CO₂ hydrogenation to methanol: the structure–activity relationships of different catalyst systems

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Received: 31 January 2020 / Revised: 6 March 2020 / Accepted: 11 March 2020 / Published online: 20 March 2020
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Abstract CO₂ hydrogenation to methanol is a promising environmental-friendly route for combatting CO₂ emissions. Methanol can be used to produce a variety of chemicals and is also an alternative fuel. The CO₂-to-methanol process is mostly studied over multi-component catalysts in which both metal and oxide phases are present. The difficulty in elucidating the influence of the different phases on the catalytic performance has led to intense debate about the nature of the active site. Consequently, the main stumbling blocks in developing rational design strategies are the complexity of the multi-component catalytic systems and challenges in elucidating the active sites. In this paper, we reviewed the most promising catalyst systems for the industrial CO₂-to-methanol processes. Firstly, the copper-based catalysts are discussed. The focus is on the debate regarding the promotional effect of zinc, as well as other metal oxides typically employed to enhance the performance of copper-based catalysts. Other catalytic systems are then covered, which are mainly based on palladium and indium. Alloying and metal–metal oxide interaction also play a significant role in the hydrogenation of CO₂ to methanol over these catalysts. The purpose of this work is to give insight into these complex catalytic systems that can be utilized for advanced catalyst synthesis for the industrial CO₂-to-methanol process.

Keywords CO₂ hydrogenation · Methanol · Catalyst · Structure–activity

1 Introduction

Environmental concerns on greenhouse gas emissions have led to a large interest in CO₂ conversion and utilization from both academia and industry in the past decade. CO₂ utilization offers an alternative carbon-neutral pathway for the synthesis of valuable fuels and chemicals. CO₂ hydrogenation to methanol is an attractive process because methanol is one of the largest industrial chemicals and an essential building block for various chemical compounds (formaldehyde, olefins, acetic acid, etc.) (Behrens et al. 2012). Furthermore, methanol is widely used in fuel blends and can also be directly applied in methanol fuel cells. Besides reducing CO₂ emissions, using methanol as an alternative fuel can significantly lower the emissions of air pollutants in the transportation sector, such as hydrocarbons and NOₓ (Verhelst et al. 2019). The global methanol market is also expected to grow significantly over the next decade (Triton Market Research 2019). Furthermore, CO₂ hydrogenation to methanol has been suggested as a promising method for intermittent renewable energy storage (Kiss et al. 2016).

Today, methanol is almost exclusively synthesized from fossil sources over Cu/ZnO/Al₂O₃ catalysts by an industrial process that converts synthesis gas (H₂/CO/CO₂) into methanol at elevated pressures (50–100 bar) and temperatures (200–300 °C) (Behrens et al. 2012). The interest in converting captured CO₂ to methanol by hydrogenation (Eq. 1) has increased significantly in recent years. However, the industrial implementation of CO₂ hydrogenation to methanol has so far been limited. This is mainly due to the higher costs associated with capturing CO₂ and producing H₂ from renewable energy compared to synthesis gas. There are also more significant thermodynamic
restrictions on the conversion due to the competing reverse water–gas shift (RWGS) reaction (Eq. 2) (Álvarez et al. 2017; Stangeland et al. 2018). Furthermore, the different gaseous environment containing a larger amount of water during CO$_2$ hydrogenation to methanol can have negative effects on the activity and stability of the catalyst (Liang et al. 2019).

$$\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{H}_2\text{O} \quad \Delta H_{298K} = -49.5 \text{ kJ/mol}$$ \hfill (1)

$$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad \Delta H_{298K} = 41.2 \text{ kJ/mol}$$ \hfill (2)

The most efficient catalysts for CO$_2$ hydrogenation to methanol are multi-component catalytic systems. For example, the industrial Cu/ZnO/Al$_2$O$_3$ catalyst is often used as a reference for catalytic performance. It typically consists of intermixed Cu and ZnO nanoparticles after activation, where Al$_2$O$_3$ is primarily considered as a structural promoter (Behrens et al. 2012). A large Cu surface area is important to obtain high activity, but there are differences in intrinsic activity between Cu/ZnO-based catalysts with different preparation history. This difference in the active site “quality” implies that the reaction is structure-sensitive over Cu/ZnO-based systems. Similar observations have also been reported for the interplay of Cu with other metal oxides (Chen et al. 2019). Thus, the interaction between the catalyst’s components plays an important role in maximizing the catalytic performance of Cu-based systems. The exact nature of the interaction between Cu and metal oxides has been strongly debated and is currently not fully understood.

The key role of the metal–support interaction for CO$_2$ hydrogenation to methanol has also been demonstrated for other transition metal-based catalysts (i.e., Pd, Ni, Co). Without adequate promotion, these metals typically produce mainly CH$_4$ or CO during CO$_2$ hydrogenation. Therefore, alloying or strong metal–metal oxide interaction is needed to increase the methanol selectivity (Ojelade and Zaman 2019). More recently, In-based catalysts have gained much research interest due to the high methanol selectivity over a wide range of temperatures. Promoters can further enhance the methanol synthesis rate of In-based catalysts, which is significantly affected by the atomic-scale architecture (Frei et al. 2019).

The aim of this paper is to give insight into the interplay between species in the different multi-component catalytic systems that have been widely studied for CO$_2$ hydrogenation to methanol. Elucidating the nature of the active site is important for the development of more effective catalysts, which can aid in commercializing the process and enhance its economic viability.

### 2 Catalyst systems for CO$_2$ hydrogenation to methanol

#### 2.1 Cu-based catalysts

##### 2.1.1 Cu/ZnO-based catalysts

The industrial Cu/ZnO/Al$_2$O$_3$ catalyst is often referred to as the benchmark catalyst for CO$_2$ hydrogenation to methanol. The reported studies of Cu-based catalysts covered in this work are summarized in Table 1, where the different effects of oxides have been underlined. Initial studies led to the conclusion that Cu was the active component in methanol synthesis, while ZnO and Al$_2$O$_3$ functioned as spacers for the Cu particles and structural promoters. Single-crystal studies over different Cu facets indicate that the turnover frequencies (TOF) for methanol synthesis are lower than for the RWGS reaction for H$_2$/CO$_2$ mixtures. For instance, a TOF of $\sim 8 \times 10^3$ s$^{-1}$ was reported for methanol synthesis on Cu(110), while the TOF for CO production was $\sim 5$ s$^{-1}$ (H$_2$/CO$_2$ = 11/1, 5.1 bar, 530 K) (Yoshihara and Campbell 1996). Rasmussen et al. (1994a, 1994b) found that the methanol synthesis rate over Cu(100) was $\sim 30$ times faster than that on Cu(110). On this basis, the role of ZnO has been proposed to increase the exposure of more active Cu sites. Furthermore, several researchers have observed a linear correlation between activity and Cu surface area with catalysts supported on different metal oxides (Natesakhawat et al. 2012). Consequently, many studies report that ZnO does not have a direct influence on methanol synthesis. However, the Cu surface area is typically determined solely from N$_2$ chemisorption. Recent reports suggest that reducible metal oxides may distort the measurements and that N$_2$O probes both Cu and the partially reducible oxide (Chatterjee et al. 2019; Fichtl et al. 2014; Kuld et al. 2014).

Evidence for an increase in the intrinsic activity of Cu by metal oxide promoters can be observed from the reported TOF of different model structures and real catalysts in the literature. For instance, a TOF several magnitudes higher than single-crystal Cu has been reported for Cu/ZnO(0001) (Yang et al. 2010) and CeO$_2$/Cu(111) (Graciani et al. 2014) model surfaces. Kuld et al. (2016) found that the TOF for methanol increased with increasing Zn coverage of Cu over an industrial-type Cu/ZnO/Al$_2$O$_3$. This has also been observed in model structures by deposition of Zn on polycrystalline Cu (Nakamura et al. 1996), ZnO on Cu(111) (Senanayake et al. 2016), and ZnO nanoparticles on Cu(111)/ZnO(0001) (Kattel et al. 2017). Senanayake et al. (2016) observed that the intrinsic activity of Cu(111) showed a volcano-type behavior relative to the ZnO and CeO$_2$ coverage, as shown in Fig. 1a. Furthermore,
Table 1 Summary of the reported studies of Cu-based catalysts for CO₂ hydrogenation to methanol

| Catalyst                     | P, T, H₂/CO₂ (bar, °C) | GHSV (Ml g⁻¹ h⁻¹) | SA₃₉ (m² g⁻¹) | X₃₉ (C) | SMOH (%) | STYMeOH (mg g⁻¹ h⁻¹) | Ea, MeOH (kJ/mol) | TOFMeOH (s⁻¹ × 10⁻³) | Effect of promoterb | References                  |
|------------------------------|-------------------------|--------------------|--------------|---------|---------|----------------------|-------------------|----------------------|---------------------|------------------------|
| Cu(100)                      | 2, 270, 2               | –                  | –            | –       | –       | –                   | 69                | 0.27                 | –                   | Rasmussen et al. (1994a, b) |
| Cu(110)                      | 5.1, 257, 10            | –                  | –            | –       | –       | –                   | 67                | 8                    | –                   | Yoshihara et al. (1996)     |
| Cu/ZnO/Al₂O₃                 | 60, 250, 3              | –                  | –            | –       | –       | –                   | –                | 21                   | Zn: A, F, Al: S          | Behrens et al. (2012)        |
| Cu(111)                      | 4.9, 302, 9             | –                  | –            | –       | –       | –                   | 105               | 6.3                  | –                   | Yang et al. (2010)         |
| Cu/ZnO(0001)                 | 4.9, 302, 9             | –                  | –            | –       | –       | –                   | 67                | 93                   | ZnO: S                | Yang et al. (2010)         |
| CeO₃/Cu(111)                 | 4.9, 302, 9             | –                  | –            | –       | –       | –                   | 50                | 1300                 | CeO₂: F                | Graciani et al. (2014)      |
| Cu/ZnO/Al₂O₃                 | 30, 220, 3              | 10⁴                | 10           | 10      | 91      | 582                 | –                | 21                   | ZnO-ZrO₂: F             | Wang et al. (2019)         |
| Cu/ZnO₂ (MOF)                | 10, 200, 3              | –                  | –            | –       | –       | –                   | –                | 23                   | –                   | Rungtaweevoranit et al. (2016) |
| Cu₂ZnAl₂GaY                  | 20, 240, 3              | 30,000             | 94           | 5       | –       | –                   | –                | 21                   | Ga₂O₃, ZrO₂, Y₂O₃: D, R | Natesakhwat et al. (2012)   |
| Cu-LaO₃/SBA-15               | 30, 240, 3              | 12,000             | 76           | 7       | 81      | 190                 | –                | 19                   | LaO₃: D, F             | Chen et al. (2019)         |
| Cu/SBA-15                    | 30, 240, 3              | 12,000             | 38           | 3       | 26      | 20                  | –                | 1.3                  | –                   | Chen et al. (2019)         |
| Cu/ZnO/Al₂O₃                 | 30, 230, 3              | –                  | –            | –       | –       | –                   | 1250              | –                    | ZnO₃/Zn: I              | Lunkenbein et al. (2015)    |
| Cu@ZnO₃                      | 30, 250, 3              | 1800               | –            | 2       | 100     | 149                 | –                | –                    | ZnO₃: I                | Le Valant et al. (2015)     |
| Cu–ZnO₃                      | 30, 250, 3              | 1800               | –            | 11      | 7       | 52                  | –                | –                    | –                   | Le Valant et al. (2015)     |
| Cu/ZnO/Al₂O₃/Zr₂O₃/Y₂O₃      | 50, 230, 3              | 10,000             | 35           | 20      | 69      | 390                 | –                | –                    | Y₂O₃: D, I, S            | Gao et al. (2015)           |
| Cu/ZnO/Ga₂O₃                 | 45, 240, 2.8            | 18,000             | 85           | 27      | 50      | 837                 | –                | –                    | Ga₂O₃: A¹, S             | Li et al. (2016)            |
| Cu/ZnO/Al₂O₃                 | 30, 200, 3              | 9000⁴             | 54           | –       | –       | 181                 | –                | –                    | ZnO₃: I, R              | Liang et al. (2019)         |
| Cu/ZnO/Al₂O₃/Zr₂O₃ (MOF)     | 40, 250, 3              | 18,000⁴           | –            | 3       | 100     | 2590                | –                | –                    | ZnO₃, ZrO₂: I            | An et al. (2017)           |
| Cu/AlCeO                     | 40, 240, 3              | 6000               | 26           | 15      | 70      | 224                 | –                | –                    | CeO₃: B, I              | Li et al. (2019)            |
| Cu/ZrO₂                      | 80, 260, 3              | 3600⁴             | 3            | 15      | 86      | 98                  | –                | –                    | ZrO₂: F, I              | Samson et al. (2014)        |
| Cu/ZrO₂                      | 10, 230, 3              | 8400               | 8            | 4       | 59      | 58                  | –                | –                    | ZrO₂: D, F, I            | Tada et al. (2019)          |
| Cu/ZrO₂                      | 10, 230, 3              | 8400               | 82           | 4       | 45      | 35                  | –                | –                    | –                   | Tada et al. (2019)          |
| Cu/ZrO₂/Al₂O₃/Zr             | 50, 250, 3              | 12,000             | 25           | 25      | 48      | 490                 | –                | –                    | ZrO₂: B, D              | Gao et al. (2013)           |
| Cu/ZrO₂                      | 10, 200, 3              | 8800               | 9            | 2       | 83      | –                   | 57                | –                    | –                   | Arena et al. (2008)         |
| Cu–ZnO/ZrO₂                  | 10, 200, 3              | 8800               | 61           | 3       | 65      | –                   | 69                | –                    | ZnO₂: D, F, I, R         | Arena et al. (2008)         |
they found that the TOF of the inverse oxide/Cu configuration \([\text{CeO}_x/\text{Cu(111)}\) and \(\text{ZnO}_x/\text{Cu(111)}\)] was about 2 times higher than the corresponding Cu/oxide structure (\(\text{Cu/ZnO}\) and \(\text{Cu/CeO}_2\)). These structure effects are schematically illustrated in Fig. 1b. The reactivity of Cu particles deposited on ZnO single-crystal surfaces has also been reported to depend on the surface plane of ZnO \(\text{[i.e., (0001), (000\bar{1}), and (10\bar{1}0)]\) (Didziulis et al. 1989; Ludviksson et al. 1993). Moreover, the morphology of ZnO could also influence the \(\text{Cu–ZnO}\) interaction. Liao et al. (2011) detected a strong electronic interaction between Cu and platelike ZnO, which was proposed to facilitate \(\text{CO}_2\) activation and hydrogenation at the interface.

The increased activity due to the presence of ZnO in Cu/ZnO-based catalysts is often referred to as the Cu–ZnO synergy or strong metal–support interaction (SMSI). There has been intense debate regarding the nature of the active site and the role of Zn in promoting methanol synthesis (Behrens et al. 2012; Kattel et al. 2017; Kuld et al. 2016; Lunkenbein et al. 2015). Kasatkin et al. (2007) found that lattice strain and defect in Cu particles enhanced the catalytic activity of \(\text{Cu/ZnO/Al}_2\text{O}_3\). Theoretical studies have also indicated that defects can improve the energetics of the reaction pathway for methanol synthesis (Kopač et al. 2019; Wu and Yang 2017).

Recently, based on a combination of experimental measurements and theoretical calculations, the synergy between Cu and ZnO arising from SMSI was attributed to the formation of surface CuZn alloy (Kuld et al. 2016). Furthermore, the Zn\(^0\) atoms at the step edges of Cu nanoparticles (NPs) were proposed to be the active sites, and the Zn coverage was quantitatively correlated with the methanol synthesis activity. Studt et al. (2015) proposed that metallic Zn on the surface of Cu increased the binding energy of O-bound intermediates \(\text{(i.e., formate)}\), which facilitates the hydrogenation pathway from \(\text{CO}_2\). The lower activity in the absence of ZnO was suggested to result from formate poisoning of the Cu surface. These findings were supported by activity tests in methanol synthesis from various mixtures of \(\text{H}_2/\text{CO}_2/\text{CO}\) and DFT calculations. Martinez-Suárez et al. (2015) found that the formation of metallic Zn was thermodynamically favorable at low \(\text{O}_2\) partial pressures based on molecular dynamics modeling of a Cu eight-atom cluster on a ZnO substrate.

Several authors have concluded that metallic Zn generated during reduction is not stable under reaction conditions. TEM studies revealed encapsulation of Cu particles by a ZnO overlayer (Lunkenbein et al. 2015). It has also been observed that Zn\(^0\) in the \(\text{ZnCu}(111)\) catalyst underwent oxidation to ZnO during \(\text{CO}_2\) hydrogenation to methanol (Kattel et al. 2017). Le Valant et al. (2015) found that the Cu and CuZn particles were inactive, while...
particles composed of a CuZn core with a ZnO shell (CuZn@ZnO) showed low activity with 100% methanol selectivity. In contrast, the Cu@ZnO core–shell particles exhibited similar selectivity but an eightfold increase in activity compared to that of CuZn@ZnO. They concluded that the ZnO overlayer was directly involved in the active site for methanol production. Moreover, in situ neutron diffraction characterization of an industrial Cu/Zn/Al methanol synthesis catalyst operated at industrially relevant conditions indicated that the CuZn alloy is not present during syngas conversion to methanol (Kandemir et al. 2013). From the discussion so far, there are conflicting reports on whether Zn or ZnO is the component responsible for promoting the reaction. Furthermore, the promotion mechanism of Zn is also debated. It has been suggested to directly participate in the reaction through the Cu/ZnO interface or CuZn alloy, enhance the rate through electronic promotion, and increase the exposure of certain geometrical or structural active sites in Cu.

It has been demonstrated that the interaction between Cu and Zn can be tuned through the composition of the catalysts, preparation method, and addition of promoters. A higher Zn/(Cu + Zn) surface ratio can be obtained at higher Zn content, which can benefit the methanol selectivity (Martin et al. 2015). Brown et al. (2015) reported a one-pot synthesis approach, where colloidal particles consisting of zinc oxide and Cu(0) were produced from diethyl zinc and bis(carboxylato/phosphinato)copper(II) precursors. The optimum system comprised a 55:45 loading of ZnO/Cu and showed equivalent activity to a commercial Cu/ZnO/Al2O3/MgO catalyst. There have also been reports of more effective catalysts with higher Cu dispersion and Cu–ZnO interaction for catalysts derived from Cu/Zn/Al georgeite precursors (Kondrat et al. 2016; Smith et al. 2017), as well as higher intrinsic activity of Cu/Zn/Al produced from hydrotalcite (Kühl et al. 2014). Gao et al. (2015) explored the effect of Y loading (Y = 0, 1.5, 3.0, 5.8, and 14.5 mol%) of Cu/ZnO/Al2O3/3Y3O3 derived from hydrotalcite precursors. A volcano-shaped trend was observed for the methanol selectivity with a maximum at 3 mol% Y. This was attributed to improved Cu dispersion at moderate Y loading, resulting in enhanced Cu–ZnO interaction. Li et al. (2016) investigated the effect of Ga loading in Ga modified Cu/ZnO catalysts. Apart from the structural promotion provided by Ga, their results indicated that it also facilitated the deep reduction of ZnO to Zn, which formed CuZn alloy after reduction. The improvement in catalytic activity and methanol selectivity could be correlated with the increased Zn concentration. Gao et al. (2013) investigated the influence of different modifiers (Mn, La, Ce, Zr, and Y) on Cu/Zn/Al catalyst obtained via a hydrotalcite-like precursor. They found that the methanol selectivity increased in the series Cu/Zn/Al < Cu/Zn/Al/Mn < Cu/Zn/Al/La < Cu/Zn/Al/Ce < Cu/Zn/Al/Y < Cu/Zn/Al/Zr. This trend was related to the fraction of strong basic sites of the catalysts that facilitated the activation and hydrogenation of CO2, indicating that the basic sites of the metal oxides influenced the selectivity.

Recent investigations of the deactivation mechanisms of Cu/ZnO/Al2O3 catalysts during CO2 hydrogenation further illustrate the importance of metal–support interaction. Liang et al. (2019) studied a Cu/ZnO/Al2O3 catalyst and found that the main causes of deactivation were aggregation of ZnO and partial oxidation of the Cu phase. Prasnikar et al. (2019) found that separate Cu regions formed during CO2 hydrogenation and that the segregation of Cu/ZnO was promoted when water was added to the feed. Interestingly, Cu/ZnO segregation was not observed when the catalyst was applied for syngas conversion to methanol. Instead, migration of ZnO and partial coverage of Cu were evident during syngas experiments. Thus, the behavior of the catalyst is significantly affected by the gaseous environment, and different strategies might be needed to enhance Cu/ZnO-based catalysts for CO2 hydrogenation compared to syngas conversion.

There are works that indicate that the reaction pathway on non-promoted and promoted Cu surfaces is different (Studt et al. 2015). In complex real catalyst systems, there

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**Fig. 1 a** Rates for CO2 conversion to methanol on Cu(111) as a function of the fraction of metal surface covered by zinc oxide or ceria oxide. [Reproduced from Ref. Senanayake et al. (2016) with permission from the American Chemical Society, copyright 2016] and **b** illustration of the role of metal oxides on intrinsic methanol synthesis activity of Cu catalysts [Adapted from Ref. Senanayake et al. (2016) | Springer]
is a combination of different active sites, such as the coexistence of fully covered Cu nanoparticles with partially covered and practically uncovered ones in typical Cu/ZnO/Al2O3 catalysts. Consequently, methanol is likely produced from a combination of different reaction pathways (Martinez-Suarez et al. 2015). Therefore, understanding and tuning the interaction between Cu and the promoter(s) is a crucial component of optimizing the activity of Cu-based catalysts. A second observation is that enhancing the stability of the “optimum” catalytic structure(s) is another key challenge in Cu-based catalyst design.

2.1.2 Effect of other metal oxide components on Cu-based catalysts

The interaction of Cu with other metal oxides has also been reported, which indicate that the nonstructural promoting role of the metal oxide significantly affects the catalytic behavior. Studt et al. (2015) observed that high methanol formation rates could be obtained over Cu/MgO in CO hydrogenation, whereas the catalyst was significantly less active when CO₂-rich syngas or H₂/CO₂ feedstock was used. This was attributed to poisoning of the Cu surface by CO₂ through the generation of spectator formate species. Chen et al. (2019) found that the addition of La to Cu/SBA-15 increased the methanol selectivity from 26 to 81%. The increase in methanol selectivity was attributed to Cu-LaOₓ interfacial sites or the pure metal surface modified by the adjacent oxides could be responsible for methanol production.

Samson et al. (2014) showed that Cu supported on t-ZrO₂ crystallite phase had a higher activity than Cu supported on m-ZrO₂. The presence of oxygen vacancies stabilized both the thermodynamically unstable t-ZrO₂ phase and Cu⁺ cations, which were present in the vicinity of oxygen vacancies. The catalytic activity toward methanol increased with increasing t-ZrO₂ content. Hence, the complexes built from Cu cations and oxygen vacancies preferentially on t-ZrO₂ were proposed as the active site for the methanol synthesis reaction. Tada et al. (2019) demonstrated the importance of the interfacial area and surface basicity on the catalytic activity for Cu/ZrO₂ catalysts. Utilizing a Cu nitrate precursor resulted in residual nitrogen that bound to basic sites of the ZrO₂ support, thereby significantly reducing the methanol synthesis reaction. Tada et al. (2019) demonstrated the importance of the interfacial area and surface basicity on the catalytic activity for Cu/ZrO₂ catalysts. Utilizing a Cu nitrate precursor resulted in residual nitrogen that bound to basic sites of the ZrO₂ support, which reduced the activity of the catalysts. In addition, high calcination temperature transformed the amorphous ZrO₂ phase to t-ZrO₂, thereby significantly reducing the number of basic sites and, consequently, the activity of the catalyst. Interestingly, an inverse relationship between the Cu surface area determined by N₂O chemisorption and the activity was observed. Calcination at 500 °C resulted in a tenfold increase in Cu surface area compared to the catalyst calcined at 350 °C, but the catalytic activity and the methanol selectivity were significantly lower.
Both direct and indirect promotion of Cu by ZrO$_2$ has been suggested based on theoretical and experimental investigations. Polierer et al. (2019) studied the Cu/ZrO$_2$ interface by density functional theory (DFT) calculations. Their results indicate that the intermediates bind too strongly on the ZrO$_2$ surface as well as on the Cu/ZrO$_2$ interface for further hydrogenation to methanol. However, electronic promotion of Cu atoms in the vicinity of the Cu/ZrO$_2$ interface was identified. This increased the binding energy of the key intermediates on the Cu surface and promoted the formation of methanol.

A dual-site reaction path has also been proposed in which Cu activates hydrogen, whereas CO$_2$ is adsorbed and hydrogenated at the metal/metal oxide interface or neighboring defective sites in the metal oxide. Arena et al. (2008) observed that the specific activity relative to the number of interfacial sites remained constant for Cu–ZnO–ZrO$_2$ catalysts with different Cu dispersion. The number of interfacial sites was quantified by two independent methods, namely CO and N$_2$O chemisorption, as well as the oxide-to-metal surface area ratio. Furthermore, they found that the activation energy was lower for Cu/ZrO$_2$ (57 kJ/mol) compared to Cu–ZnO–ZrO$_2$ catalysts (69 kJ/mol). This was attributed to a higher reactivity of CO$_2$ adsorbed on the zirconia surface, where the formate intermediate was further hydrogenated to methanol. Wang et al. (2019) examined the interaction between Cu, ZnO, and ZrO$_2$ by dispersing ZnO and ZrO$_2$ on a Cu framework. The Cu–ZnO–ZrO$_2$ ternary system was more efficient for CO$_2$ adsorption and subsequent hydrogenation than Cu–ZnO and Cu–ZrO$_2$. The Cu–ZnO–ZrO$_2$ catalyst showed excellent activity of 18% conversion and 80% methanol selectivity at relatively mild conditions (220 °C, 30 bar). Based on in situ FTIR combined with DFT calculations, the ZnO–ZrO$_2$ interface was proposed as the active site for CO$_2$ adsorption and conversion, while metallic Cu was necessary for generating hydrogen.

The ability of ZnO–ZrO$_2$ to produce methanol from CO$_2$ has also been confirmed experimentally. Wang et al. (2017) prepared a ZnO–ZrO$_2$ solid solution catalyst, which showed methanol selectivity of 86–91% at CO$_2$ conversion of more than 10% (reaction conditions: 50 bar, 24,000 mLg$_{\text{cat}}^{-1}$ h$^{-1}$, H$_2$/CO$_2$ = 3:1 to 4:1, 320 to 315 °C, respectively). Based on the observed surface species and DFT calculations, the high methanol selectivity was attributed to a synergetic effect in H$_2$ activation between the Zn and Zr sites.

### 2.1.3 Effect of metal alloying on Cu-based catalysts

There are also studies that investigate the effect of metal-doped Cu and Cu alloys. Martin et al. (2015) showed that the addition of small amounts of Au to Cu/ZnO/Al$_2$O$_3$ significantly enhanced the methanol formation rate. This was attributed to an increase in Cu$^0$ surface species, and it was suggested that Au had a stabilizing effect on Cu$^0$. Choi et al. (2017) found that suitable amounts of Pd added to Cu/ CeO$_2$ generated more reduced Cu sites and also created oxygen vacancies in CeO$_2$, which enhanced the activity of the catalyst. Jiang et al. (2015) linked the production of methanol to PdCu alloy particles for PdCu supported on different SiO$_2$ supports. Interestingly, the best performance was obtained with well-mixed PdCu and PdCu$_3$ alloy phases, but further in-depth study is needed to elucidate the synergy between these phases. Whereas a higher amount of Cu$^0$ enhanced the performance of the catalyst when ZnO or CeO$_2$ was present, the formation of separate Cu$^0$ particles lowered the methanol selectivity for Pd–Cu/SiO$_2$.

Yang et al. (2011) calculated that the methanol yield followed the order of Au/Cu(111) < Cu(111) < Pd/Cu(111) < Rh/Cu(111) < Pt/Cu(111) < Ni/Cu(111) based on DFT computations and kinetic Monte Carlo (kMC) simulations. Zhao et al. (2017) demonstrated that Ni–Cu/Al$_2$O$_3$ prepared by ALD was significantly more active and selective in CO$_2$ hydrogenation to methanol than the catalyst prepared by impregnation. This was attributed to improved dispersion and stronger interaction between Ni and Cu. Tan et al. (2018) found that both the CuNi alloy and CeO$_2$ support enhanced the conversion to methanol. The role of oxygen vacancies in CeO$_2$ was to enhance the adsorption of CO$_2$, while Ni promoted the adsorption and hydrogenation of CO to methanol.

### 2.2 Pd-based catalysts

Pd-based catalysts have also been extensively studied for CO$_2$ hydrogenation to methanol, and the performance of different catalysts is summarized in Table 2. They typically exhibit comparable activity and methanol selectivity to Cu-based catalysts during methanol synthesis from CO$_2$.

The interaction between Pd and the promoter is also crucial for Pd-based catalysts to obtain high methanol selectivity. Bahrui et al. (2016) investigated the structure–activity relationship over Pd/ZnO catalysts prepared by different methods. They found that the preparation method considerably affected the selectivity of the catalyst. Pd/ZnO prepared by impregnation produced almost exclusively CO, whereas the catalyst prepared by sol immobilization had an initial methanol selectivity of 70%. This was attributed to the presence of a mixture of metallic Pd and PdZn alloy clusters, where the former was the active site for CO formation and the latter produced methanol. The methanol selectivity was found to decrease with increasing PdZn alloy particle size. In a later work, Bahrui et al. (2017) found that PdZn supported on TiO$_2$ was much more active than PdZn supported on Al$_2$O$_3$, which was...
attributed to higher PdZn dispersion on the TiO₂ support. A Pd/Zn ratio of 1:5 yielded the highest methanol formation rate, while a ratio of 1:10 maximized the methanol selectivity. Liao et al. (2017) prepared PdZn core–shell catalysts with varying degree of Zn decoration of Pd. It was found that the methanol selectivity increased with an increase in neighboring Zn around Pd atoms. Furthermore, the activation energy for the RWGS reaction was increased to 98 kJ/mol. Compared to a conventional Pd/ZnO (71 kJ/mol) and a commercial Cu catalyst (69 kJ/mol), the heavy decoration of Pd with Zn strongly inhibited the RWGS reaction. Xu et al. (2016) also observed that increasing the PdZn alloy content was beneficial to the methanol selectivity. However, Pd species modified by ZnOₓ islands were also detected over Pd/ZnO/Al₂O₃ catalysts at low Pd loadings. The methanol selectivity of high alloy content PdZn and ZnOₓ containing samples was similar under comparable CO₂ conversion. Therefore, it was proposed that ZnOₓ islands could also play a role in methanol synthesis from CO₂. Malik et al. (2018) investigated the effect of Ca-doping on PdZn/CeO₂ catalysts. It was found that the methanol synthesis activity was increased by Ca-doping, which was attributed to an increase in basicity that enhanced CO₂ activation. Fiodaliso et al. (2015) reported that the GaPd₂/SiO₂ catalyst exhibited higher intrinsic activity than that of the conventional Cu/ZnO/Al₂O₃ at atmospheric pressure. The high intrinsic activity was attributed to the GaPd₂ intermetallic phase generated during activation. Furthermore, the GaPd₂ phase remained stable during CO₂ hydrogenation. García-Trenco et al. (2017) utilized a pyrolysis–reduction method to prepare colloidal Pd/Ga catalysts, which led to the formation of GaPd₂ alloy NPs with an average size of 5–6 nm. The colloidal catalyst was tested in liquid-phase methanol synthesis and showed a fourfold increase in activity compared to Cu/ZnO/Al₂O₃ and Pd/ZnO, comparable methanol selectivity, and high stability at 210 °C and 50 bar. Qu et al. (2014) prepared Pd supported on plate and rod Ga₂O₃ nanocrystals. It was observed that Pd supported on plate nanocrystals resulted in higher Pd dispersion and stronger metal–support interaction compared to that of rod nanocrystals supported Pd. This was attributed to the highly unstable surface of the low indexed (002) polar Ga₂O₃ surface present on plate nanocrystals. It contained more oxygen defects and mobile electrons in the conduction band, which was favorable for the formation of Pd/Gaₓ active sites for methanol production.

### 2.3 Indium-based catalysts

Over the last decade, indium-based catalysts have gained significant interest for CO₂ hydrogenation to methanol. The indium-based catalysts typically show low activity for the reverse water–gas shift reaction, which results in high methanol selectivity over a wide temperature range (Table 3). Ye et al. (2013) predicted that methanol formation is favorable on the defective In₂O₃(110) surface containing oxygen vacancies by DFT calculations. Martin et al. (2016) found that In₂O₃ prepared by precipitation had 100% selectivity toward methanol up to 300 °C (50 bar, H₂/CO₂ = 4:1). They also examined In₂O₃ impregnated on various supports and found that ZrO₂ supported In₂O₃ was significantly more active than the others. This was ascribed to the formation of inactive metallic In in samples with

| Table 2 | Summary of the reported studies of Pd-based catalysts for CO₂ hydrogenation to methanol |
|---------|-----------------------------------|
| Catalyst | P, T, H₂/CO₂ (bar, °C) | XₓCO₂ (%) | SMEOH (%) | GHSV (mL g⁻¹ h⁻¹) | STYMeOH (mg g⁻¹ h⁻¹) | TOFMeOH (s⁻¹ × 10⁻²) | References |
| Pd/ZnO | 20, 250, 3 | 11 | 60 | 3600 | 78 | – | Bahruij et al. (2016) |
| PdZn/TiO₂ | 20, 250, 3 | 10 | 40 | 3600 | 59 | – | Bahruij et al. (2017) |
| Pd/ZnO-CdSe | 20, 250, 3 | – | 70 | 18,000 | – | 19 | Liao et al. (2017) |
| Pd/ZnO/Al₂O₃ | 30, 220, 3 | 8 | 50 | 3600 | 43 | 1.37 | Xu et al. (2016) |
| Ca-PdZn/Al₂O₃ | 30, 250, 3 | 11 | 92 | 2400 | 80 | – | Malik et al. (2018) |
| GaPd₂/SiO₂ | 1, 210, 3 | – | 39 | 88 | – | 0.37ᵇ | Fiodaliso et al. (2015) |
| Pd₂Ga(CSTR)ᵇ | 50, 210, 3 | – | 46 | 67,000 | 276 | 0.06ᵇ | García-Trenco et al. (2017) |
| Pd/Ga₂O₃ | 50, 210, 3 | 17 | 52 | 6000 | 69 | – | Qu et al. (2014) |

ᵃContinuous stirred tank reactor (CSTR) ᵇTOF given in mmol m⁻² s⁻¹
other carriers than ZrO2. Only a moderate decrease in the reaction rate was observed over the In2O3/ZrO2 catalyst with H2O co-feeding (H2O/CO2/H2 = 0.3:1:4) at 300 °C. Furthermore, it remained stable over 1000 h on stream, which makes it a very promising catalyst for CO2 hydrogenation to methanol. Zhang et al. (2018) studied ZrO2-doped In2O3 surfaces through DFT calculations. They found that ZrO2 can prohibit the excessive formation of oxygen vacancies on the In2O3 surface by enhancing the In–O bond near Zr atoms, which is consistent with the effect of different supports on In2O3 reported by Martin et al. (2016). In addition, the ZrO2 species was able to stabilize and activate the intermediates involved in methanol synthesis. Chou and Lobo (2019) found that Y and La promotion of In2O3/ZrO2 can further improve the methanol selectivity by increasing the amount of oxygen defects and CO2 adsorption sites.

Noble metals have been studied to improve the activity of indium-based catalysts. DFT and microkinetic studies have found that the pathway for methanol formation on Pd–In intermetallic surfaces is comparable to that over Cu surfaces (Wu and Yang 2019). Furthermore, it has been shown that methanol is a more favorable product than CO. Rui et al. (2017) prepared a Pd/In2O3 catalyst by mixing In2O3 powder with a Pd/peptide composite. The catalyst showed a CO2 conversion above 20% and methanol selectivity higher than 70% at 300 °C and 50 bar. Both interfacial sites and oxygen vacancies played important roles, while Pd–In bimetallic species was found to reduce the methanol yield. This is consistent with the observation that Pd–In bimetallic NPs supported on SiO2 are efficient RWGS catalysts at atmospheric pressure (Ye et al. 2015). On the other hand, Garcia-Trenco et al. (2018) found that Pd-In intermetallic compound was highly active and selective for liquid-phase methanol synthesis from CO2. They observed that the surface was enriched in indium with a significant fraction present as In2O3. It was concluded that a synergistic effect between the alloy and In2O3 might play an important role in the methanol synthesis reaction pathway over Pd–In catalysts.

Both experimental and theoretical work by Snider et al. (2019) indicated a synergy between PdIn alloy and In2O3/SiO2 catalysts. The highest methanol selectivity (61%) was obtained at an In/Pd ratio of 2:1, whereas In2O3/SiO2 only had a methanol selectivity of 24%. Frei et al. (2019) showed that the size and location of Pd species influence the performance of Pd-promoted In2O3, and their findings are illustrated in Fig. 2. Pd-promoted In2O3 prepared by dry impregnation leads to agglomeration of Pd atoms, which lowered the activation energy of the RWGS reaction. On the other hand, a higher methanol selectivity was observed when the catalyst was prepared by co-precipitation, where the Pd species were more strongly embedded into the indium oxide phase. This configuration resulted in a lower activation energy for methanol synthesis (84 kJ/mol), while the activation energy for the RWGS reaction remained unchanged. The lack of agglomeration of Pd species resulted in excellent stability over 500 h time on stream with a CO2 conversion of 9% and methanol selectivity of 78%. This illustrates the delicate interaction

### Table 3  Summary of the reported studies of In-based catalysts for CO2 hydrogenation to methanol

| Catalyst       | P, T, H2/CO2 (bar, °C) | XCO2 (%) | SMEOH (%) | GHSV (mL gcat⁻¹ h⁻¹) | STYMeOH (mg gcat⁻¹ h⁻¹) | Ea, MeOH (kJ/mol) | References            |
|----------------|------------------------|----------|-----------|----------------------|------------------------|---------------------|---------------------|
| In2O3          | 50, 300, 4             | –        | 100       | 16,000b              | 190                    | –                   | Martin et al. (2016) |
| In2O3/ZrO2     | 50, 300, 4             | –        | 100       | 16,000b              | 320                    | –                   | Martin et al. (2016) |
| YIn2O3/ZrO2    | 40, 300, 4             | 11       | 53        | 52,000               | 465                    | 66                  | Chou et al. (2019)   |
| Pd/In2O3       | 50, 300, 4             | 21       | 72        | 21,000               | 885                    | –                   | Rui et al. (2017)    |
| Pd/In2O3 (CSTR) | 50, 270, 3             | –        | 61        | –                    | –                      | 35                  | Garcia-Trenco et al. (2018) |
| Pd-In/SiO2     | 40, 300, 4             | –        | 61        | 7500                 | 104                    | –                   | Snider et al. (2019) |
| Pd-In2O3       | 50, 280, 4             | 9        | 78        | 48,000               | 960                    | 84                  | Frei et al. (2019)   |
| In2O3          | 50, 280, 4             | 3        | 89        | 24,000               | 180                    | 103                 | Frei et al. (2019)   |

*aContinuous stirred tank reactor (CSTR)
bGHSV given in the unit h⁻¹
that is required between the catalyst components to selectively enhance the methanol synthesis rate. Other transition metals have also been found to increase the methanol synthesis activity of In$_2$O$_3$, such as Ni (Snider et al. 2019) and Rh (Tsang et al. 2018).

2.4 Other transition metal-based catalysts

CO$_2$ hydrogenation to methanol over various transition metals has also been explored (Table 4). Wu et al. (2017) investigated the effect of Au particle size on various supports (CeO$_2$, TiO$_2$, ZnO, and ZrO$_2$). They demonstrated
that the activity and selectivity of Au particles with an average size smaller than 2 nm were much higher than the catalysts containing particles with an average size larger than 2 nm. In addition, the support significantly influenced the product selectivity as well as the activity. The methanol selectivity followed the order of Au/ZrO2 > Au/ZnO > Au/TiO2 > Au/Fe2O3, and the Au/ZrO2 catalyst achieved a substantially higher intrinsic activity than the others. There have been different reports regarding the effect of different supports on the activity and selectivity of Au-based catalysts. Hartadi et al. (2015) found that only Au/ZnO was selective toward methanol in CO2 hydrogenation, while Au/TiO2 and Au/ZrO2 mainly produced CO. Vourros et al. (2017) found that Au/TiO2 and Au/Fe2O3 exhibited high CO2 conversion with low methanol selectivity, whereas Au NPs supported on ZnO and CeO2 were highly selective toward methanol, but without adequate CO2 conversion. The discrepancies reported by these groups could be ascribed to the preparation method, the Au particle size of the supported catalysts, and the reaction conditions.

Studt et al. (2014) discovered a Ni-Ga catalyst presenting superior performance than Cu/ZnO/Al2O3 for CO2 hydrogenation to methanol at ambient pressure. They prepared different Ni-Ga intermetallic compounds (Ni3Ga, Ni5Ga3, and NiGa). The Ni5Ga3 phase displayed the highest methanol selectivity, as it was able to inhibit methane generation and suppress the RWGS reaction. Sharafutdinov et al. (2014) reported a detailed study of the relationship between active components and product distribution in intermetallic NiGa catalysts. Methane production was attributed to Ni-rich Ni3Ga phase, which is present on adjacent Ni–Ni sites on the surface of Ni5Ga3. Richard and Fan (2017) synthesized Ni–In–Al/SiO2 catalysts via phyllosilicate precursor and observed that methanol was hardly produced at atmospheric pressure when Ni or In was absent. However, the selectivity toward methanol was below 4% for Ni–In–Al/SiO2. Hengne et al. (2018) discovered that NiSn alloy was selective toward methanol. It was observed that Sn introduction to Ni/ZrO2 increased the methanol selectivity to 54%. The selectivity was further increased for NiSn supported on In-modified ZrO2, which showed 99% methanol selectivity and a significant increase in intrinsic activity for CO2 hydrogenation. This was attributed to improved redox ability of Ni species and enhanced basic strength of the catalyst.

Although Co typically acts as a methanation catalyst during CO2 hydrogenation, the selectivity can partially be tuned toward methanol by utilizing promoters. Li et al. (2015) investigated MnOx NPs supported on mesoporous Co3O4 and found that MnOx significantly increased the methanol selectivity of Co3O4. The active phase of the catalyst after reduction was proposed to be MnO NPs dispersed over grains of Co comprised of a CoO surface with metallic Co cores. The MnO/CoO interface facilitated an activity enhancement toward methanol synthesis compared with the separate Co/Mn NPs and supports. A methanol selectivity of 45% was achieved at relatively mild conditions (4 bar and 250 °C), but the hydrocarbon selectivity was approximately 50%. Mn-doped mesoporous Co3O4 spinel has also been shown to be selective toward methanol and significantly increase the methanol formation rate compared to Co3O4 (Stangeland et al. 2019). Khan et al. (2016) prepared Pt3Co and Pt nanocrystals. The Pt3Co octapods showed the best catalytic activity, which was attributed to both the presence of multiple sharp tips and charge transfer between Pt and Co. This charge transfer enabled the accumulation of negative charges on the Pt atoms in the vertices of the Pt3Co octapods, which promoted the activation of CO2.

Duyar et al. (2018) reported a highly active molybdenum phosphide (MoP) catalysts for methanol synthesis. Interestingly, the catalysts showed a stable performance irrespective of the composition of CO and CO2 in the feed. The most promising catalyst was comprised of CeO2 promoted MoP supported on K promoted SiO2 (K-SiO2). The addition of CeO2 to the MoP/K-SiO2 catalyst enhanced the methanol selectivity, while both methane and CO production was inhibited. The effect of the CeO2 promoter was to block Mo-rich sites that were responsible for the methanation activity.

3 Conclusions and perspectives

CO2 hydrogenation to methanol is a promising environment-friendly route to produce fuels and chemicals. One of the main obstacles for industrial implementation is developing effective catalysts. Multi-component catalyst systems are required for this process. The interaction between components is essential for high activity and selectivity of CO2-to-methanol catalysts. This has been demonstrated by numerous catalyst systems comprised of various metals (i.e., Cu, Pd, Ni) and metal oxides (i.e., ZnO, ZrO2, In2O3). These complex systems can contain a mixture of metallic, alloy, and metal oxide phases, which presents challenges in identifying the structure–activity relationship. Therefore, understanding and tailoring the interaction between the different phases is key to develop more active and stable catalysts. The most promising catalyst systems for large-scale industrial processes are currently Cu-based and In-based catalysts due to their superior catalytic performance.

The synergy between Cu and various metal oxides has been well documented, but different and conflicting mechanistic models have been proposed to explain this effect. These include direct effects such as participating in...
the reaction through the Cu-metal oxide interface or partial formation of Cu alloy sites. In addition, electronic promotion or increasing the exposure of certain geometrical or structural active Cu sites has been suggested as indirect promotional mechanisms. Identifying effective active site configurations as well as stabilizing the structure is key to enhance the performance of Cu-based catalysts.

For In-based catalysts, the activity can be increased by promotion with suitable metals and metal oxides. Both noble metals and transition metals have been shown to increase the activity of In-based catalysts. It is important to avoid the formation of metal promoter clusters (i.e., Pd), which leads to higher rates of undesired side reactions. Metal oxides can enhance the activity by providing additional sites for CO₂ activation. Further exploration of In-based catalysts could lead to the development of promising industrial CO₂-to-methanol catalysts.

Acknowledgements Open Access funding provided by University of Stavanger. The authors would like to thank the financial support from the Norwegian Ministry of Education and Research and the Department of Energy and Petroleum Engineering, University of Stavanger, for this project.

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