ORIGINAL ARTICLE

CO_2 hydrogenation to methanol: the structure–activity relationships of different catalyst systems

Kristian Stangeland[1] · Hailong Li[2] · Zhixin Yu[1]

[1] Department of Energy and Petroleum Engineering, University of Stavanger, 4036 Stavanger, Norway
[2] Department of Energy, Building and Environment, Mälardalen University, 73123 Västerås, Sweden

Abstract CO_2 hydrogenation to methanol is a promising environmental-friendly route for combatting CO_2 emissions. Methanol can be used to produce a variety of chemicals and is also an alternative fuel. The CO_2-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 CO_2-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 CO_2 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 CO_2-to-methanol process.

Keywords CO_2 hydrogenation · Methanol · Catalyst · Structure–activity
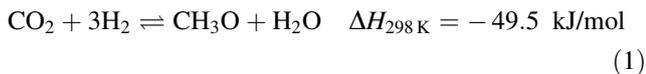
✉ Zhixin Yu
 Zhixin.yu@uis.no

1 Introduction

Environmental concerns on greenhouse gas emissions have led to a large interest in CO_2 conversion and utilization from both academia and industry in the past decade. CO_2 utilization offers an alternative carbon-neutral pathway for the synthesis of valuable fuels and chemicals. CO_2 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 CO_2 emissions, using methanol as an alternative fuel can significantly lower the emissions of air pollutants in the transportation sector, such as hydrocarbons and NO_x (Verhelst et al. 2019). The global methanol market is also expected to grow significantly over the next decade (Triton Market Research 2019). Furthermore, CO_2 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 $Cu/ZnO/Al_2O_3$ catalysts by an industrial process that converts synthesis gas (H_2/CO/CO_2) into methanol at elevated pressures (50–100 bar) and temperatures (200–300 °C) (Behrens et al. 2012). The interest in converting captured CO_2 to methanol by hydrogenation (Eq. 1) has increased significantly in recent years. However, the industrial implementation of CO_2 hydrogenation to methanol has so far been limited. This is mainly due to the higher costs associated with capturing CO_2 and producing H_2 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).

$$CO_2 + 3H_2 \rightleftharpoons CH_3O + H_2O \quad \Delta H_{298\,K} = -49.5 \text{ kJ/mol} \tag{1}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad \Delta H_{298\,K} = 41.2 \text{ kJ/mol} \tag{2}$$

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 its 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 ~ 5 s^{-1} (H$_2$/CO$_2$ = 11/1, 5.1 bar, 530 K) (Yoshihara and Campbell 1996). Rasmussen et al. (1994a, b) found that the methanol synthesis rate over Cu(100) was ~ 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$_2$O 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(000$\bar{1}$) (Yang et al. 2010) and CeO$_x$/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(000$\bar{1}$) (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$_x$ coverage, as shown in Fig. 1a. Furthermore,

Table 1 Summary of the reported studies of Cu-based catalysts for CO_2 hydrogenation to methanol

Catalyst	P, T, H_2/CO_2 (bar, °C)	GHSV (Ml g_{cat}^{-1} h^{-1})	SA_{Cu} (m^2 g^{-1})	X_{CO_2} (%)	SMeOH (%)	STYMeOH (mg g_{cat}^{-1} h^{-1})	Ea, MeOH (kJ/mol)	TOF_{MeOH} ($s^{-1} \times 10^{-3}$)	Effect of promoter[b]	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/Al$_2$O$_3$	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(000ī)	4.9, 302, 9	–	–	–	–	–	67	93	ZnO: S	Yang et al. (2010)
CeO$_x$/Cu(111)	4.9, 302, 9	–	–	–	–	–	50	1300	CeO$_x$: F	Graciani et al. (2014)
Cu/ZnO/ZrO$_2$	30, 220, 3	10[a]	10	10	91	582	–	21	ZnO-ZrO$_2$: F	Wang et al. (2019)
Cu/ZrO$_2$ (MOF)	10, 200, 3	–	–	5	–	–	–	23	–	Rungtaweevoranit et al. (2016)
CuZnAlZrGaY	20, 240, 3	30,000	94	5	–	–	–	21	Ga$_2$O$_3$, ZrO$_2$, Y$_2$O$_3$: D, R	Natesakhawat et al. (2012)
Cu-LaO$_x$/SBA-15	30, 240, 3	12,000	76	7	81	190	–	19	LaO$_x$: 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/Al$_2$O$_3$	30, 230, 3	–	–	–	–	1250	–	–	ZnO$_x$/Zn: I	Lunkenbein et al. (2015)
Cu@ZnO$_x$	30, 250, 3	1800	–	2	100	149	–	–	ZnO$_x$: I	Le Valant et al. (2015)
Cu–ZnO	30, 250, 3	1800	–	11	7	52	–	–	–	Le Valant et al. (2015)
Cu/ZnO/ Zr$_2$O$_3$/Y$_2$O$_3$	50, 230, 3	10,000	35	20	69	390	–	–	Y$_2$O$_3$: D, I, S	Gao et al. (2015)
Cu/ZnO/Ga$_2$O$_3$	45, 240, 2.8	18,000	85	27	50	837	–	–	Ga$_2$O$_3$: A[c], S	Li et al. (2016)
Cu/ZnO/Al$_2$O$_3$	30, 200, 3	9000[a]	54	–	–	181	–	–	ZnO: I, R	Liang et al. (2019)
Cu/ZnO-ZrO$_2$ (MOF)	40, 250, 3	18,000[a]	–	3	100	2590	–	–	ZnO$_x$, ZrO$_x$: I	An et al. (2017)
Cu/AlCeO	40, 240, 3	6000	26	15	70	224	–	–	CeO$_x$: B, I	Li et al. (2019)
Cu/ZrO$_2$	80, 260, 3	3600[a]	3	15	86	98	–	–	ZrO$_2$: F, I	Samson et al. (2014)
Cu/ZrO$_2$	10, 230, 3	8400	8	4	59	58	–	–	ZrO$_2$: D, F, I	Tada et al. (2019)
Cu/ZrO$_2$	10, 230, 3	8400	82	4	45	35	–	–	–	Tada et al. (2019)
Cu/ZnO/ Al$_2$O$_3$/Zr	50, 250, 3	12,000	25	25	48	490	–	–	ZrO$_2$: B, D	Gao et al. (2013)
Cu/ZrO$_2$	10, 200, 3	8800	9	2	83	–	57	–	–	Arena et al. (2008)
Cu–ZnO/ZrO$_2$	10, 200, 3	8800	61	3	65	–	69	–	ZnO: D, F, I, R; ZrO$_2$: F, I	Arena et al. (2008)

Table 1 continued

Catalyst	P, T, H$_2$/CO$_2$ (bar, °C)	GHSV (Ml g$_{cat}$$^{-1}$ h^{-1})	SA$_{Cu}$ (m^2 g^{-1})	X$_{CO_2}$ (%)	SMeOH (%)	STYMeOH (mg g$_{cat}$$^{-1}$ h^{-1})	Ea, MeOH (kJ/mol)	TOF$_{MeOH}$ (s^{-1} × 10^{-3})	Effect of promoter[b]	References
ZnO–ZrO$_2$	50, 320, 3	24,000	–	10	86	730	–	–	–	Wang et al. (2017)
Au–Cu/ZnO/Al2O3	50, 230, 4	600,000[a]	11	1	92	5700	–	–	Au: A, E	Martin et al. (2015)
Pd–Cu/CeO$_2$	30, 250, 3	3000	–	16	27	–	–	–	Pd: D, E, R,	Choi et al. (2017)
Pd–Cu/SiO$_2$	41, 250, 3	3600	–	7	34	36	–	–	Pd: A	Jiang et al. (2015)
Ni–Cu/Al$_2$O$_3$	20, 250, 3	3600	–	6	59	48	–	–	Ni: A	Zhao et al. (2017)
Cu–Ni/CeO$_2$	30, 260, 3	6000[a]	–	18	79	580	–	–	Ni: A, D, R	Tan et al. (2018)

[a] GHSV given in the unit h^{-1}

[b] A, Alloy; I, enhanced metal–support interaction; B; enhanced surface basicity; D, dispersion; E, electronic promotion; F, facilitates CO$_2$ activation; R, reducibility; S, structural promoter

[c] Ga enhances CuZn alloy formation

they found that the TOF of the inverse oxide/Cu configuration [CeO$_x$/Cu(111) and ZnO$_x$/Cu(111)] was about 2 times higher than the corresponding Cu/oxide structure (Cu/ZnO and 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 [i.e., (0001), (000$\bar{1}$), and (10$\bar{1}$0)] (Didziulis et al. 1989; Ludviksson et al. 1993). Moreover, the morphology of ZnO could also influence the Cu–ZnO interaction. Liao et al. (2011) detected a strong electronic interaction between Cu and platelike ZnO, which was proposed to facilitate CO$_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 Cu/ZnO/Al$_2$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 (i.e., formate), which facilitates the hydrogenation pathway from 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 H$_2$/CO$_2$/CO and DFT calculations. Martinez-Suáres et al. (2015) found that the formation of metallic Zn was thermodynamically favorable at low 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 ZnCu(111) catalyst underwent oxidation to ZnO during CO$_2$ hydrogenation to methanol (Kattel et al. 2017). Le Valant et al. (2015) found that the Cu and CuZn particles were inactive, while

Fig. 1 a Rates for CO_2 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)]
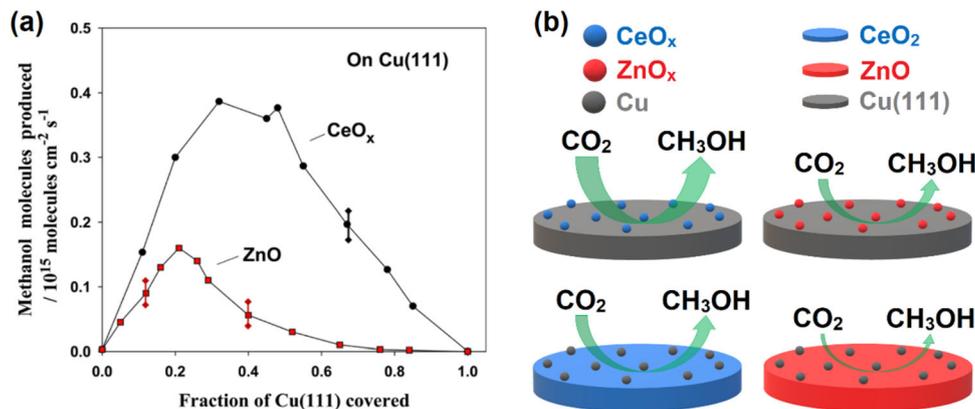
particles composed of a CuZn core with a ZnO_x shell (CuZn@ZnO_x) showed low activity with 100% methanol selectivity. In contrast, the Cu@ZnO_x core–shell particles exhibited similar selectivity but an eightfold increase in activity compared to that of CuZn@ZnO_x. They concluded that the ZnO_x overlayer 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^0 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_x 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/Al_2O_3/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/Al_2O_3/Y_2O_3 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^0, which formed CuZn alloy after reduction. The improvement in catalytic activity and methanol selectivity could be correlated with the increased Zn^0 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 CO_2, indicating that the basic sites of the metal oxides influenced the selectivity.

Recent investigations of the deactivation mechanisms of Cu/ZnO/Al_2O_3 catalysts during CO_2 hydrogenation further illustrate the importance of metal–support interaction. Liang et al. (2019) studied a Cu/ZnO/Al_2O_3 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 CO_2 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 CO_2 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

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/Al$_2$O$_3$ 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 CO$_2$-rich syngas or H$_2$/CO$_2$ feedstock was used. This was attributed to poisoning of the Cu surface by CO$_2$ 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-LaO$_x$ interface that enhanced the adsorption capacity of CO$_2$ and facilitated the conversion of CO$_2$ to methanol. Furthermore, the TOF for methanol synthesis over Cu-LaO$_x$/SiO$_2$ was 19×10^{-3} s^{-1} while only 1.3×10^{-3} s^{-1} over Cu/SiO$_2$.

Graciani et al. (2014) investigated CO$_2$ hydrogenation to methanol over a model CeO$_x$/Cu(111) surface. The activation energy of methanol synthesis over the CeO$_x$/Cu(111) surface was 50 kJ/mol, which is much lower than that obtained over a Cu/ZnO(000$\bar{1}$) surface (67 kJ/mol). The reaction mechanism was investigated by in situ infrared reflection adsorption spectroscopy and DFT calculations. The results indicated that methanol and CO were produced through the carboxyl intermediate (HOCO), whereas hydrogenation of formate (HCOO) was inhibited by high barriers. Li et al. (2019) prepared Cu supported on mesostructured Al$_2$O$_3$ and AlCeO with different Ce content. They found that Ce enhanced the surface basicity of the catalyst, which could be correlated with the increase in methanol selectivity. Cu/AlCeO showed higher methanol yields than a Cu/ZnO/Al$_2$O$_3$ catalyst prepared by co-precipitation despite having a significantly lower Cu surface area.

Zr is by far the most investigated promoter for Cu-based catalysts besides Zn, and it is often combined with Zn in tricomponent catalysts. Rungtaweevoranit et al. (2016) studied Cu confined in Zr-based metal–organic framework (MOF). The XPS analysis indicated a strong interaction between Cu and ZrO$_2$. They proposed that the presence of multiple Cu oxidation states and the high interfacial contact area between Cu and ZrO$_x$ lead to superior performance relative to a Cu/ZnO/Al$_2$O$_3$ catalyst. An et al. (2017) anchored ultra-small Cu/ZnO$_x$ NPs to a pre-assembled 2,2'-bipyridine-5,5'-dicarboxylate and Zr$_6$(μ$_3$-O)4(μ$_3$-OH)$_4$ sites in a UiO-bpy MOF. The MOF-cavity-confinement prevented the agglomeration of Cu NPs and phase separation between Cu and ZnO$_x$, resulting in a highly stable catalyst for 100 h. The catalyst showed a high space-time yield of methanol and a methanol selectivity of 100%, which was attributed to SMSI due to the presence of both Zn and Zr in close proximity to Cu. Ro et al. (2016) prepared Cu/ZrO$_2$ via controlled surface reactions and atomic layer deposition (ALD) to study the Cu/Zr interface. The oxidation state of Cu and Zr species was primarily Cu^0 and Zr^{4+}. However, Cu$^+$ and Zr$^{\delta+}$ ($\delta < 4$) were present at the interfacial sites, suggesting partial Cu diffusion into the ZrO$_2$ lattice to form Cu-ZrO$_x$. It was found that the formation of Cu–ZrO$_2$ interfacial sites increased the intrinsic activity of Cu by an order of magnitude. The exact nature of the active site was not addressed, meaning that either the 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-ZrO$_2$ crystallite phase had a higher activity than Cu supported on m-ZrO$_2$. The presence of oxygen vacancies stabilized both the thermodynamically unstable t-ZrO$_2$ phase and Cu$^+$ cations, which were present in the vicinity of oxygen vacancies. The catalytic activity toward methanol increased with increasing t-ZrO$_2$ content. Hence, the complexes built from Cu cations and oxygen vacancies preferentially on t-ZrO$_2$ 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/ZrO$_2$ catalysts. Utilizing a Cu nitrate precursor resulted in residual nitrogen that bound to basic sites of the ZrO$_2$ support, which reduced the activity of the catalysts. In addition, high calcination temperature transformed the amorphous ZrO$_2$ phase to t-ZrO$_2$, 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 N$_2$O 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 duel-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_2O 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 $mLg_{cat}^{-1} h^{-1}$, $H_2/CO_2 = 3:1$ 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 $Cu/ZnO/Al_2O_3$

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 $Ni–Cu/Al_2O_3$ 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. Bahruji 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, Bahruji et al. (2017) found that PdZn supported on TiO_2 was much more active than PdZn supported on Al_2O_3, which was

Table 2 Summary of the reported studies of Pd-based catalysts for CO_2 hydrogenation to methanol

Catalyst	P, T, H₂/CO₂ (bar, °C)	X_{CO_2} (%)	SMeOH (%)	GHSV (mL g_{cat}^{-1} h^{-1})	STYMeOH (mg g_{cat}^{-1} h^{-1})	TOFMeOH ($s^{-1} \times 10^{-2}$)	References
Pd/ZnO	20, 250, 3	11	60	3600	78	–	Bahruji et al. (2016)
PdZn/TiO₂	20, 250, 3	10	40	3600	59	–	Bahruji 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/CeO₂	30, 250, 3	11	92	2400	80	–	Malik et al. (2018)
GaPd₂/SiO₂	1, 210, 3	–	39	88	–	0.37[b]	Fiordaliso et al. (2015)
Pd₂Ga (CSTR)[a]	50, 210, 3	–	46	67,000	276	0.06[b]	García-Trenco et al. (2017)
Pd/Ga₂O₃	50, 210, 3	17	52	6000	69	–	Qu et al. (2014)

[a]Continuous stirred tank reactor (CSTR)

[b]TOF given in mmol m^{-2} s^{-1}

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 ZnO_x islands were also detected over Pd/ZnO/Al₂O₃ catalysts at low Pd loadings. The methanol selectivity of high alloy content PdZn and ZnO_x containing samples was similar under comparable CO_2 conversion. Therefore, it was proposed that ZnO_x islands could also play a role in methanol synthesis from CO_2. 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 CO_2 activation.

Fiordaliso 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 CO_2 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/Ga_x active sites for methanol production.

2.3 Indium-based catalysts

Over the last decade, indium-based catalysts have gained significant interest for CO_2 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 3 Summary of the reported studies of In-based catalysts for CO_2 hydrogenation to methanol

Catalyst	P, T, H_2/CO_2 (bar, °C)	X_{CO_2} (%)	SMeOH (%)	GHSV (mL g_{cat}^{-1} h^{-1})	STYMeOH (mg g_{cat}^{-1} h^{-1})	Ea, MeOH (kJ/mol)	References
In_2O_3	50, 300, 4	–	100	16,000[b]	190	–	Martin et al. (2016)
In_2O_3/ ZrO_2	50, 300, 4	–	100	16,000[b]	320	–	Martin et al. (2016)
In_2O_3/ ZrO_2	40, 300, 4	11	53	52,000	465	66	Chou et al. (2019)
YIn_2O_3/ ZrO_2	40, 300, 4	8	69	52,000	420	92	Chou et al. (2019)
Pd/In_2O_3	50, 300, 4	21	72	21,000	885	–	Rui et al. (2017)
PdIn (CSTR)[a]	50, 270, 3	–	61	–	–	35	García-Trenco et al. (2018)
Pd-In/SiO_2	40, 300, 4	–	61	7500	104	–	Snider et al. (2019)
Pd-In_2O_3	50, 280, 4	9	78	48,000	960	84	Frei et al. (2019)
In_2O_3	50, 280, 4	3	89	24,000	180	103	Frei et al. (2019)

[a]Continuous stirred tank reactor (CSTR)

[b]GHSV given in the unit h^{-1}

other carriers than ZrO_2. Only a moderate decrease in the reaction rate was observed over the In_2O_3/ZrO_2 catalyst with H_2O co-feeding (H_2O/CO_2/H_2 = 0.3:1:4) at 300 °C. Furthermore, it remained stable over 1000 h on stream, which makes it a very promising catalyst for CO_2 hydrogenation to methanol. Zhang et al. (2018) studied ZrO_2-doped In_2O_3 surfaces through DFT calculations. They found that ZrO_2 can prohibit the excessive formation of oxygen vacancies on the In_2O_3 surface by enhancing the In–O bond near Zr atoms, which is consistent with the effect of different supports on In_2O_3 reported by Martin et al. (2016). In addition, the ZrO_2 species was able to stabilize and activate the intermediates involved in methanol synthesis. Chou and Lobo (2019) found that Y and La promotion of In_2O_3/ZrO_2 can further improve the methanol selectivity by increasing the amount of oxygen defects and CO_2 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/In_2O_3 catalyst by mixing In_2O_3 powder with a Pd/peptide composite. The catalyst showed a CO_2 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 SiO_2 are efficient RWGS catalysts at atmospheric pressure (Ye et al. 2015). On the other hand, García-Trenco et al. (2018) found that Pd-In intermetallic compound was highly active and selective for liquid-phase methanol synthesis from CO_2. They observed that the surface was enriched in indium with a significant fraction present as In_2O_3. It was concluded that a synergistic effect between the alloy and In_2O_3 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 In_2O_3 for Pd–In/SiO_2 catalysts. The highest methanol selectivity (61%) was obtained at an In/Pd ratio of 2:1, whereas In_2O_3/ SiO_2 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 In_2O_3, and their findings are illustrated in Fig. 2. Pd-promoted In_2O_3 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 CO_2 conversion of 9% and methanol selectivity of 78%. This illustrates the delicate interaction
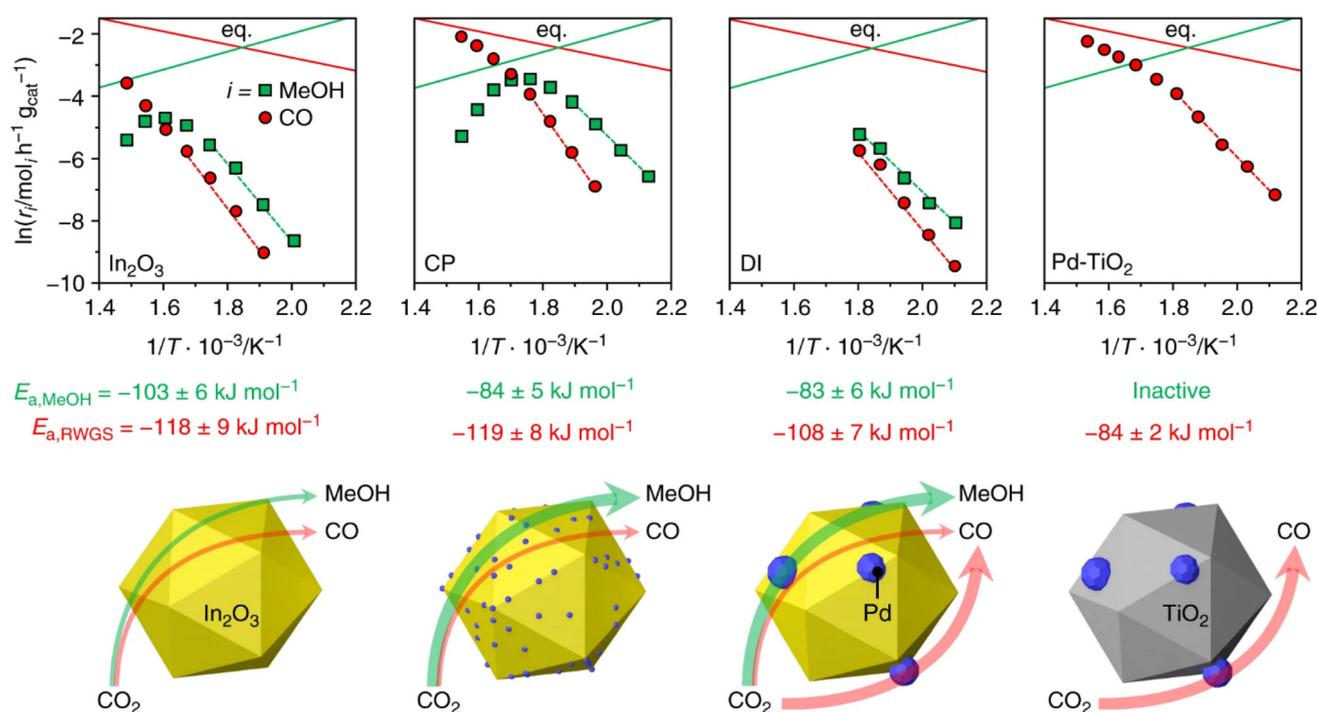
Fig. 2 Activation energies for the main reactions during CO$_2$ hydrogenation and schematic illustration of the role of Pd in Pd-promoted In$_2$O$_3$ and Pd supported on TiO$_2$. Reproduced from Ref. (Frei et al. 2019) with permission from Springer Nature, copyright 2019

Table 4 Summary of the reported studies of transition metal-based catalysts for CO$_2$ hydrogenation to methanol

Catalyst	P, T, H$_2$/CO$_2$ (bar, °C)	X$_{CO2}$ (%)	SMeOH (%)	GHSV (mL g$_{cat}^{-1}$ h^{-1})	STYMeOH (mg g$_{cat}^{-1}$ h^{-1})	Ea, MeOH (kJ/mol)	References
Au/ZrO$_2$ (BR)[a]	45, 180, 3	–	73	–	–	51	Wu et al. (2017)
Au/CeO$_2$	1, 225, 3	–	–	–	1	–	Vourros et al. (2017)
Ni$_5$Ga$_3$	1, 200, 3	–	–	–	80	–	Studt et al. (2014)
Ni-In-Al/SiO$_2$	1, 260, 3	4	2	4000[b]	18	–	Richard et al. (2017)
NiSn/InZrO$_2$	25, 250, 3	–	99	30,000[b]	120	–	Hengne et al (2018)
MnO$_x$/Co$_3$O$_4$	4, 250, 3	50–60	45	150,000[b]	–	–	Li et al. (2015)
Mn$_x$Co$_y$O$_4$	10, 250, 3	45	22	88,800[b]	3106	–	Stangeland et al. (2019)
CeO$_2$-MoP/K-SiO$_2$	31, 230, 3	< 2	76	10.8[b]	–	–	Duyar et al. (2018)

[a]Batch reactor (BR)

[b]GHSV 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 $Au/ZrO_2 > Au/ZnO > Au/TiO_2 > Au/CeO_2$, and the Au/ZrO_2 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 CO_2 hydrogenation, while Au/TiO_2 and Au/ZrO_2 mainly produced CO. Vourros et al. (2017) found that Au/TiO_2 and Au/Fe_2O_3 exhibited high CO_2 conversion with low methanol selectivity, whereas Au NPs supported on ZnO and CeO_2 were highly selective toward methanol, but without adequate CO_2 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 $Cu/ZnO/Al_2O_3$ for CO_2 hydrogenation to methanol at ambient pressure. They prepared different Ni-Ga intermetallic compounds (Ni_3Ga, Ni_5Ga_3, and NiGa). The Ni_5Ga_3 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 Ni_3Ga phase, which is present on adjacent Ni–Ni sites on the surface of Ni_5Ga_3. Richard and Fan (2017) synthesized $Ni–In–Al/SiO_2$ 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 $Ni–In–Al/SiO_2$. Hengne et al. (2018) discovered that NiSn alloy was selective toward methanol. It was observed that Sn introduction to Ni/ZrO_2 increased the methanol selectivity to 54%. The selectivity was further increased for NiSn supported on In-modified ZrO_2, which showed 99% methanol selectivity and a significant increase in intrinsic activity for CO_2 hydrogenation. This was attributed to improved reducibility of Ni species and enhanced basic strength of the catalyst.

Although Co typically acts as a methanation catalyst during CO_2 hydrogenation, the selectivity can partially be tuned toward methanol by utilizing promoters. Li et al. (2015) investigated MnO_x NPs supported on mesoporous Co_3O_4 and found that MnO_x significantly increased the methanol selectivity of Co_3O_4. 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 Co_3O_4 spinel has also been shown to be selective toward methanol and significantly increase the methanol formation rate compared to Co_3O_4 (Stangeland et al. 2019). Khan et al. (2016) prepared Pt_3Co and Pt nanocrystals. The Pt_3Co 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 Pt_3Co octapods, which promoted the activation of CO_2.

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 CO_2 in the feed. The most promising catalyst was comprised of CeO_2 promoted MoP supported on K promoted SiO_2 ($K-SiO_2$). The addition of CeO_2 to the $MoP/K-SiO_2$ catalyst enhanced the methanol selectivity, while both methane and CO production was inhibited. The effect of the CeO_2 promoter was to block Mo-rich sites that were responsible for the methanation activity.

3 Conclusions and perspectives

CO_2 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 CO_2-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, ZrO_2, In_2O_3). 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 CO_2 activation. Further exploration of In-based catalysts could lead to the development of promising industrial CO_2-to-methanol catalysts.

References

Álvarez A et al (2017) Challenges in the greener production of formates/formic acid, methanol, and DME by heterogeneously catalyzed CO_2 hydrogenation processes. Chem Rev 117:9804–9838

An B, Zhang J, Cheng K, Ji P, Wang C, Lin W (2017) Confinement of ultrasmall Cu/ZnO$_x$ nanoparticles in metal-organic frameworks for selective methanol synthesis from catalytic hydrogenation of CO_2. J Am Chem Soc 139:3834–3840

Arena F, Italiano G, Barbera K, Bordiga S, Bonura G, Spadaro L, Frusteri F (2008) Solid-state interactions, adsorption sites and functionality of Cu–ZnO/ZrO₂ catalysts in the CO_2 hydrogenation to CH₃OH. Appl Catal A Gen 350:16–23

Bahruji H et al (2016) Pd/ZnO catalysts for direct CO_2 hydrogenation to methanol. J Catal 343:133–146

Bahruji H, Bowker M, Jones W, Hayward J, Esquius JR, Morgan DJ, Hutchings GJ (2017) PdZn catalysts for CO_2 hydrogenation to methanol using chemical vapour impregnation (CVI). Faraday Discuss 197:309–324

Behrens M et al (2012) The active site of methanol synthesis over Cu/ZnO/Al₂O₃ industrial catalysts. Science 336:893–897

Brown NJ et al (2015) From organometallic zinc and copper complexes to highly active colloidal catalysts for the conversion of CO_2 to methanol. ACS Catal 5:2895–2902

Chatterjee R et al (2019) Mapping support interactions in copper catalysts. Top Catal 62:649–659

Chen K et al (2019) CO_2 hydrogenation to methanol over Cu catalysts supported on La-modified SBA-15: the crucial role of Cu–LaO$_x$ interfaces. Appl Catal B Environ 251:119–129

Choi EJ, Lee YH, Lee D-W, Moon D-J, Lee K-Y (2017) Hydrogenation of CO_2 to methanol over Pd–Cu/CeO₂ catalysts. Mol Catal 434:146–153

Chou C-Y, Lobo RF (2019) Direct conversion of CO_2 into methanol over promoted indium oxide-based catalysts. Appl Catal A Gen 583:117144

Didziulis SV, Butcher KD, Cohen SL, Solomon EI (1989) Chemistry of copper overlayers on zinc oxide single-crystal surfaces: model active sites for copper/zinc oxide methanol synthesis catalysts. J Am Chem Soc 111:7110–7123

Duyar MS et al (2018) A highly active molybdenum phosphide catalyst for methanol synthesis from CO and CO_2. Angew Chem Int Ed 57:15045–15050

Fichtl MB et al (2014) Counting of oxygen defects versus metal surface sites in methanol synthesis catalysts by different probe molecules. Angew Chem Int Ed 53:7043–7047

Fiordaliso EM et al (2015) Intermetallic GaPd₂ nanoparticles on SiO₂ for low-pressure CO_2 hydrogenation to methanol: catalytic performance and in situ characterization. ACS Catal 5:5827–5836

Frei MS et al (2019) Atomic-scale engineering of indium oxide promotion by palladium for methanol production via CO_2 hydrogenation. Nat Commun 10:1–11

Gao P, Li F, Zhao N, Xiao F, Wei W, Zhong L, Sun Y (2013) Influence of modifier (Mn, La, Ce, Zr and Y) on the performance of Cu/Zn/Al catalysts via hydrotalcite-like precursors for CO_2 hydrogenation to methanol. Appl Catal A Gen 468:442–452

Gao P, Zhong L, Zhang L, Wang H, Zhao N, Wei W, Sun Y (2015) Yttrium oxide modified Cu/ZnO/Al₂O₃ catalysts via hydrotalcite-like precursors for CO_2 hydrogenation to methanol. Catal Sci Technol 5:4365–4377

García-Trenco A, White ER, Regoutz A, Payne DJ, Shaffer MS, Williams CK (2017) Pd₂Ga-based colloids as highly active catalysts for the hydrogenation of CO_2 to methanol. ACS Catal. 7:1186–1196

García-Trenco A, Regoutz A, White ER, Payne DJ, Shaffer MS, Williams CK (2018) PdIn intermetallic nanoparticles for the hydrogenation of CO_2 to methanol. Appl Catal B Environ 220:9–18

Graciani J et al (2014) Highly active copper-ceria and copper-ceria-titania catalysts for methanol synthesis from CO_2. Science 345:546–550

Hartadi Y, Widmann D, Behm RJ (2015) CO_2 hydrogenation to methanol on supported Au catalysts under moderate reaction conditions: support and particle size effects. Chemsuschem 8:456–465

Hengne AM et al (2018) Ni–Sn-supported ZrO₂ catalysts modified by indium for selective CO_2 hydrogenation to methanol. ACS Omega 3:3688–3701

Jiang X, Koizumi N, Guo X, Song C (2015) Bimetallic Pd–Cu catalysts for selective CO_2 hydrogenation to methanol. Appl Catal B Environ 170:173–185

Kandemir T et al (2013) In situ study of catalytic processes: neutron diffraction of a methanol synthesis catalyst at industrially relevant pressure. Angew Chem Int Ed 52:5166–5170

Kasatkin I, Kurr P, Kniep B, Trunschke A, Schlögl R (2007) Role of lattice strain and defects in copper particles on the activity of Cu/

ZnO/Al$_2$O$_3$ catalysts for methanol synthesis. Angew Chem Int Ed 46:7324–7327

Kattel S, Ramírez PJ, Chen JG, Rodriguez JA, Liu P (2017) Active sites for CO$_2$ hydrogenation to methanol on Cu/ZnO catalysts. Science 355:1296–1299

Khan MU et al (2016) Pt$_3$Co octapods as superior catalysts of CO$_2$ hydrogenation. Angew Chem Int Ed 55:9548–9552

Kiss AA, Pragt J, Vos H, Bargeman G, De Groot M (2016) Novel efficient process for methanol synthesis by CO$_2$ hydrogenation. Chem Eng J 284:260–269

Kondrat SA et al (2016) Stable amorphous georgeite as a precursor to a high-activity catalyst. Nature 531:83

Kopač D, Likozar B, Huš M (2019) Catalysis of material surface defects: Multiscale modeling of methanol synthesis by CO$_2$ reduction on copper. Appl Surf Sci 497:143783

Kühl S, Tarasov A, Zander S, Kasatkin I, Behrens M (2014) Cu-based catalyst resulting from a Cu, Zn, Al hydrotalcite-like compound: a microstructural, thermoanalytical, and in situ XAS study chemistry. Eur J 20:3782–3792

Kuld S, Conradsen C, Moses PG, Chorkendorff I, Sehested J (2014) Quantification of zinc atoms in a surface alloy on copper in an industrial-type methanol synthesis catalyst. Angew Chem Int Ed 53:5941–5945

Kuld S, Thorhauge M, Falsig H, Elkjær CF, Helveg S, Chorkendorff I, Sehested J (2016) Quantifying the promotion of Cu catalysts by ZnO for methanol synthesis. Science 352:969–974

Le Valant A, Comminges C, Tisseraud C, Canaff C, Pinard L, Pouilloux Y (2015) The Cu–ZnO synergy in methanol synthesis from CO$_2$, Part 1: origin of active site explained by experimental studies and a sphere contact quantification model on Cu+ZnO mechanical mixtures. J Catal 324:41–49

Li C-S et al (2015) High-performance hybrid oxide catalyst of manganese and cobalt for low-pressure methanol synthesis. Nat Commun 6:6538

Li MM-J, Zeng Z, Liao F, Hong X, Tsang SCE (2016) Enhanced CO$_2$ hydrogenation to methanol over CuZn nanoalloy in Ga modified Cu/ZnO catalysts. J Catal 343:157–167

Li S, Wang Y, Yang B, Guo LJ (2019) A highly active and selective mesostructured Cu/AlCeO catalyst for CO$_2$ hydrogenation to methanol. Appl Catal A Gen 571:51–60

Liang B et al (2019) Investigation on deactivation of Cu/ZnO/Al$_2$O$_3$ catalyst for CO$_2$ hydrogenation to methanol. Ind Eng Chem Res 58(21):9030–9037

Liao F et al (2011) Morphology-dependent interactions of ZnO with Cu nanoparticles at the materials' interface in selective hydrogenation of CO$_2$ to CH$_3$OH. Angew Chem Int Ed 50:2162–2165

Liao F et al (2017) A promising low pressure methanol synthesis route from CO$_2$ hydrogenation over Pd@Zn core–shell catalysts. Green Chem 19:270–280

Ludviksson A, Ernst K, Zhang R, Campbell CJ (1993) The chemisorption of CO on Cu films on ZnO (0001)-O. J Catal 141:380–388

Lunkenbein T, Schumann J, Behrens M, Schlögl R, Willinger MG (2015) Formation of a ZnO overlayer in industrial Cu/ZnO/Al$_2$O$_3$ catalysts induced by strong metal–support interactions. Angew Chem Int Ed 54:4544–4548

Malik AS, Zaman SF, Al-Zahrani AA, Daous MA, Driss H, Petrov LA (2018) Development of highly selective PdZn/CeO$_2$ and Ca-doped PdZn/CeO$_2$ catalysts for methanol synthesis from CO$_2$ hydrogenation. Appl Catal A Gen 560:42–53

Martin O, Mondelli C, Curulla-Ferré D, Drouilly C, Hauert R, Pérez-Ramírez J (2015) Zinc-rich copper catalysts promoted by gold for methanol synthesis. ACS Catal 5:5607–5616

Martin O et al (2016) Indium oxide as a superior catalyst for methanol synthesis by CO$_2$ hydrogenation. Angew Chem Int Ed 55:6261–6265

Martinez-Suarez L, Siemer N, Frenzel J, Marx D (2015) Reaction network of methanol synthesis over Cu/ZnO nanocatalysts. ACS Catal 5:4201–4218

Nakamura J, Nakamura I, Uchijima T, Kanai Y, Watanabe T, Saito M, Fujitani T (1996) A surface science investigation of methanol synthesis over a Zn-deposited polycrystalline Cu surface. J Catal 160:65–75

Natesakhawat S, Lekse JW, Baltrus JP, Ohodnicki PR Jr, Howard BH, Deng X, Matranga C (2012) Active sites and structure–activity relationships of copper-based catalysts for carbon dioxide hydrogenation to methanol. ACS Catal 2:1667–1676

Ojelade OA, Zaman SF (2019) A review on Pd based catalysts for CO$_2$ hydrogenation to methanol: in-depth activity and DRIFTS mechanistic study. Catal Surv Asia 4:11–37

Polierer S, Jelic J, Pitter S, Studt F (2019) On the reactivity of the Cu/ZrO$_2$ system for the hydrogenation of CO$_2$ to methanol: a density functional theory study. J Phys Chem C 123:26904–26911

Prašnikar A, Pavlišič A, Ruiz-Zepeda F, Kovač J, Likozar B (2019) Mechanisms of copper-based catalyst deactivation during CO$_2$ reduction to methanol. Ind Eng Chem Res 58:13021–13029

Qu J, Zhou X, Xu F, Gong X-Q, Tsang SCE (2014) Shape effect of Pd-promoted Ga$_2$O$_3$ nanocatalysts for methanol synthesis by CO$_2$ hydrogenation. J Phys Chem C 118:24452–24466

Rasmussen P, Holmblad P, Askgaard T, Ovesen C, Stoltze P, Nørskov J, Chorkendorff I (1994a) Methanol synthesis on Cu(100) from a binary gas mixture of CO$_2$ and H$_2$. Catal Lett 26:373–381

Rasmussen P, Kazuta M, Chorkendorff I (1994b) Synthesis of methanol from a mixture of H$_2$ and CO$_2$ on Cu(100). Surf Sci 318:267–280

Richard AR, Fan M (2017) Low-pressure hydrogenation of CO$_2$ to CH$_3$OH using Ni–In–Al/SiO$_2$ catalyst synthesized via a phyllosilicate precursor. ACS Catal 7:5679–5692

Ro I et al (2016) Role of the Cu-ZrO$_2$ interfacial sites for conversion of ethanol to ethyl acetate and synthesis of methanol from CO$_2$ and H$_2$. ACS Catal 6:7040–7050

Rui N, Wang Z, Sun K, Ye J, Ge Q, Liu C-j (2017) CO$_2$ hydrogenation to methanol over Pd/In$_2$O$_3$: effects of Pd and oxygen vacancy. Appl Catal B Environ 218:488–497

Rungtaweevoranit B, Baek J, Araujo JR, Archanjo BS, Choi KM, Yaghi OM, Somorjai GA (2016) Copper nanocrystals encapsulated in Zr-based metal–organic frameworks for highly selective CO$_2$ hydrogenation to methanol. Nano Lett 16:7645–7649

Samson K et al (2014) Influence of ZrO$_2$ structure and copper electronic state on activity of Cu/ZrO$_2$ catalysts in methanol synthesis from CO$_2$. ACS Catal 4:3730–3741

Senanayake SD et al (2016) Hydrogenation of CO$_2$ to methanol on CeO$_x$/Cu(111) and ZnO/Cu(111) catalysts: role of the metal-oxide interface and importance of Ce^{3+} sites. J Phys Chem C 120:1778–1784

Sharafutdinov I et al (2014) Intermetallic compounds of Ni and Ga as catalysts for the synthesis of methanol. J Catal 320:77–88

Smith PJ et al (2017) A new class of Cu/ZnO catalysts derived from zincian georgeite precursors prepared by co-precipitation. Chem Sci 8:2436–2447

Snider JL et al (2019) Revealing the synergy between oxide and alloy phases on the performance of bimetallic In–Pd catalysts for CO$_2$ hydrogenation to methanol. ACS Catal 9:3399–3412

Stangeland K, Li H, Yu Z (2018) Thermodynamic analysis of chemical and phase equilibria in CO$_2$ hydrogenation to methanol, dimethyl ether, and higher alcohols. Ind Eng Chem Res 57:4081–4094

Stangeland K, Kalai DY, Ding Y, Yu Z (2019) Mesoporous manganese-cobalt oxide spinel catalysts for CO$_2$ hydrogenation to methanol. J CO2 Util 32:146–154

Studt F et al (2014) Discovery of a Ni–Ga catalyst for carbon dioxide reduction to methanol. Nat Chem 6:320

Studt F et al (2015) The mechanism of CO and CO_2 hydrogenation to methanol over Cu-based catalysts. ChemCatChem 7:1105–1111

Tada S, Oshima K, Noda Y, Kikuchi R, Sohmiya M, Honma T, Satokawa S (2019) Effects of Cu precursor types on the catalytic activity of Cu/ZrO_2 toward methanol synthesis via CO_2 hydrogenation. Ind Eng Chem Res 58:19434–19445

Tan Q, Shi Z, Wu D (2018) CO_2 hydrogenation to methanol over a highly active Cu–Ni/CeO_2–nanotube catalyst. Ind Eng Chem Res 57:10148–10158

Triton Market Research (2019) Global methanol market 2019–2027. https://www.tritonmarketresearch.com/reports/methanol-market

Tsang SCE, Meng-Jung Li M, Zou H (2018) Catalyst composition comprising rhodium and indium, preparation methods and use in methanol synthesis and steam reforming. Patent number WO2019/053452A1

Verhelst S, Turner JW, Sileghem L, Vancoillie J (2019) Methanol as a fuel for internal combustion engines. Prog Energy Combust Sci 70:43–88

Vourros A, Garagounis I, Kyriakou V, Carabineiro S, Maldonado-Hódar F, Marnellos G, Konsolakis M (2017) Carbon dioxide hydrogenation over supported Au nanoparticles: effect of the support. J CO2 Util 19:247–256

Wang J et al (2017) A highly selective and stable ZnO–ZrO_2 solid solution catalyst for CO_2 hydrogenation to methanol. Sci Adv 3:e1701290

Wang Y, Kattel S, Gao W, Li K, Liu P, Chen JG, Wang H (2019) Exploring the ternary interactions in Cu–ZnO–ZrO_2 catalysts for efficient CO_2 hydrogenation to methanol. Nat Commun 10:1166

Wu P, Yang B (2017) Significance of surface formate coverage on the reaction kinetics of methanol synthesis from CO_2 hydrogenation over Cu. ACS Catal 7:7187–7195

Wu P, Yang B (2019) Intermetallic PdIn catalyst for CO_2 hydrogenation to methanol: mechanistic studies with a combined DFT and microkinetic modeling method. Catal Sci Technol 9:6102–6113

Wu C, Zhang P, Zhang Z, Zhang L, Yang G, Han B (2017) Efficient hydrogenation of CO_2 to methanol over supported subnanometer gold catalysts at low temperature. ChemCatChem 9:3691–3696

Xu J et al (2016) Methanol synthesis from CO_2 and H_2 over Pd/ZnO/Al_2O_3: catalyst structure dependence of methanol selectivity. Appl Catal A Gen 514:51–59

Yang Y, Evans J, Rodriguez JA, White MG, Liu PJPCCP (2010) Fundamental studies of methanol synthesis from CO_2 hydrogenation on Cu(111), Cu clusters, and Cu/ZnO(000$\bar{1}$). Phys Chem Chem Phys 12:9909–9917

Yang Y, White MG, Liu P (2011) Theoretical study of methanol synthesis from CO_2 hydrogenation on metal-doped Cu(111) surfaces. J Phys Chem C 116:248–256

Ye J, Liu C, Mei D, Ge Q (2013) Active oxygen vacancy site for methanol synthesis from CO_2 hydrogenation on In_2O_3(110): a DFT study. ACS Catal 3:1296–1306

Ye J, Ge Q, Liu C-j (2015) Effect of PdIn bimetallic particle formation on CO_2 reduction over the Pd–In/SiO_2 catalyst. Chem Eng Sci 135:193–201

Yoshihara J, Campbell CT (1996) Methanol synthesis and reverse water–gas shift kinetics over Cu(110) model catalysts: structural sensitivity. J Catal 161:776–782

Zhang M, Dou M, Yu Y (2018) Theoretical study of the promotional effect of ZrO_2 on In_2O_3 catalyzed methanol synthesis from CO_2 hydrogenation. Appl Surf Sci 433:780–789

Zhao F, Gong M, Cao K, Zhang Y, Li J, Chen R (2017) Atomic layer deposition of Ni on Cu nanoparticles for methanol synthesis from CO_2 hydrogenation. ChemCatChem 9:3772–3778