4.85
a (Å)	3.099819(8)	20.112587(3)	20.101010(4)
b (Å)	3.099819(8)	19.944774(2)	19.903951(4)
c (Å)	22.792972(8)	13.422978(3)	13.420631(4)

Table C.6: Details of the Pawley refinement and structural parameters for CZA-Zr_{0.75}. PXRD data was collected on a Bruker D8 ECO diffractometer.

Sample	CZA-Zr _{0.75}
Phase component	LDH
Space group	R-3m
R_{wp} (%)	2.34
GOF (%)	1.11
a (Å)	3.094635(7)
b (Å)	3.099819(1)
c (Å)	22.781215(8)

Table C.7: Scherrer parameters for the calculation of the CZA LDH crystallite sizes in ZSM5@CZA-Zr_{0.75} and CZA-Zr_{0.75}.

Sample	2θ (°)	Reflection planes	FWHM (radians)	Crystal size (nm)
ZSM5@CZA-Zr _{0.25}	11.66	(003)	0.01031	13.4
	23.44	(006)	0.01321	10.3
	59.66	(110)	0.02092	5.8
CZA-Zr _{0.25}	11.63	(003)	0.01494	9.3
	23.42	(006)	0.01546	8.8
	59.78	(110)	0.02150	5.6

Table C.8: CO₂ hydrogenation results for ZSM5@CZA-Zr_{0.75}-C compared against ZSM5@Cu_{1.3}ZnAl.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)			Yield (%)	STY_{DME} (g _{DME} /g·h)
			S_{DME}	S_{CH_3OH}	S_{CO}	Y_{DME}	
^a ZSM5@Cu _{1.3} ZnAl	260	12.8	34.6	9.5	55.8	4.4	0.36
	280	17.9	25.4	9.3	65.2	4.5	0.37
	300	21.5	17.6	7.6	74.4	3.8	0.31
^a ZSM5+Cu _{1.3} ZnAl	260	13.0	33.3	9.5	57.2	4.3	0.35
	280	19.2	26.1	9.1	64.5	5.0	0.41
	300	22.4	17.1	7.5	74.2	3.8	0.31
^b ZSM5@CZA-Zr _{0.75} -C	260	7.8	42.2	10.8	47.0	3.3	0.28
	280	12.7	29.1	10.4	60.5	3.7	0.31
	300	17.2	20.8	8.7	70.4	3.6	0.30

^aPrecursor materials were calcined in air prior to *in-situ* reduction. ^bPrecursor material was calcined in O₂ prior to *in-situ* reduction. Reaction conditions:

$P = 3.0$ MPa, CO₂/H₂/N₂ = 24:72:4, and $WHSV = 18,000$ mL/g_{cat}·h.

