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Tuning Selectivity of CO₂ Hydrogenation Reactions at the Metal/Oxide Interface

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Abstract

The chemical transformation of CO₂ not only mitigates the anthropogenic CO₂ emission into the earth's atmosphere but also produces carbon compounds that can be used as precursors for the production of chemicals and fuels. The activation and conversion of CO₂ can be achieved on multifunctional catalytic sites available at the metal/oxide interface by taking advantage of the synergy between the metal nanoparticles and oxide support. Herein, we reviewed the recent progress in mechanistic studies of CO₂ hydrogenation to C1 (CO, CH₃OH and CH₄) compounds on metal/oxide catalysts. On the basis, we were able to provide better understanding of the complex reaction network, grasp the capability of manipulating structure and combination of metal and oxide at the interface in tuning selectivity, and finally identified the key descriptors to control the activity and in particular the selectivity of catalysts. Finally, we also discussed challenges and future research opportunities for tuning the selective conversion of CO₂ on metal/oxide catalysts.

1. Introduction

Carbon dioxide (CO₂) is one of the major components of greenhouse gases emitted into earth's atmosphere due to human activities. The increasing amount of greenhouse gases produced due to human civilization over the decades has a negative impact on climate change and ocean acidification.^{1,2} Considering the negative impact of CO₂ emission in global climate change, leading CO₂ emitting countries have pledged to cut CO₂ emissions significantly in the near future to limit the temperature increase to 1.5 °C above pre-industrial levels. In doing so, the rate of the atmospheric CO₂ emission is forecasted to be slower in the future. However, tens of thousands of tons of anthropogenic CO₂ will still be continuously emitted into the earth's atmosphere due to burning of fossil fuels for energy generations.

Among the different approaches explored for reducing CO₂, the chemical transformation of CO₂ to high calorific fuels is particularly attractive.³⁻¹⁴ The conversion of CO₂ (by hydrogen) to fuels not only mitigates its emission into the earth's atmosphere but also produces commodity chemicals that can be either used as fuels or as precursors in many industrial chemical processes.¹⁵ The chemical recycling of CO₂ to useful chemicals can be done using two different methods: (i) electrochemical reduction of CO₂^{10,16-27} and (ii) thermocatalytic reduction of CO₂.^{4,9,28-32} The electrochemical reduction of CO₂ to liquid fuels is achieved at room temperature while the thermocatalytic transformation of CO₂ is often carried out at high pressure and elevated temperature in the range of 200-300 °C.^{29,30} In both cases catalysts play a critical role in determining the activity and selectivity of CO₂ transformation. The focus of the present Perspective is on the thermocatalytic transformation of CO₂ to C1 chemicals.

The importance of catalytic activation of CO₂ in carbon neutral energy conversion and storage using earth abundant catalytic materials has been highlighted in several recent reviews and

Perspective articles.^{4,6,10,12,13,15,32-35} Daza et al.³⁶ summarized the various catalysts and their activities for CO₂ conversion to fuels via the reverse-water-gas-shift (RWGS) reaction. Dorner et al.³² reviewed the modified Fischer-Tropsch (FT) catalysts in converting CO₂ to value-added hydrocarbons. Porosoff et al.¹⁵ provided an overview of the various catalysts used for CO₂ conversion to CO, CH₃OH and light alkane and olefin. Rodriguez et al. recently highlighted the importance of the metal/oxide interface for the catalytic CO₂ → CH₃OH transformation,³³ showing that the catalytic activity for CO₂ conversion can be greatly promoted at the metal/oxide and metal/carbide interfaces. Another focus is on ways to convert CO₂ via photo-, electro- and thermo-reductions for instance by Kondratenko et al.¹⁰ and Hu et al.¹³ Finally, the reaction mechanisms were also outlined for CO₂ conversion to C1 fuels in a theoretical review by Li et al.⁹

Besides catalytic activity, the selectivity for CO₂ conversion is equally or maybe even more important in practice. To the best of our knowledge, the essential role of the metal/oxide interface for controlling the selectivity of CO₂ conversion has not been critically reviewed. The current Perspective aims to identify the general trends, as well as challenges and opportunities in designing metal/oxide interfaces to achieve selective CO₂ hydrogenation. Due to the complexity of the reaction network for CO₂ hydrogenation (Figure 1), multiple products can be formed and the separation of product can be very expensive in practical applications. The current Perspective provides a bottom-up review on how the synergistic interactions at the metal/oxide interface can tune the reaction mechanisms and in turn the selectivity of CO₂ hydrogenation. Typically the activity of the catalyst is associated with multiple catalytic sites available at the metal/oxide interface, according to recent studies using in-situ, operando experimental techniques and theoretical calculations, where bifunctional^{28,37-40} and/or electronic effects⁴¹⁻⁴⁶ contribute to modify the bonding strength. The metal/oxide interface provides multiple sites for the adsorption

of reaction intermediates. In some cases,^{28,38,47-49} the simultaneous participation of both the metal sites on metal nanoparticles and the M^+ or O^{2-} sites of oxides is observed to stabilize the key reaction intermediates, e.g. *CO_2 , *C_xH_y and *C_xH_yO_z species. In this regard, the metal/oxide interface is bifunctional. The electronic effect creates unique electronic properties at the metal/oxide interface due to the strong interaction between the metal and oxide support, which can be different from that of each component and be suitable for CO_2 activation and its subsequent transformation. However, it is not straightforward to isolate these two effects which can occur simultaneously.^{50,51} Here, we will focus on the catalyst selectivity, using the metal/oxide interface in determining the product selectivity of CO_2 toward C1 carbon compounds: carbon monoxide (CO), methanol (CH_3OH) and methane (CH_4). We will first summarize the activity and reaction mechanisms of the oxide-supported metal catalysts that are selective to produce CO, CH_3OH , and CH_4 . It will be followed by the discussion on the challenges and opportunities for the rational design of metal/oxide interfaces by choosing the appropriate combination of metals and oxides to achieve high activity and selectivity toward CO_2 hydrogenation.

2. CO_2 Hydrogenation to CO

CO is the simplest C1 product of the CO_2 hydrogenation through the RWGS reaction, $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$. CO is a valuable precursor molecule that can be used for CH_3OH synthesis and for the production of longer chain hydrocarbons in the FT process. Various metals including precious metals Pt,⁵²⁻⁵⁵ Pd,⁵⁶ Rh⁵⁷ and Au^{58,59} and non-precious metals Cu,⁶⁰⁻⁶⁶ Fe⁶⁷ and Ni⁶⁸⁻⁷¹ supported on oxides were reported to be active towards the production of CO (Table 1). Cu was one of the extensively studied metal catalysts for the RWGS reaction, whose catalytic activity for CO_2 hydrogenation was found to be sensitive to its dispersion, surface morphology and particle size.^{60,65,66} For example, highly dispersed Cu nanoparticles on the ZnO

support showed high activity for CO₂ hydrogenation reaction to produce CO.⁷² Pt was also widely studied as a catalyst for promoting the RWGS reaction to produce CO. The activity and selectivity of Pt catalysts were found to be influenced by the nature of the oxide support. For example, Pt/ γ -Al₂O₃ was less active and more selective to CO than Pt/CeO₂ at similar Pt loadings and CO₂ conversion.⁷³ Rh was another active metal for the RWGS reaction when deposited on different supports (MgO, Nb₂O₅, ZrO₂ and TiO₂, Table 1).^{36,57,74,75} Rh/TiO₂ with low Rh loadings was selective to CO,⁷⁵ where the RWGS activity was higher than the CO₂ methanation activity at 200 °C for two different ratios of CO₂:H₂ (Figure 2). Furthermore, a quantitative site-specific correlation between CO and CH₄ selectivity on Rh/TiO₂ was reported using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements. It was proposed that the RWGS reaction only occurred at isolated Rh atomic sites while the CO₂ methanation reaction was on Rh atoms interacted with Rh nanoparticles.⁷⁵ Bimetallic catalysts such as PtNi, PtCo and PdNi were also studied for CO₂ hydrogenation to CO.^{73,76} Results in Table 2 showed that bimetallic catalysts displayed higher activity and CO selectivity than the individual monometallic catalysts deposited on the same oxide supports.⁷³

CO₂ hydrogenation to CO via the RWGS reaction, can proceed via the carboxyl (*HOCO) intermediate (Figure 1). Alternatively, *CO₂ can dissociate into *CO + *O via the direct C-O bond cleavage pathway, and formed *CO can desorb as a product CO(g). Density functional theory (DFT) calculations showed that CO₂ was activated and bound at the metal/oxide interface via a configuration with C atom of *CO₂ bound to the metal site and one of the O atoms of CO₂ bound to the metal cation (M⁺) of the oxide support for various oxide supports e. g. SiO₂, Al₂O₃, TiO₂, CeO₂, ZrO₂, In₂O₃ and ZnO.^{28,38,47-49,77-80} The dissociation of molecular H₂ occurred relatively easily on the metal sites, and the spillover of hydrogen atoms from metal sites to oxide supports,

e.g. SiO_2 , TiO_2 , ZrO_2 , was also observed, which formed hydroxylated oxide surfaces.^{81,82} In some cases, e. g. Pt/SiO_2 ,⁵¹ Cu/TiO_2 ,³⁸ $^*\text{CO}_2$ underwent hydrogenation and formed $^*\text{HOCO}$, which dissociated to produce $^*\text{CO}$ either at the metal or metal/oxide interfacial sites. The relatively stronger binding of $^*\text{HOCO}$ was necessary for its dissociation with a low activation energy. In other cases, e.g. Cu/ZrO_2 ,⁴⁸ $^*\text{CO}_2$ preferred dissociation reaction over its hydrogenation according to the DFT and kinetic Monte Carlo (KMC) study.

The nature of oxide supports influence the activity of metal/oxide catalysts toward CO_2 conversion via the direct participation in CO_2 binding. In term of activity, the reducibility of oxide is important,⁵⁵ and the presence of an O-vacancy provided the site for CO_2 adsorption which is otherwise a difficult step.⁸³⁻⁸⁷ On Pt/SiO_2 , a non-reducible support, O vacancies were difficult to be formed and CO_2 bound weakly at the Pt- SiO_2 interface; in contrast, the presence of an O vacancy on TiO_2 , a reducible support, provided much stronger binding for CO_2 (Figure 3).⁵¹ The stronger binding of CO_2 on Pt/TiO_2 compared to Pt/SiO_2 was likely responsible for the experimentally observed higher activity of CO_2 conversion to CO on Pt/TiO_2 .⁵¹ The effect on selectivity rather depend on the binding of CO.^{28,88,89} A similar CO selectivity was observed on both Pt/TiO_2 and Pt/SiO_2 , because on both catalysts CO primarily interacted with Pt, and the similarity in CO binding energy. Besides Pt/oxides, the importance of CO binding in determining CO selectivity was also observed for Pt alloy/oxides and Cu/oxides.^{38,39} A combination of ambient pressure X-ray photoelectron spectroscopy (APXPS) and DFT calculations for the model surfaces and transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, DRIFTS, and extended X-ray absorption fine structure (EXAFS) analysis for the corresponding powder catalysts showed that changing the support from TiO_2 to CeO_2 and ZrO_2 did not affect the CO_2 hydrogenation pathway of the PtCo alloy; however, CO selectivity was greatly influenced.³⁹

Figure 4 shows the FTIR spectra recorded during CO₂ hydrogenation on the PtCo/oxides catalysts. The vibrational modes $\nu(\text{C}=\text{O})$ at 2358 cm⁻¹, $\nu(\text{C}\equiv\text{O})$ at 2170 cm⁻¹, and $\nu(\text{C}-\text{H})$ at 3016 cm⁻¹ were used to monitor the presence of CO₂, CO, and CH₄, respectively. On PtCo/TiO₂, a sharp band corresponding to CO was detected (Figure 4a) while on PtCo/CeO₂, vibrational peaks corresponding to the formation of CH₄ were observed in addition to the peaks corresponding to CO. Even though CO was observed as a product on both PtCo/TiO₂ and PtCo/CeO₂ model and powder catalysts, PtCo/TiO₂ was found to selectively promote CO₂ → CO conversion because of weak CO binding at the PtCo/TiO₂ interface. In addition, both DFT calculations and experiments using the steady state flow reactor demonstrated that Cu/TiO₂ was more selective for CO production than Cu/ZrO₂.³⁸ This was associated with the weakened interaction of *CO at the Cu/TiO₂ interface compared to the Cu/ZrO₂ interface.

Overall, the previous studies on Pt, Cu/oxide catalysts shined the light on the principles to tune the activity and selectivity of metal/oxide catalysts during CO₂ hydrogenation to CO. The promotion in activity required the strengthened interaction to CO₂ at the metal/oxide interface, being able to facilitate the overall conversion via either the RWGS or the direct C-O bond cleavage pathway. CO selectivity of a metal/oxide catalyst is primarily determined by the binding capability of the metal/oxide interface for CO.^{38,39,51,90} The metal/oxide interface that binds CO weakly should be selective to CO simply because of facile desorption of *CO. Conversely, when *CO is strongly bound, its hydrogenation or dissociation is likely more favorable than desorption, and consequently the catalyst is likely to show lower CO selectivity.

3. CO₂ Hydrogenation to CH₃OH

CH₃OH synthesis from the thermocatalytic CO₂ transformation, $\text{CO}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{*CH}_3\text{OH}(\text{g}) + \text{H}_2\text{O}(\text{g})$, has gained tremendous interests in recent years.²⁸⁻³⁰ Among many materials

studied, oxide-supported metals have emerged as promising catalysts and the metal/oxide interfaces have been identified to play a critical role in controlling the activity and selectivity for CH₃OH synthesis from CO₂ hydrogenation.^{91,92} For example, the synergistic effect between the metal and oxide in promoting CO₂ conversion to CH₃OH was observed in Cu/oxide catalysts, surpassing the activity of Cu catalysts without oxide supports.^{28,30,38,91} Pd^{93-95,96-99} and Au^{31,37,100} supported on oxides have also been reported to be active for CH₃OH synthesis from the CO₂ hydrogenation at moderate reaction temperature and pressures (Table 1).

Cu/ZnO/Al₂O₃ is an industrially used catalyst for the transformation of CO₂ to CH₃OH at high pressures (50-100 atm) and elevated temperatures (200-300 °C),^{29,30,101} though CO is still the major product. Significant efforts have been made to understand the nature of the active sites in Cu/ZnO/Al₂O₃ for CO₂ activation and conversion.^{29,30,91,102-107} Recently, the synergy between Cu and ZnO arising from the strong-metal-support-interaction (SMSI) was attributed to the formation of CuZn alloy, where Zn atoms at the step edges of Cu nanoparticles were proposed to be active sites using a combination of experimental measurements and theoretical calculations and the Zn coverage was quantitatively correlated with the methanol synthesis activity (Figure 5).^{30,102} On the other hand, recent TEM studies revealed that the SMSI between Cu and ZnO led to the encapsulation of ZnO overlayers (Figure 6) over Cu particles during CH₃OH synthesis on the Cu/ZnO/Al₂O₃ catalyst, which could potentially create new catalytically active sites.^{101,103} Indeed, the combined X-ray photoemission spectroscopy (XPS) measurements, DFT calculations and kinetic Monte Carlo (KMC) simulations on model ZnCu(111) catalysts showed that the CuZn alloy underwent surface oxidation under the reaction conditions and the surface Zn was transformed into ZnO, creating a catalytically active Cu/ZnO interface (Figure 7) for CH₃OH synthesis.⁴⁷ In another example, the CH₃OH synthesis activity of Cu/CeO_x/TiO₂(110) was found

to be ~1280 times higher than Cu(111) (Figure 8).²⁸ The unique Cu/CeO_x interface not only activated CO₂ but also selectively stabilized the reaction intermediates and facilitated the overall CO₂ conversion to CH₃OH with an apparent activation energy lower than Cu(111).

Pd catalysts supported on various oxides (Al₂O₃, SiO₂, TiO₂, CeO₂, Ga₂O₃, MgO and ZnO) have also been studied for CO₂ transformation to CH₃OH.^{97,98,108,109} An earlier study by Erdohelyi et al.¹⁰⁸ showed that Pd supported on TiO₂ displayed the highest activity for CO₂ hydrogenation among Pd supported on Al₂O₃, SiO₂, TiO₂ and MgO. The selectivity of CO₂ hydrogenation on Pd/oxides catalysts was shown to largely depend on Pd particle size; CO and CH₃OH were produced on poorly dispersed Pd while CH₄ was the main product on highly dispersed Pd.¹⁰⁸ Pd/CeO₂ was reported to be highly selective to CH₃OH (CH₃OH selectivity ~90 %) at a temperature of 230 °C and a pressure of 30 bar when CO₂:H₂ ratio is 1:3.¹¹⁰ The SMSI effect between Pd and oxides such as CeO₂ or TiO₂ created catalytically active interfacial sites for CO₂ hydrogenation.^{98,111} Fujitani et al.⁹⁴ showed that Pd/Ga₂O₃ was more active than Cu/ZnO by a factor of 2 in yield and 20 in turnover frequency for CO₂ hydrogenation. Pd/ZnO was another metal/oxide catalyst studied which showed high CH₃OH selectivity, where Pd/ZnO prepared by sol immobilization method exhibited much higher than that prepared by impregnation method for identical Pd loadings (Figure 9).^{92,103,106} The promotional effect of ZnO, similar to that on Cu/ZnO, on Pd forming catalytically active Pd-Zn alloy has been proposed.⁹⁹

Au/oxide was reported to have comparable activity in CO₂ hydrogenation as Cu/oxide in the temperature range of 150-400 °C.^{31,37,100,112} Smaller Au particles were shown to give higher CH₃OH productivity.¹⁰⁰ The oxide supports also matter. The CH₃OH production was observed following the order of Au/ZrO₂ > Au/ZnO > Au/TiO₂ > Au/Al₂O₃ with similar Au nanoparticle size (Figure 10).³¹ The catalytic performance of Au/ZnO catalyst for CH₃OH production^{87,100} was

impressive given that the metal mass-normalized activity was comparable to and the selectivity for CH₃OH formation was significantly higher than (> 50% compared to 37%) those of a commercial Cu/ZnO/Al₂O₃ catalyst. Finally, the mixed oxide, CeO_x/TiO₂, supports was found to be able to promote the CO₂ conversion to CH₃OH at the Au/CeO_x/TiO₂ interface to a level comparable to those of Cu/CeO_x/TiO₂ catalysts.³⁷

There are two major reactions pathways proposed for the production of CH₃OH from CO₂ hydrogenation based on experimental observations and theoretical calculations (Figure 1).^{38,48,77,83,113-117} The first pathway is featured by the *CO intermediate, which is produced from the RWGS reaction via the carboxylate (*HOCO) species or via the direct C-O bond cleavage of *CO₂ and is further hydrogenated to the final product CH₃OH (designated as the RWGS + CO-Hydro pathway); the other pathway is associated with the formate (*HCOO) intermediate formed by the initial step in *CO₂ hydrogenation, which eventually produces CH₃OH via the C-O bond cleavage of the *H₂COOH intermediate (designated as the Formate pathway). As shown in Figure 1, the CH₃OH production from both pathways involves many reaction intermediates and can occur in various possible routes. The identification of the active reaction intermediates is essential to fully explore the preferred pathways in which CO₂ is hydrogenated to CH₃OH, which requires the combination of experimental observations and theoretical calculations.³⁸

The preferred pathway for the CO₂ hydrogenation is primarily controlled by the binding capability of the catalyst with the key reaction intermediates.³⁸ As shown in Figure 11, the metal/oxide (e.g. Cu/TiO₂) interface directly participates in binding and stabilizing of the reaction intermediates. The initial hydrogenation of CO₂ determines the pathway for CO₂ hydrogenation. In general, at the metal/oxide interface, *HCOO along the Formate pathway adsorbs through two O atoms in the bidentate configuration (Figure 11d), while *HOCO along the RWGS pathway

binds through a single O atom (Figure 11c). Consequently, the stability of $^*\text{HCOO}$ is mostly higher than that of $^*\text{HOCO}$ and the barrier for the formation of $^*\text{HCOO}$ is expected to be lower than that for the formation of $^*\text{HOCO}$.³⁸ This was the case for Cu/ZnO where the Formate pathway was preferred over the RWGS + CO-Hydro pathway for CH_3OH production.^{30,47} Along the Formate pathway, the hydrogenation of $^*\text{HCOO}$ to $^*\text{HCOOH}$ and $^*\text{H}_3\text{CO}$ hydrogenation to $^*\text{CH}_3\text{OH}$ displayed the highest barrier among the elementary steps according to the DFT calculations.⁴⁷ That is, the interaction of $^*\text{HCOO}$ with the surface can be one of the keys to facilitate CH_3OH production along the Formate pathway, being strong enough to facilitate CO_2 hydrogenation, but weakly enough to allow further hydrogenation.

The over stabilization of the $^*\text{HCOO}$ species can result in surface poisoning of metal/oxide catalysts over time, which hinders the Formate pathway.^{28,38} DFT calculations (Figure 12) and KMC simulations performed at experimental reaction conditions on Cu/TiO₂ and Cu/ZrO₂ catalysts predicted the poisoning of catalysts due to accumulation of surface $^*\text{HCOO}$ species during CO_2 hydrogenation.³⁸ On Cu/TiO₂, Cu/CeO₂ and Cu/ZrO₂, $^*\text{HCOO}$ acted as a spectator, and the CH_3OH production did not occur via the Formate pathway..^{28,38} Under such situation, the CH_3OH formation can occur via the $^*\text{HOCO}$ intermediate along the RWGS + CO-Hydro pathway.^{28,38} For Cu/oxide catalysts, in particular, the binding strength of $^*\text{CO}$ to the catalysts was again critical to the production of CH_3OH , similar to that of CO production (see Section 2).^{38,90} The main difference is that the conversion to CH_3OH requires a catalyst that binds $^*\text{CO}$ strongly enough to enhance its hydrogenation to formyl species ($^*\text{HCO}$), rather than its desorption.³⁸ Besides, the stability of $^*\text{HCO}$, $^*\text{H}_2\text{CO}$ and $^*\text{H}_3\text{CO}$ intermediates is also important. An ideal Cu/oxide catalyst for $\text{CO}_2 \rightarrow \text{CH}_3\text{OH}$ conversion via the RWGS + CO-Hydro pathway should promote the initial hydrogenation of $^*\text{CO}_2$ to $^*\text{HOCO}$ and simultaneously stabilize the $^*\text{CO}$,

*HCO and *H₂CO active intermediates, while *H₃CO should be destabilized to allow its hydrogenation to CH₃OH. Herein, the reduced M^{δ+} sites at the metal/oxide interface can play a critical role in stabilizing the *CO, *HCO and *H₂CO intermediates through a M^{δ+}-O interaction. Indeed, a combined theory-experiment study showed that upon going from Cu/TiO₂ to Cu/ZrO₂, the CO₂ conversion was facilitated due to the fine-tuning capability of ZrO₂, being strong enough to stabilize *CO₂, *CO, *HCO, and *H₂CO at the Cu/ZrO₂ interface and therefore to promote its hydrogenation to CH₃OH via the RWGS + CO-Hydro pathway, but weak enough to prevent the poisoning of the active sites.³⁸

The variation in the size of metal nanoparticles also affects the selectivity. The Cu₄/hydroxylated-Al₂O₃ model catalyst showed high activity for CO₂ conversion to CH₃OH at a low CO₂ partial pressure.¹¹⁷ According to DFT calculations, the CO₂ hydrogenation on Cu₄/Al₂O₃ was highly selective to CH₃OH via the Formate pathway; by comparison the production of CO or CH₃OH along the RWGS reaction was kinetically less favorable (Figure 13).¹¹⁷ The unique coordination environment of Cu atoms in small Cu clusters on Al₂O₃ was able to tune the bindings of Cu with reaction intermediates, leading to the selective production of CH₃OH.

The mechanistic studies of Cu/oxide catalysts indicated that the conversion of CO₂ to CH₃OH can proceed via both the Formate and the RWGS + CO-Hydro pathways. Along the Formate pathway, the binding of *HCOO is important, which should be tuned being able to promote the hydrogenation of *CO₂ to *HCOO, but not over-stabilized to prevent surface poisoning. In term of selectivity, *H₃CO should be destabilized on the surface to allow the production of CH₃OH. By comparison, the situation along the RWGS + CO-Hydro pathway is more complex. To achieve high activity, the metal/oxide interfacial sites should selectively provide stabilization to *CO₂ and facilitate *HOCO formation. To enhance CH₃OH selectivity, the

bindings of *CO, *HCO, and *H₂CO should be increased, while that of *H₃CO should be decreased. For such complex reaction network, the binding energy of a single intermediate, or single descriptor, may not be adequate enough to well describe the catalytic performance; instead it is likely controlled by several key species, which work in a cooperative way. The binding strength of adsorbates on the catalysts can be tuned by selecting different metal/oxide catalysts and by controlling the metal particle size. The combination of DFT calculations, KMC simulations, and experimental measurements is essential to provide significant insight into the complex reaction mechanisms of CO₂ hydrogenation to CH₃OH.

4. CO₂ Hydrogenation to CH₄

Converting CO₂ to CH₄ by H₂, or CO₂ methanation, $\text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g})$, is a promising way to produce synthetic natural gas. As summarized in Table 1, Ni catalysts supported on various oxides, SiO₂,^{118,119} Al₂O₃,¹²⁰⁻¹²³ TiO₂,¹²⁴ CeO₂,¹²⁵⁻¹²⁷ and ZrO₂^{127,128} have been shown to promote the CO₂ methanation reaction. The activity of Ni-based catalysts for CO₂ methanation was found to be promoted by the addition of second metals or other oxides.^{93,129,130} For example, the synergy between the precious metals Rh or Ru and Ni was observed on both activity and selectivity of Ni based Ce_xZr_{1-x}O₂ catalysts.¹²⁹ Furthermore, Ni loading also played a major role in both activity and selectivity for CO₂ methanation. A recent experimental study showed that both CO₂ conversion and CH₄ selectivity of Ni/γ-Al₂O₃ catalyst were affected by Ni content and 20 wt.% of Ni loading showed the highest activity and selectivity.¹²⁰ Ru¹³⁰⁻¹⁴⁰ and Rh^{75,141} supported on oxides (Table 1) were also widely studied. HRSTEM and XPS measurements on Ru/TiO₂ catalysts showed encapsulation of Ru particles by the TiO₂ support due to the SMSI. Time-resolved in-situ EXAFS measurements showed that the presence of H₂O increased the CH₄ selectivity of Ru/TiO₂ catalysts due to the promotion of the OH group for CO₂ adsorption and

dissociation.¹⁴² Ru-doped CeO₂ showed a higher selectivity for CO₂ methanation reaction than that of doping Ni, Co or Pd.¹³¹ The promoting effect of adding a secondary oxide or metal component on the overall rate was also observed for Ru/Al₂O₃ with the addition of CeO₂¹³⁰ and Pd/SiO₂ with addition of Mg,⁹³ respectively.

The possible pathways for CO₂ hydrogenation to CH₄ are summarized in Figure 1.^{39,51,124,132,139,140,143-145} The CH₄ formation can occur via the Direct C-O bond cleavage, the RWGS + CO-Hydro and Formate pathways. Along the Direct C-O bond cleavage pathway, *CO₂ dissociates to *CO and *O and the produced *CO undergoes dissociation reaction to form *O and *C, which is subsequently hydrogenated to CH₄.¹⁴³ Alternatively, *CO may be hydrogenated to *HCO, which dissociates to *CH + *O and *CH is hydrogenated to CH₄.¹²⁴ Along the RWGS + CO-Hydro pathway the C-O bond scission of *HCOH, *H₂COH or *H₃CO leads to the formation of CH_x species which undergo subsequent hydrogenation reactions to form CH₄.^{39,51} Along the Formate pathway, CH₄ formation occurs via the C-O bond cleavage in H₂COH or H₃CO.⁵¹ The CH₄ selectivity is therefore ultimately determined by the competition between C-O bond scission in H_xCO species and their hydrogenation reactions.^{39,51} Thus along all three pathways, the C-O bond scission of the H_xCO species is a critical step and likely determines the overall CH₄ selectivity in CO₂ hydrogenation.

Compared to mechanistic studies for CO and CH₃OH productions on metal/oxide catalysts, much less attention has been paid to CH₄ production. On Ni/ γ -Al₂O₃ catalysts, the kinetics of CO₂ methanation was found to follow the Direct C-O bond cleavage pathway in which the rate-limiting step was the subsequent dissociation of adsorbed *CO.¹²¹ The detailed mechanisms of CO₂ methanation on Ru(0001) was studied by combined DFT calculations and microkinetic modeling.¹⁴⁶ It was found that the CH₄ production primarily occurred via the direct *CO₂

dissociation to $^*\text{CO} + ^*\text{O}$ followed by several steps: hydrogenation of $^*\text{CO}$ to $^*\text{HCO}$, $^*\text{HCO}$ dissociation to $^*\text{CH} + ^*\text{O}$, and $^*\text{CH}$ hydrogenation to $^*\text{CH}_4$. The reaction of $^*\text{HCO}$ dissociation to $^*\text{CH} + ^*\text{O}$ was predicted to be the rate-limiting step. The mechanism of CH_4 formation on Pt/oxide and Cu/oxide catalysts was well described, though the catalysts were highly selective to CO or CH_3OH .^{51,117} The addition of a secondary Co component on Pt/CeO₂ or Pt/ZrO₂ tuned the selectivity more toward CH_4 than that without Co, though CO was still the major product.³⁹ According to DFT calculations, CH_4 formation occurred via the RWGS reaction via the $^*\text{H}_3\text{CO}$ intermediate at the PtCo/oxide interface (Figure 14).³⁹ The DFT prediction of the presence of the H_3CO intermediate as a precursor for the formation of CH_4 on PtCo/oxides, such as PtCo/ZrO₂, was also confirmed in the corresponding experiments.³⁹ As shown in Figure 13, $^*\text{H}_3\text{CO}$ was also a precursor for the C-O bond cleavage for the production of CH_4 on Cu₄/Al₂O₃; however, the C-O bond cleavage could not compete with the hydrogenation of $^*\text{H}_3\text{CO}$, as a result CH_3OH was the major product of CO₂ hydrogenation.¹¹⁷

In general, on a metal/oxide catalyst, several of the steps involved in CO₂ methanation are similar to the steps in the RWGS + CO-Hydro and Formate pathways for the formation of CH_3OH . The selectivity of CO₂ hydrogenation towards CH_3OH or CH_4 is primarily determined by the competition between the pathways of C-O bond scission and the hydrogenation of H_xCO species. To tune the selectivity of metal/oxide catalysts toward CH_4 rather than CH_3OH during CO₂ hydrogenation, metal/oxide interfaces should strengthen the binding for H_xCO species to facilitate the C-O bond scission.

5. Conclusions, Challenges and Future Opportunities

The chemical transformation of CO₂, however challenging because of its high thermochemical stability, is one of the potential ways to utilize CO₂ and to store energy in the form

of chemical energy. Recent progress made based on experimental and atomistic theoretical simulations have shown that CO₂ can be activated and subsequently hydrogenated to C1 carbon compounds on metal/oxide catalysts by utilizing multifunctional catalytic sites available at the metal/oxide interface.^{28,38,39} It has been shown that the binding strengths of key reaction intermediates at the metal/oxide interface determine the reaction pathways and selectivity in CO₂ hydrogenation reactions. Oxides are found to be able to promote CO₂ conversion to CO and/or CH₃OH on the supported Au, Pd, Cu catalysts at moderate temperatures and pressures.^{28-30,38} The combination of oxide with Pt tunes the selectivity toward the production of CO. When Ni^{118,121-123,126-128,143,147,148} or Ru^{124,130,131,134,136} particles are deposited on oxides, CO₂ → CH₄ conversion is selectively promoted. Furthermore, the additions of a secondary oxide or metal component, as well as the variations in metal or oxide particle size, also demonstrate the potential in tuning the binding strengths of key intermediates at the metal/oxide interface and consequently the selectivity for CO₂ hydrogenation.

The production of CO proceeds following the RWGS reaction via *HOCO intermediate and/or the direct C-O bond cleavage pathways (Figure 1), where the binding strength of CO₂ at the metal/oxide interface is likely the key to determine the preferred pathway.^{38,39,48,51} The CO selectivity is controlled by the CO binding energy. On both Pt/oxide and Cu/oxide systems, the RWGS is preferred and the CO binding is weak enough to enable facile desorption of *CO rather than its hydrogenation or dissociation under reaction conditions. For CH₃OH synthesis, two possible reaction routes are proposed (Figure 1).^{30,38,39,48,51,90,113,149,150} The first pathway is featured by the *CO intermediate from the RWGS reaction and is further hydrogenated to the final product CH₃OH; the other pathway is associated with the *HCOO intermediate formed by the initial step in CO₂ hydrogenation, which eventually produces CH₃OH via the C-O bond cleavage of the

*H₂COOH intermediate. Depending on the oxides used, the preferred reaction pathway can go from the Formate pathway on Cu/ZnO,^{30,47} to the RWGS + CO-Hydro pathway on Cu/CeO₂,²⁸ Cu/TiO₂ and Cu/ZrO₂,³⁸ where the Formate pathway is hindered for CH₃OH production due to the accumulation of strongly bound *HCOO species on the surface.³⁸ Thus ideally, the binding property of Cu/oxide catalysts should be tuned selectively, improving the stability of *CO₂, *CO, *HCO, and *H₂CO while destabilizing *HCOO and *H₃CO, to achieve a high selectivity toward CH₃OH. The CH₄ selectivity is associated with the Direct C-O bond cleavage, the RWGS + CO-Hydro or Formate pathways (Figure 1), where the Direct C-O bond cleavage is identified for Ru-based catalysts.^{39,117,124,143} The CH₄ selectivity is likely determined by the competition between the hydrogenation and C-O bond scission reactions of the *H_xCO intermediates.⁵¹ To achieve high CH₄ selectivity, the binding of *H_xCO species should be strong enough to facilitate the C-O bond cleavage. Overall, the formation of any of the three C1 products involves complex reaction network and catalyst. Therefore, the binding energy of a single intermediate, or a single descriptor, may not be adequate to well describe the catalytic performance; instead it is likely controlled by several key species that work in a cooperative way.

The selective conversion of CO₂ to C1 compounds at the metal/oxide interface of oxide-supported metal catalysts offers challenging research opportunities in the following areas:

(1) *Understanding reaction pathways for CO₂ conversion under realistic conditions.*

Although oxide-supported metal materials are widely studied as catalysts for CO₂ hydrogenation reaction,^{28,30,38,39,101,103} there are very limited comprehensive studies utilizing in-situ/operando experimental techniques and theoretical simulations at relevant experimental reaction conditions on the reaction mechanisms and key steps that control the activity and selectivity. Such atomic level understanding is essential

for the realization of a better catalyst by design. At present possible pathways for CO₂ conversion are proposed primarily based on DFT calculations.^{30,48,113-116} Future experimental measurements should focus on identifying the active reaction intermediates using in-situ spectroscopic techniques. Meanwhile, theoretical simulations should be performed at experimental reaction conditions using more realistic models, where the combination of KMC or microkinetic simulations with DFT calculations is necessary.^{38,51,113,115}

- (2) *Theoretical modeling of metal/oxide interfaces to minimize the gap between theory and experiments.* Current DFT calculations about CO₂ conversion, due to their intense computational demand, are often performed using small metal clusters of less than 1 nm.^{37,48,51,77} However, the average particle size in experimentally synthesized catalysts is typically larger and is of the order of several nm.^{39,73} Given that the particle size could play a major role in CO₂ conversion with different activity and selectivity,⁷⁵ future theoretical calculations should minimize this gap by using models relevant to experiments. In this aspect, the cooperation between the in-situ experimental measurements and theoretical calculations on both model surfaces and powder catalysts is essential to shed light on the possible reaction routes for the complex CO₂ conversion at the metal/oxide interface.
- (3) *Identifying descriptors of activity and selectivity for CO₂ conversion.* Despite numerous studies,^{38,48,51,90,113,116,117,149,150} those aiming to identify the descriptors for CO₂ conversion at the metal/oxide interface, especially for selectivity, are still limited. The descriptors for CO₂ hydrogenation to CO, CH₄ and CH₃OH on transition metal surfaces have been proposed using analytical approaches based on the DFT

microkinetic modeling.^{146,151} It was shown that the selectivity of catalytic CO₂ hydrogenation to CO and CH₄ on the transition metal catalysts could correlate well with the oxygen binding energy: weaker oxygen binding metals only converted CO₂ mildly to CO, whereas stronger oxygen binding metals enabled more deep conversion to CH₄.¹⁴⁶ Even though some progress has been made in identifying the descriptors of selectivity in CO₂ hydrogenation on transition metal surfaces, it remains a challenge in identifying such descriptors for catalytic systems that explicitly include nanoscale effects that are introduced via size and shape or oxide supports. Therefore, systematic theoretical studies, similar to what has been successfully done for other reactions such as oxygen reduction reaction (ORR),^{152,153} oxygen evolution reaction (OER)^{89,154} etc, should be carried out toward the identification of universal descriptors. The descriptor-based catalyst screening could potentially help find the next generation of highly active and selective catalysts for CO₂ transformation. The CO₂ hydrogenation is much more complex in kinetics than ORR and OER. Therefore, descriptors can be associated with a variety of reaction intermediates and the optimal performance may require the complex coordination between different descriptors.

- (4) *Tuning the activity and selectivity in CO₂ conversion using promoters.* The promoters can help tune the activity and selectivity of CO₂ hydrogenation.^{38,39,90} A promoter can be a defect site, a doped metal component, the adsorbed surface species (e.g. *O and *H), the deposited/grown nanostructures (e.g. oxide nanoparticles and thin films), etc. on the existing catalysts. The presence of such promoter is able to enhance the catalytic activity/selectivity of the CO₂ hydrogenation reaction. In particular, the effect of promoters on the currently working catalysts should be considered, e.g. bimetallic

alloys, defects, dopants and mixed oxide supports. The incorporation of promoters could lead to the discovery of selective and active catalysts. The future experimental studies, therefore, should focus on controlled synthesis of promoters incorporated into the oxide-supported metal catalysts. Complementary to the experimental studies, theoretical modeling should be performed on promising catalysts to elucidate how the the rate and selectivity controlling steps are affected by the promoters.

- (5) *Synthesizing catalysts with optimized metal/oxide interfaces.* The size of metal nanoparticles deposited on oxide supports, which most likely determines true nature of the metal/oxide interface, has been shown to influence the activity and selectivity of CO₂ hydrogenation.⁷⁵ For example, the CO selectivity of sol-immobilized Pd/ZnO catalysts increased from 40 to 80% with the PdZn particle size increasing from 3 to 7 nm at 250 °C and 20 bar.⁹⁹ In contrast, the intrinsic CO₂ methanation activity of Rh/ γ -Al₂O₃ catalysts with particle size in the range 3.6 to 15.4 nm did not appear to depend on particle size at temperatures between 185 to 200 °C, whereas at lower temperatures larger particles favored higher activity.¹⁵⁵ CO₂ hydrogenation studied using Co nanoparticles supported on SiO₂ showed an increase of the turnover frequency with increasing average particle size from 3-10 nm, however, the selectivity was independent of the particle size.¹⁵⁶ For CO₂ hydrogenation to CH₃OH on Au/ZnO catalysts, it was found that the activity increased while the selectivity decreased with decreasing particle size from ~3-10 nm. A similar trend in activity was observed on Cu/Al₂O₃ catalysts for CO₂ to CH₃OH transformation.⁷⁸ Thus, controlling particle morphology, size and dispersion may also help in optimizing the metal/oxide interface and consequently tuning selectivity. The optimized metal/oxide interface can be in

various forms. It is known that the selectivity for CO₂ hydrogenation to CO, CH₃OH and CH₄ depends on many factors: e. g. size, morphology and dispersion of deposited metal particles, nature of oxide supports, etc. For example, the selective transformation of CO₂ to CH₃OH on the Cu/oxide catalysts requires well dispersed subnanometer Cu particles deposited on oxide supports.^{78,117} Future research in this area should be directed at identifying an optimized combination of metal and oxide support that selectively promotes CO₂ to CO, CH₃OH or CH₄. Once such combination is identified, the selectivity could potentially be further enhanced via tuning the particle size and the dispersion of deposited metal nanoparticles. Furthermore, the activation of CO₂ typically occurs at the metal/oxide interface with a nearby oxygen vacancy in the oxide support.⁵¹ As a result, the reduced oxide supports heavily influence the activity and selectivity of CO₂ hydrogenation. Controlled synthesis of both metal particles and oxide substrates, using techniques such as chemical vapor deposition or atomic layer deposition, would play an important role in optimizing metal/oxide interfaces for selective CO₂ conversion.

- (6) *Investigating stability of catalysts under reaction conditions.* The morphological changes and chemical transformation of the catalysts during CO₂ hydrogenations have been reported for example on Cu/ZnO/Al₂O₃ catalysts.¹⁰¹ Another recent study has identified adsorbate-induced strong metal support interaction during CO₂ hydrogenation.¹⁵⁷ Any changes in the electronic and/or physical structures of the metal or oxide would modify the nature of metal/oxide interface and consequently the activity and selectivity of CO₂ conversion. Current experimental studies about the structure of the catalysts are mainly based on the ex-situ characterization techniques.

Future experimental studies should focus on in-situ monitoring of the dynamics of the catalyst structure and transformation. Such information would be extremely useful to design stable metal/oxide interface at the operating conditions of CO₂ hydrogenation.

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Table 1. Summary of reaction conditions with CO₂ conversion and selectivity on metal/oxide catalysts.

Catalyst	H ₂ :CO ₂ ratio	Temperature (°C)	Pressure (MPa)	Conversion (%)	Selectivity (%)		
					CO	CH ₃ OH	CH ₄
Cu/TiO ₂ ³⁸	3:1	220	0.1	0.54	83.6	13.8	
Cu/ZrO ₂ ³⁸	3:1	220	0.1	0.53	80.2	19.8	
Cu/ZrO ₂ ¹⁵⁸	3:1	220	1.7	6		67	
Cu/ZrO ₂ ¹⁵⁹	3:1	350	1.7	6.9		70	
Cu/Al ₂ O ₃ ¹⁶⁰	5:1	250	3	N/A	44.54	54.91	0.55
Cu/CeO ₂ /γ-Al ₂ O ₃ ¹⁶⁰	5:1	250	3	N/A	27.97	71.94	0.09
Cu/YDC//γ-Al ₂ O ₃ ¹⁶⁰	5:1	250	3	N/A	21.28	78.69	0.03
Cu/MnO _x /ZrO ₂ ¹⁵⁹	3:1	350	1.7	4.8		58	
Cu/CrO _x /ZrO ₂ ¹⁵⁹	3:1	350	1.7	4		87	
Cu/ZnO ⁹⁴	3:1	250	5	11.7	63.9	36.1	0
Cu/ZnO-rod ¹⁶¹	3:1	240	3	8		61.8	
Cu/ZnO-filament ¹⁶¹	3:1	240	3	16.5		78.2	
Cu/ZnO/Al ₂ O ₃ ¹⁶²	3:1	230	3	18.7		43	
Cu/ZnO ¹⁶³	2.8:1	170	5	5.2	85.4	11.9	
Cu/ZnO/Al ₂ O ₃ ¹⁶³	2.8:1	170	5	14.3	45.1	54.8	
Cu/ZnO/ZrO ₂ /Al ₂ O ₃ ¹⁶²	3:1	230	3	23.2		60.3	
Cu/ZnO/ZrO ₂ ¹⁶²	3:1	230	3	19.3		48.6	
Cu/ZnO/ZrO ₂ ¹⁶⁴	3:1	220	8	21		68	
Cu/Zn/ZrO ₂ -Mn-promoted ¹⁶⁵	3:1	280	10	16		91	
Cu/rod ZnO/Al ₂ O ₃ ¹⁶⁶	2.2:1	270	4.5	12.3		42.3	
Cu/plate ZnO/Al ₂ O ₃ ¹⁶⁶	2.2:1	270	4.5	10.9		72.7	
Pd/CeO ₂ ¹¹⁰	3:1	200	3	2.1	6.3	92.9	0.8
Pd/CeO ₂ ¹¹⁰	3:1	220	3	2.5	7.1	92.1	0.8
Pd/CeO ₂ ¹¹⁰	3:1	230	3	3.1	7.1	91.7	1.1
Pd/CeO ₂ ¹¹⁰	3:1	240	3	4.4	11.2	85.2	3.5
Pd/CeO ₂ ¹¹⁰	3:1	260	3	5.2	11	84.7	4.3
Pd/Al ₂ O ₃ ⁹⁴	3:1	250	5	3.4	51.5	29.9	18.6
Pd/Cr ₂ O ₃ ⁹⁴	3:1	250	5	2.1	65	22.4	12.6
Pd/β-Ga ₂ O ₃ ¹⁶⁷	3:1	250	3	0.86	48	52	0
Pd/Ga ₂ O ₃ ⁹⁴	3:1	250	5	19.6	47.9	51.5	0.5
Pd/rod Ga ₂ O ₃ ⁴¹	3:1	250	5	11		41.3	

Pd/plate Ga ₂ O ₃ ⁴¹	3:1	250	5	17.3		51.6	
Pd/SiO ₂ ⁹⁴	3:1	250	5	0.05	0	100	0
Pd/TiO ₂ ⁹⁴	3:1	250	5	15.5	95.9	3.9	0.2
Pd/ZnO ⁹⁴	3:1	250	5	13.8	62.3	37.5	0.1
Pd/ZnO (1% Pd), SI ⁹⁹ ; SI = sol immobilization,	3:1	250	2	1.7	24	76	
Pd/ZnO (1% Pd), IM ⁹⁹ ; IM = impregnation	3:1	250	2	3.2	78	22	
Pd/ZnO (5% Pd), SI	3:1	250	2	10.7	39	60	
Pd/ZnO (5% Pd), IM	3:1	250	2	8.7	99	1	
Pd/ZrO ₂ ⁹⁴	3:1	250	5	0.4	81.7	4.3	14
Pd/Al ₂ O ₃ ¹⁰⁸	4:1	275	0.95	1.2		5.4	
Pd/Al ₂ O ₃ ¹⁰⁸	2:1	275	0.95	0.23		49.1	
Pd/TiO ₂ ¹⁰⁸	4:1	275	0.95	3.9		1.98	
Pd/SiO ₂ ¹⁰⁸	4:1	275	0.95	0.8		9.5	
Pd/SiO ₂ ¹⁰⁸	2:1	275	0.95	0.7		89.0	
Pd/MgO ¹⁰⁸	4:1	275	0.95	0.77		7.8	
Pd/MgO ¹⁰⁸	2:1	275	0.95	0.65		96.5	
Pd/Al ₂ O ₃ -fresh ⁵⁶	1:1	240	0.1	30			22
Pd/Al ₂ O ₃ -aged ⁵⁶	1:1	240	0.1	30			39
Pd/La ₂ O ₃ /Al ₂ O ₃ ⁵⁶	1:1	240	0.1	30			30
Pd/PrO ₂ /Al ₂ O ₃ ⁵⁶	1:1	240	0.1	30			24
Pd/CeO ₂ (5)/Al ₂ O ₃ ⁵⁶	1:1	240	0.1	30			13
Pd/CeO ₂ (10)/Al ₂ O ₃ ⁵⁶	1:1	240	0.1	30			19
Pd/SiO ₂ ⁹³	4:1	450	0.1	40.8	89.6		10.4
Au/ZrO ₂ ³¹	3:1	220	0.5	5.3		5	
Au/ZrO ₂ ³¹	3:1	240	0.5	9.3		3.4	
Au/ZnO ³¹	3:1	220	0.5	0.2		56.2	
Au/ZnO ³¹	3:1	240	0.5	0.4		50.6	
Au/ZnO/ZrO ₂ ¹⁶⁴	3:1	220	8	1.5		100	
Au/Al ₂ O ₃ ³¹	3:1	220	0.5	2		1.5	
Au/Al ₂ O ₃ ³¹	3:1	240	0.5	3.7		0.4	
Pt/SiO ₂ ⁵¹	2:1	553	0.1	2.03	100		0
Pt/TiO ₂ ⁵¹	2:1	553	0.1	2.99	99.22		0.78
Ni/SiO ₂ ⁹³	4:1	450	0.1	36.8	18.2		81.8
Ni/ γ -Al ₂ O ₃ ¹²⁰	3.5	350	0.1	~75			100

Ni/Al ₂ O ₃ ¹²³	4:1	250	0.1	39			97
Ni/SiO ₂ ¹²⁷	4:1	350	0.1	27.6	11.6		85.5
Ni/SiO ₂ ¹¹⁸	4:1	300	0.1	42.4	3.4		96.6
0.5%Ni/SiO ₂ ¹¹⁹	N/A	350	0.1	~10	~40		~60
10%Ni/SiO ₂ ¹¹⁹	N/A	350	0.1	~10	~10		~90
Ni/CeO ₂ ¹²⁵	5:1	450	0.1	~80			~100
Ni/CeO ₂ ¹²⁶	4.6	340	0.1	91.1			100
Ni/ZrO ₂ ¹²⁸	12.5	377	0.1	~100			~100
Ni/Ce _x Zr _{1-x} O ₂ ¹²⁹	4:1	350	0.1	71.5	0.9		98.5
Ni/CeO ₂ /ZrO ₂ -sol-gel ¹²⁷	4:1	350	0.1	67.9	1.4		98.4
Ni/CeO ₂ /ZrO ₂ -imp ¹²⁷	4:1	350	0.1	25.4	14.5		84.7
Re/ZrO ₂ ⁸⁸	N/A	160	1	N/A		73.2	25.5
Re/Nb ₂ O ₅ ⁸⁸	N/A	220	1	N/A		52.0	37.6
Re/MgO ⁸⁸	N/A	260	1	N/A		17.5	80.6
Re/SiO ₂ ⁸⁸	N/A	180	1	N/A		22.6	74.7
Re/Zeolon ⁸⁸	N/A	220	1	N/A		18.2	75.7
Rh/ γ -Al ₂ O ₃ ¹⁴¹	4:1	200	0.1	~98			~100
Rh/SiO ₂ ⁷⁴	3:1	200	5	0.52	88.1	6.8	5.1
Rh/TiO ₂ ¹⁶⁸	1:1	270	2	7.89	14.5	0.80	72.7
Rh/TiO ₂ ⁵⁷	3:1	240	1	N/A		60.7	32.4
Rh/ZrO ₂ ⁵⁷	3:1	240	1	N/A			99.9
Rh/MgO ⁵⁷	3:1	240	1	N/A		1	99
Rh/Nb ₂ O ₅ ⁵⁷	3:1	260	1	N/A			100
Ru/TiO ₂ ¹³⁷	4:1	160	0.1	N/A			100
Ru _{0.01} Ce _{0.99} O ₂ ¹³¹	4:1	500	N/A	16			90
Ru/CeO ₂ ¹⁴⁰	4:1	250	0.1	92.7			
Ru/Al ₂ O ₃ ¹³³	~5:1	190	0.1	N/A			42
Ru/CeO ₂ /Al ₂ O ₃ ¹³⁰	4:1	250	0.1	~20			~100
Ag/ZnO/ZrO ₂ ¹⁶⁴	3:1	220	8	2		97	
Co/CeO ₂ ⁷⁶	3:1	300	0.1	3.8	39.4		
Co/ γ -Al ₂ O ₃ ⁷⁶	3:1	300	0.1	3.8	67.0		
Fe/TiO ₂ ¹⁶⁸	1:1	270	2	2.65	73	0.0	11.6
Mg/SiO ₂ ⁹³	4:1	450	0.1	0.8	89.7		10.3
Mo/ γ -Al ₂ O ₃ ¹⁶⁹	1:1	600	1	34.2	97		
Cu-Ni/ γ -Al ₂ O ₃ ¹⁷⁰	1:1	600	0.1	28.7	79.7		20.3
Pd-Fe/SiO ₂ ⁹³	4:1	450	0.1	44.7	97.2		2.8

Pd-Mg/SiO ₂ ⁹³	4:1	450	0.1	59.2	4.7		95.3
Pd-Li/SiO ₂ ⁹³	4:1	450	0.1	42.6	11.5		88.5
Pd-Ni/SiO ₂ ⁹³	4:1	450	0.1	50.5	11.0		89
PtCo/CeO ₂ ⁷⁶	3:1	300	0.1	3.3	71		
PtCo/ γ -Al ₂ O ₃ ⁷⁶	3:1	300	0.1	5.1	89.4		
PtCo/TiO ₂ ³⁹	2:1	300	0.1	8.2	~99		~1
PtCo/CeO ₂ ³⁹	2:1	300	0.1	9.1	~92		~8
PtCo/ZrO ₂ ³⁹	2:1	300	0.1	7.8	~89		~11
15Ni-5Co/Al ₂ O ₃ -CeO ₂ ¹⁴⁷	~19	300	2	N/A			100
15Ni-5Co/Zr _{0.75} Ce _{0.25} O ₂ ¹⁴⁷	~19	300	2	N/A			99
15Ni-5Co/Al ₂ O ₃ -ZrO ₂ ¹⁴⁷	~19	300	2	N/A			98
Fe-Mo/ γ -Al ₂ O ₃ ¹⁷¹	1:1	600	1	~45	~100		
Rh-Fe/TiO ₂ ¹⁶⁸	1:1	270	2	9.16	28.4	1.26	57.2
Co ₄ N/ γ -Al ₂ O ₃ ¹⁷²	~19	300	1.5	~98			~98

Table 2. First-order consumption rate constants for CO₂ conversion by H₂ normalized by catalyst weight and CO uptake values. For bimetallic catalysts, the metal loading corresponds to a Ni/Pt (Co/Pt or Ni/Pd) atomic ratio of 3 to 1. Reproduced with permission from ref ⁷³. Copyright 2013 Elsevier.

Catalysts	Metal loading (wt%)	CO uptake (μ mol g ⁻¹ cat)	k _r (10 ⁻³ min ⁻¹ g ⁻¹ cat)	Normalized k _r (10 ⁻³ min ⁻¹ mol CO ⁻¹)	CO/CH ₄ ratio at 10% conversion
PtNi/CeO ₂	1.7% Pt, 1.5% Ni	35.4	11.43	0.323	60.7
Pt/CeO ₂	1.7% Pt	14.1	2.88	0.204	150.7
Ni/CeO ₂	1.5% Ni	11.2	9.26	0.827	27.5
PdNi/CeO ₂	0.91% Pd, 1.5% Ni	36.0	12.51	0.347	31.9
PtCo/CeO ₂	1.7% Pt, 1.5% Co	37.2	6.29	0.169	259.4
Co/CeO ₂	1.5% Co	4.0	3.56	0.889	43.0
PtNi/ γ -Al ₂ O ₃	1.7% Pt, 1.5% Ni	44.4	4.18	0.094	62.1
Pt/ γ -Al ₂ O ₃	1.7% Pt	45.0	1.62	0.036	200.5
Ni/ γ -Al ₂ O ₃	1.5% Ni	14.4	2.65	0.184	40.1
PdNi/ γ -Al ₂ O ₃	0.91% Pd, 1.5% Ni	22.3	2.93	0.131	46.5
PtCo/ γ -Al ₂ O ₃	1.7% Pt, 1.5% Co	35.0	2.51	0.072	245.8
Co/ γ -Al ₂ O ₃	1.5% Co	6.5	2.12	0.326	73.9

Figure 1. Possible reaction pathways of CO₂ hydrogenation to CO, CH₃OH and CH₄. *(X) indicates adsorbed species.

Figure 2. Rate of turn over frequency (TOF) change ($d(TOF)/dt$) for both reaction pathways as a function of wt % Rh measured at 200 °C and feed ratio of (a) 0.25CO₂:H₂ and (b) 10CO₂:H₂. Rates of change for the RWGS TOF are shown in blue points and methanation TOF in red points. The linear fits to the data are added for visual clarity. Reproduced with permission from ref ⁷⁵. Copyright 2015 American Chemical Society.

Figure 3. Adsorption geometry of CO₂ on (a) Pt/SiO₂ and (b) Pt/TiO₂. Reproduced with permission from ref ⁵¹. Copyright 2016 Elsevier.

Figure 4. Fourier transform infrared spectroscopy (FTIR) spectra during the reaction of (a) CO₂ reduction by H₂ and (b) formic acid and methanol on PtCo/CeO₂ and PtCo/TiO₂ catalysts. Reproduced with permission from ref ³⁹. Copyright 2016 Wiley.

Figure 5. Methanol activities as a function of the Zn coverages at the Cu nanoparticles of a Cu/ZnO/Al₂O₃ methanol catalyst. (A) Temperature ramp and exit methanol concentrations after pretreatment as a function of time and temperature in a CO/CO₂/H₂ = 18/18/64 gas mixture at ambient pressure and space velocity (SV) = 30 to 33 NL/g/h. (B) Relative measured methanol exit concentrations at 130 °C (temperature ramp-down) as a function of postreaction values of θ_{Zn} . The varying values of θ_{Zn} are obtained by pretreatments in H₂ at different pressures and temperatures prior to activity tests. The dashed line is a second-order polynomial fit to the data. Reproduced with permission from ref ²⁹. Copyright 2016 AAAS.

Figure 6. Transformation from graphitic-like ZnO_x to the wurtzite structure. A–C) aberration-corrected high resolution transmission electron microscopy (HRTEM) images of $\text{Cu/ZnO/Al}_2\text{O}_3$ after different times of electron beam exposure. For improved assignment of the lattice fringes, the particle in (C) was slightly tilted towards a zone axis of ZnO by 128. The colors indicate the different state during phase transformation. The red-colored sites correspond to Cu particles. Yellow indicates graphitic-like ZnO_x . Green highlights the rock salt ZnO and blue regions correspond to the wurtzite ZnO structure. Reproduced with permission from ref ¹⁰¹. Copyright 2015 Wiley.

Figure 7. A) Rate for the conversion of CO_2 to methanol on Cu(111) as a function of the fraction of the metal surface covered by zinc oxide. Reaction conditions: T (temperature) = 525, 550, or 575 K; P_{H_2} (partial pressure of H_2) = 4.5 atm; P_{CO_2} (partial pressure of CO_2) = 0.5 atm. (B) (Bottom trace) Rates for the production of methanol on Cu/ZnO(0001̄) surfaces at 550 K, P_{CO_2} = 0.5 atm, P_{H_2} = 4.5 atm. (Top trace) Rates measured after depositing 0.4 ML of ZnO on the Cu/ZnO(0001̄) surfaces. Reproduced with permission from ref ⁴⁷. Copyright 2017 AAAS.

Figure 8. Kinetics and scanning tunneling microscope (STM) studies. (A) Arrhenius plot for methanol synthesis on Cu(111), a 0.2 ML of Cu on ZnO(000 $\bar{1}$), a Cu(111) surface covered 20% by ceria, and a 0.1 ML of Cu on a TiO₂(110) surface precovered 15% with ceria. In a batch reactor, the catalysts were exposed to 0.5 atm of CO₂ and 4.5 atm of H₂. The reported values are steady-state rates measured at 600, 575, 550, 525, and 500 K. (B) STM image of a CeO_x/Cu(111) surface as prepared. (C) In situ STM image taken during exposure to 1.5 torr of H₂ at 300 K after 26 hours of reaction. Scanning parameters: 0.3 nA, 1.0 V. Reproduced with permission from ref ²⁸. Copyright 2014 AAAS.

Figure 9. CO₂ hydrogenation reaction on (a) 5% Pd/ZnO by impregnation and (b) 5% Pd/ZnO catalyst prepared by sol immobilization method. The catalysts were pre-reduced prior to the reaction at 400 °C under flow of H₂. The reaction was carried out at 250 °C at 20 bar with 1CO₂: 3H₂ at 30 ml/min. Reproduced with permission from ref ⁹⁹. Copyright 2016 Elsevier.

Figure 10. Au mass-normalized formation rates and selectivity for CH₃OH formation during CO₂ hydrogenation at 220–240 °C and 5 bar in 25% CO₂/rest H₂ over Au catalysts supported on different metal oxides after calcination in 20 NmLmin⁻¹ of 1% O₂/N₂ at 400 °C for 1 h (O400). Error bars represent the standard deviation from several repeat measurements. Reproduced with permission from ref ³¹. Copyright 2015 Wiley.

Figure 11. DFT optimized geometries. (a) $^*\text{CO}_2$, (b) $^*\text{CO}$, (c) $^*\text{HOCO}$, (d) $^*\text{HCOO}$, (e) $^*\text{HCO}$, (f) $^*\text{H}_2\text{CO}$, (g) $^*\text{H}_3\text{CO}$, (h) $^*\text{HCOH}$, (i) $^*\text{H}_2\text{COH}$, (j) $^*\text{HCOOH}$, (k) $^*\text{H}_2\text{COOH}$ (l) $^*\text{CH}_3\text{OH}$, (m) $^*\text{OH}$ and (n) $^*\text{H}_2\text{O}$ on $\text{Ti}_3\text{O}_6\text{H}_6/\text{Cu}(111)$. Cu: reddish-orange, Ti: blue, O: red, C: grey and H: white. Reproduced with permission from ref ³⁸. Copyright 2016 American Chemical Society.

Figure 12. Potential energy diagrams for the hydrogenation of $\text{CO}_2(\text{g})$ to $\text{CH}_3\text{OH}(\text{g})$ on (a) $\text{Ti}_3\text{O}_6\text{H}_6/\text{Cu}(111)$ and (b) $\text{Zr}_3\text{O}_6\text{H}_6/\text{Cu}(111)$ via the RWGS + CO-Hydro and Formate pathways. “TS” corresponds to the transition state. Reproduced with permission from ref ³⁸. Copyright 2016 American Chemical Society.

Figure 13. Calculated reaction pathways of CO₂ reduction to CH₃OH, CO and CH₄ on Al₂O₃ supported Cu₄ clusters. To improve legibility, “H₂” was omitted from the labels after the initial state. Reproduced with permission from ref ¹¹⁷. Copyright 2015 American Chemical Society.

Figure 14. Potential energy diagrams for the CO, and CH₄ synthesis via the RWGS + CO-Hydro pathways on model hydroxylated Ti₃O₆/PtCo(111) (a) and Zr₃O₆/PtCo(111) (b) surfaces. Reproduced with permission from ref ³⁹. Copyright 2016 Wiley.

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