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

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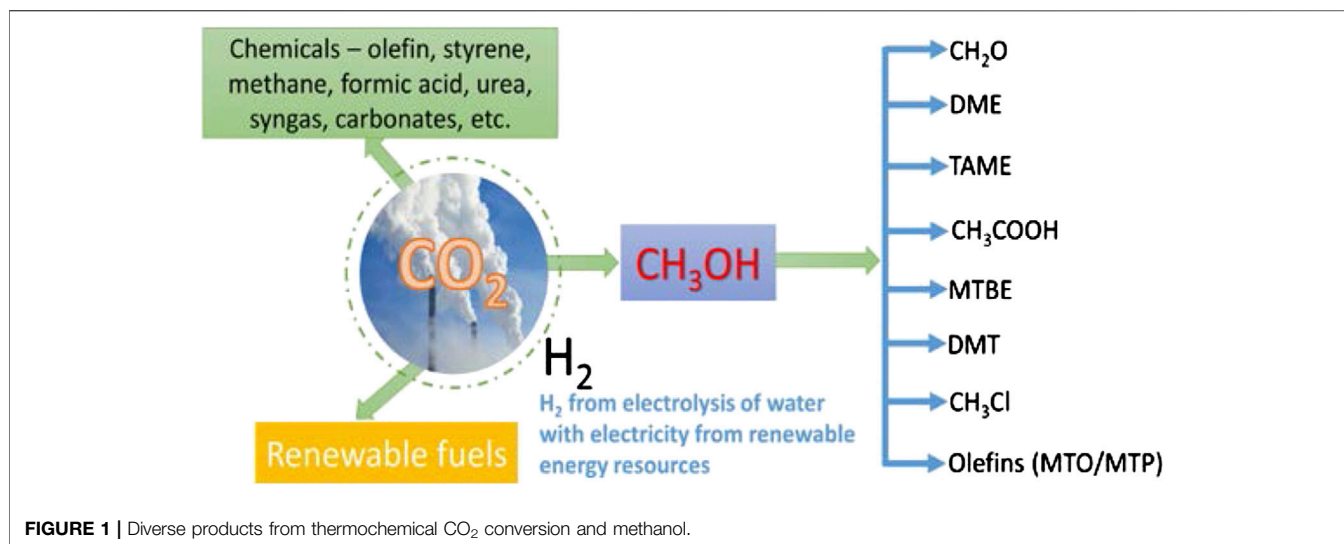
Heterogeneous catalytic hydrogenation of carbon dioxide (CO_2) to methanol is a practical approach to mitigating its greenhouse effect in the environment while generating good economic profits. Though applicable on the industrial scale through the syngas route, the catalyst of $Cu/ZnO/Al_2O_3$ suffers from a series of technical problems when converting CO_2 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 CO_2 methanolizing reaction or not? This paper reviews the history of the methanol production in industry, the impact of CO_2 emission on the environment, and analyzes the possibility of the Cu/ZnO-based catalysts for the direct hydrogenation of CO_2 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 (CO_2) 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 CO_2 from these sources, the earth heats up, resulting in global warming. A recent report shows that as of 2017, the global average concentration of CO_2 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 CO_2 control approaches. In recent times, this has been one of the reasons why discussion of CO_2 emission reduction tops agenda in most environmental pollution control submits, globally.

The reduction of CO_2 to economically relevant products represents an eco-friendly and green route toward value-added CO_2 emissions mitigation for environmental sustainability. For example, converting CO_2 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

FIGURE 1 | Diverse products from thermochemical CO_2 conversion and methanol.

successfully implemented by heterogeneous catalytic processes using cheaply available hydrogen, e.g., H_2 from natural gas and shale gas, or renewable sources of energy (Dang et al., 2018; Ouda et al., 2019). The catalytic reduction of CO_2 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 CO_2 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 CO_2 emission, with associated potential economic benefits.

Generally, conversion to methanol and other value-added products is an effective strategy for CO_2 valorization. Some literature reports in the past have reviewed the CO_2 reduction with hydrogen over heterogeneous catalysts focusing on the different aspect of the field, including the CO_2 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 CO_2 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 CO_2 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.
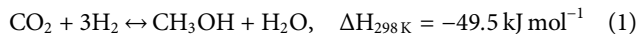
Although new catalysts have been developed in the last five years, the conventional Cu-based catalysts for CO_2 hydrogenation to methanol are still extensively investigated for further improvements. Considering the significant progress achieved in this area, we will discuss and focus on the recent advancements in the application of Cu/ZnO-based catalysts for the direct synthesis of methanol from CO_2, i.e., using CO_2 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 CO_2 feedstock to a desirable product, the performance of a catalyst will be determined by the thermodynamics of the reaction. Thus, the maximum conversion of CO_2 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 CO_2 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 CO_2, 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 H_2O 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.
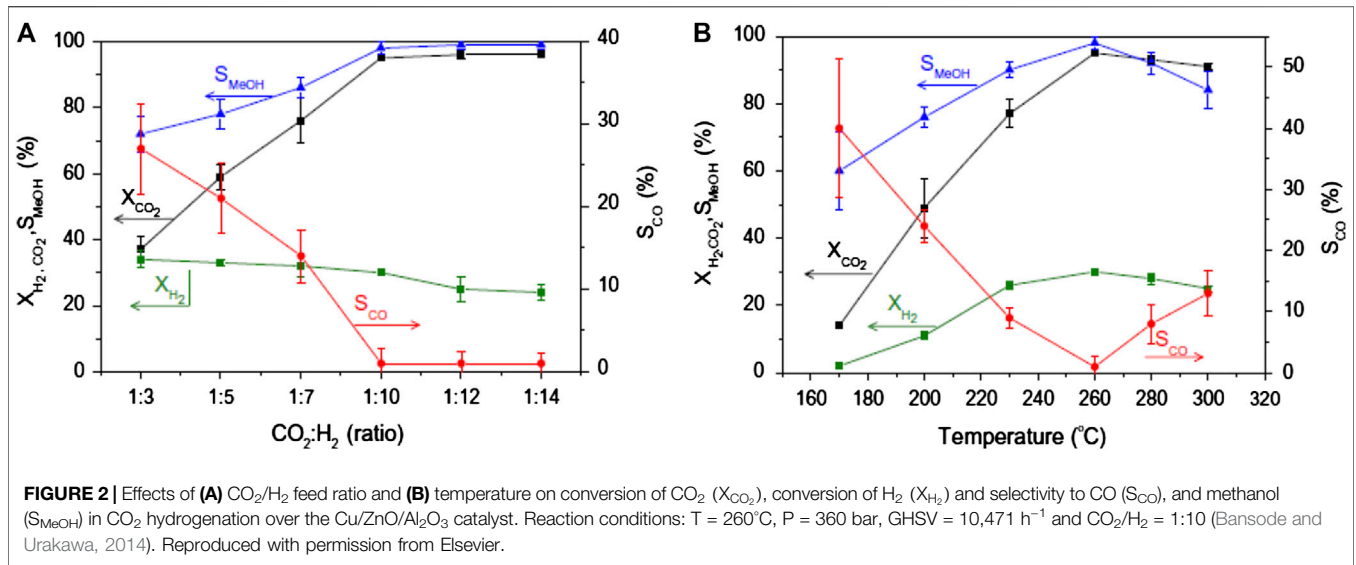
$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O, \quad \Delta H_{298\,K} = -49.5\,kJ\,mol^{-1} \quad (1)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O, \quad \Delta H_{298\,K} = 41.2\,kJ\,mol^{-1} \quad (2)$$

Breaking the thermodynamics/kinetics limitation by increasing one-pass CO_2 conversion (CO_2 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 $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst was applied to CO_2 hydrogenation to methanol (**Figure 2**). Under the specified reaction conditions, methanol selectivity, and productivity were remarkably boosted at high pressure by increasing H_2 partial pressure to enhance the reaction rate and thermodynamically favor high CO_2 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 CO_2 conversion at low temperatures. Moreover, lowering the concentration of CO_2 in the feed stream can increase the CO_2 conversion, and this can be achieved by using excess H_2 to shift the equilibrium to the products side. Thus, a high H_2/CO_2 ratio leads to high methanol and low CO selectivity. The selection of the appropriate H_2/CO_2 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 H_2 concentrations (Stangeland et al., 2018). Irrespective of the pressure, increasing the H_2/CO_2 ratio will lead to an increase in the CO_2 conversion to methanol owing to the sensitivity of H_2 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 CO_2 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 CO_2 from methanol combustion, and this can increase the conversion to almost 100% (Goeppert et al., 2014; Huš 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 CO_2 hydrogenation catalysts. Generally, two mechanistic pathways have been proposed from many studies for CO_2 hydrogenation to methanol over Cu-based catalysts, as shown in **Figure 3** (Kattel et al., 2016; Huš et al., 2017a; Huš et al., 2017b; Yang B. et al., 2017; Karelovic et al., 2019). The first pathway features the CO intermediate, which is produced from RWGS: $CO_2 + H_2 \rightarrow CO + H_2O$ reaction via carboxyl (*HOCO) species and is further hydrogenated to methanol; the other pathway is associated with the formate (*HCOO) intermediate formed by CO_2 hydrogenation which eventually produces methanol via the C–O bond cleavage and *HCO or *H_2CO intermediates (Liu and Liu, 2015). According to the density functional theory (DFT) calculations, CO_2 hydrogenation prefers the formate pathway on ZnCu(211) via *HCOOH, *H_2COOH, and *CH_3O intermediates over the RWGS + CO-hydro pathway for methanol synthesis (Kattel et al., 2017b). On the same ZnCu(211) surface, hydrogenation of CO_2 can proceed through the Eley–Rideal mechanism, as with pure Cu catalysts, as a result of the unfavorable CO_2 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 *CH_3OH. The direct dissociation of *CO_2 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 (Kunkes et al., 2015). For the industrial $Cu/ZnO/Al_2O_3$ 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 CO_2 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 CO_2 hydrogenation pathways (Grabow and Mavrikakis, 2011). Under conditions typical of the industrial methanol synthesis, CO_2 hydrogenation was responsible for about 65% of the methanol produced from the intermediates *HCOO, *HCOOH, *CH_3O_2, *CH_2O, and *CH_3O (Grabow and Mavrikakis, 2011; Kattel et al., 2016). The formation of *HCOO species from *CO_2 and *H on Cu(111) involved no intermediate carbonate species and the hydrogenation of *HCOO led to

FIGURE 2 | Effects of **(A)** CO_2/H_2 feed ratio and **(B)** temperature on conversion of CO_2 (X_{CO_2}), conversion of H_2 (X_{H_2}) and selectivity to CO (S_{CO}), and methanol (S_{MeOH}) in CO_2 hydrogenation over the Cu/ZnO/Al_2O_3 catalyst. Reaction conditions: T = 260°C, P = 360 bar, GHSV = 10,471 h^{-1} and CO_2/H_2 = 1:10 (Bansode and Urakawa, 2014). Reproduced with permission from Elsevier.

*HCOOH instead of *H_2CO_2 (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 CO_2 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 H_2COO. Formate, formaldehyde, and methoxy radicals are unlikely to be reaction intermediates for methanol synthesis. CO is also hydrogenated in significant amounts to *HCO, *CH_2O, *CH_3O, and *CH_3OH, and plays a promotional role in methanol synthesis, which include two possibilities: a) removal of *OH via *COOH to form CO_2 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 *CH_3O at low $CO_2/(CO + CO_2)$ ratios and by its hydrogenation in CO_2-rich feeds. Thus, the *CH_3O hydrogenation is a slow step during methanol synthesis from both the CO and CO_2 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 CO_2 Conversion to Methanol

The use of Cu-based catalysts for methanol synthesis via the CO_2 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.

FIGURE 3 | Pathways for the $CO_{2(g)}$ hydrogenation to $CH_3OH_{(g)}$ over the surface of Cu-based catalysts.
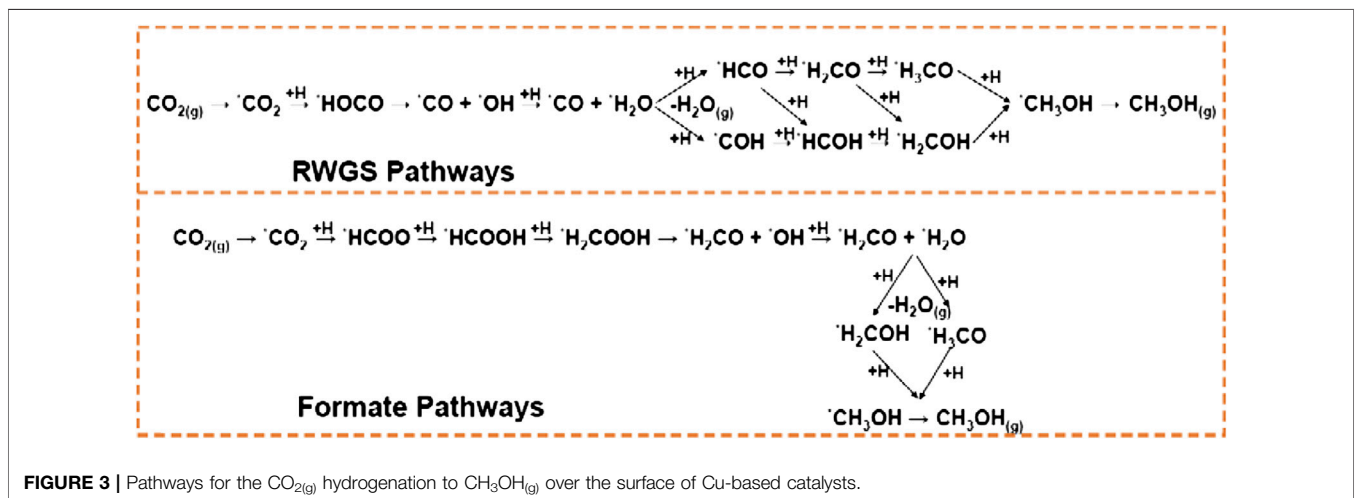
The Imperial Chemical Industries developed the Cu/ZnO catalyst in the late 1960s, which was operative at pressure and temperature of 50–100 bar and 200–300°C, respectively, and using syngas (CO + H_2) as feedstock (Din et al., 2019). Following the successful industrialization of the process and development 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 CO_2 as the sole feedstock was known. As then known, methanol catalysts produced CO_2 or H_2O 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 CO_2 formed CO and H_2O over methanol catalysts at atmospheric pressure. In the like manner, CO and H_2O react over the Cu-based catalysts to form CO_2 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 CO_2 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 Al_2O_3 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 ($CO/CO_2/H_2$) with $CO:CO_2$ 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 CO_2 and hydrogen under pressure may proceed along two paths. The developmental milestone of the Cu-based catalysts for the direct CO_2 to methanol conversion is presented in **Figure 4**.
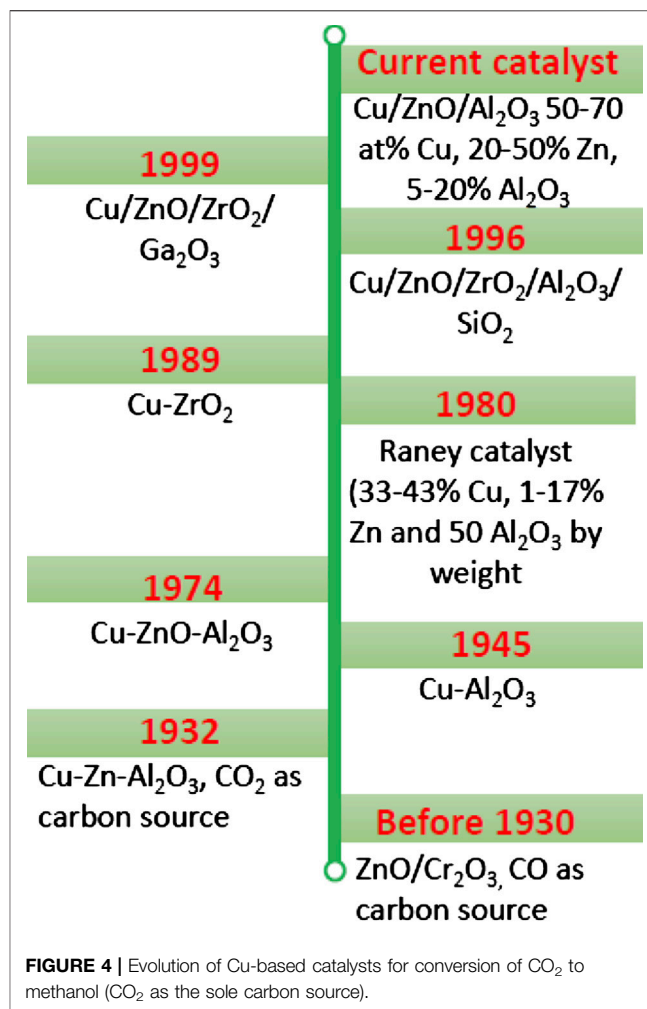
FIGURE 4 | Evolution of Cu-based catalysts for conversion of CO_2 to methanol (CO_2 as the sole carbon source).

Ren et al. provided the evidence than Cu species promoted by Zn were essential for the hydrogenation of CO_2 in the CO_2 promoted $CO–H_2$ gas system. They observed that CO_2 inhibited the CO hydrogenation over Pd/Al_2O_3, and $ZnO–Cr_2O_3$ catalysts, but promoted it over $Cu–ZnO/Al_2O_3$, at their respective optimum temperatures and under pressures that ensured low conversions (Ren et al., 1989).

Intensive research on the methanol synthesis from CO_2 and the active catalysts started growing in the 1980s. Currently, the ternary copper-based catalyst ($Cu/ZnO/Al_2O_3$) is still used for the industrial synthesis of methanol from CO_2 in the gas phase from a mixture of syngas and CO_2 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 CO_2, whereas CO acts as a scavenger of surface oxygen. Due to the availability of CO_2 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 CO_2 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/ Al_2O_3 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 Al_2O_3 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/ Al_2O_3 (Behrens et al., 2013). It should be noted that the commercial Cu/ZnO/ Al_2O_3 catalysts for methanol synthesis are not a "supported system" although researchers often mistake it as one because neither ZnO nor Al_2O_3 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/ Al_2O_3 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 ZnO_x species that act as co-catalysts in the methanol synthesis. The overlayer growth protects the Cu from particle size growth and reshaping. ZnO can also act as a spacer, avoiding the direct contact of the Cu particles with the Al_2O_3, enabling dispersion of the Cu particles and preventing them from sintering (Kasatkin et al., 2007). The Al_2O_3 component, although it can interact with the ZnO phase, does not generally change the evolution 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). Al_2O_3 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 Al^{3+} doping into ZnO, which specifically tailors the reduction properties of the latter. Also, Al_2O_3 surface acidity affects the byproducts' selectivity (Xiao K. et al., 2017). **Table 1** summaries the performance of the Cu/ZnO/ Al_2O_3 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.

Catalyst	T (°C)	P (MPa)	H₂/CO₂	WHSV (mL g꜀ₐₜ⁻¹ h⁻¹)	CO₂ conv. (%)	CH₃OH sel. (%)	References
JM-HiFUEL (50 wt% Cu/ZnO/Al₂O₃)	270	4.5	3:1	18,000	—	0.38[a]	Li et al. (2018)
Industrial CuO/ZnO/Al₂O₃	220	8.0	—	3,400 L h⁻¹		40	Lachowska and Skrzypek (2004)
Cu/ZnO/Al₂O₃	250	4.1	—	3,600 L h⁻¹	18.2	27	Jiang et al. (2015)
Cu/ZnO/Al₂O₃	270	5.0	3:1	4,000	10.7	81.8	Xiao S. et al. (2017)
Cu/ZnO/Al₂O₃	240	2.0	—	3,600 L h⁻¹	20.1	31.3	Hong et al. (2002)
Cu/ZnO/Al₂O₃	240	2.0	—	7,200 L h⁻¹	17.3	32.4	Hong et al. (2002)
Cu/ZnO/Al₂O₃	260	36.0	—	—	37	72	Bansode and Urakawa (2014)
Cu/ZnO/Al₂O₃	250	3.0	—	18,000	16.9	42.3	Lee et al. (2000)
Cu/ZnO/Al₂O₃	250	3.0	—	54,000	7.0	65.2	Lee et al. (2000)
Cu/ZnO/Al₂O₃	250	3.0	—	108,000	7.1	61.7	Lee et al. (2000)
Cu/ZnO/Al₂O₃	250	3.0	—	73,000	13.5	61.8	Lee et al. (2000)
Cu/ZnO/Al₂O₃	230	3.0	3:1	—	18.7	43.0	Li et al. (2014)
Cu/ZnO/Al₂O₃	170	5.0	2.8:1	—	4.3	45.1	Liu et al. (2007)
Cu/ZnO/Al₂O₃	270	4.5	2.2:1	—	12.3	42.3	Liao et al. (2011)
Cu/ZnO/Al₂O₃	270	4.5	2.2:1	—	10.9	72.7	Liao et al. (2011)

[a]Space-time yield (STY) (g_ml⁻¹ h⁻¹); weight hourly space velocity (WHSV).

FIGURE 5 | Properties, challenges and possible solutions.
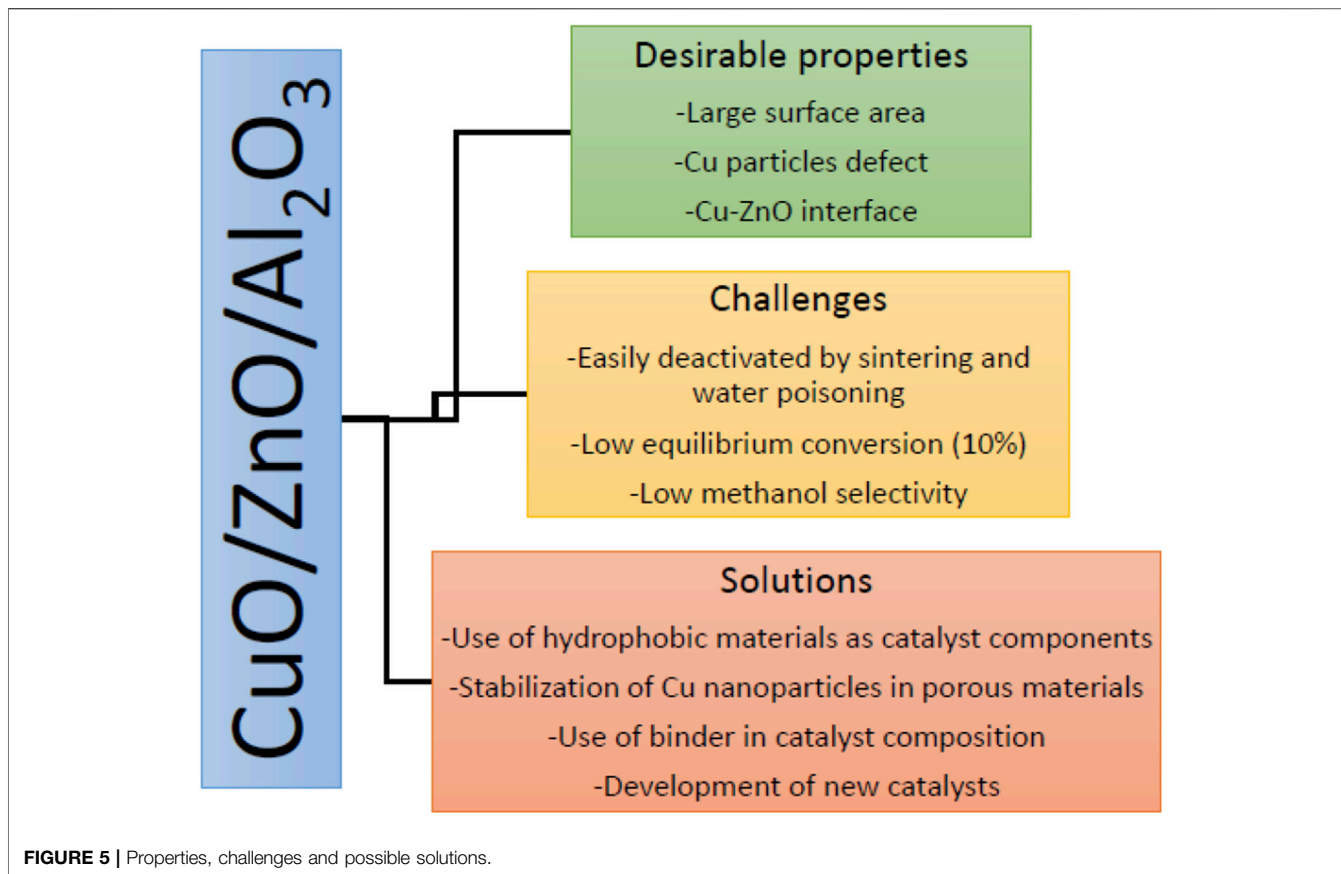
decreases under the same condition (Guo et al., 2011). Usually, the calcination temperatures of 300–400°C are optimum for forming a suitable catalyst. The detailed description of the synthesis of this catalyst can be found in the literature (Behrens and Schlögl, 2013).

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 CO_2 hydrogenation to methanol. Although Cu/ZnO/ Al₂O₃ exhibits promising performance (space-time yield up to 7,729 g_{MeOH} kg_{cat}^{-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
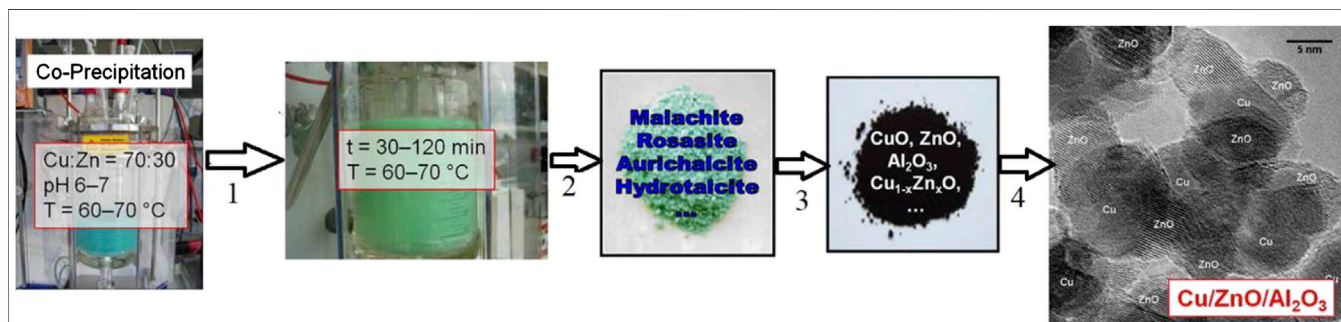
FIGURE 6 | Major steps in co-precipitation synthesis of Cu–ZnO–Al₂O₃ catalyst developed by ICI. Stages 1–4 refer to aging, washing/drying, calcination and reduction, respectively (Behrens and Schlögl, 2013). Reproduced with permission from John Wiley and Sons.

exact reaction pathway, including energetics and kinetics of every 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 (Pavlišič 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 modellings were found to conform well to the experiments over Cu–ZnO–Al$_2$O$_3$ or Cu–MgO–Al$_2$O$_3$. 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/Al$_2$O$_3$ 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 H$_2$COH hydrogenation pathway, resulting in higher CH$_3$OH yields. Over (ZrO$_2$)$_3$/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 (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 CH$_3$O instead of CH$_2$OH species. The rate-limiting step over Cu(211) was the reaction, CO$_2$ + H → HCOO, whereas that over ZnCu(211) was HCOOH + H → H$_2$COOH, 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/Al$_2$O$_3$ 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 (Cu^0) 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 (Natesakhawat 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 Cu^0 upon exposure to H$_2$ 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 (Natesakhawat 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 CO$_2$ hydrogenation to MeOH. They attributed the effect of incorporation of Ga^{3+} to the formation of the ZnGa$_2$O$_4$ spinel structure, which created electronic heterojunction with excess ZnO phase that eased the reduction of Zn^{2+} to Zn^0 to form CuZn alloy upon contact with Cu nanoparticle. They also correlated the concentration of Zn^0 in the CuZn alloy nanoparticle with the catalytic performance (CO$_2$ conversion and methanol selectivity) and found that the latter could be significantly improved by increasing the Zn^0 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).
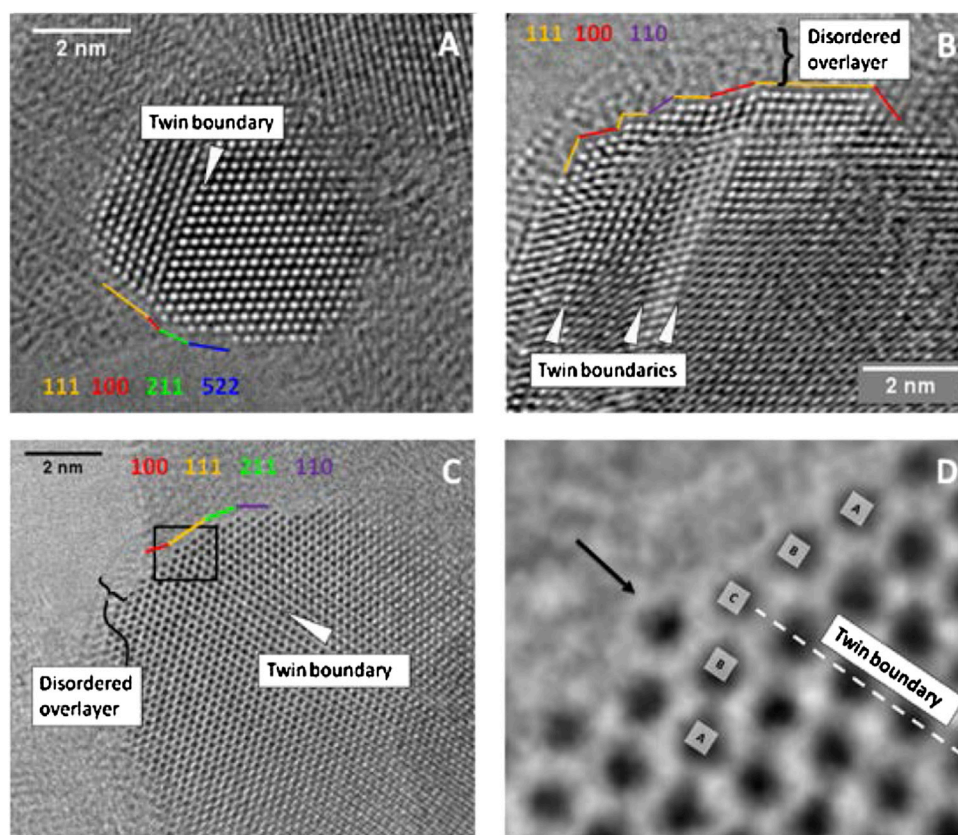
FIGURE 7 | (A-C) Aberration-corrected HRTEM images of Cu particles in the commercially active Cu/ZnO/Al$_2$O$_3$ catalyst. **(D)** is a zoom-in of the marked area in **(C)** (Behrens et al., 2012). Reproduced with permission from American Association for the Advancement of Science.

The active site of Cu catalysts can also exist in the form of other species. Recent studies have shown that stepped and ZnO$_x$-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 CO$_2$ 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/Al$_2$O$_3$ catalyst under reaction conditions that could create a metal oxide interface with catalytic activity (**Figure 7**). 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
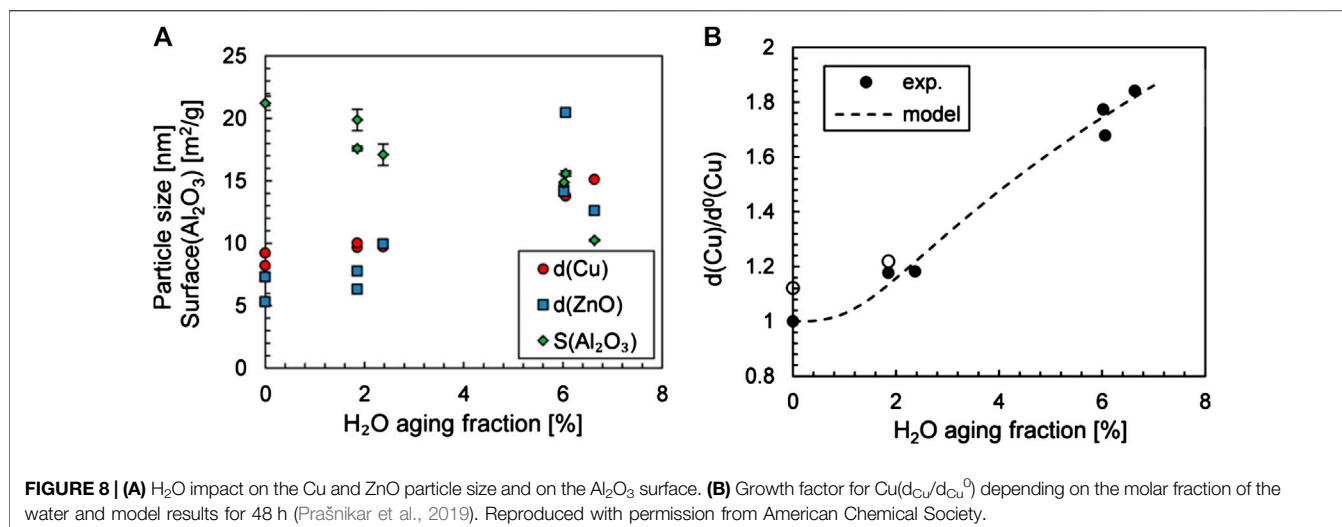
FIGURE 8 | (A) H_2O impact on the Cu and ZnO particle size and on the Al_2O_3 surface. **(B)** Growth factor for Cu(d_{Cu}/d_{Cu}^0) depending on the molar fraction of the water and model results for 48 h (Prašnikar et al., 2019). Reproduced with permission from American Chemical Society.

intermediates, especially water, and carbonated species (Roberts et al., 1993). It was found that the cause of catalyst deactivation was sintering of both Al_2O_3 and Cu with water due to the decreasing Al_2O_3 surface, and Cu particle size with increasing content of H_2O (Prašnikar 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 (Prašnikar et al., 2019). The structures of ZnO and Al_2O_3 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 CO_2 reduction to methanol deactivates the catalyst, causing speciation of Cu active phase and phase separation (Kung, 1992; Liang et al., 2019; Prašnikar et al., 2019). Sahibzada et al. observed a lower rate of methanol production in the presence of water in the H_2/CO_2 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/ZrO_2/Al_2O_3 catalyst. The inhibiting effect of water during CO_2 reduction to methanol was caused by the adsorption on and blocking of the active sites for CO_2 hydrogenation (Liu et al., 1985). Water reacts with CO_2, forming carbonate species that have been proven to block the active sites for CO_2 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–Al$_2$O$_3$ Catalyst
Use of Promoters

To further increase the activity and stability of the Cu–ZnO or Cu–ZnO–Al_2O_3 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, CO_2 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 CO_2 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 CH_3OH 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

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$_2$O$_3$. 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ and the adsorption of CO$_2$ and increases the methanol selectivity (Dybbert et al., 2019).

Although the CuO–ZnO–ZrO$_2$ ternary catalysts have exhibited comparative activity with the commercial catalyst, the introduction of promoters such as SiO$_2$, CeO$_2$, Ga$_2$O$_3$, 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. Słoczyński 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$_2$O$_3$ has been particularly useful in promoting methanol yield. Saito et al. (1996) developed a Cu/ZnO/ZrO$_2$/Al$_2$O$_3$/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$_2$O$_3$/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.

Catalyst	Conversion (%)		Selectivity (%)			MeOH yield (%)	CO:CO$_2$ conversion ratio
	CO	CO$_2$	CH$_4$	DME (10^{-3})	MeOH		
CZA	17.9	7.0	1.51	0.13	98.49	16.0	2.57
CZA–Mg	9.2	2.8	0.73	1.54	99.27	8.2	3.24
CZA–Zr	20.9	2.3	0.21	3.90	99.79	18.1	8.98
CZA–Ga	14.7	4.5	0.43	3.22	99.57	13.1	3.27

Reaction conditions: 240°C and 30 bar; space velocity of 6,000 L/kg$_{cat.}$ h.

TABLE 3 | Catalytic activities of recently studied Cu-catalysts for methanol synthesis from CO$_2$ hydrogenation in fixed bed reactors.

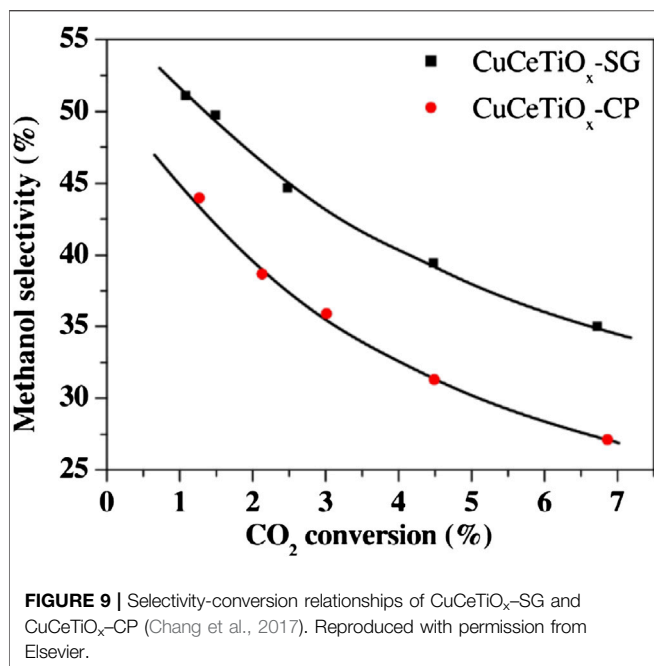| Catalyst	Preparation method	T (°C)	P (MPa)	H$_2$/CO$_2$	WHSV (ml g$_{cat}^{-1}$ h^{-1})	CO$_2$ conv. (%)	CH$_3$OH sel. (%)	STY g$_{ml}^{-1}$ h^{-1}	References
CuO-ZnO-ZrO$_2$	PR	503–543	5	3:1	4,600 h^{-1}	23	66.8	0.21	Dong et al. (2016)
Cu/ZnO/Al$_2$O$_3$/ZrO$_2$	CP	190	5.0	3:1	4,000 h^{-1}	10.7	81.8	0.087	Xiao S. et al. (2017)
CuO-ZnO-ZrO$_2$-WO$_3$	CP	240	3.0	3:1	2,400	5.6	64.0	—	Wang et al. (2018)
Cu-LaO$_x$/SBA-15	IP	240	3.0	3:1	12,000	6.0	81.2	0.244	Chen et al. (2019)
Cu-In-Zr-O	CP	250	25	—	18,000	1.48	79.7	0.087	Yao et al. (2019)
LDH30-Ga (33.5)	CP	297	4.5	—	18,000	—	49	0.60	Li et al. (2018)
Cu-ZnO-ZrO$_2$/LDH	US-CP	250	3	3:1	2,000 h^{-1}	4.9	78.3	0.365	Fang et al. (2019)
Cu/AlCeO	CP	260	3	3:1	14,400	~17	85	11.9[a]	Li et al. (2020)
ZnCuCe	RCP	240	3	3:1	8.8 N L g^{-1} h^{-1}	—	—	0.69[a]	Bonura et al. (2011)
CuCeTiO$_x$	CP	235	3	3:1	2,000	—	—	0.47[a]	Chang et al. (2017)
1Pd-10Cu/CeO$_2$	IP	273	3	3:1	—	17.8	23.7	0.9[a]	Choi et al. (2017)
10Cu/CeO$_2$	IP	273	3	3:1	—	6.4	42.8	—	Choi et al. (2017)
15 wt% CuCu/Al$_2$O$_3$	IP	200–280	4	3:1	6,000	16.4	59	—	Li et al. (2019)
15 wt% CuCu/AlCeO	IP	200–280	4	3:1	6,000	22.5	94	—	Li et al. (2019)
Cu/La$_2$O$_2$CO$_3$-R	DP	280	3.0	3:1	12,000 ml	5.6	92.5	110.2[b]	Chen et al. (2018)
Cu/ZrO$_2$	IWP	493–553	3	3:1	—	13	76.4	—	Witoon et al. (2016)
CuZn@UiO-bpy	DSM	523	4	—	—	17.4	85.6	—	An et al. (2017)

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 molmol$_{Cu}^{-1}$ h^{-1}.

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 Na$_2$CO$_3$ solution at a constant pH 6 or 7 and at temperatures ranging from 60–70°C (Li and Inui, 1996; Baltes et al., 2008). The initial precipitate, which is made of hydroxycarbonates (Mota et al., 2018; Ghosh et al., 2019), is aged for around 30 min to a few hours (Li and Inui, 1996; Kniep et al., 2004; Behrens et al., 2011) followed by washing, drying, and calcination at temperatures around 600–700 K to form CuO–ZnO species with some carbonate residues, responsible for the porous microstructure and surface area. The following further reduction of the obtained phases yields the active catalyst phase—usually metallic Cu nanoparticles, although other species of Cu, including Cu$^+$, ZnO decorated Cu, or partially reduced ZnO$_x$, have been reported (Schumann et al., 2016; Mota et al., 2018). The conditions during the precipitation and aging stages, as well as residual Na$^+$ ions in the system and elemental composition (Cu:Zn—65:25), are crucial for the properties of the final catalyst (Zhao et al., 2011; Behrens, 2016; Kondrat et al., 2017; Mota et al., 2018; Ghosh et al., 2019; Guil-López et al., 2019b).

To further improve the microstructural and porous properties of the methanol synthesis catalysts, other synthesis methods have also been studied (Guo et al., 2009; Natesakhawat et al., 2012; Dong et al., 2016; Dasireddy and Likozar, 2019). The precipitation–reduction method involves first the co-precipitation step, followed by a reduction in the second step by a reducing agent such as NaBH$_4$. Typically, a solution of metal nitrates and a solution of Na$_2$CO$_3$ 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 Cu^0 species contributed to the activity of CO$_2$ hydrogenation to methanol is accepted (Dong et al., 2016).

The sol–gel (SG) method is another way to prepare mixed oxides, especially for M–CeTiO$_x$ systems (Chen et al., 2014; Matějová et al., 2014; Bo et al., 2016). In a study utilizing CuCeTiO$_x$ 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 CuCeTiO$_x$ on their catalytic properties. By this method, a catalyst composite (CuCeTiO$_x$–SG) with the composition (30%CuO35%CeO$_2$35%TiO$_2$) was prepared and compared with the co-precipitation method derived catalyst (CuCeTiO$_x$–CP). The preparation methods show an important influence on catalytic performance (**Figure 9**). The CuCeTiOx–CP catalyst showed a higher CO$_2$ conversion than CuCeTiOx–SG. However, the CuCeTiOx–SG catalyst showed a higher selectivity to methanol than CuCeTiOx–CP at the same CO$_2$ 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

FIGURE 9 | Selectivity-conversion relationships of CuCeTiO$_x$–SG and CuCeTiO$_x$–CP (Chang et al., 2017). Reproduced with permission from Elsevier.

concluded that the preparation methods had noticeable effects on the dispersion of Cu particles and the catalyst structure. These effects were more pronounced for the catalysts prepared by homogeneous precipitation and co-precipitation (Sanches et al., 2012). The hydrogenation of CO_2 was conducted over a series of Cu/ZnO/Al$_2$O$_3$ 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 significant methanol selectivity in comparison with that prepared from the conventional co-precipitation route. This method also improved the dispersion of metallic Cu particles, which altered the intrinsic reactivity of CuO–ZnO. Since the methanol production rate was proportional to the ratio of Cu$^+$/Cu^0, 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).

OTHER Cu-CONTAINING CATALYSTS

Supported and Promoted Cu Catalysts

Until the present, Cu-based catalysts present the most desirable properties for the direct CO_2 hydrogenation to methanol at the industrial scale, thus proper to refer it as the methanol synthesis catalyst. However, the low conversion of CO_2 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

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; Díez-Ramírez 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/Al$_2$O$_3$) 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, ZrO$_2$, Al$_2$O$_3$, Ga$_2$O$_3$, SiO$_2$, and CeO$_2$ 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 CO_2 or a mixture of both have been in existence and applied for nearly six decades. Before the standardization of the ternary Cu/ZnO/Al$_2$O$_3$ 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 (Lei 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., 2007). The active Cu surface area of Cu/ZnO catalysts correlated with the degree of Zn incorporated into the precursor phase. The metallic copper surface areas in the reduced catalysts could be determined by the N$_2$O titration technique (Guo et al., 2009; Guo et al., 2011).

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$^{(2-\delta)+}$ which created active sites like Cu$^+$–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 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 H$_2$ was studied by Fierro et al. (1996). The temperature programmed reduction investigation of the CuO–ZnO catalyst synthesized by the co-precipitation method revealed ZnO promoted the reducibility of CuO. It is believed that

FIGURE 10 | Classification of supports for Cu-based methanol synthesis catalysts.
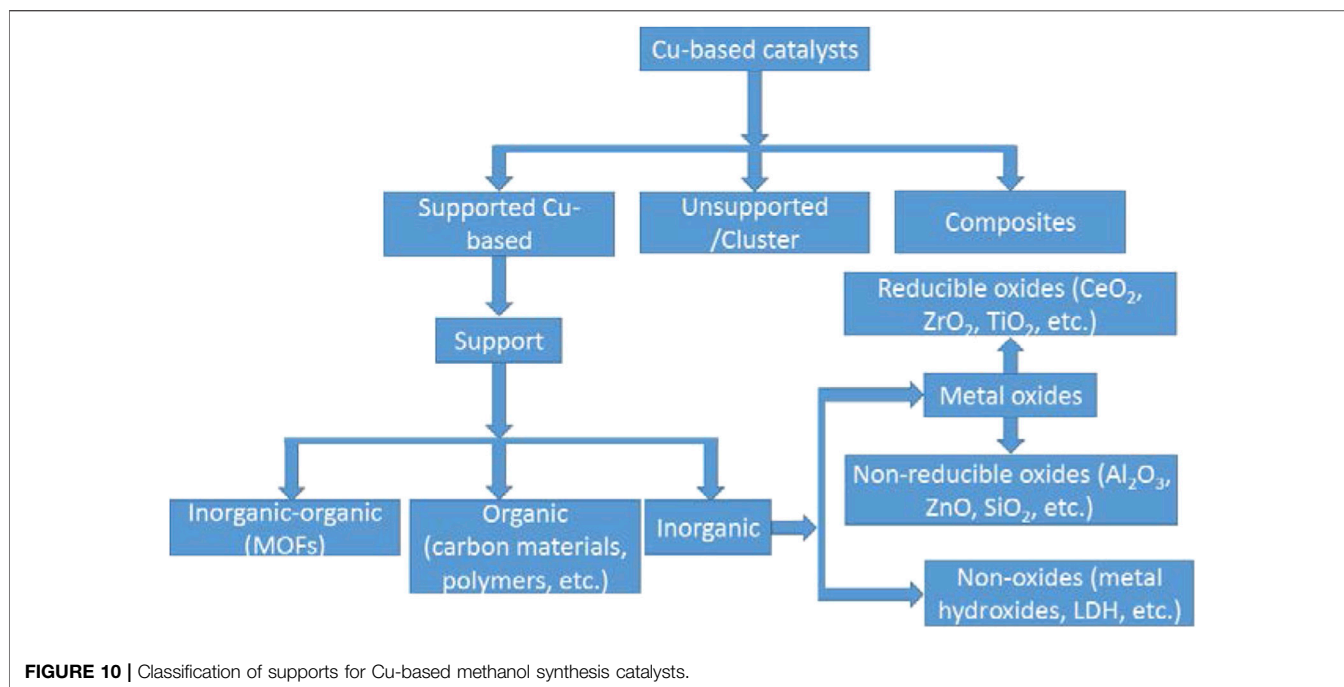
ZnO acts as a reservoir of atomic hydrogen and provides it for the CO_2 hydrogenation on the Cu surface, or as a binding site facilitating the adsorption of H_2 species and CO_2 via a spillover (Chen et al., 1999). The atomic hydrogen then transfers from the Cu onto the ZnO surface and gradually hydrogenates the adsorbed CO_2 to methanol (Sun et al., 2003; Dang et al., 2018).
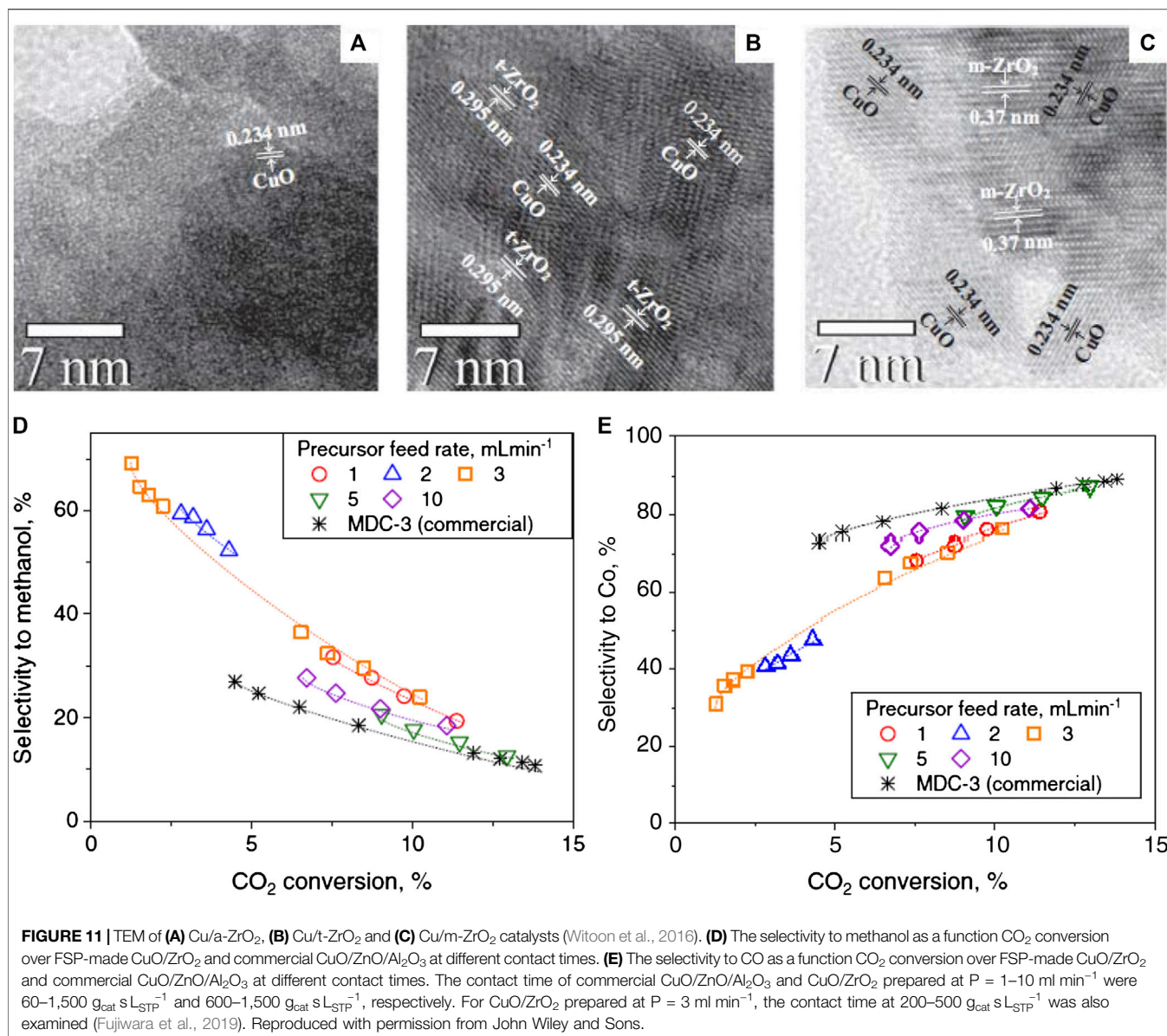
ZnO, as a support, is also suggested to be an active component in the methanol synthesis catalyst (Fujitani and Nakamura, 2000; Choi et al., 2001). In a physical mixture of Cu/SiO_2 and ZnO/SiO_2, it was found that Zn species could migrate to the Cu surface upon reduction with H_2, creating Cu–Zn active 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_2CO, and H_3CO 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 $ZnCl_2$, respectively, militating against deactivation of the catalyst. On the negative, ZnO is a basic oxide that can neutralize the acidity of Al_2O_3 in the commercial catalyst, preventing the transformation of CO_2 to methanol and promoting the agglomeration of active Cu particles (Twigg and Spencer, 2001).

Cu/ZrO$_2$ and Cu/ZnO/ZrO$_2$

ZrO_2 is a good support due to its hydrophobicity, and surface basicity. Besides, its high thermal stability is superior to Al_2O_3 under reducing and oxidizing atmospheres (Li and Chen, 2019). The catalytic activity of ZrO_2 as a support is superior to that of Al_2O_3, SiO_2, or ZnO (Li and Chen, 2019). The addition of ZrO_2 has been reported to improve the surface area of Cu species and can alter the Cu^+/Cu^0 ratio in the surface (Fisher et al., 1997; Słoczyński et al., 2003). CuO can be uniformly dispersed on the ZrO_2 surface, forming an interface favorable for the methanol synthesis reaction (Li and Chen, 2019).

ZrO_2 exists in different crystal structural phases (polymorphs)–amorphous (a)-ZrO_2 and tetragonal (t)-ZrO_2 and monoclinic (m)-ZrO_2 (**Figures 11A–C**). The a-ZrO_2 and t-ZrO_2 transform to m-ZrO_2 at high temperatures. The calcination of $Zr(OH)_4$ at temperatures greater than 400°C transforms it mainly to m-ZrO_2, so Cu species are easily incorporated into a-ZrO_2 (Tada et al., 2018). The effects of ZrO_2 polymorphs, including -a, -t and -m phases on the structure of Cu, Cu–ZrO_2 interaction and adsorption–desorption of H_2 and CO_2 were systematically investigated, and the catalytic performance of the catalysts, Cu/a-ZrO_2, Cu/t-ZrO_2, and Cu/m-ZrO_2 catalysts explored (Witoon et al., 2016). By a variety of analytical techniques, the Cu surface area followed the trend: Cu/a-ZrO_2 > Cu/t-ZrO_2 > Cu/m-ZrO_2. The increase in the yield of methanol is correlated with the increase in Cu surface area, thus the Cu/a-ZrO_2 exhibited the highest methanol yield. However, the methanol turn over frequency ($TOF_{Methanol}$) of Cu/t-ZrO_2 was higher than those of Cu/a-ZrO_2 and Cu/m-ZrO_2. In general, the high $TOF_{Methanol}$ is due to a strong Cu–ZrO_2 interaction and a high

FIGURE 11 | TEM of (A) Cu/a-ZrO_2, (B) Cu/t-ZrO_2 and (C) Cu/m-ZrO_2 catalysts (Witoon et al., 2016). (D) The selectivity to methanol as a function CO_2 conversion over FSP-made CuO/ZrO_2 and commercial $CuO/ZnO/Al_2O_3$ at different contact times. (E) The selectivity to CO as a function CO_2 conversion over FSP-made CuO/ZrO_2 and commercial $CuO/ZnO/Al_2O_3$ at different contact times. The contact time of commercial $CuO/ZnO/Al_2O_3$ and CuO/ZrO_2 prepared at P = 1–10 ml min^{-1} were 60–1,500 g_{cat} s L_{STP}^{-1} and 600–1,500 g_{cat} s L_{STP}^{-1}, respectively. For CuO/ZrO_2 prepared at P = 3 ml min^{-1}, the contact time at 200–500 g_{cat} s L_{STP}^{-1} was also examined (Fujiwara et al., 2019). Reproduced with permission from John Wiley and Sons.

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 $CuO/ZnO/Al_2O_3$ (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_2O_3 and exhibits high performance in methanol synthesis from CO_2 hydrogenation. Compared with Al_2O_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_2O_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 ZrO$_2$ 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/ZrO$_2$ catalyst arises from the structural and surface modifications of the Cu/ZnO by ZrO$_2$, it is important also to note that the crystallinity of ZrO$_2$ strongly affects the Cu–ZrO$_2$ interaction (Baiker et al., 1993). Thus, the co-presence of amorphous ZrO$_2$ and crystalline Cu/ZnO enhances the synergistic effect of Cu/ZnO/ZrO$_2$, facilitating the dissociative adsorption of CO$_2$ and the selective conversion of CO$_2$ to methanol (Słoczyński et al., 2004).

Both experiments and DFT calculations using Cu–ZnO–ZrO$_2$ have provided evidence on the separate functions of the Cu species and ZnO–ZrO$_2$ interface in the catalytic conversion of CO$_2$ to methanol by hydrogenation (Wang Y. et al., 2019). The catalytic evaluation at 220°C under 3.0 MPa showed very high activity (CO$_2$ conversion of 18.2% and selectivity to methanol of 80.2%). The binary oxides of ZnO–ZrO$_2$ showed a higher ability for CO$_2$ adsorption and the hydrogenation of carbonate species to formate and methoxy intermediates than the Cu–ZnO or Cu–ZrO$_2$ systems. Cu/ZrO$_2$ and Cu/ZnO catalysts synthesized by various methods show different catalytic performance. While Cu/ZrO$_2$ is more effective for the selective formation of methanol from CO$_2$, higher activity for CO$_2$ conversion is associated with Cu/ZnO (Li and Chen, 2019).

So far, efforts have been made to enhance the catalytic performance of CuO–ZnO–ZrO$_2$ catalysts further. Modification of CuO–ZnO–ZrO$_2$ 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–ZrO$_2$ 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 CO$_2$ and H$_2$. 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–ZrO$_2$ 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 a hydrogen spillover from the Cu surface to the carbon-containing species adsorbed on the metal oxide particles (Witoon et al., 2018). The mixed oxides of Cr, Mo, or W and CuO–ZnO–ZrO$_2$ 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–ZrO$_2$ catalyst upon addition of MoO$_3$ or WO$_3$ but slightly dropped when doped with Cr$_2$O$_3$. The improved methanol yield over these catalysts can be attributed to the differences in their Brunauer-Emmett-Teller surface areas and adsorption capacities for CO$_2$. 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–ZrO$_2$ catalyst synthesized by the co-precipitation
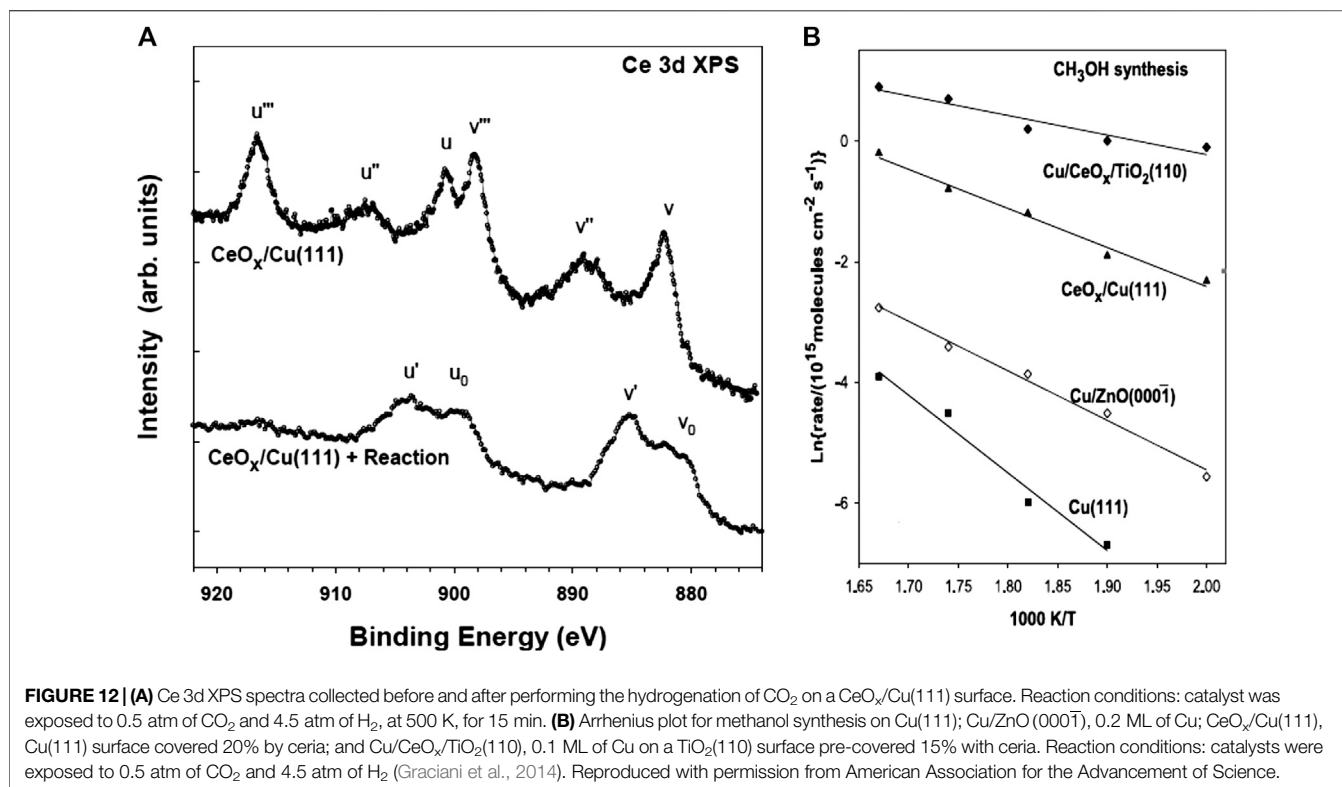
method. Characterization results revealed CuO–ZnO–ZrO$_2$ nanoparticles were uniformly dispersed and attached to the surface of the LDH, which improved the specific surface area and Cu dispersion compared with a reference catalyst without the support. The catalyst showed a high methanol selectivity of 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–ZrO$_2$–LDH catalyst slightly decreased the conversion. Very promising is that the activity of the can be recovered by reduction with H$_2$ (Fang et al., 2019).

Cu/CeO$_2$ and Cu/ZnO/CeO$_2$

CeO$_2$ has also been studied as a support or co-support for the methanol synthesis catalysts via the CO$_2$ 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 CO$_2$ 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–CeO$_2$ interface affords favorable reaction pathways for the conversion of CO$_2$ to methanol (Graciani et al., 2014). By theoretical methods, the CO$_2$ hydrogenation over a CeO$_x$/Cu(111) surface was demonstrated. The complementary surface analysis with XPS indicated Ce$_2$O$_3$/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(000$\bar{1}$) (**Figure 12B**). It was also found that the catalytic activity of CeO$_x$/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 CO$_2$ to methanol decreased from 25 kcal/mol on Cu(111) to 16 and 13 kcal/mol on ZnO/Cu(111) and CeO$_x$/Cu(111), respectively. The analysis of the surface of the CeO$_x$–Cu(111) interface by ambient pressure—XPS and ambient pressure infrared reflection absorption spectroscopy revealed the formation of formates and carboxylates (CO$_2^{\delta-}$) during the reaction. These results demonstrate CeO$_x$–Cu as an active catalyst riched in Ce^{3+} sites, which stabilized the CO$_2^{\delta-}$ species, an essential intermediate for the production of methanol (Graciani et al., 2014).

In ceria-containing Cu–ZnO oxide catalysts, the presence of CeO$_2$ promoted the surface activity of the Cu–ZnO system, although negatively influenced the catalyst texture and metal surface area in comparison to ZrO$_2$ (Bonura et al., 2011). As discussed earlier, CeO$_x$ 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 CeO$_x$ nanoparticles. Thus, the ternary CuZnCeO$_x$ exhibited higher performance than the binary CuZnO$_x$ catalyst (Shi et al., 2019); but had relatively very high selectivity toward CO (Hu et al., 2018). A CuZnCeO$_x$ catalyst prepared by a parallel flow co-precipitation technique was evaluated in the hydrogenation of CO$_2$ to methanol and CO.

FIGURE 12 | (A) Ce 3d XPS spectra collected before and after performing the hydrogenation of CO$_2$ on a CeO$_x$/Cu(111) surface. Reaction conditions: catalyst was exposed to 0.5 atm of CO$_2$ and 4.5 atm of H$_2$, at 500 K, for 15 min. **(B)** Arrhenius plot for methanol synthesis on Cu(111); Cu/ZnO (000$\bar{1}$), 0.2 ML of Cu; CeO$_x$/Cu(111), Cu(111) surface covered 20% by ceria; and Cu/CeO$_x$/TiO$_2$(110), 0.1 ML of Cu on a TiO$_2$(110) surface pre-covered 15% with ceria. Reaction conditions: catalysts were exposed to 0.5 atm of CO$_2$ and 4.5 atm of H$_2$ (Graciani et al., 2014). Reproduced with permission from American Association for the Advancement of Science.

The amount of CeO$_x$ in the catalyst controlled the selectivity of the products. Characterization results revealed a significant synergistic effect between Cu and metal oxides (ZnO and/or CeO$_x$) in the catalyst. Cu played a critical role in the activation of H$_2$, and CeO$_x$ strongly adsorbed CO$_2$, improved the dispersion of Cu nanoparticles, and promoted the spillover of atomic hydrogen (Shi et al., 2019). The results of these studies suggest that CeO$_2$ in Cu–ZnO catalysts can offer a viable way to produce methanol or CO from CO$_2$ 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 CuZnCeTiO$_x$ showed significantly enhanced activity in comparison with the CuCeTiO$_x$ 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/Al$_2$O$_3$ 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 CO$_2$ by improving the adsorption

properties (Słoczyński 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 CuAl$_2$O$_4$ and MgAl$_2$O$_4$ spinel phases in Cu/MgO/Al$_2$O$_3$ catalysts were observed (Dasireddy et al., 2018).

Gallium Oxide (Ga$_2$O$_3$)

Ga$_2$O$_3$ is reported to increase the activity per unit Cu surface area of methanol synthesis catalyst (Toyir et al., 2009). Ga^{3+} 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–ZnO$_x$ sites, which enhanced the efficiency of Cu–ZnGa catalyst system for CO$_2$ hydrogenation to methanol (An et al., 2007). One reason for this improvement is that the hydrotalcite derived catalysts could maintain their morphology in ultrafine 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 CO$_2$ hydrogenation to methanol. LDH30Ga (Cu: 33.5 wt%) yielded STY of 0.59 $g_{ml}^{-1} h^{-1}$, higher than the commercial JM-HiFUEL (50 wt% Cu/ZnO/Al$_2$O$_3$) with a STY of 0.38 $g_{ml}^{-1} h^{-1}$ 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 (TiO$_2$)

The incorporation of titanium nanotubes (TNTs) support into CuO–ZnO–CeO$_2$ catalysts can promote CuO reducibility, improve metallic Cu dispersion and increase the specific surface area. The CuO–ZnO–CeO$_2$/TNTs composite catalysts with different TNTs contents prepared by a deposition–precipitation method gave high CO$_2$ conversion and methanol selectivity. The selectivity was positively correlated with the number of basic sites, whereas the CO$_2$ conversion was a function of the specific surface area of Cu. The catalyst prepared with 10 wt% TNTs (CuO–ZnO–CeO$_2$/10 TNTs) possessed high metallic Cu surface area, high CO$_2$ adsorption capacity and a large number of basic sites, translating into excellent catalytic performance (methanol selectivity of 59.8%, CO$_2$ conversion of 23.3% and STY of 9.33 $mmol_{MeOH} h^{-1} g_{cat}^{-1}$ at 260°C, H$_2$/CO$_2$ 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, SiO$_2$ 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 CO$_2$, 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/SiO$_2$ catalyst exhibited a low selectivity to methanol (Sugawa et al., 1995). A 10 wt% Cu/SiO$_2$ exhibited higher methanol formation rate (2.1%) than 10 wt% Pd/SiO$_2$ (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). SiO$_2$ 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 SiO$_2$ 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 SiO$_2$ 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 SiO$_2$. Beyond this loading, CO$_2$ 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 SiO$_2$ facilitated the formation of both Cu$^+$ and Cu^0 species on the surface of the reduced Cu/ZnO/SiO$_2$ catalysts (Jiang et al., 2018). Other examples of the SiO$_2$ 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 H$_2$ dissociation. All these properties contribute to the increasing rate of CO$_2$ 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 CO$_2$ hydrogenation to methanol. The results found that 10 wt% CuZn/rGO catalyst exhibited a good activity for the CO$_2$ hydrogenation, achieving 26 % CO$_2$ conversion, methanol selectivity of 51%, and 424 ± 18 mg$_{methanol}$ 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 CO$_2$ hydrogenation to methanol. The results found that 10 wt% CuZn/rGO catalyst exhibited a good activity for the CO$_2$ hydrogenation, achieving 26% CO$_2$ conversion, methanol selectivity of 51%, and 424 ± 18 mg$_{methanol}$ 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$_{cat}$. h and H$_2$/CO$_2$ of 3, the catalyst presented a methanol yield of 10.4%, CO$_2$ 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 CO$_2$ 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 Klabunde, 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 CeO$_2$ support (Choi et al., 2017). According to the XPS results, the peaks for Cu 2p electrons in Pd–Cu/CeO$_2$ catalysts appeared at relatively lower binding energy than those in Cu/CeO$_2$ catalyst, meaning that Cu sites in Pd–Cu/CeO$_2$ 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 CO$_2$ by interaction with the carbon atom of CO$_2$ (Choi et al., 2017). A strong Pd–Cu bimetallic promoting effect on the formation of methanol from CO$_2$ 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/SiO$_2$ or Pd/SiO$_2$ for CO$_2$ 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 CH$_3$OH synthesis at 250°C and 4.1 MPa. The improvement in catalytic performance was realized at lower metal loadings, and Pd–Cu(2.4)/SiO$_2$ catalyst could yield approx. 1.6 times higher methanol than the commercial Cu/ZnO/Al$_2$O$_3$ 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 g$_{Cu}^{-1}$ h^{-1} at CO$_2$ conversion of 9.9% and methanol selectivity of 82.7% under reaction conditions of 3 MPa and 250°C at a high WHSV of 20,000 ml g$_{cat}^{-1}$ 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 CO$_2$ to renewable fuels and commodity chemicals represents an economic aspect of the CO$_2$ mitigation. Methanol, a primary liquid product derived from the hydrogenation of CO$_2$, 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 CO$_2$, which can be recycled back effectively, forming a carbon loop (Goeppert et al., 2014). Biomass is a form of recycled CO$_2$ that can be converted into DME, for example. Since CO$_2$ hydrogenation is carried out using hydrogen produced from renewable energy sources—electrical, wind, hydro or solar energy (Goeppert 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; Goeppert 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, including ethylene 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 CO$_2$ 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 CO$_2$ is also produced in the first step. Methanol cannot be directly generated electrochemically from CO$_2$ with high

selectivities or current densities (Malik et al., 2016; Yang D. et al., 2019).

Researches are continuously seeking new technologies to recycle CO_2 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 CO_2 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 H_2 and extract CO_2 from seawater, where it is in equilibrium with the atmosphere. H_2 and CO_2 then react to form methanol. H_2 is electrochemically generated and the extraction of CO_2 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 CO_2 capture because CO_2 in seawater (0.099 kg CO_2/m^3) is about 125 greater than the amount in the atmosphere (0.00079 kg/m^3) (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 CO_2 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 CO_2 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 H_2 from seawater? iii) Can electrodialysis be deployed for large-scale CO_2 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 CO_2 air capture with CO_2 and H_2O 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 CO_2 electrolyzers to convert atmospheric CO_2 into solar fuels using renewable electricity. This technology has the potential of producing 10,000 tons of methanol/day. The CO_2 and water electrolyzers can replace the steam-methane reforming step of current methanol synthesis by producing CO and H_2 from CO_2 and H_2O. Essentially, the carbon and hydrogen content of methane is replaced by CO_2, H_2O 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 CO_2 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 CO_2 reduction with hydrogen; however, low temperature is kinetically unfavorable for breaking the O–C–O bonds in CO_2 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 CO_2 conversion and a high methanol selectivity with the current industrial catalyst via the direct CO_2 hydrogenation. Consequently, developing Cu-based catalysts with high activity (high single-pass CO_2 conversion and high selectivity to methanol) at lower temperatures and pressures are crucial for the CO_2 to methanol hydrogenation.

With the Cu/ZnO/Al$_2$O$_3$ 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 SiO$_2$ (SBA-15) and porous ZrO$_2$; 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 multi-metallic 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 CO_2. Several materials acting both as support or co-catalysts are effective as the traditional alumina in the Cu/ZnO/Al$_2$O$_3$. Specifically, ZrO$_2$ is a good substitute for Al$_2$O$_3$ 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 ZrO$_2$ 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 CO$_2$ 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, CO$_2$ 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 CO$_2$ to renewable fuels and platform chemicals is an important aspect of CO$_2$ mitigation. Methanol, a major liquid product of CO$_2$ 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 CO$_2$ from the marine environment in combination with catalysis, and "air-to-barrel" process, which uses CO$_2$ electrolyzers to convert atmospheric CO$_2$ into solar fuels. It is not yet developed a practical design of solar-powered artificial marine-islands to recycle CO$_2$ into methanol and other synthetic liquid fuels. Several issues, including deployment at marine environment on large-scale, proper maintenance, efficient production of H$_2$ 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.

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