Bimetallic Catalysts for Green Methanol Production via CO_2 and Renewable Hydrogen: A Mini-review and Prospects

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Abstract

Recently, the increasing level of atmospheric CO_2 has been well noted due to its association with global warming, provoking a growth in environmental concerns toward the continued use of fossil fuels. To mitigate the concentration of atmospheric CO_2, various strategies have been implemented. Carbon capture and utilisation along with renewable hydrogen production as the raw materials for methanol production are one of the options to turn waste CO_2 into useful fuels and chemicals. In the 1960s, the highly active and cost effective $Cu/ZnO/Al_2O_3$ catalyst was developed for the synthesis of methanol from carbon oxides and hydrogen derived from natural gas. Since then, metal nanoparticles and nanocomposites have been extensively investigated and applied on CO_2 hydrogenation reaction to methanol. Particularly, bimetallic catalysts have emerged as an important class of catalysts due to their unique properties and enhanced catalytic performances compared to their monometallic counterparts. In this minireview, after giving the introduction of the main motivation for the development of green methanol production via CO_2 hydrogenation, we first summarise the recent promising research activities in the fields of generating renewable CO_2/H_2 sources from carbon capture technologies, green hydrogen production, and biomass-derived CO_2/H_2 mixture. Then we provide an overview of the developments in the preparation of some new bimetallic catalysts for CO_2 hydrogenation reactions to methanol with the emphasis on the synergistic effects and the enhancement of catalytic performances over monometallic counterparts. Finally, the main conclusions are summarised and an outlook is presented for the future development in this research area.

Keywords: Methanol synthesis, carbon dioxide, renewable hydrogen, bimetallic alloy, heterogeneous catalysts, sustainable development.

1. Introduction

Along with the benefits brought by the advance of industrialisation, more and more problems of greenhouse gas emissions have emerged, which result in global warming and lead to extreme weather change[1,2]. Although it is well-known that burning of fossil fuels accounts for the major greenhouse gas production, the world energy supply is still strongly reliant on this limited and non-environmentally friendly source[3] as shown in Fig. 1a. According to the World Meteorological Organisation (WMO), the concentration of CO_2 in the Earth's atmosphere surged to a record high, hitting 403.3 ppm in 2016. Researchers suggested that a combination of human activities and the El Niño weather phenomenon drove CO_2 to a level not seen in 800,000 years[4]. This has become an international concern, and increasing efforts are being made to end this carbon emission problem.

Carbon capture and storage (CCS) is one of the options that could help towards the target for mitigating climate change. According to theInternational Energy Agency (IEA) report in 2017, among many human activities, the use of energy represents by far the largest source of emissions[5]. It can be seen from Fig. 1b that c.a. 42% of the global CO_2 emissions from fuel combustion are related to electricity and heat generation, indicating that CO_2 capture technologies could effectively alleviate the current carbon emission problem if it was applied at large point sources, i.e., power plants. However, the main economic obstacles for CCS is that it is not a profitable activity which requires large capital investment[6]. Therefore, an alternative, carbon capture and utilisation (CCU), has started to attract the attention of people who are interested in this area because it can turn waste CO_2 into valuable products such as chemical feedstocks and fuels. In addition, its application for enhanced oil recovery (EOR) has also attracted commercial interests since 1970s[7]. By storing CO_2 in oil fields, EOR has the advantages of the enhanced oil production and reduced carbon emissions that may offset the cost of the CO_2 capture process. With the development of the CCU technologies, CO_2 is no longer considered as a waste but as an alternative carbon feedstock. Chemical fixation of CO_2 using renewable hydrogen from biomass or decomposition of water from solar, tidal wave, and wind powers through its hydrogenation to methanol, as suggested in the “Methanol economy” strategy[8], has prompted intense research activities because methanol not only can be a platform chemical for many chemical products manufacture but also act as a high energy density and easy storable/transportable liquid hence it is suitable for replacing fossil fuels.

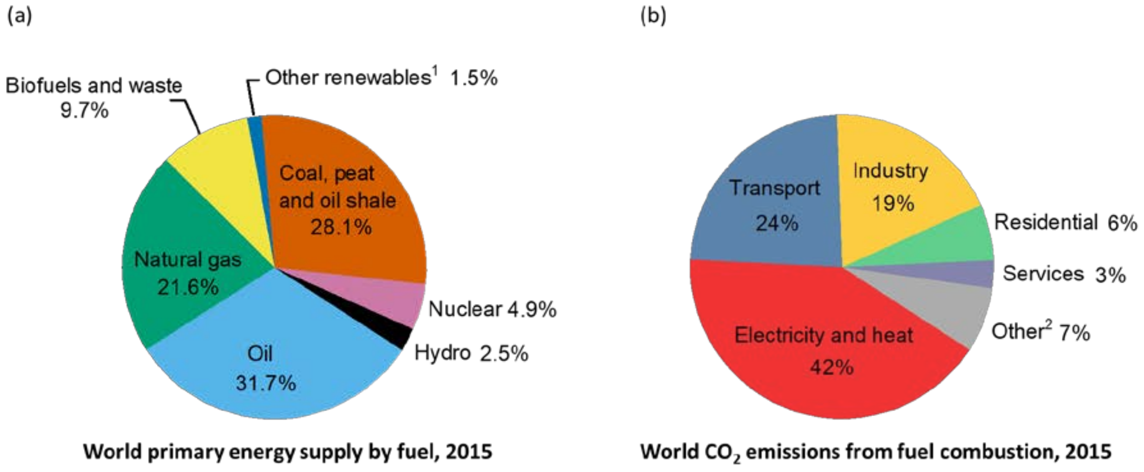

Fig. 1 The sources of (a) the global primary energy supply by fuel, and (b) the global CO_2 emissions from fuel combustion by sector; data retrieved from the reports of IEA Statistics[3,5], 2017. [1]*Includes geothermal, solar, wind, tide/wave/ocean, heat, and other renewables;* [2]*Includes agriculture/forestry, fishing, energy industries other than electricity and heat generation.*

The advancements in understanding the heterogeneous catalysts for methanol synthesis from CO_2 and hydrogen have progressively been made, especially on the $Cu/ZnO/Al_2O_3$ based system that was initially developed in the 1960s. This catalyst is still currently the centre of the focus, which reflects the fact that heterogeneous catalysts are preferable than the homogeneous systems owing to its high stability, easier handling, and reusability that help to fulfil large-scale productions with lower costs[9]. Over the years, a great amount of effort has been put into the development of active and stable heterogeneous catalysts for CO_2 hydrogenation to methanol, and several influential publications have reviewed it. A review published by Liu et al.[10] summarised the catalyst innovation for methanol synthesis via CO_2 and CO through the detailed aspects including active site, support effect, promoter, synthesis and pre-treatment effect. However, this report was published 15 years ago hence an update of recent studies is desirable. In a review on recent advances in catalytic hydrogenation of CO_2, various catalyst systems such as Cu-based catalysts, Pd-based catalysts, and other novel catalysts are discussed in detail[11]. Álvarez et al.[12] provided a statistical result on types of catalyst reported for methanol synthesis from CO_2 hydrogenation published in the past 10 years, which shows that 79% of the reports described catalysts based on Cu, followed by 11.5% based on Pd, and 9.5% on bimetallic systems. It can recently be seen that CO_2 hydrogenation to methanol over bimetallic catalysts has emerged as an important subject in this area. In many cases, there is a great enhancement in their specific physical and chemical properties owing to a synergistic effect over the monometallic counterparts, therefore leading to a desirable catalytic performance toward methanol production.

So far, numerous solutions have been proposed to alleviate the problems associated with the emission of CO_2. Among all the options, green methanol synthesis that consists of CO_2 capturing/recycling together with renewable hydrogen production seems to be a promising way to achieve carbon neutral process and sustainable development. In recent years, many efforts have been made towards carbon capture and utilisation, hydrogen synthesis via green routes, and methanol synthesis from CO_2 hydrogenation over promising bimetallic materials. This minireview is therefore intended to provide an overview of the research advancements on those topics.

2. Renewable CO_2/H_2 sources

2.1 CO_2 sources

Carbon dioxide capture and storage (CCS) is an emerging combination of technologies which can help to reduce CO_2 emissions from the use of fossil fuels. However, CCS faces many economic and technical barriers, such as the shortage of capital investment, the uncertain CO_2 leakage rate, and the geological incapability in certain areas, that must be overcome before it can be applied on a large scale[13]. More recently, carbon capture and utilisation (CCU) has started to attract attention because it can turn waste CO_2 into valuable products, such as methanol and many other chemicals. Utilisation of CO_2 has the advantages of being a renewable, low in cost, and non-toxic process. In addition, the CCU is generally a profitable activity as the produced chemicals or fuels can be sold, which makes it a promising way to help with the climate change mitigation[6].

Elimination of CO_2 from the flue gases of power plants would greatly reduce the global annual emissions, as the CO_2 produced from the electric power industry represents almost half of the global greenhouse gas emissions[14]. There are three CO_2 capture strategies that have been considered to possess the greatest possibility of reducing the emissions of CO_2 from fossil fuel-based power plants, namely, post-combustion, pre-combustion, and oxy-fuel capture[12]. In the post-combustion strategy, CO_2 is separated from the flue gas stream which allows for an easy adaptation to use with an existing power plant. As for the pre-combustion strategy, the fossil fuel is gasified under certain temperature and pressure for the removal of carbon prior to combustion. Given the higher partial pressure of CO_2 in this stream, an easy separation by utilising a variety of solvents can be achieved. In the last scenario of CO_2

capture, the oxy-fuel capture, pure oxygen is used for the combustion, resulting in a flue gas containing mainly water vapour and CO_2 so that the process can be easily recovered through a simple condensation method.

Presently, the biggest challenge for the implementation of CO_2 capture within power plants is the development of new materials. Many researchers are devoted to finding a material that displays suitable physical and chemical properties, and can reduce the large energy requirements when conducting the capture process[15]. The aqueous amine solutions such as monoethanolamine (MEA), diethanolamine (DEA) methyl diethanolamine (MDEA), as well as the amine blends solutions, show highly selective for acid gases[16,17]. Those amine scrubbers have been commonly employed industrially for post-combustion CO_2 capture because of their rapid reaction rate and low cost[16]. However, due to the considerable energy penalty for desorbing CO_2 from the liquids, other materials with lower heat capacities are frequently proposed as alternatives. For example, ammonia-based solvents for CO_2 separation has been applied to overcome the drawbacks of amine-based capture technologies[18]. Ionic liquids show the advantages of high CO_2 solubility, good thermal stability and tuneable structures, hence they have also been proposed as promising solvents to replace the existing amine-based solvents[19]. On the other hand, solid sorbents such as zeolites[20,21], carbon-based adsorbents (activated carbons[21], carbon nanotubes[22], and graphenes[23]), layered double hydroxides (LDHs), and metal-organic frameworks (MOFs)[24] are considered to be good candidates for CO_2 capture owing to their promising adsorption capacity, CO_2 selectivity, stability and regenerability[21]. The high costs in the syntheses for some of these solid absorbers are presently the prime concerns.

Very recently, another method is by the use of a membrane system which has been introduced for CO_2 separation. The advantage of using membrane technologies is that they are simple, flexible, and less space-demanding. Most importantly, the potential to perform separations at low energy penalties makes the membrane strategies attractive for the practical CO_2 removal applications[25]. Apart from the polymer-based membranes, the inorganic solid sorbents mentioned above can also be used as inorganic fillers to form mixed-matrix membranes, which were found to improve both the permeability and selectivity of the membranes compared to the base polymer when applying for CO_2 capture[26].

Overall, current CO_2 capture technologies still require a substantial energy input, therefore it is unlikely that CO_2 capture will become profitable in the near future. If the government can develop policies that help the development of CO_2 capture projects, for example, including CO_2 capture costs into the electricity bill[12], allowing tax-exempt financing for the acquisition of capital equipment that is used to capture CO_2, etc., then the implementation of CO_2 capture and the subsequent CO_2 mitigation may be able to take effect in a shorter time scale.

2.2 Hydrogen sources

In the current industrial production, hydrogen is commercially produced by steam methane reforming, coal gasification, and partial oxidation of light oil residues, which accelerates the depletion of fossil fuels and lead to an increasing CO_2 level in the atmosphere[27,28]. For the renewable methanol production from H_2 and CO_2, it must be pointed out that the consumed CO_2 in this process has to be more than that produced in hydrogen manufacturing, which means hydrogen sources must come from the green production routes. Water electrolysis with the electricity generated from green energy, i.e., photovoltaic power plant, wind power plant, and ocean energy converted into electricity[29], is considered to be one of the potential options for green hydrogen productions. Today, the most common electrolysis technology is alkaline-based water electrolysis[30]. Alkaline electrolysers operate by having two electrodes in a liquid alkaline electrolyte solution that transports hydroxide ions (OH^-) from the cathode to the anode with hydrogen being generated on the cathode side. State-of-the-art nickel-based cathode materials show good corrosion resistance in an alkaline solution water thus attracting extensive research efforts[30]. Although alkaline systems are the most developed electrolysis technologies with the lowest in capital cost, they have the lowest efficiency which leads to the highest electrical energy costs. Other ways toward green water electrolysis such as polymer electrolyte membranes (PEM) and solid oxide electrolysers (SOEC) are the developing technologies[28]. PEM electrolysers have no corrosion and seals issues, and they are more efficient than alkaline systems but more expensive. SOEC technology has a huge potential for industrial application because it can produce hydrogen while achieving 100% Faradaic efficiency[12]. However, it has problems with corrosion, seals, thermal cycling, and chromium migration[27].

In addition to the above-mentioned processes, photocatalytic water splitting has a high potential for application as a clean and renewable way to generate hydrogen, because it is a process with negligible CO_2 emission: Decomposition of water directly into hydrogen and oxygen under sunlight irradiation with a semiconductor material (photocatalyst) is investigated. To efficiently exploit solar energy, myriad efforts have been made to develop photocatalysts that can be used not only under UV light but also under visible light[31]. Up to now, TiO_2 has been a widely used catalyst for photocatalytic water splitting, due to the fact that it is environmentally benign, stable, abundant and economical. However, the main obstacles of TiO_2-based photocatalysts are the rapid recombination of electrons and holes of photo-generated excitons, fast backward reaction, and its poor activation by sunlight[32]. In response to these weaknesses, modification of its structure through the introduction of surface oxygen vacancies by controlled reduction (blue or black TiO_2) and incorporation of dopers (N, F) to alter surface defect concentration are the common strategy. Employing composite photocatalysts is also an up-and-coming approach to increase the photocatalytic performance. For example, the composites are prepared by combining non-oxide materials with oxides or other non-oxides to form heterojunctions such as CdS-TiO_2, CdS-ZnO, CdS-MoS_2, CdS-AgI, etc.,[31,33,34] which lead to new photocatalysts with more efficient charge separation and widened absorption spectrum.

So far, a tremendous amount of research has been pursued in developing the hydrogen production via green routes. Among all the strategies, water electrolysis coupled with renewable resources should be at this moment the preferable option for low CO_2 emission hydrogen synthesis technology in short term. The availability of inexpensive electric power generated by wind, photovoltaic, tidal, or ground heat in special locations or countries may justify the implantation of this technology. It is however, for most industrial areas of major CO_2 emission sources, the high installation and operational cost are still the major hindrances. Further research to address the cost issues is urgently needed. For photocatalytic generation of H_2, with the rapid development of new photocatalytic materials that overcoming the current deficiencies such as low stability of the catalysts and low energy efficiencies, it is anticipated that the low cost, environmentally friendly photocatalytic water-splitting for hydrogen production can contribute more significantly to the green hydrogen economy in further future. Particularly, the direct conversion of light energy to H_2 over the indirect conversion via photovoltaic and electrolysis would in principle offer lesser energy losts for the stepwise conversions.

2.3 CO_2/H_2 mixtures from biomass

Biomass is currently considered as one of the potential alternatives to produce renewable methanol. It can be obtained from various sources, including agricultural and forest residues, animal wastes, municipal paper wastes, sawdust, aquatic plants, and many more[28]. The currently accepted procedure to catalytically convert biomass into methanol is first via biomass conversion in the aqueous phase at temperatures ranging from 275 to 800 ^{o}C to produce syngas (CO, CO_2 and H_2), followed by water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) which leads to the outcome with lower amounts of CO and higher yield of hydrogen[35], and ultimately by hydrogenation of CO_2 to methanol ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$). Among the various gasification options, supercritical water (SCW) gasification[36] has received a great deal of attention as a promising method for utilising high moisture content biomass and allowing maximum conversion. In addition, SCW gasification is non-toxic, safe, readily available, economically feasible and environmentally friendly[37]. However, high temperature and pressure ($T > 500$ °C and $P > 23$ MPa) are usually required to satisfy the SCW operating condition, which are very energy intensive[36]. On the other hand, aqueous-phase reforming (APR) of biomass-derivatives is a recently developed process and is preferable over other methods owing to its wide renewable resource, mild reaction conditions ($T = 230$ °C and $P = 2$ MPa), and low processing cost[38]. These biomass conversion technologies have been found promising in generating a CO_2/H_2 mixture that can incorporate with the downstream CO_2 hydrogenation reactions. However, most biomasses and their derived molecules generally contain lower carbon to hydrogen ratios. As a result, the utilisation of biomass for methanol production faces the main problem in producing reformate gas of large excess CO_2 to H_2, while in practice $H_2/CO_2 \geq 3$ is preferable for methanol synthesis over most catalyst formulations. Therefore, the stoichiometric adjustment has to be introduced either by adding hydrogen gas or applying a CO_2 removal step, which requires burdensome equipment and high costs[39]. Alternatively, developing a new catalyst that can efficiently catalyse CO_2 hydrogenation to methanol under excess CO_2 but H_2-deficient conditions would be highly desirable.

3. Bimetallic catalysts on CO_2 hydrogenation to methanol

Bimetallic catalysts have emerged as an important class of catalysts due to their unique properties that are combined with two constituent metals. In many cases, bimetallic surfaces have enhanced catalytic properties owing to strong synergies to contribute the electronic or geometric alterations to monometallic counterparts. For the studies on CO_2 hydrogenation to methanol, Cu-Zn based system is prominently chosen. Other bimetallic catalysts such as Pd-Zn, Pd-Ga, Cu-Ni and Ni-Ga have also been investigated. In this part, we survey the research progress on CO_2 hydrogenation reaction to methanol over many of diversified bimetallic catalysts in the literature. This section will start with a brief introduction of thermodynamic equilibrium of the methanol synthesis reactions, followed by a discussion of the possible reaction pathways and reaction intermediates. The correlation between reaction products and the adsorption properties of the metallic surfaces will also be addressed. Then reviewing different synthesis methods of the selected bimetallic systems and their catalytic performance toward methanol synthesis will be carried out.

3.1 Methanol synthesis mechanism

Owing to the increasing focuses and interests in the methanol synthesis processes, numerous studies on the mechanism of CO_2 hydrogenation have been conducted. To fully understand the catalytic performance of CO_2 hydrogenation to methanol, the kinetics and thermodynamics of the catalytic system of concern are therefore required. Section 3.1.1 gives a brief review of the existing literature that provides information on the thermodynamic and kinetic aspects. Section 3.1.2 then discloses the reaction pathways and intermediates of methanol production reported in the literature. It is noted, however, that the mechanistic investigations on methanol synthesis from CO_2/H_2 were predominately conducted in the most studied system, i.e., the Cu-based system, hence the mechanisms derived from Cu-based catalysts are usually adopted to describe the reaction pathways/intermediates in different bimetallic systems due to the lack of the knowledge in understanding the underlying reaction mechanisms of CO_2 hydrogenation to methanol over other bimetallic catalysts. Therefore, in this section, the discussion of the reaction pathways and the key reaction intermediates is focused on the Cu-based system, after that, the influences of adding foreign metals (to form bimetallic system) on the reaction mechanisms are introduced.

3.1.1 Thermodynamic and kinetic considerations

In general, direct CO_2 hydrogenation to methanol contains two major competing reactions[12]. The first reaction is the synthesis of methanol from CO_2 and hydrogen:

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$. $\Delta H^0_{298K} = -49.5$ kJ/mol (1)

The second reaction is the reverse water gas shift (RWGS) reaction that produces CO:

$CO_2 + H_2 \rightarrow CO + H_2O$. $\Delta H^0_{298K} = 41.2$kJ/mol   (2)

Moreover, the catalytic hydrogenation of CO_2 to methanol can also occur indirectly from CO formed through the RWGS reaction[40]:

$CO + 2H_2 \rightarrow CH_3OH$. $\Delta H^0_{298K} = -90.6$kJ/mol   (3)

It can be seen from equations (1) and (3) that, according to Le Chatelier's principle, increasing pressures and decreasing temperatures will cause the reaction to shift toward the products to produce more methanol over the CO production from RWGS (equation 2). In addition, using a high molar ratio of H_2/CO_2 is also thermodynamically as well as kinetically favourable in methanol synthesis with taking the two equilibria into account[41]. Early studies have demonstrated the necessity of using extremely high-pressure conditions in the synthesis of methanol from syngas with CO_2 as reactants[42–44]. Thanks to the development of active Cu-Zn based catalysts, the reaction pressure of methanol synthesis has been substantially reduced to 5-10 MPa while a satisfactory methanol selectivity of 50% can be attained compared to previous catalyst formulations[45]. Nevertheless, due to the advantages of applying high-pressure conditions in CO_2 hydrogenation to methanol such as boosting methanol yield, handling hydrogen more safely, reduction in reactor volume and plant area thus decreasing capital costs, etc., high-pressure methanol synthesis over Cu based catalysts have been explored and documented by some research groups. Ipatieff et al.[46] conducted a high-pressure study up to 41.4 MPa over Cu/Al_2O_3 catalysts in a fixed-bed reactor, which showed remarkable conversion (94%) from CO_2 to methanol. By using co-precipitated $Cu/ZnO/Al_2O_3$ catalysts, Bansode et al.[47] demonstrated that one-pass CO_2 conversion (>95%) and methanol selectivity (>98%) were achieved under the reaction conditions of $H_2/CO_2 = 10$, reaction temperature of 260 ^{o}C, reactant pressure of 33.1 MPa, and gas hourly space velocity (GHSV) of 10,471 h^{-1}. Gaikwad et al.[48] also showed that at the stoichiometric molar ratio of $H_2/CO_2 = 3$, ca. 90% CO_2 conversion and > 95% methanol selectivity could be achieved at 44.2 MPa. In contrast, some researchers devoted to the development of catalysts that can work under low reaction pressures. It is mainly because the low-pressure CO_2 hydrogenation processes are more economically attractive with lower installation and operation (pumping) costs. Moreover, they have the advantages of safer operation and can be readily coupled with the upstream feedstocks generation processes. For example, hydrogen production from standard alkaline electrolyser is typically operated at ambient pressure or less than 3 MPa[49], and some low-pressure biomass conversion processes (e.g., APR) to form CO_2/H_2 mixture are operated at around 2 MPa[38]. However, the conversion of CO_2/H_2 to methanol by using low-pressure technologies is limited by thermodynamic and kinetic considerations. It has to be emphasised that obtaining satisfactory single-pass CO_2 conversion and methanol selectivity is important for practical catalytic application since recycling processes are costly and also required cumbersome facilities. So far, very little research has demonstrated high methanol production rate at the pressure lower than 2 MPa. In fact, most of the reported catalysts perform poorly at low-pressure conditions. Taking Cu-Zn system as an example, when the reaction pressures are applied at less than 2 MPa, the rate of RWGS is generally 1–3 orders of magnitude higher than that of methanol production over the Cu-Zn surface[50], thus resulting very poor selectivity toward methanol. It was reported previously by Toyir et al.[51] that under pressure of 2 MPa, silica-supported Cu/ZnO based catalysts showed methanol selectivity around 99%. In addition, In_2O_3/ZrO_2 catalyst reported more recently by Martin et al.[52] also achieved nearly 100% methanol selectivity under relatively low pressure (5 MPa). Although these catalysts presented unexpectedly high selectivity toward methanol, they showed very low CO_2 conversion (2% to 5%) hence leading to an overall low methanol production yield. Other Cu-based systems and novel catalyst materials such as the catalysts with copper-ceria interface[53] as well as Ni-Ga/SiO_2 system[54] have proven their potential on highly efficient methanol synthesis. However, those systems were evaluated for CO_2 to methanol at the pressure around ambient pressure where the obtained methanol yields are not impressive, hence little information on their realistic application of CO_2 hydrogenation is known from the results provided by the authors. Nevertheless, it has been recently reported that the production of methanol is more favourable than that of CO on the PdZn site of Pd@Zn core–shell nanoparticles from the kinetic perspectives[55]. From density functional theory (DFT) calculations, the relatively higher stability of the key adsorbed intermediate for methanol synthesis than that for CO production was revealed on this PdZn bimetallic surface. In addition, it was found that the PdZn surface could offer an unusually high kinetic (activation) barrier for the RWGS reaction and thus effectively enhancing methanol production while reducing CO levels under low pressure (2 MPa) conditions[56]. Therefore, this Pd-Zn catalyst system apparently opens up a promising possibility for low-pressure CO_2 hydrogenation application.

3.1.2 Reaction pathways and intermediates of methanol production

As stated, the catalytic hydrogenation of CO_2 to methanol can proceed directly or indirectly. In the former, two different mechanistic routes have been proposed according to their key reaction intermediates: the formate (HCOO) pathway or the hydrocarboxyl (COOH) pathway. Methanol synthesis via the HCOO-mediated mechanism has been proposed by many studies due to the fact that the formation barrier of the HCOO is considerably lower than the formation barrier of the COOH[50,57–59]. In addition, formate species were found to be the most abundant surface intermediates during CO_2 hydrogenation reaction from the experimental observations[60–64]. By performing DFT (GGA-PW91) calculations and microkinetic modelling for Cu surfaces, Grabow et al.[57] found that under typical methanol synthesis conditions, CO_2 hydrogenation is responsible for ~2/3 of the methanol produced, and the intermediates of the formate pathway for methanol production include HCOO*, HCOOH*, CH_3O_2*, CH_2O*, and CH_3O*, see Fig. 2. Another example of the formate pathway, proposed by Yang et al.[50] who employed DFT (GGA-PW91) calculation for Cu(111) and Cu nanoparticle surfaces, showed that methanol synthesis on Cu surfaces followed the formate pathway via HCOO, H_2COO, H_2CO and H_3CO intermediates, which were considered to be less stable from the above-mentioned calculations done by Grabow et al.[57] However, the authors indicated that the presence of the active low-coordinated Cu sites in the Cu nanoparticle could stabilise the key intermediates (HCOO and H_2COO) therefore lowered the barrier for the rate-limiting hydrogenation process. On the contrary, other researchers also investigated CO_2 hydrogenation to methanol on Cu(111) by using DFT (GGA-PW91) calculations and proposed that the H_2O-promoted hydrocarboxyl (COOH) mediated mechanism, following the sequence of COOH → HCOOH → HCO → HCOH → CH_2OH → CH_3OH, is kinetically more favourable than the formate pathway for the hydrogenation of CO_2 to methanol on Cu(111)[65]. In this proposed COOH pathway, it has been suggested that the formate species only plays a spectating co-adsorbate role[66], and the direct HCOO hydrogenation is even believed to be the "dead end" for methanol production[65]. For an easy comparison, the above-mentioned pathways for CO_2 hydrogenation to methanol and the intermediates are displayed in Fig. 2. On the other hand, it is also believed that hydrocarboxyl (COOH) is the chemical precursor of CO from RWGS reaction[56,67]. Hence, an indirect CO_2 hydrogenation mechanism has also been suggested, which involves the formation of CO from the RWGS reaction as the first step, then methanol is formed by the hydrogenation of CO. However, for the Cu-based catalyst system, this claim is not as widely accepted as the other two, because CO_2 hydrogenation to methanol was found to proceed much faster than CO hydrogenation to methanol over the industrial Cu/ZnO catalyst[68,69]. Moreover, it has already been demonstrated by several researchers that methanol is mainly produced by hydrogenation of CO_2 rather than CO under industrial conditions based on their isotopic labelling studies[69–72].

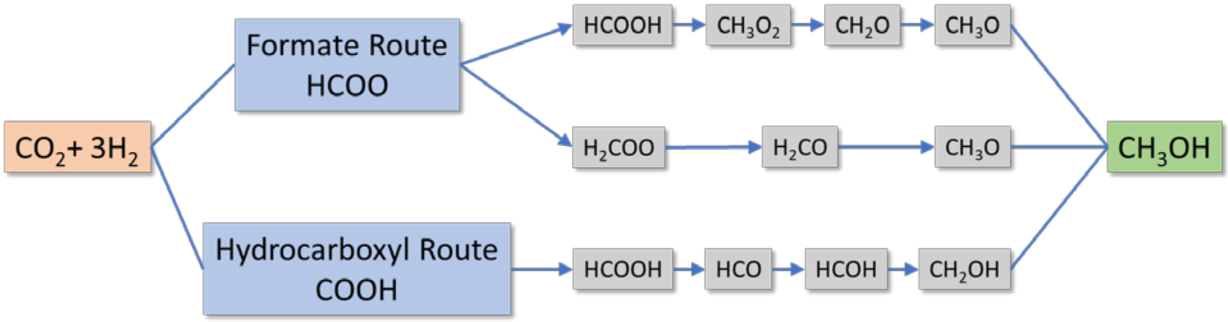

Fig. 2 CO_2 hydrogenation to methanol through formate route and hydrocarboxyl route and the intermediates[50,57,65] discussed in this minireview.

3.1.3 Synergistic enhancement in bimetallic catalysts

Adding foreign atoms to an existing metal system is used frequently to modify the chemical properties of metal surfaces. In catalysis, bimetallic alloys usually have different catalytic properties from their primary mono-metallic surfaces, which depend strongly on their electronic or geometric structures. Fig. 3 illustrates the main types of mixing patterns and structures of bimetallic, namely, mixed, core-shell or Janus alloys[73,74]. For the transition metals, the d-band model is often employed in understanding bond formation at the surface and their catalytic trends. Nørskov and co-workers have illustrated the correlation between the adsorption energy and the d-band structure on the surface metal atom that the adsorbate binds to[75,76]. By forming a bimetallic alloy, the structure of the surface d-electron bands and filling could change substantially owing to the modification of the electronic properties driven by i) the formation of heteroatomic bonds that lead to the electronic interaction between the two metals. This can alter the electronic environment of the primary metal, giving rise to modifications in the electronic configuration of it, and consequently, change its chemical properties. This is so-called electronic (or ligand) effect[77,78]; ii) geometric irregularity, that is, lattice distortion induced by alloying of two metals with different sizes, and lattice compression or expansion occurs often in the core-shell (see Fig. 3) bimetallic structure. Those geometric differences can cause the changes in surface bond lengths and bond angles, giving rise to the so-called geometrical (or ensemble) effect that modifies the electronic properties of the parent metal atoms[77–79]. According to theoretical calculations[54,67,80–82], catalytic activity and selectivity of CO_2 hydrogenation to methanol is critically dependent on the overall adsorptivity of the active surfaces. For a better understanding on the differences in product specificity and methanol production rate caused by the alteration of molecule adsorption through forming bimetallic alloys, we have surveyed the reported CO_2 hydrogenation studies and some examples are given as below.

In the literature, it has been suggested that Cu/Zn interface plays a significant role in methanol synthesis from CO_2 hydrogenation as these two species (Cu and Zn) work synergistically. Indeed, placing Zn in a proximity to Cu showed enhanced methanol production has been demonstrated by many researchers[83–85]. Behrens et al.[84] have reported the stabilisation of adsorbed intermediates with decreased energy barriers when Zn atoms were introduced on Cu step sites, which significantly increased the methanol production rate of Cu-Zn surface compared to the unmodified Cu surface. Moreover, catalysts containing Cu/ZnO were recently found to show 10 times higher activity than Cu catalysts of the same sizes but without in contact with ZnO[86]. Another non-precious bimetallic system, discovered by Studt et al.[54], showed that by alloying of Ga into Ni, the adsorption strength of Ni surface was modified hence accelerated the methanol formation. In contrast, Ni alone binds oxygen too strongly that would result in surface poisoning by formate or the surface would mainly perform methanation in CO_2 hydrogenation reaction[54]. Kusama et al. found that the formation of bimetallic alloys on the catalyst surface could change the electronic states of rhodium and lead to different adsorption properties: Rhodium-based catalysts are known to effectively catalyse CO_2 hydrogenation to CH_4 or CO, but alloying with Fe to form Fe-Rh catalysts could improve the ethanol selectivity remarkably[87], while alloying with Co and Rh resulted in promotion of methanol formation[88]. The authors concluded that the changes of product specificity could be correlated with the electronic state of rhodium changed with the foreign atom addition. The changes of the adsorptivity of the active surfaces can also be illustrated in the Pd-Zn bimetallic system. Liao et al.[56] found that alloying of Pd with Zn to form Pd core-Zn shell (Pd@Zn) structure could increase the adsorption strength of the bidentate formate species (the key intermediate to methanol). From density functional theory (DFT) calculation, a strong electronic charge transfer from Zn to Pd was revealed. The Zn-rich Pd-Zn bimetallic surfaces showed more selective and active for the formation of surface HCOO rather than COOH species in the first step of CO_2 hydrogenation, leading to a higher selectivity towards methanol production. Overall, from the above-mentioned examples, it can be seen that the changes in the adsorption properties of the primary mono-metallic surface are obvious when forming bimetallic system, giving rise to a different catalytic behaviour.

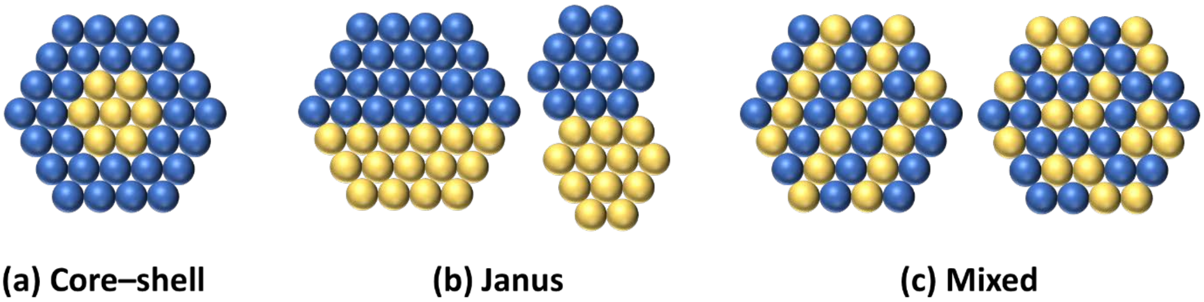

Fig. 3 Schematic representation of the types of structures of bimetallic alloy nanoparticles (based on Ref. [68, 69]).

3.2 Bimetallic catalysts made by different methods and their catalytic performances

The high-pressure methanol synthesis process from CO/CO_2 and H_2 mixture using mixed metals and metal oxides was firstly investigated in the early 20th century[42–44]. In the 1960s, the highly active and economic Cu/ZnO/Al_2O_3 catalyst was developed and it is still currently the preferred industrial catalyst for methanol synthesis operated at 240 °C – 260 °C and 50 – 100 bar[45]. At present, the major challenges for catalyst development to methanol synthesis from CO_2 are to develop a more efficient catalyst, thus the academic and industrial research efforts on catalyst preparation using different catalyst compositions and preparation methods are continuously built. Recently, bimetallic nanoparticles/alloys have emerged as an important class of catalysts because they show the intimate contacts of the two elements which can modify their electronic properties and change the adsorption properties of the metal surfaces. It is well-known that catalytic conversion of CO_2 to methanol is a structural-sensitive reaction[86]. Therefore, the differences in synthesis methods can influence the structure of the catalysts and then lead to a different catalytic performance. This section will focus on the review of synthesis methods of those bimetallic catalysts that showed enhanced ability to catalyse CO_2 hydrogenation to methanol than their monometallic counterparts. The catalytic performance of the selected catalysts is compared in Table 1. Please note that only the bimetallic catalyst systems with detailed disclosure of the catalytic testing results including CO_2 conversion, methanol selectivity, methanol yield, or turnover frequency, were selected for their comparison in this minireview.

Table 1 Catalytic performance of selected bimetallic catalysts in CO_2 hydrogenation to methanol

Synthesis method	Catalyst Active species/ (support)	Reaction conditions			Catalytic performance					Ref.
		P (MPa), T (°C)	Space velocity	H_2/CO_2	CO_2 conversion (%)	Methanol selectivity (%)	STY_{MeOH}[e] ($g_{MeOH}·g_{cat}^{-1}·h^{-1}$)	WTY_{MeOH}[f] ($g_{MeOH}·.g_{active\ metal}^{-1}·h^{-1}$)	TOF (s^{-1})	
Imp.[a]	PdGa/(β-Ga_2O_3)	3, 250	(G)[d] 80000 h^{-1}	3	<1	52	N.A.	N.A.	0.075	89
	Pd/(SiO_2)					12			0.002	
	PdGa/(rod Ga_2O_3)	5, 250	(W) 6000 mL g^{-1} h^{-1}	3	11.04	41.27	N.A.	N.A.	N.A.	90
	PdGa/(plate Ga_2O_3)				17.33	51.62				
	PdZn/(h-CNTs)	3, 250	(W) 1800 mL g^{-1} h^{-1}	3	N.A.	99.6	0.371	N.A.	0.0115	91
	PdZn / (activated carbon)					96.5	0.281		0.0098	
	PdZn/(γ-Al_2O_3)					92.1	0.242		0.0097	
	PdCu/(SiO_2)	4.1, 250	(W) 3600 mL g^{-1} h^{-1}	3	6.7	30	0.032	N.A.	N.A.	92
	Pd/(SiO_2)				3.0	23	0.010			
	Cu/(SiO_2)				2.8	15	0.006			
	Ni_5Ga_3/(SiO_2)	0.1, 210	(G) 6000 h^{-1}	3	N.A.	N.A.	~0.02	~0.12	N.A.	54
Co-precip.[b]	Cu/ZnO/Al_2O_3	5, 250	(W) 18000 mL g^{-1} h^{-1}	3	19.7	48.1	0.637	N.A.	N.A.	93
	Zincian georgeite-derived catalyst	2.5, 190	(W) 7000 mL g^{-1} h^{-1}	CO:CO_2: H_2:N_2 =6:9.2:67:17.8	N.A.	N.A.	0.102	0.167	N.A.	94
	Zincian malachite-derived catalyst						0.083	0.136		
	Commercial Cu/ZnO/Al_2O_3						0.116	0.243		
	PdGa/(Ga_2O_3)	5, 250	(W) 18000 mL g^{-1} h^{-1}	3	19.6	51.5	N.A.	N.A.	0.1139	95
	CuZn/(ZnO)				11.7	36.1	N.A.	N.A.	0.0048	
	Catalyst derived from Cu,Zn,Al-LDH	6, 250	(W) 20000 mL g^{-1} h^{-1}	H_2:CO:CO_2:He =72:10:4:14	N.A.	N.A.	N.A.	N.A.	0.0268	96
	Conventional Cu/ZnO/Al_2O_3								0.018	
	Catalyst derived from Cu,Zn,Al,Y-LDH	5, 250	(W) 10000 mL g^{-1} h^{-1}	3	20.2	69.3	0.39	N.A.	0.00666	97
	Cu/(Zn,Al,Zr-LDH)	5, 250	(W) 7500 mL g^{-1} h^{-1}	3	22.2	45.8	0.30	N.A.	N.A.	98
	Catalyst derived from Cu,Zn,Al,Y-LDH	5, 250	(W) 12000 mL g^{-1} h^{-1}	3	26.9	47.1	0.52	N.A.	N.A.	99
	CuZn catalyst derived from CuZnGa-CO_3 AMO-LDH	4.5, 270	(W) 18000 mL g^{-1} h^{-1}	3	18.8	47.8	0.6	N.A.	N.A.	100,101
	PdZn catalyst derived from PdZnAl LDH	3, 250	(W) 15000 mL g^{-1} h^{-1}	3, with 4 vol% Ar	0.6	60	0.017	N.A.	0.002	102
	Pd_2Ga catalyst derived from PdMgGa LDH				1.0	47	0.020	N.A.	0.0085	
	Pd catalyst derived from PdMgAl LDH				3	4	0.0006	N.A.	0.00005	
bimetal carbonyl hydride	PtCr/(SiO_2)	3, 200	W/F = 10 g_{cat} h/mol.	3	2.2	51.1	N.A.	N.A.	N.A.	103
	PtW/(SiO_2)				2.6	92.2				
Imp.	Pt/(SiO_2)				0.4	1.9				
Sol-immob.[c]	PdZn/(ZnO)	2, 250	(W) 3600 mL g^{-1} h^{-1}	3	10.7	60	0.07744	N.A.	N.A.	104
Imp.	PdZn/(ZnO)				8.7	1	0.00176			
Hetero-junction	Pd@Zn/(ZnO+CdSe)	4.5, 270	(W) 18000 mL g^{-1} h^{-1}	3	14.4	64.9	0.60	12.0	0.33	55
		2, 270			7	67.3	0.30	6.1	0.19	56
Commercial Cu/ZnO/Al_2O_3		4.5, 270	(W) 18000 mL g^{-1} h^{-1}	3	N.A.	N.A.	0.38	N.A.	N.A.	101

[a] Impregnation method

[b] Co-precipitation method

[c] Sol-immobilisation

[d] (G) = GHSV = volume flow rate/bed volume, (W) = WHSV = mass flow rate/catalyst mass.

[e] Space time yield of methanol ($g_{MeOH}·g_{cat}^{-1}·h^{-1}$)

[f] Weight time yield of methanol ($g_{MeOH}·.g_{active\ metal}^{-1}·h^{-1}$)

3.2.1 Impregnation method

Impregnation is the simplest method for mounting of dissolved aqueous metal precursors on oxide supports to prepare supported catalysts. A knowable advantage of impregnation method is that the materials dissolved in the solution will not get lost, which makes this method attractive when preparing precious metal-containing catalysts. Pd-containing bimetallic catalysts made via impregnation method were first discovered in the 1900s by Iwasa et al.[105] The authors observed that the original catalytic functions of monometallic Pd for steam reforming of methanol, the reverse reaction of CO_2 hydrogenation to methanol, was greatly modified by the formation of bimetallic alloys, i.e., Pd-Zn, Pd-Ga and Pd-In, upon the reduction of the Pd-metal oxides. It was found that the reactions proceeded selectively when using the catalysts having the alloy phase, whereas poor selectivities were exhibited on the catalysts having monometallic phase.[106] A few years later the Pd-Ga system was further investigated by other researchers[89], and the Pd-Ga bimetallic particles were found to be the sites responsible for the increased selectivity to methanol in CO_2 hydrogenation as well as the inhibition of the methanol decomposition and/or reverse water-gas shift (RWGS) reaction to produce CO. As a result, the Ga-modified Pd catalyst showed much better selectivity and TOF toward methanol production[89]. Qu et al. [90] further proposed that using the plate-form Ga_2O_3, which has a higher degree of defects and electron-richer polar (002) surface, could exert a stronger electronic interaction with Pd than the rod-form surface Ga_2O_3. This would lead to a deep reduction of Ga^{3+} to generate bimetallic $PdGa_x$ nanoparticles with superior catalytic properties for methanol synthesis by CO_2 hydrogenation. As the importance of bimetallic nanoparticles has been increasingly recognised, the characterisation techniques for revealing the structures of bimetallic catalysts become more and more valuable. By using a combination of advanced electron microscopy techniques and structure characterisation tools, highly dispersed $GaPd_2$ nanoparticles on a high-surface-area SiO_2 support synthesised by impregnation of the high-surface-area SiO_2 with Pd and Ga nitrates were identified. Besides, this nanodispersed intermetallic $GaPd_2$ catalyst showed a much better methanol selectivity than the traditional $Cu/ZnO/Al_2O_3$ catalyst under ambient pressure[107].

Apart from the Pd-Ga system, several supported Pd catalysts have also been found to exhibit considerable activity and selectivity for hydrogenation of CO_2 to methanol. Liang et al.[91] incorporated multi-walled carbon nanotubes (MWCNTs) into Pd/ZnO catalysts prepared via a stepwise incipient wetness method. They found that the unique features of MWCNTs were leading to the increase of the surface concentration of the Pd^0 species in the form of

PdZn alloys as well as helping with H_2 activation, thus increasing the rate of surface hydrogenation reactions. On the other hand, amorphous silica supported Pd-Cu bimetallic catalysts prepared by co-impregnation method also found to have a strong synergistic promotion compared to the monometallic Pd and Cu catalysts[92]: The production rate of methanol on the Pd-Cu bimetallic catalyst is 2 times as much as the sum of those on the monometallic catalysts, indicating a considerable bimetallic promotion on methanol synthesis from hydrogenation of CO_2. Another example of the precious bimetallic metal surface for enhancing methanol production can be found in the Rh-Co catalyst[88]. Although the methanol selectivity was very low (< 20%), Rh-Co alloy was suggested to change the electronic states of rhodium, resulting in promotion of methanol formation. On the other hand, non-precious Ni-Ga catalysts synthesised via impregnation method was recently discovered to be superior to the traditional $Cu/ZnO/Al_2O_3$ catalyst with respect to their ability to inhibit the RWGS activity[54]. The Ni-Ga intermetallic compounds were found to possess mixed sites: the gallium-rich sites facilitate methanol synthesis, whereas the nickel-rich sites perform RWGS and methanation until they get poisoned by CO and carbon, which makes the Ni-Ga catalysts to display good methanol synthesis activity with considerably lower production of CO as compared to the conventional $Cu/ZnO/Al_2O_3$ catalysts under atmospheric pressure[54].

3.2.2 Co-precipitation method

The catalysts based on more than one component can be prepared by the simultaneous precipitation from a solution containing desired soluble species to generate a homogeneous distribution of catalyst components or catalyst precursors with a definite stoichiometry. Co-precipitation method provides the advantage of obtaining high dispersions of catalyst components, which is difficult to achieve by other synthesis approaches. Therefore, it is very suitable to use in preparing multi-component catalysts and catalyst precursors.

3.2.2.1 Cu/ZnO based catalysts

The industrial $Cu/ZnO/Al_2O_3$ catalyst for methanol synthesis is made via coprecipitation method. Since the prevailing of $Cu/ZnO/Al_2O_3$ catalyst, the Cu/ZnO based catalysts have attracted increasing attention and many systematic studies have focused on elucidating the structure of active sites[58,84,108]. Although the active sites of methanol synthesis over commercial $Cu/ZnO/Al_2O_3$ catalysts have recently been the subject of intense debate, many studies over the past 20 years have shown that the good performance of Cu/ZnO based catalysts for methanol synthesis could be attributed to the active Zn-Cu bimetallic sites. Early researches done by Fujitani et al.[93,109,110] focused on the promotion mechanism of ZnO to Cu catalysts for methanol synthesis. Their result revealed that the partially reduced ZnO_x could migrate to the surface of Cu particles to form Cu-Zn alloy when reducing a Cu/ZnO catalyst with H_2 at above 600 K. The Cu-Zn alloy phase was then believed to be a catalytically active species for the methanol synthesis from CO_2 and H_2 [111,112]. Topsøe and co-workers observed that Cu/ZnO changed the CO adsorption properties under severe reducing conditions from in-situ IR during methanol synthesis, suggesting that Cu-Zn alloy structures could be formed due to the migration of reduced ZnO species[113]. After conducting careful investigations using other in-situ techniques, which includes electron energy loss spectroscopy (EELS), high-resolution transmission electron microscopy (HR-TEM) and extended X-ray absorption fine structure (EXAFS), the presence of Cu-Zn alloy in the reduced Cu/ZnO catalysts was further confirmed[114,115]. Recently, with the rapid development of advanced characterisation techniques, it has been shown that Cu steps stabilised by bulk defects and decorated with Zn atoms upon reduction can lead to a subtle change in the geometric and electronic structure of Cu due to the desirable bimetallic properties[84]. Consequently, the high activity of $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst is attributed to the surface alloy of Zn and Cu[83,108].

It is noted that Cu/ZnO based catalysts prepared by coprecipitation are much more active than those prepared by impregnation methods. Moreover, the structure of catalyst precursor obtained in the coprecipitation synthesis, such as malachite $Cu_2CO_3(OH)_2$, zincian malachite (sometimes called rosasite) $(Cu,Zn)_2CO_3(OH)_2$, aurichalcite $(Cu,Zn)_5(CO_3)_2(OH)_6$, or hydrozincite $Zn_5(CO_3)_2(OH)_6$, can significantly affect the catalytic activity for methanol production[112,116,117]. Baltes et al.[118] discovered that the synthesis history would influence strongly to the catalytic activity of methanol production. In their study, ternary $Cu/ZnO/Al_2O_3$ catalysts were systematically prepared via the coprecipitation method under various synthetic parameters, and the best methanol productivity was found in the catalysts with the following preparation conditions: Precipitation temperature of 70 ^oC, pH of 6-8, time of aging in the mother liquor of 20-60 min, and calcination at 300 ^oC, which resulted in the catalysts with relatively high BET and Cu^0 surface areas[118]. Other studies on this system by Behrens et al.[119–121] further concluded that zincian malachite was the optimum precursor for the methanol synthesis catalyst due to its interwoven, nano-scale needle morphology that facilitates the formation of a highly porous mesostructure catalyst. On the other hand, it was recently reported that a disordered zincian georgeite catalyst precursor could be prepared using supercritical antisolvent (SAS) precipitation method[122], which enabled the preparation of an active Cu/ZnO catalysts that could compete with those catalysts prepared from other hydroxycarbonates precursors. Soon after it was found that zincian georgeite could be readily prepared by co-precipitation method[94]. Although the zincian georgeite made by co-precipitation led to a catalyst with a slightly poorer performance than those derived from SAS precipitation due to the impurity contamination and less-disordered structure in the co-precipitated phases, it still displayed superior performance for methanol synthesis compared to a conventional preferred zincian malachite derived catalyst[94].

3.2.2.2 Precious metal based bimetallic catalysts

Apart from the Cu/ZnO based catalysts, co-precipitation method was also widely employed in the preparation of precious metal based bimetallic catalysts. Fujitani et al.[95] synthesised a series of palladium catalysts by co-precipitation method. The authors found that the Pd/Ga_2O_3 catalyst was more active than Cu/ZnO by a factor of 2 in term of yield and 20 in term of turnover frequency (TOF) for the synthesis of methanol from CO_2 and hydrogen, due to the optimal amount of Pd^{n+} ($0 < n < 2$) stabilised by Ga_xO_y on the surface of palladium. Remember that many studies have identified the formation of Pd-Ga bimetallic alloys in such catalyst composition, as discussed previously in section 3.2.1 of this minireview, which are experimentally proven to be active for methanol production from CO_2 and hydrogen. On the other hand, carbon nanotubes (CNTs) was found to play a dual role (acting as a catalyst supporter as well as a promoter) for Pd-based catalysts[91]. CNTs-promoted Pd-Zn and Pd-Ga catalysts were synthesised via co-precipitation method and studied for methanol production from CO_2 hydrogenation by Zhang and co-workers[91,123]. The authors found that Pd-Zn and Pd-Ga catalyst with an appropriate incorporation of CNTs displayed enhanced activity for CO_2 hydrogenation to methanol compared to those non-promoted Pd-based bimetallic catalysts.

3.2.2.3 Layered double hydroxide (LDH)-derived catalysts

Recently, hydrotalcite-like compounds (or layered double hydroxide, LDH) with the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(An^{-})_{x/n}\cdot mH_2O$ where M^{2+} and M^{3+} are divalent and trivalent cations, respectively, have attracted increasing attention. LDH structure provides a homogeneous distribution of all metal cations inside the layers, which is believed to offer a suitable matrix for generating small, stable, and well-dispersed metal nanoparticles after calcination and reduction. It was reported that monophasic catalyst precursor containing M^{2+} and M^{3+} could be obtained by controlled thermal treatment of an LDH structure[124], since that, the application of LDH as a catalyst precursor for CO_2 hydrogenation reaction has been developed accordingly. Many studies have discussed the advantages of LDH precursors for Cu/ZnO-based catalysts[125,126], such as good dispersion of M^{2+} (Cu^{2+}, Zn^{2+}) and M^{3+} (Al^{3+}, Y^{3+} or Ga^{3+}) at an atomic level, homogeneous microstructure, good thermal stability against sintering/reduction, high dispersion for small Cu clusters, and high specific surface area. An active catalyst derived from a phase pure Cu, Zn, Al hydrotalcite-like precursor was prepared and studied by Kühl et al[96]. This sample showed intrinsically more active than a conventionally prepared reference catalyst. Furthermore, Gao et al.[97–99] synthesised a series of $Cu/ZnO/Al_2O_3$ catalysts derived from hydrotalcite-like precursors with modifier (Mn, La, Ce, Zr and Y) or promoter (Y_2O_3) and tested for the CO_2 hydrogenation to methanol. They have concluded that the introduction of additives to $Cu/ZnO/Al_2O_3$ catalysts derived from hydrotalcite-like compounds could give higher BET specific surface area, Cu surface area and Cu dispersion, thus leading to an enhanced catalytic performance with high stability[97–99]. Tsang and co-workers[100,101] have recently reported a new CuZnGa catalyst derived from ultra-thin (1-3 cationic-layers) $(CuZn)_{1-x}Ga_x$-CO_3 layered double hydroxides (AMO-LDH) nanosheets using the aqueous miscible organic solvent method (AMOST)[127]. It has been found that upon reduction, the AMO-LDH-derived catalysts give consistently and significantly higher Cu surface areas and dispersions than the catalysts prepared from conventional co-precipitation methods. It is also evident that Zn metal atoms decorating on Cu nanoparticles can be formed in the catalyst derived from ultrathin LDH precursor, thus exerting a great promoting effect to the CO_2 hydrogenation reaction to methanol and leading to a high methanol production rate. On the other hand, Ota et al.[102] synthesised Pd-based catalysts derived from ternary hydrotalcite-like compounds obtained by co-precipitation from aqueous solutions. They found that the intermetallic Pd_2Ga and PdZn nanoparticles with a homogeneous distribution of Pd and intimate interaction with the other reducible metal species were formed upon reduction in hydrogen, which were more active for methanol synthesis from CO_2 hydrogenation than the monometallic Pd catalyst.

3.2.3 Other synthesis method.

Shao et al.[103] reported the supported PtW and PtCr bimetallic catalysts made by the bimetal carbonyl hydride complexes precursors. The PtW and PtCr bimetallic catalysts exhibited higher activity and methanol selectivity in CO_2 hydrogenation reaction than the monometallic or bimetallic catalysts prepared via impregnation method. Nerlov et al.[128] applied CO as a promoter in the catalyst system and observed a CO gas phase induced surface segregation of Ni on Cu(100). The authors also found that the Ni/Cu(100) bimetallic sites were 60 times more active for CO_2 activation compared with pure Cu ones[129]. Hartadi et al.[70] found that a commercially available Au/ZnO catalyst prepared by deposition-precipitation could benefit from the same effect as the Cu/ZnO catalyst: the partially reduced ZnO in the highly reductive atmosphere could induce the formation of AuZn (surface) alloys or the formation of a partially reduced ZnO_x shell, implying the potential of Au/ZnO catalysts for the application in hydrogenation of CO_2 to methanol. Bahruji et al.[104] identified the PdZn alloy nanoparticles with a controlled particle size from the Pd/ZnO catalysts prepared by sol-immobilisation. The authors suggested that the catalysts prepared by sol-immobilisation were relatively stable to thermal treatment and showed a higher conversion of CO_2 towards methanol than the classic impregnated catalysts.

Tsang and co-workers[55,56] reported a novel hetero-junction approach to synthesize supported Pd@Zn nano-structures with tuneable Zn shell thickness by a simple reduction of Pd/CdSe-ZnO solid precursors in hydrogen. The precursors contained CdSe-ZnO type II hetero-junction interfaces that could promote the reduction process of ZnO to metallic Zn^0 atom and form Zn decorate Pd nanoparticles, which would exert enhanced catalytic performance in methanol production from CO_2 hydrogenation. The similar hetero-junction approach was then applied to the Cu/ZnO based catalyst. It was found that the presence of a small amount of Ga^{3+} in the Cu/ZnO system could lead to the formation of Ga-containing spinel structure, which would create electronic heterojunction with excess ZnO phase to account for the facilitated reduction of Zn^{2+} to Zn^0 in contact with Cu to form highly active CuZn bimetallic nanoparticles and offer catalytic sites. The authors also discovered a correlation between Zn^0 concentration in the CuZn alloy nanoparticle to the catalytic performance, showing that CO_2 conversion and methanol selectivity were significantly improved by increasing the Zn^0 content in these CuZn bimetallic catalysts[85].

4. Conclusion

To deal with the problems imposed by global warming, an immediate action toward reducing CO_2 emissions is necessary. Recent years have seen a growing interest in capturing CO_2 with hydrogen generated from renewables to produce green methanol, which can contribute to the mitigation of greenhouse gasses. This minireview has provided a survey of the recent advancements in the CO_2 capture, hydrogen production, CO_2/H_2 derived from biomass, and the use of bimetallic alloy catalysts for methanol production via CO_2 hydrogenation. To assess whether the green methanol production process is technological and economically attractive, the availability of upstream feedstocks including CO_2 capture as well as H_2 production technologies should be considered. On the other hand, biomass conversion is a feasible way to obtain both CO_2 and H_2 for methanol synthesis. However, a large excess CO_2 exists in the biomass-derived gas mixture is not favourable for the direct methanol production, hence the stoichiometric adjustment is required either by adding hydrogen or by removing CO_2. As for the catalyst systems for CO_2 hydrogenation to methanol, at present the commonly used Cu-based catalyst, especially Cu-Zn based catalysts, still at the benchmark position due to their superior activity and economic advantages. However, Cu-based catalysts often show low methanol selectivity under low reaction pressure or low H_2/CO_2 conditions, presumably due to the poor intrinsic H_2 activation capability of Cu. Therefore, the development of new non-Cu based catalysts with low cost, good performance, and high stability that can be effectively coupled with the above-mentioned feedstocks generation processes, would be highly desirable. In this context, rational design of novel bimetallic alloy systems as well as developing new synthesis approaches that can lead to unique structural properties and enhanced activities toward methanol synthesis are required.

Conflicts of interest

There are no conflicts of interest to declare.

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