Improving the Cu/ZnO-Based Catalysts for Carbon Dioxide Hydrogenation to Methanol, and the Use of Methanol As a Renewable Energy Storage Media

Ubong J. Etim1, Yibing Song2 and Ziyi Zhong1,3*

1Guangdong Technion Israel Institute of Technology (GTIIT), Shantou, Guangdong, China, 2Department of Chemistry, Shantou University, Shantou, China, 3Technion-Israel Institute of Technology (IIT), Haifa, Israel

Heterogeneous catalytic hydrogenation of carbon dioxide (CO₂) to methanol is a practical approach to mitigating its greenhouse effect in the environment while generating good economic profits. Though applicable on the industrial scale through the syngas route, the catalyst of Cu/ZnO/Al₂O₃ suffers from a series of technical problems when converting CO₂ to methanol directly, which include low single-pass conversion, low methanol selectivity, requiring high pressure and fast deactivation by the reverse water gas shift reaction. Over the years, intensive research efforts have been devoted to proffering solutions to these problems by modifying the existing catalyst or developing new active catalysts. However, the open question is if this type of widely used industrial catalyst still promising for CO₂ methanolizing reaction or not? This paper reviews the history of the methanol production in industry, the impact of CO₂ emission on the environment, and analyzes the possibility of the Cu/ZnO-based catalysts for the direct hydrogenation of CO₂ to methanol. We not only address the theoretical and technical aspects but also provide insightful views on catalyst development.

Keywords: carbon dioxide, hydrogenation, methanol, Cu/ZnO catalyst, microstructure

INTRODUCTION

Carbon dioxide (CO₂) is a greenhouse gas emitted into the atmosphere via the combustion of fossil fuels (oil, coal, natural gas) in vehicles and power plants, from many industrial processes, and household operations, etc. (Karl and Trenberth, 2003; Hansen et al., 2006; Lim, 2015). On receiving the CO₂ from these sources, the earth heats up, resulting in global warming. A recent report shows that as of 2017, the global average concentration of CO₂ in the atmosphere was 405 ppm, and it is expected to reach 410 ppm by 2020, which shows a clear increasing level in the atmosphere. Therefore, it is urgent to develop and establish practical and reliable emission reduction technologies and CO₂ control approaches. In recent times, this has been one of the reasons why discussion of CO₂ emission reduction tops agenda in most environmental pollution control submits, globally.

The reduction of CO₂ to economically relevant products represents an eco-friendly and green route toward value-added CO₂ emissions mitigation for environmental sustainability. For example, converting CO₂ to liquid fuels and chemicals is essential to cushion the shortage of fossil fuels and to provide cheap availability of chemical feedstock (Kattel et al., 2017a). This kind of conversions can be
successfully implemented by heterogeneous catalytic processes using cheaply available hydrogen, e.g., H₂ from natural gas and shale gas, or renewable sources of energy (Dang et al., 2018; Ouda et al., 2019). The catalytic reduction of CO₂ can produce carbon monoxide (CO), methanol, or hydrocarbons. CO is a feedstock in the Fischer–Tropsch process, while the applications of methanol and hydrocarbon are diversified.

Methanol is an essential industrial commodity chemical, with a global production capacity higher than 100 MTY (Bertau et al., 2014; Jadhav et al., 2014; Wang et al., 2014; Sehested, 2019). In 2018, the demand for methanol was approximately 80–90 million tons and will exceed 110 MTY by 2023. Methanol can be directly used as a clean-burning biodegradable fuel in combustion engines and fuel cells, and can be transformed by various chemical processes into a wide range of useful chemicals (Figure 1). The latter can be subsequently applied to produce a broad range of daily products—fuel additives, resins, plastics, paints, polyester, and building materials (Goeppert et al., 2014; Sehested, 2019). With the increasing use of these products, more methanol is required to meet the large-scale precursor chemical production and other applications. Hence, the catalytic conversion of CO₂ to methanol is highly desirable to meet the high demand and to ensure a cleaner environment by reducing the burden of global warming caused by CO₂ emission, with associated potential economic benefits.

Generally, conversion to methanol and other value-added products is an effective strategy for CO₂ valorization. Some literature reports in the past have reviewed the CO₂ reduction with hydrogen over heterogeneous catalysts focusing on the different aspect of the field, including the CO₂ reduction to CO, methanol and hydrocarbons, their challenges and prospects (Porosoff et al., 2016; Yang H. et al., 2017; Whang et al., 2019; Zhou et al., 2019). According to the thermodynamics, the most stable reaction path for CO₂ hydrogenation yields methane as the product. The pathway to a particular reaction can be selectively controlled by selecting appropriate catalysts and reaction conditions (Porosoff et al., 2016). Owning to a low equilibrium conversion of CO₂ to methanol at high temperatures, the development of efficient catalysts to break the thermodynamics barriers is of extreme importance. Thus, a selective catalyst is required to optimize methanol synthesis.

Although new catalysts have been developed in the last five years, the conventional Cu-based catalysts for CO₂ hydrogenation to methanol are still extensively investigated for further improvements. Considering the significant progress achieved in this area, we will discuss and focus on the recent advancements in the application of Cu/ZnO-based catalysts for the direct synthesis of methanol from CO₂, i.e., using CO₂ as the sole feed. We will also retrospect and review the history of the methanol production in industry, the reaction thermodynamics, mechanism, and kinetics, as well as the catalyst structures and suitable conditions for surpassing the equilibrium catalyst activity.

**THERMODYNAMICS AND REACTION MECHANISM**

**Thermodynamics**

In the hydrogenation of CO₂ feedstock to a desirable product, the performance of a catalyst will be determined by the thermodynamics of the reaction. Thus, the maximum conversion of CO₂ at a given pressure and temperature is defined by the thermodynamic equilibrium conversion under the given reaction conditions (Mutschler et al., 2018). The transformation of CO₂ to methanol is an exothermic reaction (Eq. 1), and therefore, favored at low reaction temperature and high pressure. Consequently, elevated pressure and reduced temperature favor an increased methanol yield. However, considering the reaction kinetics and the inert nature of CO₂, a high reaction temperature greater than 240°C is often applied (Ma et al., 2009). In addition, this reaction often accompanies the reverse water gas shift (RWGS) reaction, that is endothermically (Eq. 2) favorable at high temperatures and low pressures,
generating CO, which lowers the selectivity to methanol, and H2O that deactivates the catalyst. These factors reduce catalyst activity and increase the difficulty in process design (Grabow and Mavrikakis, 2011; Graciani et al., 2014; Hartadi et al., 2015). Thus, the overall process is limited by the thermodynamic equilibrium, and the equilibrium-shift chemistry plays out to control the conversion and selectivity of the products.

\[
\begin{align*}
\text{CO}_2 + 3\text{H}_2 & \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H_{\text{298 K}} = -49.5 \text{ kJ mol}^{-1} \\
\text{CO}_2 + \text{H}_2 & \leftrightarrow \text{CO} + \text{H}_2\text{O}, \quad \Delta H_{\text{298 K}} = 41.2 \text{ kJ mol}^{-1}
\end{align*}
\]

Breaking the thermodynamics/kinetics limitation by increasing one-pass CO2 conversion (CO2 conversion at a single step) can tune the selectivity away from CO and toward methanol (Stangeland et al., 2018). One way to actualize this is by applying high pressure. The high-pressure approach using a conventional Cu/ZnO/Al2O3 methanol synthesis catalyst was applied to CO2 hydrogenation to methanol (Figure 2). Under the specified reaction conditions, methanol selectivity, and productivity were remarkably boosted at high pressure by increasing H2 partial pressure to enhance the reaction rate and thermodynamically favor high CO2 conversion and methanol selectivity (Bansode and Urakawa, 2014). As reported by Stangeland et al. (2018), both temperature and pressure have considerable effects on the equilibrium conversion. The methanol synthesis reaction becomes less favored, and the RWGS reaction more favored as the temperature is increased. On the other hand, increasing the pressure strongly enhances the CO2 conversion at low temperatures. Moreover, lowering the concentration of CO2 in the feed stream can increase the CO2 conversion, and this can be achieved by using excess H2 to shift the equilibrium to the products side. Thus, a high H2/CO2 ratio leads to high methanol and low CO selectivity. The selection of the appropriate H2/CO2 ratio, therefore, depends on the requirements of the methanol synthesis system. For example, if high conversions are targeted, it is preferable to work at high H2 concentrations (Stangeland et al., 2018). Irrespective of the pressure, increasing the H2/CO2 ratio will lead to an increase in the CO2 conversion to methanol owing to the sensitivity of H2 partial pressure to the methanol synthesis (Jia et al., 2016; Stangeland et al., 2018). It was demonstrated that product condensation could be utilized to circumvent thermodynamic restrictions on the product yield. Thus, significant improvements in CO2 conversion can be achieved by operating at conditions favorable for product condensation (Stangeland et al., 2018). Also, the thermodynamic limitation can be overcome with reactors, which can recycle the waste CO2 from methanol combustion, and this can increase the conversion to almost 100% (Goepert et al., 2014; Hu et al., 2017a). Thus, performing multiple separation/recycling loops can produce high conversion under practical temperature and pressure. The use of microstructured catalytic reactors with transverse diameter channels on a millimeter-scale has advantages over larger systems of better heat management, more efficient use of catalysts and controlled operation at high pressure (Renken and Kiwi-Minsker, 2010).

### Reaction Mechanism

Knowledge of the mechanistic details is a decisive catalyst design criterion for CO2 hydrogenation catalysts. Generally, two mechanistic pathways have been proposed from many studies for CO2 hydrogenation to methanol over Cu-based catalysts, as shown in Figure 3 (Kattel et al., 2016; Hu et al., 2017a; Hu et al., 2017b; Yang B. et al., 2017; Karelovic et al., 2019). The first pathway features the CO intermediate, which is produced from RWGS: CO2 + H2 → CO + H2O reaction via carboxyl (*HOCO) species and is further hydrogenated to methanol; the other pathway is associated with the formate (*HCOO) intermediate formed by CO2 hydrogenation which eventually produces methanol via the C–O bond cleavage and *HCOOH or *H2O intermediates (Liu and Liu, 2015). According to the density functional theory (DFT) calculations, CO2 hydrogenation prefers the formate pathway on ZnCu(211) via *HCOOH, *H2COOH, and *CH3O intermediates over the RWGS + CO-hydro pathway for methanol synthesis (Kattel et al., 2017b). On the same ZnCu(211) surface, hydrogenation of CO2 can proceed through the Eley–Rideal mechanism, as with pure Cu catalysts, as a result of the unfavorable CO2 binding at the Zn–Cu interfacial site. CO is the main product along the RWGS pathway, and only a relatively small proportion of *HCO could further be hydrogenated to *CH3OH. The direct dissociation of *CO to *CO and *O was also evident, and the strong oxygen affinity for Zn sites kinetically favored the formation of *O more than hydrogenation to *HOCO. On unsupported or unalloyed Cu catalysts, *HCOO species act as spectators for methanol synthesis (Yang et al., 2015; Kattel et al., 2017b). The addition of Zn or ZnO stabilized the *HCOOH intermediates via direct Zn–O interaction and by activating *HCOO via hydrogenation. Chances to suppress the undesired CO formation for an increased methanol yield are high, and different strategies can be applied if the two reactions are known to proceed independently via parallel pathways (and on various surface sites). In turn, it will be a hard task to suppress CO formation for a catalyst that produces methanol by a mechanism that shares a common intermediate with CO formation or even uses CO as a reactant (Kunke et al., 2015). For the industrial Cu/ZnO/Al2O3 catalyst, the Fourier-transform infrared spectroscopy analysis has shown that the hydrogenation of both formate and methoxy species is the rate-determining step in the methanol synthesis over Cu-based catalysts (Ojelade and Zaman, 2019). Formates are the dominant species when CO2 is used as the feed, whereas methoxy species would result in the case with CO as the main reactant.

Theoretical studies deciphered that the WGS reaction followed the carboxyl mediated mechanism, and the methanol synthesis followed both CO and CO2 hydrogenation pathways (Grabow and Mavrikakis, 2011). Under conditions typical of the industrial methanol synthesis, CO2 hydrogenation was responsible for about 65% of the methanol produced from the intermediates *HCOO, *HCOOH, *CH3O*, *CH3O*, and *CH3OH (Grabow and Mavrikakis, 2011; Kattel et al., 2016). The formation of *HCOO species from *CO2 and *H on Cu(111) involved no intermediate carbonate species and the hydrogenation of *HCOO led to
HCOOH instead of H2CO2 (Grabow and Mavrikakis, 2011). However, the direct hydrogenation of formate over Cu(111) is not a feasible pathway for methanol production under dry hydrogen conditions (Zhao et al., 2011). Thus, the presence of small amounts of water is essential in methanol synthesis from CO2 hydrogenation on Cu-based catalysts (Yang et al., 2013). It is shown that direct formate hydrogenation does not lead to methanol due to the high hydrogenation barriers of HCOO and H2COO. Formate, formaldehyde, and methoxy radicals are unlikely to be reaction intermediates for methanol synthesis.

CO is also hydrogenated in significant amounts to *HCO, *CH2O, *CH3O, and *CH3OH, and plays a promotional role in methanol synthesis, which include two possibilities: a) removal of *OH via *COOH to form CO2 and hydrogen via WGS, and b) assisted hydrogenation of various surface intermediates (Grabow and Mavrikakis, 2011). Route a) also contributes to methanol production, although its effect is minute compared with the direct hydrogenation of CO to methanol. However, the rates of methanol synthesis are limited by the formation of *CH3O at low CO2/(CO + CO2) ratios and by its hydrogenation in CO2-rich feeds. Thus, the *CH3O hydrogenation is a slow step during methanol synthesis from both the CO and CO2 routes. Factors such as their rate-determining steps, feed composition, and reaction conditions influence the relative contribution of each route (Grabow and Mavrikakis, 2011).

**METHANOL SYNTHESIS CATALYSTS**

**Historical Development of the Industrial Catalysts for CO2 Conversion to Methanol**

The use of Cu-based catalysts for methanol synthesis via the CO2 dehydrogenation route is as old as the process itself. In 1921, the first patent for methanol synthesis on Cu-based catalyst was filed by Patart (1922), but the catalyst failed to get attention for commercial use due to its susceptibility to sulfur poisoning.
The Imperial Chemical Industries developed the Cu/ZnO catalyst in the late 1960s, which was operative at pressure and temperature of 50–100 bar and 200–300°C, respectively, and using syngas (CO + H₂) as feedstock (Din et al., 2019). Following the successful industrialization of the process and development of gas purification system, which freed the syngas produced from coal, natural gas and crude oil from poisoning by sulfur (Supp., 1973), interest in Cu-based catalysts revived with a ternary Cu-based catalyst—copper oxide, zinc oxide, and chromium oxide (synthesized by in situ reductions) (Davies and Snowdon, 1967). Subsequent studies found that replacing chromium oxide with alumina prolonged the catalyst life. The copper–zinc–alumina catalysts were prepared by co-precipitation of soluble zinc and copper salts (usually the nitrates) with an alkali carbonate solution. The resulting mixture of carbonates was heated to form a mixture of oxides, which were then mixed with aluminum oxide (Casey and Chapman, 1974).

To improve the activity, selectivity, thermal stability, and resistance to poisoning, the Raney copper catalysts consisting of 50% aluminum and 50% copper–zinc mixture by precipitation with NaOH (Marsden et al., 1980). These catalysts were active for methanol production comparable to that of the commercial copper-based methanol synthesis catalyst, but selective to small amounts of dimethyl ether (DME) by-product.

As early as 1930, the possibility of synthesizing methanol from CO₂ as the sole feedstock was known. As then known, methanol catalysts produced CO₂ or H₂O or both along with methanol. It was proposed that the formation of methanol from CO and hydrogen may not be direct, especially when approaching a steady state. Smith and Hirst (1930) observed that hydrogen and CO₂ formed CO and H₂O over methanol catalysts at atmospheric pressure. In the like manner, CO and H₂O react over the Cu-based catalysts to form CO₂ and hydrogen, and equilibrium could be closely approached in the water-gas shift reaction. In 1932, the reaction was confirmed in addition to the regular methanol formation over the unsupported zinc–copper–aluminum catalyst under a certain pressure at high temperatures (Boomer and Morris, 1932). Although the catalyst was not particularly active, it indicated the course of the reaction. In 1945, it was found that methanol from CO₂ could be produced over copper–alumina catalysts in the temperature range of 282–487°C and the pressure range of 117–410 atm. Catalysts consisting of Cu or Al₂O₃ alone had no catalytic activity. The most active catalyst had a Cu content of 8–25% and gave a conversion of 94% under 410 atm at a temperature of 285°C. With CO as the carbon source, similar experiments gave 39–43% conversions, with about 15 and 41% of the CO charge converted to methane and DME, respectively (Ipatieff and Monroe, 1945). In the reaction gas mixture (CO/CO₂/H₂) with CO:CO₂ of 3:1:1, the methanol conversion was 64%, and the formation of DME reduced to about 1%. The results led to the postulation that the formation of methanol from CO₂ and hydrogen under pressure may proceed along two paths. The developmental milestone of the Cu-based catalysts for the direct CO₂ to methanol conversion is presented in Figure 4.

Ren et al. provided the evidence than Cu species promoted by Zn were essential for the hydrogenation of CO₂ in the CO₂ promoted CO–H₂ gas system. They observed that CO₂ inhibited the CO hydrogenation over Pd/Al₂O₃, and ZnO–Cr₂O₃ catalysts, but promoted it over Cu–ZnO/Al₂O₃, at their respective optimum temperatures and under pressures that ensured low conversions (Ren et al., 1989).

Intensive research on the methanol synthesis from CO₂ and the active catalysts started growing in the 1980s. Currently, the ternary copper-based catalyst (Cu/ZnO/Al₂O₃) is still used for the industrial synthesis of methanol from CO₂ in the gas phase from a mixture of syngas and CO₂ under the operations conditions: temperature and pressure of 220–300°C and 50–100 bar, respectively (Din et al., 2019; Sehested, 2019). In this process, methanol formation is believed to originate mainly from CO₂, whereas CO acts as a scavenger of surface oxygen. Due to the availability of CO₂ in large volumes from emissions into the atmosphere and the need for environmental cleaning to reduce the incidence of global warming and demand for clean fuel, research efforts are devoted to the use of CO₂ as the sole reactant gas which is challenged by the unavailability of efficient catalysts (Din et al., 2019).
The Present Commercial Catalyst (Cu–Zn–Al)

At the commercial scale, methanol is synthesized over Cu/ZnO/Al2O3 catalyst at a pressure of 50–100 bar and temperature of 220–300°C. This catalyst contains 50–70 atomic% CuO, 20–50% ZnO, and 5–20% of the Al2O3 promoter. These combinations allow the formation of stabilized Zn-incorporated Cu surfaces, which are highly defective, and enable the maximization or optimization of the density of the active sites. The resulting oxide catalyst is activated with diluted hydrogen at 190–250°C, at which CuO is completely reduced to metallic crystallites interspersed by ZnO/Al2O3 (Behrens et al., 2013). It should be noted that the commercial Cu/ZnO/Al2O3 catalysts for methanol synthesis are not a “supported system” although researchers often mistake it as one because neither ZnO nor Al2O3 component is classical porous oxide support to qualify it as such, and the active phase has a high loading in the system (Behrens et al., 2013). The Cu-rich composition of the industrial catalyst possesses a peculiar microstructure, which is composed of spherical copper nanoparticles of sizes 5–15 nm and even smaller ZnO nanoparticles arranged in a regular pattern (Lunkenbein et al., 2015). In the catalyst, ZnO affords typical promoting functions, partakes in active sites creation, and supports and stabilizes the mesostructure of the Cu phase. In the Cu/ZnO/Al2O3 catalyst, there is a strong metal–support interaction layer of metastable “graphitic-like” ZnO after reductive activation, which was kinetically stabilized by interacting with the defective and Cu surface (Lunkenbein et al., 2015). The defects are crucial for the stability of the ZnO overlayer and may lead to the presence of some ZnOx species that act as co-catalysts in the methanol stability of the ZnO overlayer and may lead to the presence of kinetically stabilized by interacting with the defective and Cu phase (Kasatkin et al., 2007). The Al2O3 component, although it can interact with the ZnO phase, does not generally change the evolvement of the Cu/ZnO binary phase. It helps to modify the ZnO surface, introducing defective sites by doping (Schumann et al., 2014; Mota et al., 2018). Al2O3 incorporation into the catalyst is necessary to enhance catalyst stability and resistance to thermal sintering of the Cu crystallites. In addition, studies suggest that alumina also acts as a promoter, though there is evidence of Al3+ doping into ZnO, which specifically tailors the reduction properties of the latter. Also, Al2O3 surface acidity affects the byproducts’ selectivity (Xiao K. et al., 2017). Table 1 summaries the performance of the Cu/ZnO/Al2O3 catalysts investigated in recent years.

The catalyst must fulfill three important technical requirements (Figure 5) for high catalytic activity, which can be ensured by the nanoparticulate and porous Cu/ZnO aggregates (Zander et al., 2013). Different methods have been investigated for the preparation of the commercial catalysts by researchers, including solid-state combustion, solid-state reaction, reduction–precipitation, reversed co-precipitation and deposition precipitation (Natesakhawat et al., 2012; Dong et al., 2016; Dasireddy and Likozar, 2019); however, desirable properties for the industrial applications are more often achieved by the co-precipitation method. Initially developed by the Imperial Chemical Industries in the 1960s, the method involves co-precipitation, aging of the mixed metal Cu, Zn, and (Al) hydroxyl-carbonate precursor materials, thermal decomposition and finally activation by reduction of Cu component to active species as shown in Figure 6 (Waller et al., 1989; Fierro et al., 1996; Spencer, 1999; Whittle et al., 2002; Kniep et al., 2004; Behrens et al., 2011). During the synthesis, the initially formed solids from co-precipitation of Cu, Zn and Al precursors are amorphous hydroxycarbonates, which evolve during aging in contact with the mother liquor to crystalline forms with different composition, morphology, and structure as a result of Ostwald ripening dissolution/re-precipitation or agglomeration (Mota et al., 2018). Aging can increase the exposed Cu surface area, ZnO crystallite size, the stability of ZnO, and the Cu–ZnO contacts due to the change in the structure of precipitates with a strong influence on the microstructure of the final Cu/ZnO–Al catalysts (Mota et al., 2018). Calcination influences the precursor decomposition and the CuO structure of the catalyst (Zhang et al., 2010). The average CuO crystallite size increases with an increase in calcination temperature, whereas the dispersion of Cu species

### Table 1 | Performance of various Cu/ZnO/Al2O3 ternary industrial catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>H2/CO2</th>
<th>WHSV (mL gcat⁻¹ h⁻¹)</th>
<th>CO2 conv. (%)</th>
<th>CH3OH sel. (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>JM-HiFUEL (50 wt% Cu/ZnO/Al2O3)</td>
<td>270</td>
<td>4.5</td>
<td>3:1</td>
<td>18,000</td>
<td>—</td>
<td>0.38</td>
<td>Li et al. (2018)</td>
</tr>
<tr>
<td>Industrial CuO/ZnO/Al2O3</td>
<td>220</td>
<td>8.0</td>
<td>—</td>
<td>3,400 L h⁻¹</td>
<td>18.2</td>
<td>85.6</td>
<td>Lachowska and Skrzypek (2004)</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3</td>
<td>250</td>
<td>4.1</td>
<td>—</td>
<td>3,600 L h⁻¹</td>
<td>20.1</td>
<td>31.3</td>
<td>Jiang et al. (2015)</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3</td>
<td>270</td>
<td>5.0</td>
<td>3:1</td>
<td>4,000</td>
<td>10.7</td>
<td>81.8</td>
<td>Xiao S. et al. (2017)</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3</td>
<td>240</td>
<td>2.0</td>
<td>—</td>
<td>3,600 L h⁻¹</td>
<td>17.3</td>
<td>32.4</td>
<td>Hong et al. (2002)</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3</td>
<td>240</td>
<td>2.0</td>
<td>—</td>
<td>7,200 L h⁻¹</td>
<td>17.3</td>
<td>32.4</td>
<td>Hong et al. (2002)</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3</td>
<td>260</td>
<td>3.0</td>
<td>3:1</td>
<td>37</td>
<td>37</td>
<td>72</td>
<td>Bansode and Uragawa (2014)</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3</td>
<td>250</td>
<td>3.0</td>
<td>—</td>
<td>18,000</td>
<td>16.9</td>
<td>42.3</td>
<td>Lee et al. (2000)</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3</td>
<td>250</td>
<td>3.0</td>
<td>—</td>
<td>54,000</td>
<td>7.0</td>
<td>65.2</td>
<td>Lee et al. (2000)</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3</td>
<td>250</td>
<td>3.0</td>
<td>—</td>
<td>108,000</td>
<td>7.1</td>
<td>61.7</td>
<td>Lee et al. (2000)</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3</td>
<td>250</td>
<td>3.0</td>
<td>—</td>
<td>73,000</td>
<td>13.5</td>
<td>61.8</td>
<td>Lee et al. (2000)</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3</td>
<td>230</td>
<td>3.0</td>
<td>3:1</td>
<td>—</td>
<td>18.7</td>
<td>43.0</td>
<td>Li et al. (2014)</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3</td>
<td>170</td>
<td>5.0</td>
<td>2:1</td>
<td>—</td>
<td>4.3</td>
<td>45.1</td>
<td>Liu et al. (2007)</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3</td>
<td>270</td>
<td>4.5</td>
<td>2:2:1</td>
<td>—</td>
<td>12.3</td>
<td>42.3</td>
<td>Liao et al. (2011)</td>
</tr>
<tr>
<td>Cu/ZnO/Al2O3</td>
<td>270</td>
<td>4.5</td>
<td>2:2:1</td>
<td>—</td>
<td>10.9</td>
<td>72.7</td>
<td>Liao et al. (2011)</td>
</tr>
</tbody>
</table>

*aSpace-time yield (STY) (gcat⁻¹ h⁻¹); weight hourly space velocity (WHSV).*

Frontiers in Energy Research | www.frontiersin.org 6 September 2020 | Volume 8 | Article 545431
decreases under the same condition (Guo et al., 2011). Usually, the calcination temperatures of 300–400°C are optimum for forming a suitable catalyst. The detailed description of the synthesis of this catalyst can be found in the literature (Behrens and Schlögl, 2013).

The Cu–ZnO–Al2O3 catalyst system has been optimized to a very high-performance level under relevant industrial conditions. Thus, one may rationally assume that the catalyst is highly active for the direct CO2 hydrogenation to methanol. Although Cu/ZnO/Al2O3 exhibits promising performance (space-time yield up to 7,729 gMeOH kgcat−1 h−1) under 36 MPa and 10:1 H2:CO2 ratio (Bansode and Urakawa, 2014), obviously this pressure is too high from an economic point of view.

Active Sites

Theoretical Modeling of the Cu–ZnO Catalyst Surface

The multiscale modeling techniques adopted for investigating the performance of the traditional Cu-based catalysts include the DFT, kinetic Monte Carlo (kMC), and microkinetic modeling (Li et al., 2015; Huš et al., 2017b; Kopač et al., 2017; Kopač et al., 2019; Park et al., 2020). These models allow for the clarification of the
exact reaction step, and help the analysis of catalyst performance over a range of operating conditions and different length and time scales (Park et al., 2020). The DFT can compute ground-state energy and its associated properties using electron density, allowing for the calculation of relatively larger systems such as nanoparticles and periodic surfaces. The atomic configurations, transition states, energetics, energy barriers, and reaction mechanisms derived from first-principles calculations can be used to predict the catalytic activities at an atomic level. The kMC showed how the catalytic surface coverages change with time and conditions on a microscopic scale, and resolve the surface coverage with atomistic detail (Pavlišić et al., 2020). Microkinetic modeling is an important continuum model with even higher accuracy and reliability than DFT and kMC. It is an ideal framework for integrating the data generated by latter. Like the kMC, it avails information on product distribution and estimates the catalyst activity in steady-state kinetics (Li et al., 2015). In many cases, the catalytic performance data form Cu-based catalysts compared qualitatively with those obtained from the experiments in the literature. For example, the results from these theoretical modelling were found to conform well to the experiments over Cu–ZnO–Al₂O₃ or Cu–MgO–Al₂O₃. The active sites of the catalysts Cu–ZnO or Cu–MgO were modeled by the DFT. Cu sites were modeled as a Cu(111) surface on top of which ZnO or MgO cluster was placed in the most energetically favorable position. The methanol synthesis was investigated under different temperatures and pressures. Both the microkinetic and kMC modeling indicated high selectivities toward methanol at low temperatures (between 95 and 100%). Cu/Mg and Cu/Zn had different reaction pathways toward methanol production, which depended on the operating conditions and the formate pathway was the energetically most favorable over the Cu/Zn surface.

The DFT calculation found that, on a commercial Cu/ZnO/Al₂O₃ catalyst, the open Cu surfaces [e.g., Cu(110) and Cu(100)] partially covered by oxygen are active for methanol synthesis, suggesting that Cu species without the effect of support are the active sites for methanol synthesis (Grabow and Mavrikakis, 2011). Different surfaces and the presence or absence of surface defects have shown the ability to catalyze the methanol synthesis. The stepped Cu(533) surface was shown to enhance the selectivity for methanol about four orders of magnitude better than a flat Cu(111) surface (Kopač et al., 2019). The defective surface relative to the Cu(111) surface promoted the H₂COH hydrogenation pathway, resulting in higher CH₃OH yields. Over (ZrO₂)x/Cu(110) interface, the adsorption energies of unsaturated species were observed to increase compared to a pure Cu(110) surface. A similar observation was recorded for the selectivity for methanol (Liu et al., 2020). A comparison between the pure Cu(211) and the Zn-doped Cu(ZnCu(211)) surfaces showed differences in the reaction steps (Zheng et al., 2020). For the ZnCu(211) surface, the methanol formation pathway included the formation of CH₃O instead of CH₂OH species. The rate-limiting step over Cu(211) was the reaction, CO₂ + H → HCOO, whereas that over ZnCu(211) was HCOOH + H → H₂COOH, which has been known as the main intermediate for the methanol synthesis over Cu/ZnO catalysts. The kinetics further deviated on Zn-promoted Cu due to the reduced activation energies of several critical reactions, leading to the improved catalytic performance of ZnCu(211).

The simple pure-copper kinetic model can sufficiently describe the catalysts with different supports after modifying the model active site concentrations (Jurković et al., 2020). Such a method can be useful for predicting the activity of the Cu/Al₂O₃ catalyst and for further reactor designs modeling and scale-up applications. Applying these could guide the rational design of multifaceted Cu catalysts for methanol synthesis by surface defects engineering.

**Experimentally Observed Active Sites**

Studies have discussed the identity of the catalysts’ active sites, with particular regard to the intermediates and precursors for methanol formation. The reported kind and nature of the active sites are closely linked with the synthesis method and/or the analytical techniques deployed for studying it (Herman et al., 1979). For the Cu-based catalysts, the active sites are considered to be metallic Cu (Cu⁰) or Cu⁺, and the activity was shown to be directly related to the Cu surface area (Baltes et al., 2008; Dong et al., 2016; Dasireddy and Likozar, 2019). However, other studies found that the catalytic activity was not certainly correlated linearly with the Cu surface area (Nakamura et al., 2003). The active sites and the activity relations of a reversed co-precipitated prepared Cu-based catalysts were investigated by various characterization techniques (Natesakhat et al., 2012). The results revealed the presence of metallic Cu on the surface of fresh but reduced and spent catalysts. CuO in the catalyst reduced to Cu⁰ upon exposure to H₂ at 250°C. This state was observed in various kinds of Cu-containing catalysts with different supports/additives, size of Cu particle, and varying degrees of ZnO crystallinity, thus it can be concluded from this study that additives, particles and support crystallite size do not affect the activity of Cu (Natesakhat et al., 2012).

Tsang and co-workers observed the formation of CuZn alloy particles by X-ray photoelectron spectroscopy (XPS) in the Ga-promoted Cu/ZnO catalyst for CO₂ hydrogenation to MeOH. They attributed the effect of incorporation of Ga³⁺ to the formation of the ZnGa₂O₄ spinel structure, which created electronic heterojunction with excess ZnO phase that eased the reduction of Zn²⁺ to Zn⁰ to form CuZn alloy upon contact with Cu nanoparticle. They also correlated the concentration of Zn⁰ in the CuZn alloy nanoparticle with the catalytic performance (CO₂ conversion and methanol selectivity) and found that the latter could be significantly improved by increasing the Zn⁰ content in the heterojunction catalysts (Li et al., 2016). With advanced characterization techniques, it is evident that Zn atoms can be reduced on Cu nanoparticles, resulting in a detectable change in the geometry and electronic structure of Cu due to Zn–Cu bimetallic properties (Sanches et al., 2012). As a result, it is concluded that the Zn–Cu alloy is an active catalytic site. On the contrary, other studies found that reactions occur at the atomic interface between ZnO and Cu. Thus, the presence of the ZnO–Cu interface and the synergy of Cu and ZnO are essential for the production of methanol (Li et al., 2018).
The active site of Cu catalysts can also exist in the form of other species. Recent studies have shown that stepped and ZnOx-decorated Cu surfaces are active sites of the industrial catalysts (Studt et al., 2015). Both experimental and theoretical investigations have found that decorated Cu stabilized by bulk defects and surface species participate in the hydrogenation of CO2 to methanol reaction (Behrens et al., 2012). The transmission electron microscopy study revealed the ZnO overlayer was formed on top of the Cu particles in the Cu/ZnO/Al2O3 catalyst under reaction conditions that could create a metal oxide interface with catalytic activity (Behrens et al., 2012). Evidence is also available for the existence of the Zn–Cu bimetallic sites or ZnO–Cu interfacial sites (Kattel et al., 2017b). Over the ZnCu bimetallic and ZnO/Cu model catalysts for methanol synthesis, it was found that ZnCu surface oxidized in situ such that the surface Zn transforms into ZnO, allowing ZnCu to form ZnO/Cu active surface in a synergistic interaction of Cu and ZnO. Cu–Zn alloy or the Cu/ZnO interface has been proposed to generate the active site responsible for the high methanol selectivity. Generally, as summarized in this section, the active sites for the Cu–ZnO catalysts can be grouped into the following categories: a) Cu species (metallic or oxidized Cu species); b) Cu–ZnO interface; c) defective Cu surface; d) Cu–Zn alloy; and e) ZnO decorated Cu. All these have led to the conclusion that the Cu species and/or Cu–Zn contact is necessary for the activity of the Cu/ZnO-based catalysts.

**Deactivation of Methanol Synthesis Catalysts**

The deactivation of heterogeneous catalysts is a severe problem in many reactions. Many studies have reported various deactivation mechanisms of the Cu-based catalyst in the literature; however, the mechanism of deactivation is not entirely clear. One of the major causes of catalysts deactivation is sintering. The sintering of catalytic materials particles results in a decrease in catalyst activity. Catalyst particles sinter in the early stages by a coalescence mechanism, which involves the migration and coalescence of particles, while the Ostwald ripening mechanism is operative in the end phase of the process (Bartholomew, 2001). The Ostwald ripening is caused by the surface diffusion of catalytic material and the higher thermodynamic stability of larger particles (Fichtl et al., 2015). The initial and rapid deactivation is due to loss of surface area when some of the finely dispersed Cu crystallites agglomerate (Roberts et al., 1993; Twigg and Spencer, 2001). The later pathway, which is slow and approaches the steady-state, is caused by the surface coverage of some reaction products and
intermediates, especially water, and carbonated species (Roberts et al., 1993). It was found that the cause of catalyst deactivation was sintering of both Al2O3 and Cu with water due to the decreasing Al2O3 surface, and Cu particle size with increasing content of H2O (Prasnikar et al., 2019).

Figure 8A shows that all phases exhibit a reduction in surface area (or increase of particle size) with an increasing amount of steam. The Cu particle growth was fitted to a coalescence model for sintering (Figure 8B), which confirms coalescence as the operating mechanism. The increased particle migration is due to weak contact between the metal and support or increased surface diffusion of catalytic material (Prasnikar et al., 2019). The structures of ZnO and Al2O3 species and metallic Cu can be stabilized to improve the catalyst lifetime, which can be accomplished by forming stable Cu interface with support material, and by stabilizing the dynamic nature of ZnO under working conditions using hydrophobic or hydrothermally stable materials. A promising approach is to confine the growth of Cu species in a porous oxide to stabilize and maximize Cu–support interface (Chen et al., 2019).

The water generated in the RWGS during CO2 reduction to methanol deactivates the catalyst, causing speciation of Cu active phase and phase separation (Kung, 1992; Liang et al., 2019; Prasnikar et al., 2019). Sahibzada et al. observed a lower rate of methanol production in the presence of water in the H2/CO2 feed (Sahibzada et al., 1998). Another possible effect of water in the deactivation of the methanol synthesis catalyst is the crystallization of ZnO and Cu particles (Lunkenbein et al., 2016). Water produced can speed up the crystallization of particles, leading to deactivation observed for the Cu/ZnO/ZrO2/Al2O3 catalyst. The inhibiting effect of water during CO2 reduction to methanol was caused by the adsorption on and blocking of the active sites for CO2 hydrogenation (Liu et al., 1985). Water reacts with CO2, forming carbonate species that have been proven to block the active sites for CO2 hydrogenation. The deactivation of Cu-based catalysts by water could also result from blocking of hydrogen adsorption sites, morphology changes of Cu, and the oxidation of the active Cu-phase (Clausen et al., 1994; Omata et al., 2004). These can be explained by recrystallization and an enhanced tendency for sintering of the Cu particles in the presence of water (Wu et al., 2001); however, this mechanism is not always true as no deactivation was observed by Omata et al. (2004) in their study in the presence of water.

**Improvements to the Conventional Cu–ZnO–Al2O3 Catalyst Use of Promoters**

To further increase the activity and stability of the Cu–ZnO or Cu–ZnO–Al2O3 catalysts, modifiers such as K, Ba, Zr, Ce, Mn, La, Si, Pd, Ga, Mg, and Y were incorporated to promote the catalytic performance (Iizuka et al., 1983; Inoue and Iizuka, 1986; Denize et al., 1989; Toyir et al., 2009; Sanches et al., 2012; Zhang L. et al., 2012; Gao et al., 2013; Zhan et al., 2014; Gao et al., 2015; Zohour et al., 2016; Larmier et al., 2017; Xiao S. et al., 2017; Zhang F. et al., 2017; Hu et al., 2018). An effective promoter should be able to achieve large Cu surface area, high Cu dispersion, and to ease the reducibility of CuO to metallic Cu (Sanches et al., 2012). Modification to the basicity, methanol selectivity, CO2 conversion, and temperature and pressure have been reportedly observed (Gao et al., 2013). A series of Cu/Zn/Al catalysts promoted with Mn, La, Ce, Zr, and Y were synthesized by the co-precipitation method and tested for the CO2 hydrogenation to methanol, and effect of the promoters on the physicochemical properties of the base catalysts was investigated (Gao et al., 2013). The results showed that the specific surface area, Cu surface area, Cu dispersion and number of basic sites increase in the order: Cu/Zn/Al < Cu/Zn/Al/Mn < Cu/Zn/Al/La Cu/Zn/Al/Ce < Cu/Zn/Al/Zr < Cu/Zn/Al/Y, whereas the CH3OH selectivity increases in the order of Cu/Zn/Al < Cu/Zn/Al/Mn < Cu/Zn/Al/La < Cu/Zn/Al/Ce < Cu/Zn/Al/Y < Cu/Zn/Al/Zr. The Zr-modified Cu/Zn/Al catalyst exhibited the highest density and proportion of strong basic sites. The addition of Mn, La, Ce, Zr, and Y enhanced the production of methanol; however, the Y- and

![Figure 8](https://www.frontiersin.org/articles/10.3389/fenre.2020.545431/full/figure8.png)
Zr-modified Cu/Zn/Al catalysts exhibited the highest CO_2 conversion and methanol selectivity, respectively (Gao et al., 2013). Lee et al. (2020) investigated the effect of adding Zr, Mg, and Ga on the conventional Cu/ZnO/Al_2O_3. The incorporation of Zr enhanced the performance for methanol synthesis by improving conversion and methanol yield, but the occurrence of intensified WGS reaction reduced CO_2 conversion. On the other hand, the addition of Ga and Mg further lowered catalytic performance (Table 2), attributed to reducibility difficulties and the increased crystalline size of Cu particles (Xiao et al., 2015). These catalysts were evaluated using a feed composed of both CO and CO_2.

The CuO–ZnO–Al_2 catalysts modified with SiO_2, TiO_2, or SiO_2–TiO_2 exhibited better catalytic performances than the CuO–ZnO–Al_2O_3 without any promoter. The conversion of CO_2 and methanol yield increased when the promoters were added, and the maximum of CO_2 conversion and methanol yield were obtained over 2 wt% SiO_2–TiO_2/CuO–ZnO–Al_2O_3 catalyst (Zhang et al., 2012). Both SiO_2 and TiO_2 eased the reduction and dispersion of CuO, while SiO_2–TiO_2 made the reduction of CuO slightly difficult. SiO_2–TiO_2 had the best performance than SiO_2 or TiO_2 as a result of synergistic interaction between SiO_2 and TiO_2, leading to a weaker acid strength and a higher acid concentration on the surface of the catalyst. This resulted in weaker adsorption of CO_2 but stronger adsorption of H_2 and the dissociated H species (Zhang et al., 2012). The catalytic results revealed higher performance for the promoted CuO–ZnO–Al_2O_3 catalysts. Maximum activity and methanol selectivity were obtained for the catalyst promoted with SiO_2–TiO_2, giving CO_2 conversion of 40.70% and methanol selectivity of 41.17% compared with the catalyst without a promoter (CO_2 conversion of 15.81% and methanol selectivity of 23.31%) under similar reaction conditions of temperature = 533 K, pressure = 2.6 MPa, H_2:CO_2 = 3:1, and space velocity = 3,600 h^{-1}. The introduction of non-metallic ions (e.g., fluoride ion) can drastically promote the basicity of Cu/ZnO/Al_2O_3 and the adsorption of CO_2 and increases the methanol selectivity (Dybbert et al., 2019).

Although the CuO–ZnO–ZrO_2 ternary catalysts exhibited comparative activity with the commercial catalyst, the introduction of promoters such as SiO_2, CeO_2, Ga_2O_3, or TiO_2 can further improve the catalytic performance (Zhang et al., 2012; Larmier et al., 2017; Phongamwong et al., 2017; Hu et al., 2018). A series of CuO–ZnO–ZrO_2–SiO_2 catalysts were synthesized by the reverse co-precipitation of copper, zinc and zirconium precursors with colloidal silica nanoparticles, and the influence of silica content (0–5 wt%) on the properties of the resulting catalysts as well as their catalytic activity in CO_2 hydrogenation were studied. Analysis with various characterization techniques revealed modification of the catalyst structures. A low content of SiO_2 was more effective for modifying the geometric structure. The addition of 1 wt% SiO_2 led to an increase in methanol synthesis activity (26%) compared to the SiO_2-free catalyst system. Phongamwong et al. (2017) concluded that the addition of SiO_2 to Cu/ZnO/ZrO_2 improves methanol synthesis activity by increasing metallic Cu surface area and surface basicity. Sloczyński et al. (2006) observed an increase in the yield of methanol upon modification of Cu/ZnO/ZrO_2 catalyst with B, Ga, In, Gd, Y, Mn, and Mg oxides. The addition of these elements also altered the textural and/or structural properties of the catalyst; Ga_2O_3 has been particularly useful in promoting methanol yield. Saito et al. (1996) developed a Cu/ZnO/ZrO_2/Al_2O_3/SiO_2 catalyst used for methanol synthesis operation in the bench plant. The catalyst was very stable during long-term methanol synthesis (Saito et al., 1996; Toyir et al., 2009). The methanol production capacity of 50 kg d^{-1} of methanol over Cu/ZnO/ZrO_2/Al_2O_3/SiO_2 was also successfully operated (Ushikoshi et al., 1998; Toyir et al., 2001; Toyir et al., 2009).

**Improvements in Catalyst Synthesis**

A unique microstructure with a proper balance of Cu dispersion and exposure of active Cu–ZnO interface sites at a high total Cu content is essential for achieving methanol selectivity (Behrens and Schlögl, 2013). Thus, the synthesis method that guarantees the structure sensitivity of methanol synthesis over Cu surfaces is appropriate. Varying the specific activity of the active sites and/or the concentration of the sites can be a result of the deployed synthesis method (Table 3). The ternary Cu-based catalysts are prepared by co-precipitation from a mixture of copper, zinc, and aluminum nitrate using a carbonate as a precipitant (Behrens and Schlögl, 2013; Behrens, 2015).

The co-precipitation involves the simultaneous solubilization and solidification of copper and zinc precursors (usually nitrate salts) in the presence of alkaline metal carbonates, forming binary precipitates under suitable conditions (Casey and Chapman, 1974; Kasatkin et al., 2007). The precipitate is aged, dried, and calcined in air to obtain the CuO/ZnO oxides. Finally, the catalyst is reduced under H_2 atmosphere during which CuO is reduced to metallic Cu. This method affords the study of hydrolysis of Cu^{2+} and Zn^{2+} at different pH relevant to the catalyst preparation. Over the years, many researchers have investigated the synthesis parameters of the co-precipitation route, and have achieved a

### TABLE 2 | Comparison of methanol synthesis performance between CZA and promoted CZA.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>MeOH yield (%)</th>
<th>CO:CO_2 conversion ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
<td>CO_2</td>
<td>CH_4</td>
<td>DME (10^{-3})</td>
</tr>
<tr>
<td>CZA</td>
<td>17.9</td>
<td>7.0</td>
<td>1.51</td>
<td>0.13</td>
</tr>
<tr>
<td>CZA–Mg</td>
<td>9.2</td>
<td>2.8</td>
<td>0.73</td>
<td>1.54</td>
</tr>
<tr>
<td>CZA–Zr</td>
<td>20.9</td>
<td>2.3</td>
<td>0.21</td>
<td>3.90</td>
</tr>
<tr>
<td>CZA–Ga</td>
<td>14.7</td>
<td>4.5</td>
<td>0.43</td>
<td>2.22</td>
</tr>
</tbody>
</table>

Reaction conditions: 240°C and 30 bar; space velocity of 6,000 L/kg_{cat}/h.
high degree of optimization, usually by empirically adjusting the synthesis conditions (Li and Inui, 1996; Baltes et al., 2008; Behrens et al., 2011). Even so, further improvement of this catalyst is still needed. The best catalyst is usually obtained by co-precipitation with Na2CO3 solution at a constant pH 6 or 7 changes in the aurichalcite precursors that were transformed into Cu-based catalysts, which directly impact their catalytic activities. The precipitation method involves a reducing agent such as NaBH4. Typically, a solution of metal nitrates and a solution of Na2CO3 or NaOH precipitant are added dropwise to deionized water simultaneously under stirring at a temperature and a constant pH (∼7.0) during precipitation. Then a reducing agent is added, and the resulting slurry is further aged at a specific temperature for sufficient time, followed by filtration and washing, drying, and calcination. Compared with the conventional co-precipitation method, catalysts with smaller Cu particles are much more easily obtained by using the precipitation–reduction method. By this method, the viewpoint that both Cu+ and Cu0 species contributed to the activity of CO2 hydrogenation to methanol is accepted (Dong et al., 2016).

The sol–gel (SG) method is another way to prepare mixed oxides, especially for M–CeTiOx systems (Chen et al., 2014; Matějová et al., 2014; Bo et al., 2016). In a study utilizing CuCeTiOx as the catalyst, Ce and Ti ions were hydrolyzed to form the framework at low pH during the sol–gel transformation. Then the Cu species were solidified through evaporation of the solvents. These steps can lead to elemental distribution that differs between the bulk and surface, resulting in catalysts with varying composition in CuCeTiOx on their catalytic properties. By this method, a catalyst composite (CuCeTiOx–SG) with the composition (30%CuO35%CeO235%TiO2) was prepared and compared with the co-precipitation method derived catalyst (CuCeTiOx–CP). The preparation methods show an important influence on catalytic performance (Figure 9). The CuCeTiOx–CP catalyst showed a higher CO2 conversion than CuCeTiOx–SG. However, the CuCeTiOx–SG catalyst showed a higher selectivity to methanol than CuCeTiOx–CP at the same CO2 conversion (Chang et al., 2017). Also, Cu/ZnO catalysts were prepared using three different methods (co-precipitation, sequential precipitation, and homogeneous precipitation). The studied preparation methods influenced the surface area of the Cu-based catalysts, which directly impact their catalytic activities. The different preparation methods resulted in various structural changes in the aurichalcite precursors that were transformed into the final catalyst. From the catalytic evaluation results, it was

Table 3. Catalytic activities of recently studied Cu-catalysts for methanol synthesis from CO2 hydrogenation in fixed bed reactors.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation method</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>H2/CO2</th>
<th>WHSV (ml gcat⁻¹ h⁻¹)</th>
<th>CO2 conv. (%)</th>
<th>CH3OH sel. (%)</th>
<th>STY gcat⁻¹ h⁻¹</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO-ZnO-ZrO2</td>
<td>PR</td>
<td>503–543</td>
<td>5</td>
<td>3:1</td>
<td>4,600 h⁻¹</td>
<td>23</td>
<td>66.8</td>
<td>0.21</td>
<td>Dong et al. (2016)</td>
</tr>
<tr>
<td>Cu/ZnO/ZrO2</td>
<td>CP</td>
<td>190</td>
<td>5.0</td>
<td>3:1</td>
<td>4,000 h⁻¹</td>
<td>10.7</td>
<td>81.8</td>
<td>0.087</td>
<td>Xiao et al. (2017)</td>
</tr>
<tr>
<td>CuO-ZnO-ZrO2</td>
<td>CP</td>
<td>240</td>
<td>3.0</td>
<td>3:1</td>
<td>2,400 h⁻¹</td>
<td>5.6</td>
<td>54.0</td>
<td>—</td>
<td>Wang et al. (2018)</td>
</tr>
<tr>
<td>WO3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-La2O3/SBA-15</td>
<td>IP</td>
<td>240</td>
<td>3.0</td>
<td>3:1</td>
<td>12,000</td>
<td>6.0</td>
<td>81.2</td>
<td>0.244</td>
<td>Chen et al. (2019)</td>
</tr>
<tr>
<td>Cu-In-Zr-O</td>
<td>CP</td>
<td>250</td>
<td>25</td>
<td>—</td>
<td>18,000</td>
<td>1.48</td>
<td>79.7</td>
<td>0.087</td>
<td>Yao et al. (2019)</td>
</tr>
<tr>
<td>LDH300-Ga (33.5)</td>
<td>CP</td>
<td>297</td>
<td>4.5</td>
<td>—</td>
<td>18,000</td>
<td>4.9</td>
<td>78.3</td>
<td>0.365</td>
<td>Li et al. (2018)</td>
</tr>
<tr>
<td>Cu-ZnO-ZrO2-LDH</td>
<td>US-CP</td>
<td>250</td>
<td>3</td>
<td>3:1</td>
<td>2,000 h⁻¹</td>
<td>4.9</td>
<td>78.3</td>
<td>0.365</td>
<td>Fang et al. (2019)</td>
</tr>
<tr>
<td>Cu/AIGeO</td>
<td>CP</td>
<td>260</td>
<td>3</td>
<td>3:1</td>
<td>14,400</td>
<td>17</td>
<td>85.0</td>
<td>11.9a</td>
<td>Li et al. (2020)</td>
</tr>
<tr>
<td>ZnCuCe</td>
<td>RCP</td>
<td>240</td>
<td>3</td>
<td>3:1</td>
<td>8.8 L g⁻¹ h⁻¹</td>
<td>—</td>
<td>—</td>
<td>0.49a</td>
<td>Bonura et al. (2011)</td>
</tr>
<tr>
<td>CuO/Al2O3</td>
<td>CP</td>
<td>235</td>
<td>3</td>
<td>3:1</td>
<td>2,000</td>
<td>—</td>
<td>—</td>
<td>0.9a</td>
<td>Choi et al. (2017)</td>
</tr>
<tr>
<td>1Pd-10Cu/Al2O3</td>
<td>IP</td>
<td>273</td>
<td>3</td>
<td>3:1</td>
<td>—</td>
<td>17.8</td>
<td>23.7</td>
<td>—</td>
<td>Choi et al. (2017)</td>
</tr>
<tr>
<td>10CuO/Al2O3</td>
<td>IP</td>
<td>273</td>
<td>3</td>
<td>3:1</td>
<td>—</td>
<td>6.4</td>
<td>42.8</td>
<td>—</td>
<td>Choi et al. (2017)</td>
</tr>
<tr>
<td>15 wt% Cu/Al2O3</td>
<td>IP</td>
<td>200–280</td>
<td>4</td>
<td>3:1</td>
<td>6,000</td>
<td>16.4</td>
<td>59</td>
<td>—</td>
<td>Li et al. (2019)</td>
</tr>
<tr>
<td>15 wt% Cu/Cu/</td>
<td>IP</td>
<td>200–280</td>
<td>4</td>
<td>3:1</td>
<td>6,000</td>
<td>22.5</td>
<td>94</td>
<td>—</td>
<td>Li et al. (2019)</td>
</tr>
<tr>
<td>ACeO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu/La2O3/CO2-R</td>
<td>DP</td>
<td>280</td>
<td>3.0</td>
<td>3:1</td>
<td>12,000 ml</td>
<td>5.6</td>
<td>92.5</td>
<td>110.2b</td>
<td>Chen et al. (2018)</td>
</tr>
<tr>
<td>Cu/ZrO2</td>
<td>IP</td>
<td>493–553</td>
<td>3</td>
<td>3:1</td>
<td>—</td>
<td>13</td>
<td>76.4</td>
<td>—</td>
<td>Wilton et al. (2016)</td>
</tr>
<tr>
<td>CuZn@Uio-bpy</td>
<td>DSM</td>
<td>523</td>
<td>4</td>
<td>—</td>
<td>17.4</td>
<td>85.6</td>
<td>—</td>
<td>An et al. (2017)</td>
<td></td>
</tr>
</tbody>
</table>

CP: co-precipitation; IP: impregnation; RCP: reversed co-precipitation; DP: deposition precipitation; DSM: double solvent method; PR: precipitation reduction; US-CP, ultrasonic assisted co-precipitation. *a* is in mmol h⁻¹ g⁻¹, *b* is in mmolmolCu⁻¹ h⁻¹.
intrinsic reactivity of CuO improved the dispersion of metallic Cu particles, which altered from the conventional co-precipitation route. This method also production rate was proportional to the ratio of Cu+/Cu0, it was concluded that the presence of high levels of Cu+ species is essential for high and low selectivity to methanol and CO, respectively (Dasireddy and Likozar, 2019).

The ultrasonic synthesis (solid-state). The characterization and catalytic performance effects were more pronounced for the catalysts prepared by different synthesis methods (co-precipitation, ultrasound-assisted, sol-gel, and solid-state). The characterization and catalytic performance showed that the preparation strategy had a strong influence on them (Dasireddy and Likozar, 2019). The ultrasonic synthesis route provided catalysts with increased basic active sites and the support not only provides a proper catalyst configuration but modify the interactions between the active component and the support (Liu et al., 2003). It can also alter the surface properties, such as the basicity/acidity and adsorption characteristics of the catalyst. Over the years, various support materials (Figure 10) for the Cu-based catalysts have been studied (Weigel et al., 1996; Tang et al., 2009; Halder et al., 2018; Lin et al., 2019; Yang B. et al., 2019). Metal oxides are the most common supports for the methanol synthesis catalysts, and their properties greatly affect the catalyst activity in several ways. The non-metallic supports, including metal organic frameworks (MOFs), porous silica materials, layered double hydroxides (LDHs), carbon materials, metal carbides, graphene, and porous polymers, have also been investigated (Rodriguez et al., 2015; Wang et al., 2015; Diez-Ramirez et al., 2016; Fan and Wu, 2016; Liu et al., 2016; Din et al., 2018; Sun et al., 2018; Witoon et al., 2018; Mureddu et al., 2019).

We discuss the supported Cu-catalysts in a different light from the above discussed ternary catalysts, noting that the commercial methanol synthesis (Cu/ZnO/Al2O3) catalyst, for example, is not a “supported catalyst.” Supported catalysts are generally prepared by the incipient or wet impregnation methods. Of the metal oxide supports investigated in the literature for Cu catalysts, ZnO, ZrO2, Al2O3, Ga2O3, SiO2, and CeO2 have drawn the most attention in methanol synthesis. These metal oxides have also been explored as promoters to the Cu-based methanol synthesis catalysts (Toyir et al., 2009; Zhan et al., 2014; Hu et al., 2018).

Cu/ZnO Catalysts—ZnO as a Support and Co-Catalyst

The Cu/ZnO-based catalysts for the production of methanol from CO or CO2 or a mixture of both have been in existence and applied for nearly six decades. Before the standardization of the ternary Cu/ZnO/Al2O3 catalyst, Cu/ZnO was used as an active catalyst for the hydrogenation of CO. The Cu/ZnO catalyst is typically prepared by the impregnation or co-precipitation method (Li et al., 2015; Lunkenbein et al., 2015).

In the Cu/ZnO catalyst, ZnO plays several important roles. The presence of ZnO improves the dispersion and stability of Cu (Bonura et al., 2011); also, the lattice oxygen vacancies and the electron pairs in ZnO are active for methanol synthesis. These functions lead to a more active Cu phase and larger surface area, thus preventing agglomeration of Cu particles (Arena et al., 2011). The catalytic activity of a Zn-doped Cu(111) surface was much higher than that of the pure Cu(111) as a result that ZnO modified the electronic properties of Cu sites by an electron exchange and interaction with Cu particles (Twigg and Spencer, 2001; Koitaya et al., 2019). The role of ZnO in the reduction of Cu by H2 was studied by Fierro et al. (1996). Synergism between Cu and ZnO reportedly exists upon the incorporation of ZnO into the Cu based catalysts (Kanai et al., 1996; Chen et al., 1999), and this resulted in the electronic interaction between Cu and Zn(2+–2+) which created active sites like Cu(1−O–Zn) (Kanai et al., 1996). The catalytic activity of a Zn-doped Cu(111) surface was much higher than that of the pure Cu(111) as a result that ZnO modified the electronic properties of Cu sites by electron exchange and interaction with Cu particles (Twigg and Spencer, 2001; Koitaya et al., 2019). The role of ZnO in the reduction of Cu by H2 was studied by Fierro et al. (1996). The temperature programmed reduction investigation of the Cu–ZnO catalyst synthesized by the co-precipitation method revealed ZnO promoted the reducibility of CuO. It is believed that

OTHER Cu-CONTAINING CATALYSTS

Supported and Promoted Cu Catalysts

Until the present, Cu-based catalysts present the most desirable properties for the direct CO2 hydrogenation to methanol at the industrial scale, thus proper to refer it as the methanol synthesis catalyst. However, the low conversion of CO2 below equilibrium and poor selectivity to methanol have necessitated further improvement of these catalysts. Although the methanol synthesis catalyst is not a classical supported catalyst, suitable support not only provides a proper catalyst configuration but modify the interactions between the active component and the

![Figure 9](https://example.com/figure9.png)

**Figure 9** | Selectivity-conversion relationships of CuCeTiOx-SG and CuCeTiOx-CP (Chang et al., 2017). Reproduced with permission from Elsevier.

![Figure 10](https://example.com/figure10.png)

**Figure 10** | Methanol selectivity (%) versus CO2 conversion (%) for CuCeTiOx-SG and CuCeTiOx-CP catalysts. Reproduced with permission from Elsevier.
ZnO acts as a reservoir of atomic hydrogen and provides it for the CO\textsubscript{2} hydrogenation on the Cu surface, or as a binding site facilitating the adsorption of H\textsubscript{2} species and CO\textsubscript{2} via a spillover (Chen et al., 1999). The atomic hydrogen then transfers from the Cu onto the ZnO surface and gradually hydrogenates the adsorbed CO\textsubscript{2} to methanol (Sun et al., 2003; Dang et al., 2018).

ZnO, as a support, is also suggested to be an active component in the methanol synthesis catalyst (Fujitani and Nakamura, 2000; Choi et al., 2001). In a physical mixture of Cu/SiO\textsubscript{2} and ZnO/SiO\textsubscript{2}, it was found that Zn species could migrate to the Cu surface upon reduction with H\textsubscript{2}, creating Cu–Zn active sites on the Cu surface (Choi et al., 2001). The formate species were firstly formed on both Cu and ZnO phases, and secondly, they were further hydrogenated to form methoxides located on the ZnO (Lei et al., 2015). Thus, ZnO is actively involved in the synthesis of methanol by creating more stable reaction intermediates, which readily convert to methanol on further hydrogenation (Chen et al., 1999). The absorption strength of reaction intermediates like HCO, H\textsubscript{2}CO, and H\textsubscript{3}CO can be enhanced by the incorporation of ZnO, thus decreasing the energy barriers. Consequently, the formation rate of methanol is increased (Behrens et al., 2012).

Sulfur and chlorine species are considered poisons for Cu-based methanol synthesis catalysts, and the addition of ZnO to the catalyst irreversibly scavenges sulfur or chlorine as ZnS or ZnCl\textsubscript{2}, respectively, mitigating against deactivation of the catalyst. On the negative, ZnO is a basic oxide that can neutralize the acidity of Al\textsubscript{2}O\textsubscript{3} in the commercial catalyst, preventing the transformation of CO\textsubscript{2} to methanol and promoting the agglomeration of active Cu particles (Twigg and Spencer, 2001).

**Cu/ZrO\textsubscript{2} and Cu/ZnO/ZrO\textsubscript{2}**

ZrO\textsubscript{2} is a good support due to its hydrophobicity, and surface basicity. Besides, its high thermal stability is superior to Al\textsubscript{2}O\textsubscript{3} under reducing and oxidizing atmospheres (Li and Chen, 2019). The catalytic activity of ZrO\textsubscript{2} as a support is superior to that of Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, or ZnO (Li and Chen, 2019). The addition of ZrO\textsubscript{2} has been reported to improve the surface area of Cu species and can alter the Cu\textsuperscript{+}/Cu\textsuperscript{0} ratio in the surface (Fisher et al., 1997; Sloczyński et al., 2003). CuO can be uniformly dispersed on the ZrO\textsubscript{2} surface, forming an interface favorable for the methanol synthesis reaction (Li and Chen, 2019).

ZrO\textsubscript{2} exists in different crystal structural phases (polymorphs)–amorphous (a)-ZrO\textsubscript{2} and tetragonal (t)-ZrO\textsubscript{2} and monoclinic (m)-ZrO\textsubscript{2} (Figures 11A–C). The a-ZrO\textsubscript{2} and t-ZrO\textsubscript{2} transform to m-ZrO\textsubscript{2} at high temperatures. The calcination of Zr(OH)\textsubscript{4} at temperatures greater than 400°C transforms it mainly to m-ZrO\textsubscript{2}, so Cu species are easily incorporated into a-ZrO\textsubscript{2} (Tada et al., 2018). The effects of ZrO\textsubscript{2} polymorphs, including -a, -t and -m phases on the structure of Cu, Cu–ZrO\textsubscript{2} interaction and adsorption–desorption of H\textsubscript{2} and CO\textsubscript{2} were systematically investigated, and the catalytic performance of the catalysts, Cu/a-ZrO\textsubscript{2}, Cu/t-ZrO\textsubscript{2}, and Cu/m-ZrO\textsubscript{2} catalysts explored (Witoon et al., 2016). By a variety of analytical techniques, the Cu surface area followed the trend: Cu/a-ZrO\textsubscript{2} > Cu/t-ZrO\textsubscript{2} > Cu/m-ZrO\textsubscript{2}. The increase in the yield of methanol is correlated with the increase in Cu surface area, thus the Cu/a-ZrO\textsubscript{2} exhibited the highest methanol yield. However, the methanol turn over frequency (TOF\textsubscript{Methanol}) of Cu/t-ZrO\textsubscript{2} was higher than those of Cu/a-ZrO\textsubscript{2} and Cu/m-ZrO\textsubscript{2}. In general, the high TOF\textsubscript{Methanol} is due to a strong Cu–ZrO\textsubscript{2} interaction and a high
surface concentration of atomic hydrogen to CO$_2$ (Witoon et al., 2016). A highly loaded CuO (65.2 wt%) on ZrO$_2$ support prepared by flame spray pyrolysis (FSP), showed a good catalyst activity compared with a commercial catalyst (Figure 11D). The production rate of methanol by CO$_2$ hydrogenation and the selectivity to methanol over FSP-made CuO/ZrO$_2$ catalysts were obviously higher compared with those of commercial CuO/ZnO/Al$_2$O$_3$ (Fujiwara et al., 2019). For all catalysts, the CO$_2$ conversion increased, with increasing contact time, while the selectivity to methanol decreased, but the selectivity to CO increased (Figure 11E). The activity and selectivity of the prepared catalysts depended on the spray pyrolysis rate. They were higher at low feed rates (2–3 ml min$^{-1}$) than those of the catalysts prepared at higher feed rates (5–10 ml min$^{-1}$). The former feed rate led to the formation of smaller ZrO$_2$ particles, which provided more surface to stabilize small Cu particles and formed interfacial Cu–ZrO$_2$ active sites. The crystallite size and crystallinity of t-ZrO$_2$ could be controlled by varying the precursor feed rate (Fujiwara et al., 2019).

Cu/ZnO/ZrO$_2$ catalyst is more resistant to water deactivation due to the hydrophobic nature of ZrO$_2$ (Li and Chen, 2019). The Cu/ZnO/ZrO$_2$ catalyst contains ZrO$_2$ instead of Al$_2$O$_3$ and exhibits high performance in methanol synthesis from CO$_2$ hydrogenation. Compared with Al$_2$O$_3$, the impressive performance is linked with the possibility of interactions between Cu-species and ZnO–ZrO$_2$ oxides (Li and Chen, 2019). Moreover, ZrO$_2$ exhibits a weaker hydrophilic character than either Al$_2$O$_3$ or CeO$_2$, which promotes the desorption of formed water, and benefits the formation of methanol (Arena et al., 2007). The presence of ZrO$_2$ in the Cu/ZnO catalysts could lower the Cu coordination with oxygen and increase the Cu–O
distance, as studied by the extended X-ray absorption fine structure. This indicates the presence of defective Cu structures resulting from the strong Cu–support interaction (Yang et al., 2006). Consequently, the Cu/ZnO catalyst containing ZrO₂ exhibited much higher activity and selectivity toward methanol production than the Cu/ZnO catalyst. While it is a proven fact that the impressive performance of the Cu/ZnO/ZrO₂ catalyst arises from the structural and surface modifications of the Cu/ZnO by ZrO₂, it is important also to note that the crystallinity of ZrO₂ strongly affects the Cu–ZrO₂ interaction (Baiker et al., 1993). Thus, the co-presence of amorphous ZrO₂ and crystalline Cu/ZnO enhances the synergistic effect of Cu/ZnO/ZrO₂, facilitating the dissociative adsorption of CO₂ and the selective conversion of CO₂ to methanol (Słoczyński et al., 2004).

Both experiments and DFT calculations using Cu–ZnO–ZrO₂ have provided evidence on the separate functions of the Cu species and ZnO–ZrO₂ interface in the catalytic conversion of CO₂ to methanol by hydrogenation (Wang Y. et al., 2019). The catalytic evaluation at 220°C under 3.0 MPa showed very high activity (CO₂ conversion of 18.2% and selectivity to methanol of 80.2%). The binary oxides of ZnO–ZrO₂ showed a higher ability for CO₂ adsorption and the hydrogenation of carbonate species to formate and methoxy intermediates than the Cu–ZnO or Cu–ZrO₂ systems. Cu/ZrO₂ and Cu/ZnO catalysts synthesized by various methods show different catalytic performance. While Cu/ZrO₂ is more effective for the selective formation of methanol from CO₂, higher activity for CO₂ conversion is associated with Cu/ZnO (Li and Chen, 2019).

So far, efforts have been made to enhance the catalytic performance of CuO–ZnO–ZrO₂ catalysts further. Modification of CuO–ZnO–ZrO₂ catalysts with various additives is a feasible option to alter the physicochemical properties of the catalysts, improving the methanol synthesis activity and preventing the Cu sintering. The CuO–ZnO–ZrO₂ catalysts supported on graphene oxide (GO) gave a higher STY in comparison with the GO-free catalyst due to the increased active sites for the adsorption of CO₂ and H₂. The methanol selectivity of GO supported catalysts was above that of the unsupported catalyst. Specifically, the highest methanol selectivity of 75.88% was obtained over the CuO–ZnO–ZrO₂ catalyst prepared with 1 wt% GO (CZZ-1GO) at 200°C and 20 bars. This performance was attributed to a promoting effect of GO nanosheet serving as a bridge between metal oxides, which enhanced the hydrogen spillover from the Cu surface to the carbon-containing species adsorbed on the metal oxide particles (Witton et al., 2018). The mixed oxides of Cr, Mo, or W and CuO–ZnO–ZrO₂ prepared by the co-precipitation method showed better activity for methanol synthesis. The results indicated an improved methanol selectivity and yield of the CuO–ZnO–ZrO₂ catalyst upon addition of MoO₃ or WO₃ but slightly dropped when doped with Cr₂O₃. The improved methanol yield over these catalysts can be attributed to the differences in their Brunauer-Emmett-Teller surface areas and adsorption capacities for CO₂. It was also found that the ratio of surface Zn to Cu, as well as the fraction of strong basic sites, improved the methanol selectivity (Wang G. et al., 2019). A layered double hydroxide (Mg-Al LDH) was used as a carrier for Cu–ZnO–ZrO₂ catalyst synthesized by the co-precipitation method. Characterization results revealed CuO–ZnO–ZrO₂ nanoparticles were uniformly dispersed and attached to the surface of the LDH, which improved the specific surface area and Cu dispersion compared with a reference catalyst without the support. The catalyst showed a high methanol selectivity of 78.3% at 250°C under a pressure of 3.0 MPa, which is about 50% higher than conventional Cu-based catalysts reported in the literature. Raising the temperature of the CuO–ZnO–ZrO₂–LDH catalyst slightly decreased the conversion. Very promising is that the activity of the can be recovered by reduction with H₂ (Fang et al., 2019).

**Cu/CO₂ and Cu/ZnO/CO₂**

CuO₂ has also been studied as a support or co-support for the methanol synthesis catalysts via the CO₂ hydrogenation route (Hu et al., 1991; Wang et al., 2016; Chang et al., 2017; Li et al., 2019). It has a strong adsorption affinity for CO₂ due to its strong basicity and oxygen vacancies. The latter can improve the dispersion of Cu particles and promote the spillover of atomic hydrogen, which benefits the production of methanol (Chang et al., 2017; Li et al., 2020); also, a negative influence on the surface area of catalysts with ceria was observed (Bonura et al., 2011). In 2014, Rodriguez and co-workers published a study that demonstrated the combination of Cu metal and oxide sites in the Cu–CeO₂ interface affords favorable reaction pathways for the conversion of CO₂ to methanol (Graciani et al., 2014). By theoretical methods, the CO₂ hydrogenation over a CeO₅/Cu(111) surface was demonstrated. The complementary surface analysis with XPS indicated Ce₂O₃/Cu(111) as the active phase of the catalyst (Figure 12A). This inverse catalyst was much better for methanol synthesis than either Cu(111) or Cu/ZnO(000T) (Figure 12B). It was also found that the catalytic activity of Ce₂O₃/Cu(111) was of an order higher than those of Cu(111) or ZnO/Cu(111) (Senanayake et al., 2016). The activation energy for the conversion of CO₂ to methanol decreased from 25 kcal/mol on Cu(111) to 16 and 13 kcal/mol on ZnO/Cu(111) and CeO₂/Cu(111), respectively. The analysis of the surface of the CeO₂–Cu(111) interface by ambient pressure—XPS and ambient pressure infrared reflection absorption spectroscopy revealed the formation of formates and carboxylates (CO₂δ−) during the reaction. These results demonstrate CeO₂–Cu as an active catalyst rich in Ce³⁺ sites, which stabilized the CO₂δ− species, an essential intermediate for the production of methanol (Graciani et al., 2014).

In ceria-containing Cu–ZnO oxide catalysts, the presence of CeO₂ promoted the surface activity of the Cu–ZnO system, although negatively influenced the catalyst texture and metal surface area in comparison to ZrO₂ (Bonura et al., 2011). As discussed earlier, CeO₂ can improve the dispersion of Cu particles and promote the spillover of atomic hydrogen. On the other hand, ZnO can improve the dispersion of the CeO₂ nanoparticles. Thus, the ternary CuZnCeOₓ exhibited higher performance than the binary CuZnOₓ catalyst (Shi et al., 2019); but had relatively very high selectivity toward CO (Hu et al., 2018). A CuZnCeOₓ catalyst prepared by a parallel flow co-precipitation technique was evaluated in the hydrogenation of CO₂ to methanol and CO.
The amount of CeOx in the catalyst controlled the selectivity of the products. Characterization results revealed a significant synergistic effect between Cu and metal oxides (ZnO and/or CeOx) in the catalyst. Cu played a critical role in the activation of H2, and CeOx strongly adsorbed CO2, improved the dispersion of Cu nanoparticles, and promoted the spillover of atomic hydrogen (Shi et al., 2019). The results of these studies suggest that CeO2 in Cu–ZnO catalysts can offer a viable way to produce methanol or CO from CO2 hydrogenation selectively. The selectivity toward the products (methanol and CO) can be regulated by changing the reaction conditions, catalyst formulation, or preparation method (Hu et al., 2018). For example, the CuZnCeTiOx showed significantly enhanced activity in comparison with the CuCeTiOx catalyst and was twice more active than the commercial catalyst as measured by TOF values. However, the stability is still not good enough, with high selectivity toward CO (Chang et al., 2019).

Other Metal Oxides Employed as Promoters or Additives

Magnesium Oxide (MgO)
Mg-containing Cu/Zn/Al industrial catalysts for methanol synthesis were developed in the 1990s (Bozzano and Manenti, 2016). The effect of metal oxides on the Cu/ZnO/Al2O3 catalyst from co-precipitation was investigated. MgO showed a negative impact on the catalytic activity, but a positive effect on the stability of the catalyst (Meshkini et al., 2010). It was concluded that Mg affects the activity of the Cu/Zn/Zr catalyst for methanol synthesis from CO2 by improving the adsorption properties (Sloczyński et al., 2003). Zander et al. (2013) found that the methanol production rate from synthesis gas by Cu/MgO/ZnO was higher than that by Cu/ZnO, ascribed to the higher Cu dispersion caused by Mg addition. Recently, the influence of Mg addition on the performance of Cu/Zn/Al/Mg methanol synthesis catalyst prepared by co-precipitation and fractional-precipitation methods was investigated. In a series on Cu/Zn/Al/Mg catalysts obtained, the preparation method was found to have a significant effect on the properties as well as the catalytic performance. The co-precipitation method resulted in catalysts with higher Brunauer-Emmett-Teller surface area and Cu dispersion, but with decreased catalytic activity. On the other hand, the fractional precipitation facilitated the Cu substitution by Zn in the sub-carbonate precursor, which cushioned the effect resulting from the former method, catalytically performed better than those prepared by the co-precipitation method (Zhang et al., 2017). In these catalysts, there was the formation of Mg–Al hydrotalcite unfavorable for methanol production. Moreover, the formation of CuAl2O4 and MgAl2O4 spinel phases in Cu/MgO/Al2O3 catalysts were observed (Dasireddy et al., 2018).

Gallium Oxide (Ga2O3)
Ga2O3 is reported to increase the activity per unit Cu surface area of methanol synthesis catalyst (Toyir et al., 2009). Ga3+ can modify the hydroxycarbonate precursors during the catalyst synthesis to form the precursors with hydrotalcite structure (An et al., 2007). The catalysts derived from the Ga-modified hydrotalcite showed improvement in the dispersion of Cu.
particles and the formation of active Cu–ZnOₓ sites, which enhanced the efficiency of Cu–ZnGa catalyst system for CO₂ hydrogenation to methanol (An et al., 2007). One reason for this improvement is that the hydrotalcite derived catalysts could maintain their morphology in ultratine layers even after heat treatment at high temperatures, which transformed the phase to amorphous (Guil-López et al., 2019a). The amorphous phase is more accessible with better dispersed metallic Cu crystal, and with a large surface area decorated with a small amount of Zn atoms. CuZnGa catalysts derived from the LDH precursor gave good catalytic activity in CO₂ hydrogenation to methanol. LDH30Ga (Cu: 33.5 wt%) yielded STY of 0.59 g·mol⁻¹·h⁻¹, higher than the commercial JM-HiFUEL (50 wt% Cu/ZnO/Al₂O₃) with a STY of 0.38 g·mol⁻¹·h⁻¹ after 25 h on stream at 290°C and 4.5 MPa (Li et al., 2018). However, there is an obvious requirement of high temperature and pressure for realizing the high activity.

**Titanium Oxide (TiO₂)**

The incorporation of titanium nanotubes (TNTs) support into CuO–ZnO–CeO₂ catalysts can promote CuO reducibility, improve metallic Cu dispersion and increase the specific surface area. The CuO–ZnO–CeO₂/TNTs composite catalysts with different TNTs contents prepared by a deposition–precipitation method gave high CO₂ conversion and methanol selectivity. The selectivity was positively correlated with the number of basic sites, whereas the CO₂ conversion was a function of the specific surface area of Cu. The catalyst prepared with 10 wt% TNTs (CuO–ZnO–CeO₂/10 TNTs) possessed high metallic Cu surface area, high CO₂ adsorption capacity and a large number of basic sites, translating into excellent catalytic performance (methanol selectivity of 59.8%, CO₂ conversion of 23.3% and STY of 9.33 mmol·MeOH·h⁻¹·g⁻¹ at 260°C, H₂/CO₂ of 3, gas hourly space velocity (GHSV) of 7,500 ml·g⁻¹·h⁻¹) (Shi et al., 2019).

**Non-Metal Oxide Supports**

In general, SiO₂ possesses large surface area and porosity, high thermal stability, and good dispersion capacity but weak interaction with metals (Nitta et al., 1994; Sugawa et al., 1995). However, the presence of steam at high temperatures weakens its thermal stability due to its transformation to Si(OH)₂. During the methanol synthesis from CO₂, the stability of Cu/ZnO-based catalysts was improved by incorporating a small amount of silica, which suppressed the crystallization of ZnO in the catalysts (Toyir et al., 2009). Cu supported on high-purity silica was nearly inactive in methanol synthesis (Fujita et al., 1995; Gotti and Prins, 1998), and the selectivity toward methanol was low. In another study, the Cu/SiO₂ catalyst exhibited a low selectivity to methanol (Sugawa et al., 1995). A 10 wt% Cu/SiO₂ exhibited higher methanol formation rate (2.1%) than 10 wt% Pd/SiO₂ (0.3%) (Kunkes et al., 2015). Some experimental results have reported higher activity and relatively better selectivity for methanol over silica-based than ZnO-based catalysts, due to the higher surface area of the former (Nitta et al., 1994). SiO₂ can function better as a support for Cu-catalyst for methanol synthesis in the presence of other metal oxides as a promoter or co-support, or for the copper bimetallic catalysts (Sugawa et al., 1995; Grandjean et al., 2011). Micro-spherical SiO₂ prepared by the spray-drying method was investigated as support for Cu/ ZnO-based catalysts synthesized with different percentages of Cu and ZnO by the ammonia-evaporation method (Jiang et al., 2018). The results revealed the deposition of Cu and Zn ions in the pores of the SiO₂ and high distribution, which depended on the metal loadings. The specific surface area of the catalysts increased with increasing loadings to a critical amount due to the formation of the porous structure of SiO₂. Beyond this loading, CO₂ conversion slightly reduced due to the blocking of the pores of the support. The combination of X-ray diffraction, XPS, X-ray Auger electron spectroscopy and CO-adsorption in situ Fourier-transform infrared spectroscopy analysis demonstrated that SiO₂ facilitated the formation of both Cu⁺ and Cu²⁺ species on the surface of the reduced Cu/ZnO/SiO₂ catalysts (Jiang et al., 2018). Other examples of the SiO₂ supported catalysts for methanol synthesis can be found in the literature (Studt et al., 2014; Fiordaliso et al., 2015; Phongamwong et al., 2017; Jiang et al., 2018).

Carbon materials possess a very large surface area, high thermal stability, high hydrogen uptake, mechanical strength, and facilitate H₂ dissociation. All these properties contribute to the increasing rate of CO₂ hydrogenation to methanol at a lower temperature with high methanol selectivity than the equilibrium when used as supports, but unsuitable for a commercial application due to low conversion. GO as support for the Cu–ZnO catalysts was studied for the CO₂ hydrogenation to methanol. The results found that 10 wt% CuZn/rGO catalyst exhibited a good activity for the CO₂ hydrogenation, achieving 26% CO₂ conversion, methanol selectivity of 51%, and 424 ± 18 mg·methanol·1 at 250°C under 15 bar after 5 h on a stream (Deerattrakul et al., 2016). With MOF as a support or component of catalyst, very high methanol selectivity (up to 100%) was reported (Rungtaweevoranit et al., 2016; An et al., 2017; Hu et al., 2019). Still, its application suffers from serious challenges that are undesirable for industrial applications—low conversion and instability at high temperatures. GO as support for the Cu–ZnO catalysts was studied for the CO₂ hydrogenation to methanol. The results found that 10 wt% CuZn/rGO catalyst exhibited a good activity for the CO₂ hydrogenation, achieving 26% CO₂ conversion, methanol selectivity of 51%, and 424 ± 18 mg·methanol·1 at 250°C under 15 bar after 5 h on a stream (Deerattrakul et al., 2016).

The promotion of the Cu/Zn catalyst supported on SBA-15 (CZ/SBA-15) with transition metals (Cr, Mn, Fe, Co, Ni) revealed impressive catalytic performances of the modified catalysts. The Mn promoted catalyst (Mn–CZ/SBA-15) was the most active due to the presence of small copper crystallites and strong interaction between CuO and other oxide species in the catalyst. At a reaction temperature of 180°C under 4.0 MPa, WHSV of 60 L·g⁻¹·h⁻¹ and H₂/CO₂ of 3, the catalyst presented a methanol yield of 10.4%, CO₂ conversion of 10.5% and a methanol selectivity of 98.6% (Koh et al., 2019).

**Bimetallic Cu-Based Catalysts**

Bimetallic Cu-based catalysts also have good catalytic performances in the direct CO₂ hydrogenation to methanol.
Noble metals such as Pd have proper properties for activating hydrogen, which could spread through a hydrogen spillover mechanism to the neighboring catalytic sites (Melián-Cabrera et al., 2002; Ponce and Klubunde, 2005). The hydrogen spillover can result in a catalyst surface with a highly reduced state that could facilitate the hydrogenation process. In the methanol synthesis application, Pd is reported with good catalyst improvement roles. It is suggested that Pd enhances the activity of Cu sites. Upon the addition of Pd, the Cu dispersion and surface concentration on the catalyst surface were improved. The Cu dispersion and the surface Cu concentration increased with an increase in the amount of loaded Pd to a certain level. It was explained that the interaction between Pd and Cu decreased the Cu–Cu bond distance due to the strong electronic perturbation, resulting in well-dispersed Cu species (Kugai et al., 2016). In this way, the aggregation or agglomeration of Cu particles was suppressed due to the interaction with Pd, which was highly dispersed on CeO2 support (Choi et al., 2017). According to the XPS results, the peaks for Cu 2p electrons in Pd–Cu/Al2O3 catalysts appeared at relatively lower binding energy than those in Cu/Al2O3 catalyst, meaning that Cu sites in Pd–Cu/Al2O3 catalysts were more abundant in electrons and could donate them to Cu, enabling Cu to stabilize in a more reduced state (Fox et al., 2008). Thus, Pd promotion generated more electron-rich Cu sites by electron transfer (Choi et al., 2017). Pd can also improve the reducibility of CuO and enrich the catalyst surface with electrons, enabling the activation of CO2 by interaction with the carbon atom of CO2 (Choi et al., 2017). A strong Pd–Cu bimetallic promoting effect on the formation of methanol from CO2 hydrogenation was observed, which is due to the synergetic effect between Pd and Cu as a result of the Pd–Cu alloy formation (Jiang et al., 2015). Pd–Cu supported on amorphous silica exhibited higher catalytic activity than monometallic Cu/SiO2 or Pd/SiO2 for CO2 hydrogenation to methanol. Some authors attribute the synergistic effect between Pd and Cu, which contributes to the improvement of catalytic activity to the alloy formation, as evidenced by the correlation between catalyst composition, structure and catalytic performance (Jiang et al., 2019a; Jiang et al., 2019b). The Pd–Cu bimetallic catalysts with total metal loadings (2.4–18.7 wt%) and optimal Pd/(Pd + Cu) atomic ratio exhibited a bimetallic effect on promoting CH4OH synthesis at 250°C and 4.1 MPa. The improvement in catalytic performance was realized at lower metal loadings, and Pd–Cu(2.4)/SiO2 catalyst could yield approx. 1.6 times higher methanol than the commercial Cu/ZnO/Al2O3 catalyst as measured with the metal-based STY. At high loadings, Pd–Cu alloy exhibited high selectivity to CO (Nie et al., 2018; Jiang et al., 2019a). The amount of alloy, as determined by quantitative X-ray diffraction, correlated with the observed promotive synergy; and the estimated TOFs, suggesting its involvement in methanol synthesis (Jiang et al., 2019b). A Cu–Zn bimetallic catalyst supported on Al foam (Cu–Zn/Al foam) gave a high methanol yield of 7.81 g gCu−1 h−1 at CO2 conversion of 99% and methanol selectivity of 82.7% under reaction conditions of 3 MPa and 250°C at a high WHSV of 20,000 ml gcat−1 h−1. It was found that the support structure played a significant role in the performance of this catalyst. Compared with the other Cu-based catalysts, the Cu–Zn/Al foam catalyst possesses a good heat/mass transferability, and an appropriate amount of basic sites (Liang et al., 2017).

**RENEWABLE ENERGY STORAGE IN AND NEW PROCESSES FOR METHANOL**

The chemical recycling of CO2 to renewable fuels and commodity chemicals represents an economic aspect of the CO2 mitigation. Methanol, a primary liquid product derived from the hydrogenation of CO2, aside being used directly as a fuel, can be efficiently processed into other products of high societal needs—DME, ethylene, propylene, gasoline, and other products currently obtained from petroleum and natural gas. The combustion of methanol and its derivatives will release CO2, which can be recycled back effectively, forming a carbon loop (Goepert et al., 2014). Biomass is a form of recycled CO2 that can be converted into DME, for example. Since CO2 hydrogenation is carried out using hydrogen produced from renewable energy sources—electrical, wind, hydro or solar energy (Goepert et al., 2014; Patterson et al., 2019), it is required to store it for use at a later time due to the obvious challenges with each of the energy sources. For example, solar and wind are seasonal, intermittent and fluctuating. The storage of electricity on a large scale and transportation at a very long distance are still challenging. The electrical energy can be conveniently stored in chemical compounds such as hydrogen, methanol, methane and higher hydrocarbons that can then be stored, transported and used when needed to produce electricity or for various other applications such as heating, cooking and transportation (Olah, 2005; Goepert et al., 2014). It has been proposed that the carbon-based liquid fuels will continue to be important energy storage media in the future because of their higher volumetric stored energy density. Methanol has great merits as a storage medium for renewable energy. As an energy storage medium, methanol displays high performance as an additive or substitute for gasoline in internal combustion engines. The direct conversion of the chemical energy in methanol to electrical power at ambient temperature has been demonstrated in methanol fuel cells (McGrath et al., 2004). Methanol is also a feedstock for a number of chemicals such as formaldehyde and acetic acid. It can produce light olefins, includingethylene and propylene, used in the synthesis of various polymers, and any hydrocarbons and products currently obtained from petroleum oil through the methanol-to-olefin process. DME produced from methanol can be easily liquefied at moderate pressure and applied as diesel fuel substitute with high cetane rating, producing little or no soot emissions (Semelsberger et al., 2006; Arcoumanis et al., 2008). It is a good substitute for liquefied petroleum gas in most applications, such as heating and cooking.

The CO2 hydrogenation to methanol can be processed by the thermochemical, electrochemical and photochemical methods. These processes are challenging in several aspects. The thermochemical process applied in the commercial methanol synthesis from natural gas is a two-step process that transforms the energy and molecules in a fossil fuel (Olah, 2013). The first step is the steam-methane reforming into synthesis gas, which subsequently converts to methanol in the second step. A few percent of CO2 is also produced in the first step. Methanol cannot be directly generated electrochemically from CO2 with high...
selectivities or current densities (Malik et al., 2016; Yang D. et al., 2019).

Researches are continuously seeking new technologies to recycle CO2 to liquid fuel most efficiently and economically. Patterson et al. (2019) developed a new approach integrating the existing conventional chemical catalytic process and energy harvesting methods. They proposed combining solar methanol islands and human-made marine structures that use renewable energy to harvest CO2 from seawater and catalysis to produce methanol. This approach uses clusters of marine-based floating islands on which photovoltaic cells convert sunlight into electrical energy to produce H2 and extract CO2 from seawater, where it is in equilibrium with the atmosphere. H2 and CO2 then react to form methanol. H2 is electrochemically generated and the extraction of CO2 is possible using a series of membrane cells. Methanol is then synthesized using a looped gas-phase heterogeneous catalytic process. They suggested that a single solar methanol island could output up to 15,300 tons/year of methanol. The process is particularly of advantage compared with the direct atmospheric CO2 capture because CO2 in seawater (0.099 kg CO2/m3) is about 125 greater than the amount in the atmosphere (0.00079 kg/m3) (Patterson et al., 2019). This innovative technology for renewable fuel synthesis from the marine environment has attractive features, such as abundant raw materials and large exposure to solar energy, and avoidance of local CO2 depletion. However, this technology relies on previously demonstrated chemical and physical processes to produce the solar methanol island on a significantly large scale. It is suggested that wind could also serve as a power source; thus, analyzing how other energy sources or energy mixture could contribute is expected to further the development of the process. For a practical design of solar-powered artificial marine-islands to recycle CO2 into methanol and other synthetic liquid fuel, some issues must be addressed. These include i) how photovoltaic modules can be deployed on a large-scale in the marine environment, and properly maintained. ii) Is combined technology such as desalination and electrolysis a possibility to efficiently produce H2 from seawater? iii) Can electrolysis be deployed for large-scale CO2 extraction from seawater? iv) What kind of reactor material and systems engineering are required to realize a large, practical marine installation? If methanol is the end product, there is the need to look into the optimal design, including reactor looping and heat and pressure management, for a marine-based synthetic fuel reactor and separation system. These frontline questions need urgent technological answers.

The integration of direct CO2 air capture with CO2 and H2O as electrolyzers and a traditional methanol synthesis step in a process termed “air-to-barrel” has been proposed (Smith et al., 2019). The process uses CO2 electrolyzers to convert atmospheric CO2 into solar fuels using renewable electricity. This technology has the potential of producing 10,000 tons of methanol/day. The CO2 and water electrolyzers can replace the steam-methane reforming step of current methanol synthesis by producing CO and H2 from CO2 and H2O. Essentially, the carbon and hydrogen content of methane is replaced by CO2, H2O and solar energy.

CONCLUSION AND OUTLOOK

In this review, we have discussed the recent developments in the direct hydrogenation of carbon dioxide to methanol over the Cu/ZnO-based catalysts. No doubt, the Cu-based catalysts are still very promising for the direct hydrogenation of CO2 to methanol in the industry. Still, they need to be improved to overcome a series of technical problems. Many studies have been conducted to understand the catalyst structures and to enhance their functionalities. From the thermodynamical aspect, both low temperature and high pressure are favorable conditions for the methanol synthesis from CO2 reduction with hydrogen; however, low temperature is kinetically unfavorable for breaking the O–C–O bonds in CO2 molecule. High temperature increases the rate of RWGS and other side reactions, whereas high pressure is economically infeasible. It is a challenge to obtain both a high single-pass CO2 conversion and a high methanol selectivity with the current industrial catalyst via the direct CO2 hydrogenation. Consequently, developing Cu-based catalysts with high activity (high single-pass CO2 conversion and high selectivity to methanol) at lower temperatures and pressures are crucial for the CO2 to methanol hydrogenation.

With the Cu/ZnO/Al2O3 catalysts, the sintering of the Cu particles is a crucial problem. Thus, high mechanical strength and thermal stability are essential to maintain a long catalyst life under typical industrial conditions. These may be achieved by 1) use of confined catalysts, such as Cu or Cu/ZnO in porous materials, e.g., mesoporous SiO2 (SBA-15) and porous ZrO2; 2) use of binders in the catalyst composition which can boost both thermal stability and water resistance, and 3) deploying suitable synthesis methods and protocols, such as adding promoters to the base catalyst, forming promoted or multimetallic catalysts.

Besides the conventional methods for catalyst preparation, several other approaches are promising for the development of modified catalysts. These catalysts can be grouped into the following: 1) solid-solution derived catalysts, e.g., the solid solution of ZnZrOx is demonstrated to possess high selectivity and stability. Therefore, opportunities exist for even better performances of some other solid solutions for methanol synthesis from CO2. Several materials acting both as support or co-catalysts are effective as the traditional alumina in the Cu/ZnO/Al2O3. Specifically, ZrO2 is a good substitute for Al2O3 due to its excellent catalytic and surface properties; 2) catalysts derived from complex metal oxide compounds, e.g., hydrotalcite, perovskites, spinel compounds, MOFs, zeolites, etc. The catalysts derived from these compounds can have a high Cu dispersion and intimate contact among various catalyst components. For example, Cu or Cu/ZnO nanoparticles derived from perovskites and hydrotalcites through a proper reduction strategy may have high dispersion of Cu; MOFs and zeolite derived catalysts may have the well-defined component composition and ratio, and precise location, which should be suitable for the reaction and the clarification of the property-structure relations of the catalysts, as the well-defined structures can enable the understanding of how catalyst micro/macrostructure affects conversion and selectivity; 3) core-shell
catalysts, e.g., Cu or Cu/ZnO with ZrO2 shells. The core–shell catalysts are highly thermally stable and could form efficient function-selective catalysts; 4) alloy and bi- or tri-metallic catalysts, and 5) metallic–nonmetallic hybrid systems.

It is believed that the CO2 reductive hydrogenation to methanol commonly proceeds mainly through two mechanisms—the RWGS (via *HOCO intermediate species) and the formate (via *HCOO intermediate species) pathways. While the former involves a CO intermediate followed by hydrogenation, in the latter, CO2 is initially hydrogenated to the formate species, further dissociating to methanol. The various active sites reported include metallic Cu, oxidized Cu, Zn decorated Cu, and isolated Cu–Zn interfaces. Although the active sites and reaction mechanisms have been explored and analyzed in the literature, yet, knowledge of the detailed structure of the catalysts is still lacking. Analytical approaches such as the in situ experimental measurements should be deployed to elucidate the active sites and reaction mechanisms. Theoretical calculations using multiscale modeling techniques should complement experiments to elucidate the structures of the traditional catalysts further and to improve the design of new ones. It should be kept in mind that a well-designed catalysts will catalyze the desired reaction but inhibit the side reactions. However, the design of suitable catalysts mainly depends on understanding the reaction mechanism and active site structures, and the advances in the catalyst preparation. Therefore, a comprehensive solution combining a fundamental understanding of catalysis with advanced catalyst preparation and process optimization is necessary.

The recycling of CO2 to renewable fuels and platform chemicals is an important aspect of CO2 mitigation. Methanol, a major liquid product of CO2 hydrogenation with hydrogen from renewable energy sources, can serve as a storage medium for future use of energy in various applications such as heating, cooking, and transportation. New processes for renewable fuel production have been developed, such as “solar methanol island” involving CO2 from the marine environment in combination with catalysts, and “air-to-barrel” process, which uses CO2 electrolyzers to convert atmospheric CO2 into solar fuels. It is not yet developed a practical design of solar-powered artificial marine-islands to recycle CO2 into methanol and other synthetic liquid fuels. Several issues, including deployment at marine environment on large-scale, proper maintenance, efficient production of H2 from seawater, and the reactor requirements for practical marine installation need to deal with.

AUTHOR CONTRIBUTIONS

UJE wrote the manuscript. YS revised the manuscript. ZZ organized, wrote and modified the manuscript.

FUNDING

This work is financially supported by 2020 Li Ka Shing Foundation Cross-Disciplinary Research Grant (2020LKSFG09A), Guangdong Province Key discipline fund (GTITT), and Department of Education of Guangdong Province (2018KTSCX063).
CO₂ Reduction to Methanol for Renewable Energy Storage


Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Copyright © 2020 Etm, Song and Zhong. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.