One-pot synthesis of Ca oxide - promoted Cr catalysts for the dehydrogenation of propane using CO₂

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Abstract

An important strategy for the reduction of levels of CO₂ in the atmosphere is to utilise it as a reagent molecule in catalytic reactions for the synthesis of high-value chemical products. Here we investigate the use of high-performance catalysts for the dehydrogenation of propane by CO₂ to the industrially - important molecule, propylene. Cr-based catalysts with a Ca oxide promoter on a ZrO₂ support have been prepared using a "one-pot" synthesis procedure. A range of structural and spectroscopic techniques revealed that this synthetic procedure produces a different catalyst morphology and structure and catalytic properties as compared to the widely - used "impregnation" synthesis protocol. The one-pot synthesis method provides a more uniform and well-dispersed catalytically active phase and the Cr species then appear more effectively involved in the dehydrogenation process. The introduction of Ca oxide as a promoter in the catalytic process increases both the overall propane conversion and propylene selectivity and, importantly, also reduces the level of carbon deposition on the catalyst particles leading to enhanced stability and performance.

1. Introduction

As the world's population grows and countries' economies continue to advance, our developing and future demands ensure that energy is now regarded as one of the defining issues of this century.¹ Currently, more than 80% of the global energy requirement is satisfied by the aerial combustion of fossil fuels, such as petroleum, coal, and natural gas which inevitably give rise to a continuous increase in CO₂ levels in the atmosphere.^{2,3} Among other greenhouse gases, such as CH₄, N₂O, and O₃, CO₂ contributes over 60% to global warming.² Anthropogenically-induced emissions of CO₂ are now believed to be the primary cause of global warming and marine acidification.⁴

The worldwide development of shale gas is one of the significant energy revolutions of the 21st century.⁵ Shale gas contains large amounts (typically some 10 percent) of light alkanes. The dehydrogenation of alkanes to produce alkenes is particularly attractive as these are one of the most important feedstocks for the chemical industry to manufacture a range of important products such as polyethylene, ethylene oxide, styrene, acetaldehyde, vinyl acetate, ethylene di(chloride/ bromide), ethanol, ethylbenzene, and many more.^{5,6} The demand for olefins, especially propylene, is expected to increase rapidly in the near future.⁷ Steam cracking, Fluid Catalytic Cracking (FCC) and oxidative dehydrogenation (ODH) are the primary current methods to obtain olefins from hydrocarbons. These two production processes are accompanied by vast quantities of emitted CO₂ and a large cost for the raw materials.⁶ Propane dehydrogenation (PDH), therefore, is a promising catalytic technology for the conversion of propane into propylene.⁸

Oxidative dehydrogenation of propane via mild oxidation with CO₂ is an emerging energy-efficient and environmentally-promising approach to convert propane to propylene.⁵ Moreover, the concomitant reduction of CO₂ to CO that occurs during the reaction will lead to syngas production, a key building block for fuels and other chemicals. The overall propane dehydrogenation process (equation 3) with CO₂ comprises two reactions; first, the dehydrogenation reaction (equation 1) and second, the reverse water-gas shift reaction (RWGS, equation 2).

The oxidative dehydrogenation of propane in the presence of molecular O₂, as an oxidising agent, is favoured in low temperature reactions. Deep oxidodehydrogenation of propane and propylene to CO_x is a major drawback, which often results in loss of propylene selectivity and yield.⁹

CO₂ is a thermodynamically stable molecule. Accordingly, most of the chemical reactions involving CO₂ are endothermic, and hence the application of high - efficiency catalysts are critical in for effective and efficient reactions utilisation of CO₂. In addition, metal oxide promoters are routinely employed, for example, to enhance the propane conversion rate.

Recent studies of propane dehydrogenation using CO₂ have tended to be focussed on the development of more active and selective catalysts. ZSM-5 supported Cr₂O₃ catalysts were found to be reasonably

efficient catalysts for the oxidative dehydrogenation of propane in the presence of CO_2 .^{9–11} Nonetheless, their stability is still a major problem and limits their industrial applications. Moreover, the propylene selectivity of zeolite supported catalysts is not high enough because of the presence of accompanying strong acid sites on, and in, the zeolites. Moreover, the Al/Si ratio itself strongly affects the support properties during PDH as it can change both the structures and surface acidity.¹² A strongly acidic site will lead to cracking processes. For the natural zeolites, the difficulty in obtaining homogenous materials and the reproducibility of samples obtained from natural ores are the main obstacles in the use of natural zeolites as catalytic materials.¹³ Acid and ion exchange treatments can be applied to improve the zeolites properties. However, it can also influence the catalytic performance of the zeolite by dealumination and removal of the ion-exchangeable cations. This leads to breaking of Al–O bonds, and would be a loss of crystallinity.¹⁴ Investigations improved zeolites as support for propane dehydrogenation are still in progress. The catalyst support itself plays a decisive role in determining surface metal oxide structures and the surface reducibility by affecting the dispersion of the metal species as the active phase. Irrespective of any metal-support interaction, the surface area of the support obviously affects the metal catalysts dispersion.

We report here our studies of Cr-based dehydrogenation catalysts supported on ZrO_2 which have been prepared by a new process which we term a “one-pot synthesis”. In this synthetic protocol, *all* precursors (the catalyst, the support and the promoters) are initially dissolved into a solution mixture, NaOH is then added to increase the pH level of the solution and co-precipitate out the solids as an intimate resulting solid mixture. The precipitate is then heated under reflux conditions for 48h.

Different Cr and Ca-oxide promoter contents are studied here in catalytic activity tests and subsequent catalyst characterisations. The support/promoter effects on the catalyst performance both with and without Ca oxide as promoter were also investigated.

2. Experimental Methods

2.1. Catalyst preparation

Cr/ ZrO_2 catalysts were prepared by both a one-pot synthesis and the conventional impregnation route. For the one-pot synthesis, an aqueous solution was prepared by mixing chromium (III) nitrate nonahydrate (Sigma-Aldrich, $\geq 99\%$) and 0.01 mol zirconium (IV) oxynitrate hydrate (Aldrich, $\geq 99\%$), the concentration of Cr was adjusted to produce 1–3 mmol of Cr. For the catalyst with Ca-oxide promoter, 2 mmol of calcium nitrate tetrahydrate (Sigma-Aldrich, $\geq 99\%$) was dissolved in the solution. The solutions were stirred vigorously at room temperature and NaOH solution (2 M) was added dropwise at 60°C until pH reached 11.0. The mixture was then aged in a water bath for 2h at 60°C. The precipitate was filtered off and washed three times with deionised water. Then 300 ml water was added to the solid in a 500 ml round bottom flask and the mixture boiled for 48h. The remaining solids were filtered off and dried in the oven at 80°C for more than 12h and then calcined at 600°C in air for 5h with the heating rate 2°C/min (Fig. 1). For comparison purposes, 10 wt% Cr- ZrO_2 catalysts were prepared by the impregnation method (Fig. 2 and Table SI). The reference catalyst is the 10wt% Cr- ZrO_2 prepared by

the impregnation method; with variable contents, $x\text{Cr-Ca/ZrO}_2$ and $x\text{Cr-ZrO}_2$ ($x=1-3$, mmol of Cr, Ca= 2 mmol) all being made by the one-pot synthesis. The summary of the catalysts details are shown in the table S2. The catalysts are regenerated after the catalytic tests by heating in air in a furnace at 550°C for 2h. This regeneration process combusts and removes surface coke. All fresh catalysts were ground thoroughly and pass through a $125\ \mu\text{m}$ mesh sieve.

Fig. 1. Catalyst preparation procedure using the one-pot synthesis protocol.

Fig. 2. Catalyst preparation procedure of the widely-used impregnation method.

2.2. Catalyst characterisation

The samples were characterised before and after reactions by a range of techniques, encompassing thermogravimetric analysis (TGA, TA Instrument, SDT Q-600), Laser-Raman spectroscopy (PerkinElmer Raman Station TM 400F spectrometer), scanning electron microscope and Energy-dispersive X-ray spectroscopy (SEM-EDX, ZEISS EVO) and X-ray photoelectron spectroscopy (XPS).

The powder X-ray diffraction (XRD) used a $\text{Cu K}\alpha$ X-ray source (45 kV, 40 mA) on a BRUKER D8 ADVANCE diffractometer. The scanning range (in 2θ) in this study was 20° to 70° . Thermogravimetric

analysis (TGA) in air was used to characterise the carbon deposited in spent samples. The sample was heated from room temperature to 1000 °C at a heating rate of 10 °C/min under air with a flow rate of 100 ml/min. A scanning electron microscope (SEM, ZEISS EVO) was used to characterise the surface morphology of the samples before and after dehydrogenation process. The surface element concentrations were analysed by Energy-dispersive X-ray spectroscopy (EDS, ZEISS EVO). The catalysts' surface acidity was tested by ammonia-TPD (Micromeritics 2920 surface characterisation system). The catalysts were pre-heated in flowing helium gas for 1 h at 450°C and cooled down to room temperature, they were then then exposed to ammonia for 1 h, and then purged with helium and heated linearly at 10°C/min to 450°C in 50 ml/min argon. The amount of ammonia in the effluent was recorded continuously as a function of temperature.

2.3. Catalyst activity tests

The performances of catalysts for propane dehydrogenation with CO₂ were examined at a temperature of 550 °C in a fixed-bed micro reactor (Fig. S1) at atmospheric pressure for a period of 10hrs. The catalyst loading was typically around 300 mg. The input gaseous reactants were carefully measured as 10% propane and 30% CO₂ with the balance being nitrogen at a total flow rate of 25 mL/min. The emerging reaction products were analyzed through a direct link to an on-line gas chromatograph (GC, Perkin Elmer, Clarus 580) with a flame ionization detector (FID) and a thermal conductivity detector (TCD) detector. The propane conversion, propylene selectivity and yields evaluated in this work are calculated using the equations (4) to (6) below. The equations (7) and (8) are for CO₂ conversion and CO yield calculation. the experimental deviations over two or three separate experiments are estimated as +/- 5%. The n is the number of moles of the chemicals in/out the reaction flow.

$$\text{Conversion of propane} = \frac{n_{\text{C}_3\text{H}_8 \text{ in}} - n_{\text{C}_3\text{H}_8 \text{ out}}}{n_{\text{C}_3\text{H}_8 \text{ in}}} \times 100 \quad \% \quad (4)$$

$$\text{Selectivity of propylene} = \frac{n_{\text{C}_3\text{H}_6}}{n_{\text{CH}_4} + n_{\text{C}_2\text{H}_4} + n_{\text{C}_3\text{H}_6}} \times 100 \quad \% \quad (5)$$

$$\text{Yield of propylene} = \text{Selectivity} \times \text{Conversion} \quad \% \quad (6)$$

$$\text{Conversion of CO}_2 = \frac{n_{\text{CO}_2 \text{ in}} - n_{\text{CO}_2 \text{ out}}}{n_{\text{CO}_2 \text{ in}}} \times 100 \quad \% \quad (7)$$

$$\text{Yield of CO} = \frac{n_{\text{CO}}^{\text{out}}}{3 \times n_{\text{CO}_2}^{\text{in}}} \times 100 \quad \% \quad (8)$$

3. Results and discussion

3.1. Catalyst Characterisation

In Fig. 3 we show the XRD patterns of Cr-ZrO₂ catalysts prepared using two different methods; namely our one-pot synthesis (shown as red, 2Cr-ZrO₂ and blue, 2Cr-Ca/ZrO₂) and the conventional impregnation method (green, 10wt%Cr-ZrO₂). These catalysts contain different oxidation states of Cr. The XRD could in principle identify the Cr₂O₃ and Cr metal easily (high content and strong crystallinity) but not Cr(VI) compounds as in the Cr(VI) is expected to be present in a non-crystalline form.¹⁵

For the samples prepared by the impregnation method, the diffraction peaks at $2\theta=24.6, 28.3, 31.7, 34.0, 40.9$ and 50.4 revealed the presence of Cr₂O₃ rhombohedral phase (α -Cr₂O₃)^{16,17}, but no metallic Cr (at $2\theta = 24.2, 28.2, 31.4, 34.3, 41.5, 50.0, 53.0, 55.5$, and 60.0° ; JCPDS 37-1484).¹⁵ In addition, the diffraction patterns of the commercial ZrO₂ support showed peaks characteristic of the monoclinic form, whereas for the samples synthesised via the one-pot reaction method, the tetragonal phase of ZrO₂ was detected. In addition, these data suggest that our one-pot reaction gives a smaller particle size for the Cr₂O₃ and ZrO₂, as evidenced by the diffraction widths (Fig. S3).

Fig. 3. XRD pattern of both the impregnation method 10wt%Cr-ZrO₂ (green), and the one-pot synthesis 2Cr-ZrO₂ (red) and that with the Ca-oxide promoter (blue).

It should be noted that the diffraction peaks of Cr₂O₃ and ZrO₂ sometimes overlap, which makes it difficult to distinguish individual components

In comparison, the 'one-pot' synthesised Cr-ZrO₂ catalysts (2Cr-ZrO₂, Fig. 3. red) showed a totally different XRD diffraction pattern where the Cr₂O₃ was either in the form of very small crystallites or had lost its bulk crystallinity. The crystallite sizes are estimated based on the Scherrer Equation. The sizes of Cr₂O₃ over 2Cr-ZrO₂ and 2Cr-Ca/ZrO₂ are 23 nm and 16 nm respectively and the 10wt% Cr-ZrO₂ is 30 nm. This suggests that the one-pot synthesised catalysts have smaller crystallite sizes as compared to the samples prepared by the impregnation method. The XRD pattern of the Ca-oxide promoted 2Cr-Ca/ZrO₂ catalyst is broadly similar to that from 2Cr-ZrO₂. Although a higher intensity was shown for the

non-promoted catalyst, the Cr_2O_3 peaks were difficult to detect. The only defined ZrO_2 peaks correspond to the tetragonal phase.

Arising from the intimate mixing of all reactants, another possibility is that the one-pot synthesis method produces a solid solution structure where the Cr and Zr are chemically linked by O-bridges in small polymeric cluster structures, or indeed incorporated into the host support structure itself. These appear, therefore, fundamentally different from the conventional metal oxide/support mixtures (Cr/ZrO_2).¹⁸ The general definition of a solid solution is that of a solid in which a second component is substitutionally incorporated into the lattice of another, "host" solid with or without a significant change of the overall crystal structure of the parent structure. For the one-pot synthesised catalysts, such a solid solution would involve Cr oxides (and potentially Ca oxide also) substituted into the (host) ZrO_2 support itself. Our proposal is that such substituted species will be located in the top few surface layers (as they are detected in XPS, an acknowledged surface -sensitive technique). This is in contrast to the situation where Cr and Ca species are deposited as particles oxides(or metal, in the case of Cr) on the exterior surface of the support. In addition, the observed (small) changes in lattice constant of the ZrO_2 would also support the solid solution concept.

The surface of the ZrO_2 catalyst appears far smoother for the one pot reaction possibly arising from the oxides being substituted within the ZrO_2 . The one-pot synthesis has been used in other areas for preparing nanoparticles where solid solutions formation has been invoked.^{19,20} For example, *Nomura et al.* showed the presence of a Li-based solid solution in Li-metal-oxide system using the same synthetic approach.²¹

Further investigation is required to completely identify the possible formation of such cluster species or the formation of a solid solution.

To investigate the distribution, nature and status of the Cr species on the catalyst, SEM and Energy-Dispersive X-ray Elemental (EDX) mapping were conducted on the samples prepared by both the one-pot synthesis and impregnation method. The EDX sample mapping (Fig. 5) shows that the sample prepared by the impregnation method shows that Cr species are not dispersed uniformly with the formation of large CrO_x particles. However, SEM only shows the material surface information, the detailed structure requires TEM. *Al. Awadi et al.* showed low-magnification TEM images of Cr-MCM-41 prepared by the impregnation method. The image shows that the metal oxides are on the surface of the support.¹⁶ As MCM-41 is a mesoporous material, the CrO_x species are also in the porous structure.²²

Our EDX elemental analysis suggests the Cr content of impregnation catalyst is 7.8%, Zr is 64.4% and O is 27.8%.

Fig. 4. SEM images of (A). impregnation 10wt% Cr-ZrO₂ catalysts prepared using the impregnation method and (B). 2Cr-ZrO₂ catalysts prepared using the one-pot synthesis method.

The surface morphologies of Cr-ZrO₂ catalysts prepared by the two different methods were studied by SEM-EDX analysis. As a general observation, catalysts prepared by the one-pot synthesis method have noticeably better distribution characteristics with smaller Cr species particle sizes (Fig. 5), which is indeed consistent with our XRD studies. Moreover, the SEM images show that 2Cr-ZrO₂ prepared by this method is more compact with a smoother surface and it appears to have something of a layered structure (Fig. 4).

The EDX elemental analysis shows that the Cr content of the impregnation catalyst sample, 10wt % Cr-ZrO₂, for Cr the concentration is 7.8%, for Zr is 64.4% and for O is 27.8%. The EDX elemental analysis of two one-pot synthesised catalysts, 2Cr-ZrO₂ had the Cr content of impregnation catalyst is 9.9%; for Zr is 56.1% and for O is 34%, and the 2Cr-Ca/ZrO₂ Cr content of impregnation catalyst is 8.9%, Zr is 49.3%, Ca is 5.8% and O is 36%.

Fig. 5. SEM images and Energy-Dispersive X-ray elemental (EDX) mapping of the elemental species on the surface of 2Cr-ZrO₂ samples prepared using one-pot synthesis. (A) SEM (backscattered electron), (B) Cr map, (C) Zr map, (D) O map, and (E) EDS spectrum

The EDX elemental mapping of both catalysts revealed presented that by the impregnation method (Fig. S4), the 10 wt.% Cr-ZrO₂ catalyst has a Cr content of 7.8%, whereas for the one-pot synthesised 2Cr-ZrO₂ catalyst the Cr content is 9.9%, noticeably, closer to the stoichiometric value used in preparation (Fig. 5). This again points to the solid solution structure as providing a more uniform distribution of Cr species in the catalyst when using one-pot preparation method.

Comparing the two preparation methods, the SEM observations shown in Fig. 4 were helpful in gaining insights into the morphologies of both CrO_x species and ZrO₂.

A good dispersion or distribution of the catalytically -active Cr species in the catalysts suggests that both the incoming reactants and outgoing reaction products can diffuse more effectively before/ during and after the catalytic process.

Fig. 6. TGA diagram (A) and derivative plots of temperature programmed oxidation (TPO) (B) of two fresh one-pot catalysts (Blue-2Cr-ZrO₂, Red-2Cr-Ca/ZrO₂) and impregnation catalyst (Yellow-10 wt.% Cr-ZrO₂).

The TGA curve diagram (Fig. 6) of shows that all samples are thermally stable between at 400-600°C (the range of out catalytic reaction temperatures) under the air. Interestingly, there was weight loss of about 1-2 % observed at around 650°C and 850°C respectively on 2Cr-ZrO₂ and 2Cr-Ca/ZrO₂ catalysts, whereas the 10 wt.% Cr-ZrO₂, prepared by the impregnation methods remained approximately the same (Fig. 6. B). In addition, all the catalysts did not have any noticeable colour change before and after the TGA heating.

In summary, the catalysts prepared by the one-pot synthesis showed different morphological structures, crystallinity and catalyst – distribution characteristics as compared to those made by the impregnation method. One assumption could be the catalysts are more likely to form a solid solution with a finer grain structure from the one-pot synthesis. The precipitation and calcination process during the one-pot synthesis could potentially result in the chemical bond as O-bridge formation between Cr -O cluster polymeric units on and within the ZrO₂ whilst the CrO_x is probably simply loaded onto the ZrO₂ surface during the impregnation process. In an attempt to determine the nature of the different catalysts produced by the two synthetic approaches, other characterisation techniques were employed.

Using X-ray diffraction, only the Cr³⁺ species can be observed. We therefore employed XPS probe the actual oxidation state of Cr species on the surface of the catalyst.

The XPS results are summarised in Table. 1. They showed that the one-pot catalyst, 2Cr-ZrO₂, has a characteristic peak splitting (Fig. S7) due to the presence of unpaired d-electrons in Cr (III) species ($3p^6 3d^3$), when an electron from in the core is excited by the photoionisation it creates a core vacancy, there will be coupling between the unpaired electron in the core and the unpaired electrons in the outer shell which creates several states. The Cr(III) species will result in 5 final states and the splitting is shown in the Fig. S6-8 for all catalysts.

To summarise, the fresh one-pot catalysts show different Cr binding energy levels compared with the impregnation catalysts with noticeably higher Cr(III) contents (Table. 1).

The oxidation states of Cr species in this kind of catalyst effectively control the redox reaction during the dehydrogenation process. With that in mind, the percentage of the different oxidation states were determined from the XPS data. These are given in Table 1. We note that the content of Cr(VI) is significantly different between the impregnation catalysts and the one-pot preparation method. From these data, we can conclude that the proportion of Cr(III) to Cr(VI) species critically depends on the catalyst preparation methods.

From the various characterisation results, it is clear that the catalysts' morphological structural and surface properties are noticeably different between the two differently prepared catalyst samples.

The impregnation method allows the metal oxides to be physically loaded onto the ZrO₂ support surface to form the conventional metal oxide-on- support catalytic system. In contrast, the one-pot synthesis method, provides an environment which allows all the precursors to co-precipitate to form more disperse and uniform solids. Furthermore, the solids then under reflux condition for 48h, might drive a change to a substituted solid phase or bonding formation between the different elements, such as O-bridges between Cr polymeric cluster species and the Zr host. Our XPS data reveal the proportions of different Cr oxidation states on the catalyst surface vary with the different preparation methods.

Table. 1. Binding energies of the various Cr species for the impregnation catalysts 10wt%CrZrO₂ and 2Cr-ZrO₂ and 2Cr-Ca/ZrO₂ from the one-pot synthesis procedure and the derived %'s of both the Cr(III) and Cr(VI) species are shown

Catalysts	Cr 2p _{3/2} Binding Energy (ev)		Cr(III)/ %	Cr(VI)/ %
	Cr(III)	Cr(VI)		
10wt%Cr-ZrO ₂ (Impregnation)	576.7	579.64	87.97	12.03
2Cr-ZrO ₂ (One-pot)	577.2	579.58	70.18	29.82
2Cr-Ca/ZrO ₂ (One-pot)	576.7	579.47	69.92	30.08

It is well established that ammonia can be used as a probe molecule to explore the overall acid properties of a catalyst surface using the technique of temperature-programmed desorption (TPD). For the ammonia gas contact with a solid catalyst, both physical absorption and chemical absorption occurs. Then the ammonia desorbed on the material is detected by temperature programming carried using nitrogen carrier gas. The acidic sites and both their strong and weak absorption sites can be calculated from the peak area change during the desorption process.

We have carried out ammonia-TPD experiments for the prepared catalyst and the relevant profiles are shown in Fig. S9-S11. The impregnation derived catalysts showed both strong and weak acid sites, clearly reflecting with different acid strengths. The peak at 150-290 °C could be attributed to the weak adsorption of the ammonia with acidity about 0.26 mmol/g. The other peak at 300-450 °C could be ascribed to strong desorption of ammonia adsorbed and the acidity is 0.15 mmol/g.^{23,24} The one-pot

synthesised catalysts show a multi-stage desorption but no obvious signs of sites of different acidities are found. The acidity of 2Cr-ZrO₂ is 0.56 mmol/g and the 2Cr-Ca/ZrO₂ is 0.02 mmol/g.

3.2. Catalyst activities

The catalytic activities of the ‘one-pot’ catalysts have been tested in a fixed-bed micro reactor at 550 °C and atmospheric pressure for 10h. In Fig. 7, we show the evolved propane conversion and the propylene selectivity with time on stream (min) for the oxidative dehydrogenation of propane with carbon dioxide using 2Cr-ZrO₂ catalysts. The conversion reached over 20% after 1h reaction, and the propylene yield was around 19% with 90% selectivity. The propylene selectivity remained at a ca. 90% for nearly 200 min whereas the conversion gradually dropped to 7% after a 10h reaction period. This is attributed to deleterious carbon deposition on the catalysts’ surface that block/cover the catalytically active sites and consequently deactivated the catalysts. The conversion of CO₂ was around 6% after 3h-reaction and the final conversion was 3.2% with 17.8% CO yield.

A previous report by *Rahmani et al.* presented a high propane conversion of ca. 40% after 0.17h using Cr-MCM-41.¹⁴ However, the conversion rate of Ce-based or Ga-based and bimetallic based catalysts was below than 10%.^{9,25,26} In essence, the conversion rates of PDH can be affected significantly by the ratio of propane to CO₂, the flow rate of the gases, the reaction temperature and amount of active metal content. It has been reported that an increase in the CO₂/propane ratio and the Cr content can improve the propane conversion during PDH.^{9,17,27,28} Therefore, in this work, we chose a 3:1 CO₂ /propane ratio and Cr-Ca/ZrO₂ catalysts with different Cr-contents were carefully compared.

Fig. 7. The propane conversion and propylene selectivity using 2Cr-ZrO₂ prepared by one-pot synthesis in a 10h catalytic test reaction.

The detailed nature of the catalyst active sites obviously plays a significant role in the catalyst performance. For the propane dehydrogenation, both acidic and basic sites of a catalyst are critically important to the catalyst performance. The dehydrogenation of propane over reducible metal oxide catalysts, such as chromium oxides, in the presence of CO₂ has been proposed to follow a redox mechanism.⁹ Shishido proposed a chemical mechanism for propane dehydrogenation with CO₂ shown

in Fig. 8.¹⁸ Thus, propane is oxidised to propylene with the simultaneous reduction of the chromium oxide and subsequently the reduced metal oxide catalyst is re-oxidised by CO₂.²⁹

Fig. 8. Proposed reaction mechanism of dehydrogenation of C₃H₈ in the presence of CO₂.¹⁸

Therefore, basic catalytic sites assist the absorption and consumption of CO₂ whereas acidic sites determine the adsorption and subsequent activation of propane. A strong acidity has been proposed to increase the metal-oxygen bond strength in the redox active cluster leading to a decrease in the reactivity.¹⁶ The acidity of chromium-based catalytic system serves as one of the crucial factors in determining the catalytic activity in oxidative dehydrogenation reactions. However, a stronger surface acidity also leads to the formation of carbonaceous cracking products, and thus less alkene selectivity is obtained.

To improve the catalyst performance, the balance between the acidity and basicity of the catalysts is very important. It is recognised that a promoter added into the catalytic system can assist and help to control the catalytically active sites. Pt is one of the common active components added for the PDH reaction. However, any such application is seriously restricted by the high cost of the noble metal and environmental problems.³⁰ Therefore, in this study, Ca oxide was chosen as a promoter and its performance has been investigated. In Fig. 9 we show the catalytic performances of Ca-oxide promoted 2Cr-Ca/ZrO₂ and 3Cr-Ca/ZrO₂ catalysts prepared through the one-pot approach for the oxidative dehydrogenation of propane with CO₂ under the same conditions.

Fig. 9. The propane conversion and propylene selectivity using a). 2Cr-Ca/ZrO₂ and b). 3Cr-Ca/ZrO₂ from one-pot synthesis during 10h reaction.

We note that the catalyst's stability as well as the propylene selectivity were significantly improved with the addition of the Ca oxide promoter. As the activity tests reveal (Fig. 9. a) the propane conversion increased for the first 180 min and reached a value of ca. 20% conversion and at this time the CO₂ conversion is about 5%. Then the propane conversion slightly decreased to about 17% and kept at this quasi-steady state for a period of 500 min. Importantly, over 95% selectivity to propylene formation was achieved. The propylene yield was 20% in first 3 hours and decreased to 15% after 10-hour reaction.

It should be noted that unlike the 2Cr-ZrO₂ catalysts, a quasi-steady conversion rate between 200 min to 500 min was observed over the Ca promoted 2Cr-Ca/ZrO₂ catalyst. This indicates, importantly, the Ca promoted Cr-Ca/ZrO₂ catalysts have enhanced stability in terms of resisting coke formation which has been evidenced in our post-reaction characterisations. The temperature programmed oxidation (TPO) analysis of spent samples showed only ca 5 wt.% carbon content in the 2Cr-Ca/ZrO₂ catalyst, whereas 2Cr-ZrO₂ catalyst contained ca 10 wt.% carbon residues (Fig. 11). The EDX results also reveals the lower surface carbon percentage (Fig. S12-S13) in the 2Cr-Ca/ZrO₂ catalyst.

By adding the Ca oxide promoter, therefore, the results show a noticeable increase in the conversion in the initial 3h with subsequent slow decrease (Table 2). Hence the deactivation of the Ca-oxide-promoted catalysts was slower compared with the non-Ca-oxide promoted catalysts, also with higher selectivity. The 2Cr-Ca/ZrO₂ shows a stable and high propane conversion, high propylene selectivity and yield. The maximum conversion reached 20% at 3h and the conversion stayed constant at around 16-18% between 3.5-8h. This constant reaction stage only occurred with the 2Cr-Ca/ZrO₂ catalyst.

The carbon balance of a reaction is the percentage of the carbon amount involved during the chemical reaction. The carbon balance of the PDH with all the catalysts is kept over 93% after the reaction as shown in Table 3. This demonstrates the CO₂ conversion of the 2Cr-Ca/ZrO₂ was 4% at 3h with CO yield 46.7%. The CO₂ conversion of different catalysts are summarised in Table 3. The carbon balance for each catalyst shows that the promoted catalysts have a higher carbon balance closer to that calculated without including coking than the non-promoted catalyst. Thus, it is clear that the Ca promoter inhibits the carbon coking on the catalysts surface as the percentage 95% is closer to 100%. This is also consistent with the TGA results of the spent catalysts.

In addition, the Ca promoter clearly affects the surface acidity. The acidity is calculated from the ammonia-TPD profile, the 2Cr-Ca/ZrO₂ shows a very low surface acidity compared with 2Cr-ZrO₂ (Fig. S10 and Fig. S11). Similar results were reported by Xu et al. showing that this kind of difference is mainly due to the surface basicity.²⁹ It seems that the low acidity would decrease the reaction rate due to the competitive adsorption effect. However, this could enhance the propylene selectivity in the DHP with CO₂ by inhibiting the further adsorption and cracking of propylene on catalyst surface.³¹

The Cr content and oxidation state are themselves important parameters that can affect the conversion rates of PDH and this has also been investigated. We prepared a series of Cr-Ca/ZrO₂ catalysts using the one-pot synthesis method, with different of Cr content (different amount of the Cr precursor were added) 1, 2 and 3 moles, as Cr-Ca/ZrO₂, 2Cr-Ca/ZrO₂ and 3Cr-Ca/ZrO₂, respectively. The results of experiments for propane dehydrogenation with CO₂ on these prepared catalysts are summarised in

Table 2. The propane conversion increased from 10 mol% of Cr to 20 mol% with the 2Cr-Ca/ZrO₂ catalyst showing the best catalytic performance in both propane conversion and propylene selectivity that had reached the maximum of 20.2% conversion and 94.6% selectivity, respectively. The propylene yield with this catalyst also showed the best about 20.1%. However, a further increase in the Cr loading resulted in a decrease of both propane conversion and propylene yields. This is attributed to the fact that at such high Cr content, the Cr₂O₃(Cr³⁺) species for propane dehydrogenation will be more dominant than the active chromate or poly-chromate ones (Cr⁶⁺).¹⁶

Table. 2. Summary of catalytic results of four separate ‘one-pot’ catalysts with different Cr loading.

	Conversion		Selectivity						Yield	
	C ₃ H ₈		C ₃ H ₆		CH ₄		C ₂ H ₄		C ₃ H ₆	
Catalyst	3h	10h	3h	10h	3h	10h	3h	10h	3h	10h
1Cr	3.6%	13.1%	87.9%	44.7%	6.5%	27.1%	5.5%	28.2%	3.2%	5.9%
2Cr	20.2%	9.5%	93.5%	94.6%	4.0%	0.5%	2.8%	5.0%	20.1%	14.9%
3Cr	12.1%	9.8%	90.1%	85.3%	7.1%	10.0%	4.3%	12.3%	15.0%	8.6%
2Cr (no Ca)	17.0%	7.7%	88.2%	78.0%	7.5%	7.9%	3.5%	14.1%	15.0%	6.0%

Table. 3. Summary of CO₂ conversion of four ‘one-pot’ catalysts with different Cr loading.

	CO ₂ Conversion		CO Yield		C-Balance
Catalyst	3h	10h	3h	10h	10h
1Cr	1.5%	7.4%	25.6%	20.8%	93.4%
2Cr	4.1%	0.7%	46.7%	32.0%	95.8%
3Cr	3.3%	1.5%	46.2%	21.8%	95.1%
2Cr (no Ca)	6.0%	3.2%	94.5%	17.8%	92.3%

3.3. Post-reaction analysis

SEM images (Fig. 10) are shown for the spent one-pot catalysts. The EDX mapping shows that the Ca-catalyst has 4% lower carbon content than 2Cr-ZrO₂ catalysts (Fig.S12-13).

Fig. 10. SEM images of spent (A) 2Cr-ZrO₂ and (B). 2Cr-Ca/ZrO₂ prepared by one-pot synthesis.

The X-ray diffraction pattern of spent sample is given in Fig. 11A. The XRD pattern shows that the deposited carbon has a graphitic structure. The EDX mappings show the C content on the catalysts surface (Fig. S12-13). Moreover, there is no obvious change in the diffraction peaks of both ZrO₂ and CrO_x when compared with fresh catalysts (Fig. 3) The ZrO₂ is still present as the tetragonal phase.

Fig. 11. XRD pattern of spent (A) and regenerated (B) 2Cr-ZrO₂ (blue) and 2Cr-Ca/ZrO₂(red) catalysts prepared by one-pot synthesis.

From our EDX mapping and XRD patterns, it is clear that the carbon is present as deposits on the catalysts after the dehydrogenation process. The carbon deposition on the catalysts' surface during the reaction is considered to be the main reason for its deactivation. This has also been demonstrated by our regeneration test where the carbon was removed by combustion at 550 °C. It can be seen from the XRD patterns of regenerated catalysts (Fig. 11. B) that the catalysts' structure remained unchanged indicating that the catalyst structure is stable during the dehydrogenation reaction.

The “spent” one-pot catalysts were also characterised further. The catalyst colour changed to black after the activity tests. The TGA of two spent ‘one-pot’ catalysts under air is shown in Fig. 12. The diagram shows the weight loss at 300°C, which suggests the presence of amorphous carbon which is burnt during the analysis. Notably, the catalysts’ original green colour returned after the TGA runs. Comparing the TGA results with the carbon balance data in Table. 3, the carbon loss observed in our TGA experiments is completely consistent with the observed carbon balance data.

Fig. 12. TGA diagram of two spent one-pot catalysts (Blue-2Cr-ZrO₂ and Red-2Cr-Ca/ZrO₂).

In addition, the representative XPS characterisation data from spent 2-Cr-ZrO₂ and 2 Cr-Ca/ZrO₂ catalysts are contained in Table 4. Comparing with fresh samples (Table. 1), a noticeable increase of Cr(III) species were observed after the dehydrogenation reaction, whilst the Cr(VI) species is found to decrease. Since the Cr(VI) ions are reported^{32–34} as the most active species in the oxidative dehydrogenation of alkanes, we therefore attribute this change to the decrease in propane conversion. Thus, the coke formation is considered to prevent or inhibit the re-oxidation of Cr(III) to Cr(VI). The detailed peak fitting results are given in Fig. S14 and Fig. S15.

Table. 4. Binding energies and relative proportions of various Cr species of spent catalysts.

Catalysts	Cr 2p _{3/2} Binding Energy (ev)		Cr(III)/ %	Cr(VI)/ %
	Cr(III)	Cr(VI)		
Spent 2Cr-ZrO ₂	576.8	578.47	95.53	4.47
Spent 2Cr-Ca/ZrO ₂	577.0	579.11	89.54	10.56

4. Conclusion

We have reported here a detailed study of the Cr-based catalysts prepared by the one-pot synthesis for propane dehydrogenation using CO₂. Firstly, the structural information of the one-pot synthesised Cr-based catalysts has been investigated. From the results-presented here, the one-pot synthesis method resulted in a different catalyst morphology and structure compared to the conventional impregnation method, as verified by XRD and SEM studies. This resulted in a marked enhancement in the CO₂ dehydrogenation of propane with high and stable propylene selectivity. The propane conversion is stable during the reaction for 4-8h. The SEM images show a more compact/layered structure of the one-pot catalysts. The EDX analysis shows that the one-pot catalyst contains Cr with a highly uniform distribution. Those characteristics are totally different as compared to the impregnation-route catalysts which revealed a consistently lower Cr (III)/Cr (VI) ratio and less dispersion on the catalyst surface. In addition, the catalysts from the one-pot synthesis show a more compact solid with a smoother surface.

We also have demonstrated the catalytic properties of two different one-pot catalysts during the propane dehydrogenation process with CO₂, the non-promoted catalyst, 2Cr-ZrO₂, and Ca-oxide promoted catalysts, 2Cr- Ca/ZrO₂. The general activity of catalysts decreases with the time on stream. The 2Cr-ZrO₂ catalyst shows a continual decrease in conversion rate, propylene selectivity and yield. The deactivation of the catalyst was significant with an extended reaction time, which is due to the carbon coking effect. To maintain the catalytic activity of the catalyst, Ca oxide was chosen as a promoter. The results show that both the propane conversion and propylene selectivity are noticeably improved with the addition of the Ca oxide promoter. The data reveal that the promoter protects the catalysts from the time-dependent deactivation by depositing carbonaceous material. This was supported by the TGA results of spent catalysts with promoter which showed a lower carbon content.

The best catalyst performance reached 18% conversion of propane and 20% yield to propylene with over 90% selectivity after 2h, and 10% conversion, 15% product yield after 10h with 93% propylene selectivity.

Our results highlight the attractiveness of the one-pot synthesis, which provides stable and active catalysts for this dehydrogenation reaction using CO₂. Also the inclusion of CaO as a promoter results in a superior catalyst selectivity and the propylene yield increases compared with non-promoted catalyst, which is resistant to carbon deposition and therefore maintains catalytic activity over an extended period. Thus, the one-pot synthesis of Ca oxide - promoted Cr catalyst demonstrated both good stability and good catalytic performance during the dehydrogenation process.

5. Supporting Information

The supporting information contains:

- Experimental procedure of impregnation method

- The setup of the catalytic activity test
- Summary of catalysts information
- XRD patterns of ZrO_2
- SEM images and EDX results of different catalysts and spent catalysts
- XPS splitting and binding energy of Cr of one-pot synthesis catalysts, both fresh and spent
- Ammonia-TPD profile

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The one-pot synthesis approach for catalyst preparation.