

Review

Hydrogenation of Carbon Dioxide to Methanol over Non-Noble Catalysts: A State-of-the-Art Review

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Abstract: The malignant environmental changes caused by the ever-increasing amount of anthropogenic CO₂ emissions have been particularly prominent in recent years. To achieve carbon mitigation and carbon neutrality, CO₂ hydrogenation to methanol is regarded as a promising and sustainable route. However, the development of catalysts with exceptional performance and the establishment of a clear structure–activity relationship remain formidable challenges. Considering the lack of a state-of-the-art review on the catalytic progress of CO₂ hydrogenation to methanol over non-noble catalysts, we conducted a detailed review in terms of the thermodynamic analysis, catalytic development, and reaction mechanism. In this work, we mainly reviewed the latest research progress of different catalysts including Cu-based, In₂O₃-based, bimetallic, solid solution, and other catalysts. Meanwhile, we summarized the effects of the support materials, promoters, and preparation methods on the catalytic performance. In addition, we also summarized the possible reaction mechanisms of direct hydrogenation of CO₂ to methanol. Overall, this work would be of importance for the researchers to obtain a comprehensive understanding of the design and development of efficient catalysts for CO₂ hydrogenation to methanol.

Keywords: CO₂ hydrogenation; methanol; progress; non-noble catalysts; mechanism



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1. Introduction

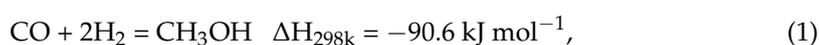
Fossil fuels such as coal, oil, and natural gas have been consumed on an unprecedented scale to meet the increasing energy demands, which have caused massive CO₂ emissions in the environment. To date, global anthropogenic CO₂ emissions have reached 37 Gton CO₂ per year, which can cause a series of environmental problems, such as serious greenhouse effects, ocean acidification, and glacier melting [1–3]. Therefore, the control and mitigation of CO₂ emissions in the atmosphere has become an urgent task to protect the environment. Carbon capture, utilization, and storage (CCUS) strategies have been proposed to reduce CO₂ emissions, which mainly can be divided into two categories: carbon capture and storage (CCS) and carbon capture and utilization (CCU) [4,5]. Compared with CCS technology, CCU technology can convert the waste CO₂ into various value-added liquid fuels and platform chemicals, such as methanol, carbon monoxide, methane, dimethyl ether, and polycarbon, and is considered as a potential and sustainable pathway to achieve carbon neutrality [6–8]. Among various products, methanol is an important platform compound, which can be further converted into low-carbon olefins, aromatics, gasoline, and other high value-added chemicals and fuels [9–11]. Therefore, CO₂ hydrogenation to methanol using green hydrogen has received wide attention due to its great economic value and industrial application prospects.

For CO₂ hydrogenation to methanol, methanol synthesis reaction and reverse water-gas-shift (RWGS) reaction are two main competitive reactions. CO₂ is firstly converted to the intermediate CO, which is hydrogenated to form *H₃CO and further hydrogenated to methanol [12–14]. From the perspective of thermodynamics, the methanol synthesis reaction is exothermic, and the volume of the molecules is reduced, so high-pressure and low-temperature reaction conditions are conducive [2,15]. At present, thermocatalytic, photocatalytic, and electrocatalytic technologies have been successfully applied in the CO₂ hydrogenation to methanol. However, the thermocatalytic technology has the most promising prospect for industrialization due to higher CO₂ conversion and fewer by-products [16]. Up to now, remarkable progress has been made for the thermocatalytic conversion of CO₂ to methanol in terms of catalyst development and mechanism study. Generally, the catalysts for the hydrogenation of CO₂ to methanol can be roughly divided into Cu-based catalysts, noble metal-based catalysts, and mixed oxide catalysts [17–20]. Cu-based catalysts are the most widely studied catalysts, but they are prone to deactivation under reaction conditions attributed to the Ostwald ripening effect and particle migration, which seriously reduces the methanol yield [21–24]. Furthermore, noble metal-based catalysts exhibit superior stability and resilience against sintering and poisoning, making them a viable alternative to Cu-based catalysts. However, the methanol selectivity of these catalysts is relatively low, their costs are relatively high, and the product distribution is difficult to regulate due to their weak binding affinity with CO₂ [25–27]. In recent years, indium oxide (In₂O₃) has been developed for the hydrogenation of CO₂ to methanol, and the oxygen vacancy on its surface plays an important role in the high selectivity and activity of methanol. However, the CO₂ conversion of the indium oxide-based catalyst is low. Therefore, it is of importance to add additives to enhance the ability to activate H₂ and generate oxygen vacancy [28–30]. In addition, some bimetallic catalysts and other novel catalysts have also been used in the hydrogenation of CO₂ to methanol [31–33].

This work is mainly divided into four sections: (1) the challenges in thermodynamics are proposed firstly. (2) The progress in conventional Cu-based catalysts with different supports, promoters, and preparation methods is deeply discussed. Additionally, an overview of the advancements of other non-noble catalysts, such as In₂O₃-based catalysts, bimetallic catalysts, and solid solution catalysts, is also provided. (3) The possible reaction mechanisms for the hydrogenation of CO₂ to methanol are summarized in detail. (4) The summary and prospects are proposed to provide comprehensive guidelines for the design and development of efficient catalysts.

2. Thermodynamic Analysis

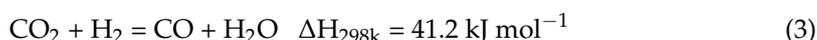
Large-scale commercial methanol production is mainly derived from syngas. Compared with CO as a raw material (Equation (1)), the conversion and activation of CO₂ generally require numerous energy due to its highly stable molecule and low Gibbs free energy (Equation (2)) [34]. Therefore, high temperature is beneficial for promoting CO₂ activation and accelerating the reaction rate. However, it should be noted that different from CO hydrogenation, the reverse water gas shift (RWGS) reaction (Equation (3)) generally competes with CO₂ hydrogenation reactions, where the RWGS reaction is endothermic, whereas the CO₂ hydrogenation reaction is exothermic [35,36]. Therefore, as shown in Equation (2), the operating conditions of low temperatures and high pressures are favorable. In addition, unlike CO hydrogenation, CO₂ hydrogenation generally consumes more H₂ and generates more water due to higher oxygen content. The presence of water accelerates the sintering of the active site in the catalyst, resulting in catalyst deactivation and the reduction of methanol production in subsequent steps [37–39]. Therefore, it is of importance to design an efficient catalytic system to promote CO₂ activation and suppress the poisonousness of the by-products for the catalysts at suitable temperatures and pressures [40]. The CO hydrogenation to methanol reaction is as follows:



The CO₂ hydrogenation to methanol reaction is as follows:



The RWGS reaction is as follows:



3. Catalyst Development of CO₂ Hydrogenation to Methanol

3.1. Cu-Based Catalyst

In the 1940s, it was possible to synthesize methanol with CO₂ as the only raw feedstock, and the relevant research report on hydrogenation of CO₂ to methanol first appeared. In the 1960s, the Cu-ZnO type catalyst used for methanol industrial production was reported by Imperial Chemical Industries [41,42]. Since then, modifying Cu-ZnO catalysts by introducing different supports and promoters and optimizing the preparation methods has received more attention and is extensively studied. The catalytic performances of some of the latest Cu-based catalysts are summarized in Table 1.

Table 1. Summary of Cu-based catalysts for the CO₂ hydrogenation to methanol.

Catalyst	T (°C)	P (MPa)	Space Velocity a	H ₂ /CO ₂ Ratio	Conv. (%)	Sel. (%)	STY c	Ref.
CuO/ZnO-400	260	3	(G) 12,000	3	18.5	41.7	0.3	[24]
CZA-r@CZM	240	3	(G) 32,000	3	11.7	73.0	0.730	[25]
CZZ@Al-TUD-1	280	2	(G) 10,000	3	10	20.3	0.180	[43]
10NG-CZA	200	3	N.A.	3	8.2	84	N.A.	[44]
aCZZ-LDH	250	3	(G) 2000	3	4.9	78.3	0.037	[45]
CuZnO@rGO	260	1	20,000 b	3	N.A.	~100	0.007	[46]
15Cu/6.4ZnO/AlFum MOF	230	5	(G) 10,000	3	45.6	3.48	0.057	[47]
CuZn10Zr	220	3	(W) 6000	3	14.0	54.4	0.65	[48]
30Cu-ZZ _{66/34}	280	5	(G) 25,000	N.A.	19.6	50	0.725	[49]
CuZnGa	270	3	N.A.	3	15.9	N.A.	0.136	[50]
Cu ₅ Sr ₃ Ti ₂ O _x	220	2	(G) 12,000	3	1.7	62.8	N.A.	[51]
CM-300	220	3	(W) 15,600	3	5.0	85	0.144	[52]
Cu _{0.3} Ce _{0.3} Zr _{0.7}	240	3	N.A.	3	4.1	55.3	0.192	[53]
Cu ₃ /LTH	250	3	(G) 3000	3	23.0	73.6	0.145	[54]
3Mg-C-ZZ SSC	320	3	(G) 2000	3	12.9	81.5	N.A.	[55]

a (W) = WHSV, mL·g_{cat}⁻¹·h⁻¹, (G) = GHSV, h⁻¹; b L_{CO₂}·g_{cat}⁻¹·h⁻¹; c STY (g_{MeOH}·g_{cat}⁻¹·h⁻¹); N.A.: Not available.

3.1.1. Supports

The type of support has a great influence on the physical properties of the catalyst, and the activity of the catalyst for CO₂ hydrogenation to methanol is proportional to the surface area of Cu. In Cu-based catalysts, the support with high specific surface area can disperse the active components well and prevent the catalyst from deactivation due to sintering [35]. The traditional supports primarily include Al₂O₃ [56–58], ZnO [59,60], and ZrO₂ [61–63]. However, the water generated by the side reaction can accelerate the sintering of the active sites, which leads to the catalyst being relatively easy to deactivate, and Al₂O₃ has hydrophilic properties, so the development of other carriers to make up for this is necessary.

Some emerging supports have been gradually successfully developed, such as mesoporous aluminosilicate support, Mg-Al layered double hydroxide (LDH) [43,45]. For example, Kubovics et al. [46] synthesized a novel Cu-ZnO multicomponent catalyst as a 3D aerogel, using reduced graphene oxide (rGO) as a support. It was found that the addition of rGO to the catalytic system significantly increased the methanol production rate by fourfold compared to pristine Cu-ZnO NPs at 220 °C. This was mainly because the intrinsic activity of Cu was enhanced due to the strain imposed at the ZnO interphase, causing a misfit at the contact surface. Recently, MOF and zeolite have been potential supports due to their abundant pore structure and tremendous surface area. Generally, MOF and zeolite are beneficial for confining the growth of Cu particles, obtaining high Cu dispersion, maximizing interface sites, and strengthening their interaction with Cu by regulating electron transfer [64]. For example, Duma et al. [47] prepared Cu-ZnO catalysts supported on an aluminum fumarate metal-organic framework (AlFum MOF) with high surface area and good porosity, which further promoted the homogenous, uniform dispersion of Cu and Zn active sites. As a result, the catalysts exhibited good activity, with a doubling loading of Cu and Zn over the AlFum MOF. Therefore, the CO₂ conversion increases from 10.8 to 45.6%, and the methanol production increases from 0.034 to 0.056 g_{MeOH}·g_{cat}⁻¹·h⁻¹. SiO₂ is widely used as a support for various heterogeneous catalysts due to its low price and high specific surface area. For instance, Shawabkeh et al. [65] studied the CO₂ adsorption on SiO₂ at different Cu loading to investigate the CO₂ interaction with the surface (mainly oxygen atom) via the sol-gel method from both experimental and theoretical points of view. The results suggested that an increase in the amount of CuO on the surface of SiO₂ improved the basicity of the adsorbent, resulting in more CO₂ uptake. Dalia Santa Cruz-Navarro et al. [66] synthesized Cu-based catalysts with ammonium salt and acidic ZSM-5 zeolite as support using the liquid phase (LPIE) and solid state (SSIE) ion exchange methods and compared their catalytic performances. The results showed that the catalyst prepared using the SSIE method had higher copper loading than the catalyst prepared using the LPIE method, which was attributed to the SSIE method promoting the diffusion of the volatile copper metal complexes through the internal channels of molecular sieves.

3.1.2. Promoters

The addition of promoters can change the acidity and alkalinity of the catalyst surface, enhance the interaction between the active components, form more defect sites on the surface, and change the product composition distribution. Cu-ZnO catalysts with various promoters have received wide attention. ZrO₂ and Ga₂O₃ are considered important catalysts for the modification of Cu-ZnO [67]. For example, Sun et al. [48] designed Cu-ZnO catalysts with different molar ratios of ZrO₂ using the co-current precipitation method and controlled the pH to regulate the distributions of Cu⁰ and Cu⁺ species. It was found that the CuZn10Zr (10 mol% ZrO₂) catalyst had the highest space-time yield to methanol with 0.65 g_{MeOH}·g_{cat}⁻¹·h⁻¹ under the reaction conditions of 220 °C and 3 MPa. Their research showed that the addition of an appropriate amount of ZrO₂ was beneficial to promoting the dispersion of Cu to provide more active sites for H₂ and CO₂ adsorption and activation. Cored et al. [68] studied two CuO/ZnO/Ga₂O₃ catalysts prepared using the co-precipitation method and compared the promoting effect of Ga³⁺-doped in the wurtzite ZnO lattice of a Cu/ZnO/Ga₂O₃ catalyst with that of a zinc gallate (ZnGa₂O₄) phase. The study indicated that Ga³⁺-doped ZnO has been considered as a more efficient promoter than ZnGa₂O₄ owing to the presence of surface vacancies with loosely bounded electrons, increasing the conductivity of the material and enhancing methanol selectivity versus CO formation. Among the different interfaces between the samples, the interaction of Cu and Ga is more favorable in the Ga³⁺-doped ZnO sample by increasing the number of surface basic centers, which is important for the stabilization of intermediate species. Sang et al. [69] systematically studied activation mechanisms of CO₂ on the Ga-modified Cu surface (Figure 1) with different forms (Cu, Cu₈Ga₁, Cu₆Ga₃, and Ga₂O₃@Cu) using

density functional theory (DFT) calculations combining the thermodynamics with chemical kinetics. DFT results and the Mulliken atomic charge of CO_2 indicated that CO_2 was transformed into chemisorbed CO_2^* with a lower reaction energy barrier, and two oxygen atoms of CO_2 obtained different charges at the interface between the metal surface and Ga_2O_3 , suggesting that the charge imbalance of the CO_2 molecule was more favorable to the activation of $\text{C}=\text{O}$. For Cu, Cu₈Ga₁, and Cu₆Ga₃ catalysts, CO_2 behaved as physical adsorption, and the oxygen atoms of CO_2 gained the same charges.

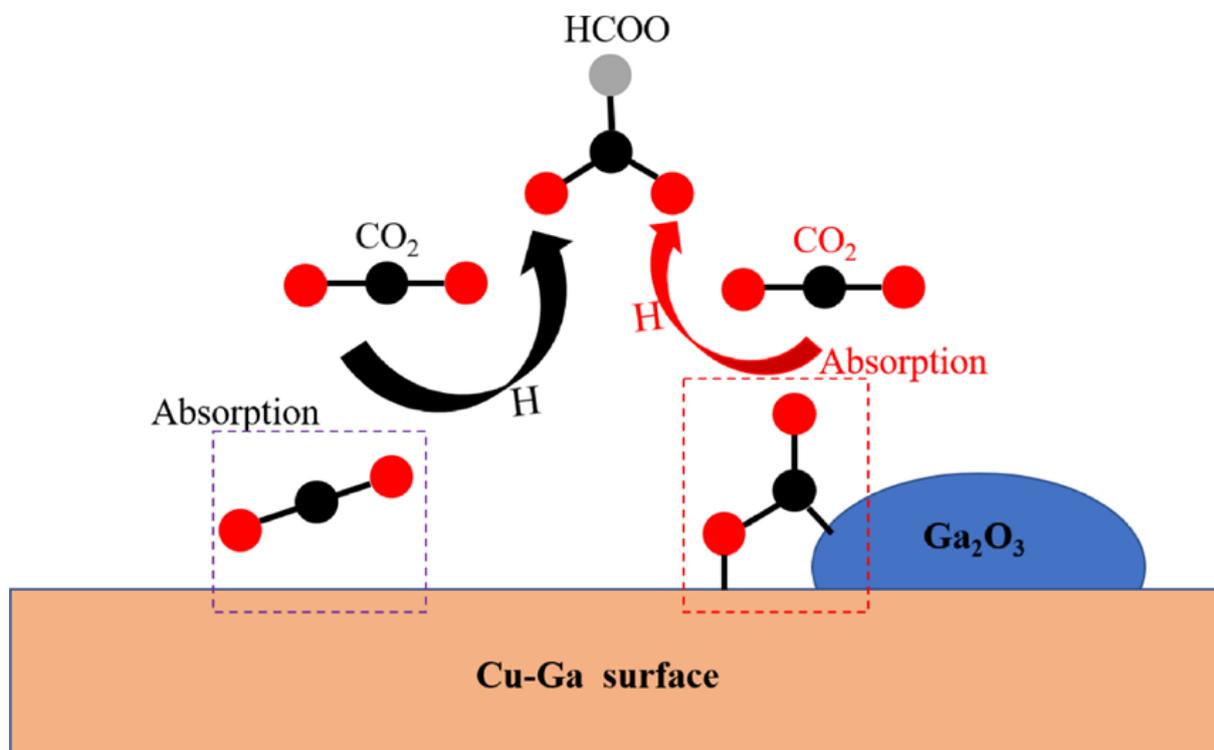


Figure 1. CO_2 activation mechanism on Ga-modified Cu-based catalysts [69].

3.1.3. Preparation Methods

It is well known that the preparation methods of catalysts have significant influences on the catalytic performances, which mainly include coprecipitation [22,23,49], impregnation [47,70,71], and sol-gel [65,70,72]. However, to further enhance the activity, selectivity, water tolerance, and stability of Cu-based catalysts, some emerging methods have appeared in recent reports [25,46,50,73,74]. For example, metal nanoparticles (NPs) attracted growing interest due to their outstanding applications in numerous fields, but so far, no large-scale synthesis of CuNPs has been reported using the disproportionation route and the reductive pathway. Ouyang et al. [75] report a method for obtaining Cu (0) nanoparticles (CuNPs) from readily available organocopper reagents (Figure 2). The method can be used to synthesize spherical CuNPs with excellent control of their size and shape on the decigram scale. Overall, the study offers many prospects for the rapidly developing field of copper plasmonic catalysis. Kubovics et al. [46] prepared its precursor CuOZnO NPs via conventional chemistry and designed rGO aerogels-supported CuZnO NPs with water repulsion as efficient 3D catalysts. Then, the supercritical CO_2 was applied for the nano-structuration and the fabrication of 3D devices with macro- and mesoporosity, and the targeted sample was obtained through H_2 reduction.

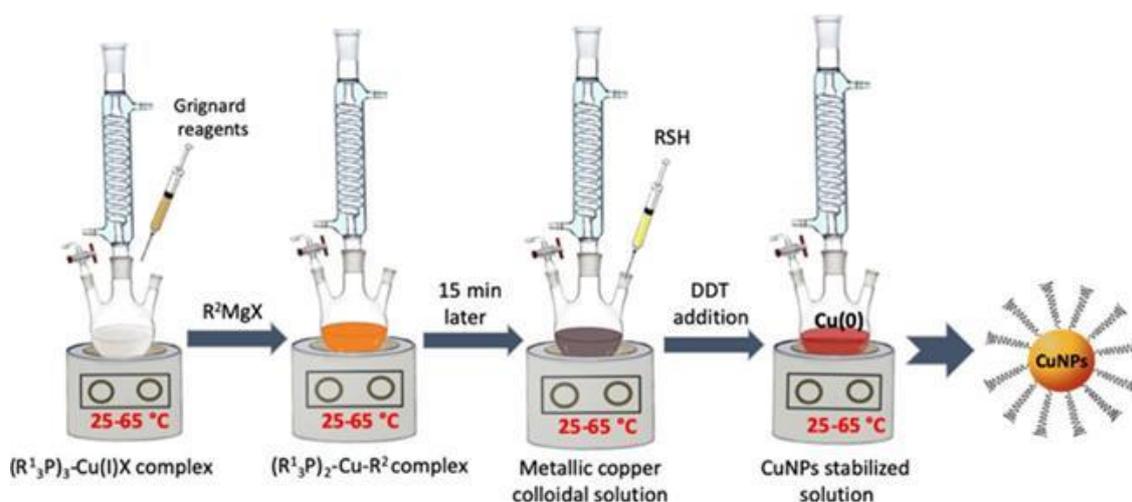


Figure 2. Schematic representation of our experimental onepot procedure [75].

Santa et al. [66] studied the effect of the synthesis method on the physicochemical properties of Cu-based catalysts through two ion exchanges. The advantage of the ion exchange method in the liquid phase and the solid phase is that the compensating cation of the zeolite can be well exchanged with the metal ions with catalytic activity, so that the metal content in the pores reaches a high level and has good metal dispersion. The results show that both ion exchange methods are suitable for the incorporation of uniformly distributed Cu into the zeolite structure, and the solid ion exchange method has the highest exchange percentage. Ali et al. [76] prepared 30 wt% CuO 49.65 wt% ZnO₂ 0.35 wt% Al₂O₃ catalyst at glycine to nitrates (G/O) ratios between 0.1 and 1.23 through the solution combustion synthesis (SCS) method. In brief, in the experimental procedure, varying quantities of glycine were used as a fuel into a mixed nitrate precursor solution, and the generated mixture was subjected to continuous stirring. The mixture gradually transformed into a soft gel upon heating on a hotplate and underwent spontaneous combustion at 150 °C. Subsequently, the synthesized powder was subjected to calcination in a muffle furnace using static air at different temperatures. The heating and cooling rates during calcination were, respectively, set at +1 and −1 °C·min^{−1} for three hours. APrašnikar et al. [51] also prepared several perovskite-containing Cu/Sr/Ti materials using the one-step solution combustion method with different fuels and conducted a long-term stability test of the catalyst with the best catalytic performances (Cu₅Sr₃Ti₂O_x, citric acid, calcination at 650 °C). The results showed that the catalyst retained 91% of initial activity after 122 h and even preserved 71% of the activity. Han et al. [52] prepared hollow Cu@ZrO₂ catalysts through the pyrolysis of Cu-loaded Zr-MOF and found that a lower pyrolysis temperature can enhance the porous structure and the metal–support interaction of Cu and ZrO₂ (Figure 3). More specifically, low-temperature pyrolysis generated highly dispersed Cu nanoparticles with balanced Cu⁰/Cu⁺ sites, more surface basic sites, and abundant Cu-ZrO₂ interface in the hollow structure, which contributed to enhancing the catalytic ability of CO₂ adsorption/activation and selective hydrogenation to methanol. Qu et al. [77] anchored a small amount of Cu on the surface of a ZnAl₂O₄ support using the ammonia evaporation method. The interaction between Cu formed through ammonia evaporation and Zn–O structure derived from the surface of ZnAl₂O₄ was stronger, and it tended to form a higher proportion of Cu⁺, which stabilized the methoxy group and improved the methanol production efficiency.

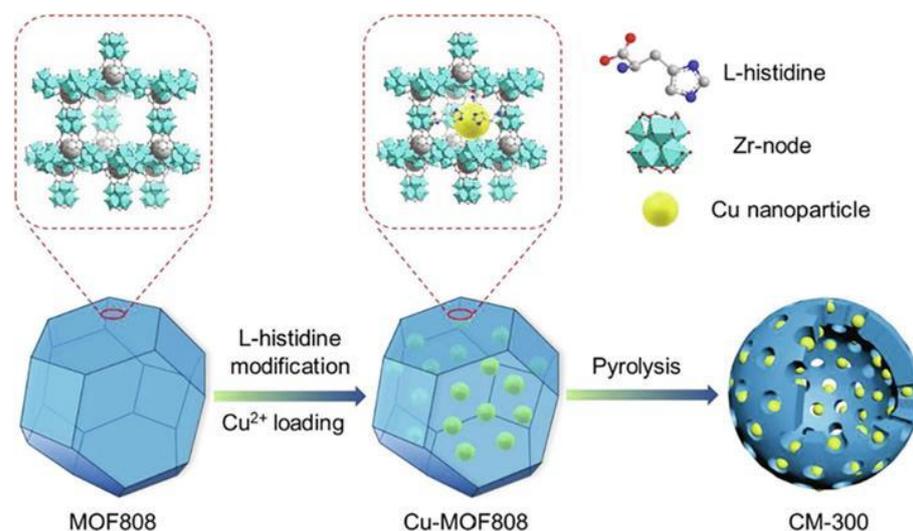


Figure 3. Illustration of synthesis of the hollow structured Cu@ZrO₂ derived from Cu-MOF808 (pyrolysis temperature was 300 °C) [52].

3.2. In₂O₃-Based Catalyst

The traditional Cu-based catalysts have been extensively studied in CO₂ hydrogenation to methanol [14,78]. However, its further application is limited by the high activity of the RWGS reaction and the poor stability and sintering of the active phase induced by H₂O. Compared with the aforementioned Cu-based catalysts, In₂O₃ has moderate adsorption capacity of CO₂ and CO and significantly better methanol selectivity than Cu, Co, and noble metal catalysts. Therefore, it has attracted extensive attention from researchers. In addition, In₂O₃ is easy to load and modify the surface, which can further promote the CO₂ and H₂ activation, and stabilize key intermediates, providing great potential for the design and preparation of efficient methanol synthesis catalysts [20,28,79].

3.2.1. Metal Promoters

Compared with traditional catalysts, In₂O₃ demonstrates better ability to adsorb and activate CO₂ owing to its abundant oxygen vacancy on the surface. However, the weak H₂ dissociation ability of In₂O₃ hinders the hydrogenation of carbon species, resulting in a significantly low CO₂ conversion rate of approximately 6%. It is a common strategy to introduce other metal elements into the In₂O₃ system and form M/In₂O₃ structure to enhance H₂ dissociation, adsorption, and overflow capacity.

As a metal with strong H₂ dissociation ability, Pd is often used to further enhance the performance of In₂O₃-based catalysts. For example, Tian et al. [80] prepared Pd-In₂O₃ catalysts with high activity using the solid phase method. Pd species have high dispersibility on the prepared Pd/In₂O₃ catalyst, which significantly promoted H₂ dissociation and provided sufficient H atoms for CO₂ hydrogenation. In addition, partial Pd²⁺ species can exist stably during CO₂ hydrogenation, which facilitated methanol synthesis. Rui et al. [81] also prepared Pd/In₂O₃ catalysts by mixing the Pd/peptide composite and In₂O₃, followed by the removal of peptide through thermal treatment. In contrast, the catalyst was also synthesized using the conventional incipient wetness impregnation method. It is notable that the CO₂ conversion of the former catalyst was higher than 20% at 300 °C, and the maximum STY was 0.89 g_{MeOH}·g_{cat}⁻¹·h⁻¹, which was higher than that of the catalyst prepared using the conventional method. This is mainly because the catalyst obtained using the former preparation method can obtain Pd-NPs with small particle size and high dispersion. The Pd NPs has a high hydrogen dissociation adsorption capacity, which can provide the hydrogen for the hydrogenation reaction and maintain the density of oxygen vacancies. Similar effects are also found for Pt, Rh, Au, and Ru supported on In₂O₃ [39]. For instance, Sun et al. [82] prepared Pt-In₂O₃ catalysts using

the deposition precipitation method (DP). The synergistic effect between Pt nanoparticles and In_2O_3 effectively modulated the relationship between H_2 activation and surface oxygen vacancy content of In_2O_3 , promoting the efficient hydrogenation of CO_2 to methanol and maintaining good stability. Rui et al. [83] prepared the $\text{Au}/\text{In}_2\text{O}_3$ catalyst using the sedimentation precipitation method. The catalyst exhibits excellent catalytic properties with 100% selectivity of the reaction below 225 °C, and the selectivity is still as high as 67.8% at 300 °C. This excellent performance is due to the $\text{Au}^{\delta+}\text{-In}_2\text{O}_{3-x}$ interface used as the active site, which gives gold the ability to activate hydrogen by regulating the electronic structure of gold. In addition, Sun et al. [84] prepared a $\text{Ag}/\text{In}_2\text{O}_3$ catalyst in the same manner. They analyzed the interaction between the surface of Ag and In_2O_3 containing oxygen vacancy based on DFT. The results showed that the interface site could promote the activation and hydrogenation of CO_2 . Moreover, the introduction of Ag can promote the formation of surface oxygen vacancy, thus promoting the increase of oxygen vacancy sites and the adsorption and dissociation of CO_2 .

Recently, a study indicated that a Ni-promoted In_2O_3 catalyst was used to produce methanol via CO_2 hydrogenation. Hensen et al. [85] prepared a Ni-promoted In_2O_3 catalyst using the one-step flame spray pyrolysis (FSP) method. The reduced Ni is conducive to the activation of H_2 molecules, and $\text{NiO-In}_2\text{O}_3$ will form oxygen vacancies and Ni-O-In during the reaction. Specifically, the metal nitrate solution is dissolved in a mixed solution of ethanol and 2-ethylhexanoic acid at room temperature, and then, the resulting solution is injected into the nozzle of the flame synthesis device, and the catalyst is collected in a quartz filter. Frei et al. [86] synthesized the catalysts with different morphology of Ni using the coprecipitation and impregnation methods. Compared with the coprecipitation method, more stable and active catalysts were obtained using the dry impregnation method. The Ni content of different impregnating catalysts has an obvious influence on the selectivity of products. To be specific, the RWGS reaction promoted methanol synthesis to some extent, and no methane was produced when Ni content was less than 10 wt%. Considering that the special wettability of the Ni-promoted In_2O_3 catalyst is beneficial for forming layered structures rather than aggregate particles, their strong anchoring on oxides through alloying can obtain high catalyst stability. DFT simulation results showed that the In_2O_3 -modulated Ni layer easily provided homogeneous cracking hydrogen to In_2O_3 , enhancing the formation of oxygen vacancy and promoting the hydrogenation of CO_2 . However, it hardly can activate CO_2 on its own, which overall explains the beneficial effects and the lack of methane generation. The catalyst consisting of 1 wt% Ni provided the best balance between charged and free radical hydrogen atoms, resulting in a twofold increase in the methanol space time yield (STY) compared to that achieved with pure In_2O_3 . Wu et al. [87] reported the experimental and theoretical results of CO_2 hydrogenation to methanol over the Ru-promoted In_2O_3 catalyst ($\text{Ru}/\text{In}_2\text{O}_3$). The results showed that the methanol selectivity of $\text{Ru}/\text{In}_2\text{O}_3$ catalyst with 1wt% Ru loading can reach 69.7%, and the STY can reach $0.57 \text{ g}_{\text{MeOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ at 300 °C and 5 MPa (Figure 4). Compared with In_2O_3 , the $\text{Ru}/\text{In}_2\text{O}_3$ catalyst has better stability. The characterization analysis showed that Ru and In_2O_3 interacted with each other. Ru increased the content of oxygen vacancy on the catalyst surface, stabilized the surface structure of the catalyst, and inhibited the excessive reduction of In_2O_3 . DFT calculation showed that the In_2O_3 surface makes Ru clusters more stable, and there is an obvious strong interaction between metal and support, which makes the surface structure of the catalyst more stable. Recently, Liu et al. [88] reported that $\text{Ir}/\text{In}_2\text{O}_{3-x}$ catalysts prepared using the traditional impregnation method show high activity, selectivity, and stability for CO_2 hydrogenation to methanol. It was found that there was a linear positive correlation between the amount of Ir and the catalytic activity within a certain range. The $\text{Ir}/\text{In}_2\text{O}_3$ catalyst with 10% Ir loading showed a methanol selectivity of 70% and methanol STY of $0.765 \text{ g}_{\text{MeOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ at 300 °C. The addition of Ir not only effectively avoids the excessive reduction of In_2O_3 but also stabilizes the oxygen vacancy on the surface of the In_2O_3 support, thus further improving the stability of the

catalyst. In turn, In_2O_3 stabilizes the highly dispersed metal Ir, avoiding the Ir aggregation observed on other oxides.

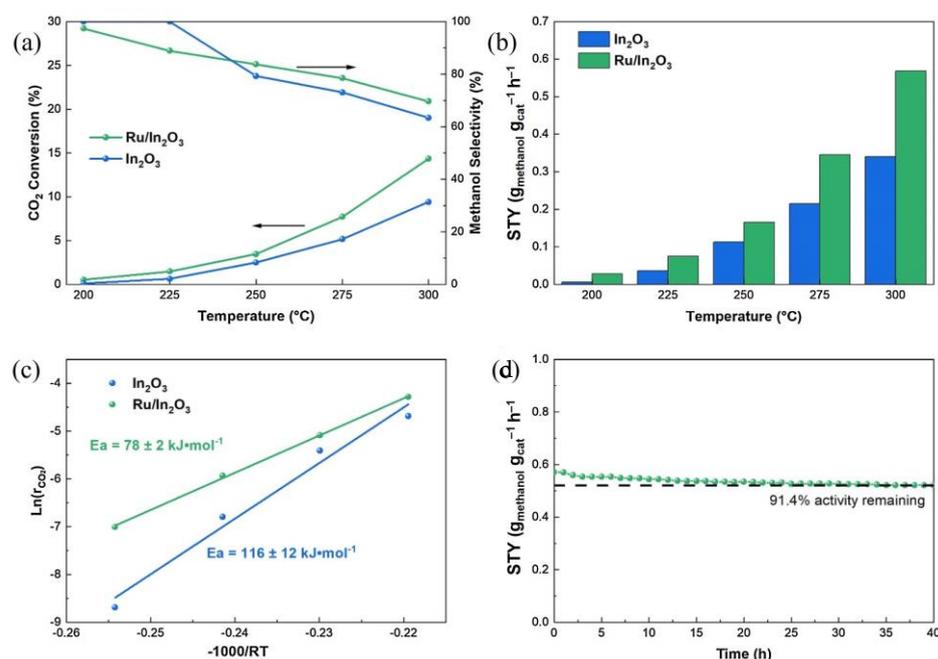


Figure 4. CO_2 hydrogenation activity of In_2O_3 and $\text{Ru}/\text{In}_2\text{O}_3$. (a) CO_2 conversion and methanol selectivity, (b) methanol STY, (c) apparent activation energy of CO_2 conversion, and (d) methanol formation rate versus time of the $\text{Ru}/\text{In}_2\text{O}_3$ catalyst for 40 h on stream [87].

3.2.2. Oxide Support

The composite oxide catalyst composed of In_2O_3 and other oxides can also promote the production of highly selective methanol. For example, Liu et al. [89] added ZrO_2 into $\text{Pt}/\text{In}_2\text{O}_3$ catalyst to explore the effect of ZrO_2 on catalytic performances of CO_2 hydrogenation. The introduction of ZrO_2 achieved high activity and stability of CO_2 hydrogenation to methanol in the presence of high CO content. This is mainly because the addition of ZrO_2 resulted in stronger electron transfer between Pt and In_2O_3 - ZrO_2 support, weakening the CO adsorption and inhibiting the overreduction of In_2O_3 and CO poisoning at the Pt site. In addition, it was found that the synergistic effect between the Zr-modified oxygen vacancy (In-OV-Zr) and the Pt site promoted the hydrogenation of CO_2 to methanol through the formate route. Sharma et al. [19] investigated the catalytic performances of ZrO_2 and CeO_2 -supported In_2O_3 catalysts for the synthesis of methanol from CO_2 hydrogenation. The selectivity of $\text{In}_{13}/\text{CeO}_2$ for methanol is higher than that of $\text{In}_{13}/\text{ZrO}_2$ at 553 K, and the methanol selectivity decreases with the increase of temperature. However, it found that the ZrO_2 -supported In_2O_3 catalyst was very stable, while In_2O_3 supported by CeO_2 was easy to be inactivated, as shown in Figure 5. This is mainly due to the hydrophilic properties [90], redox properties, and the agglomeration of CeO_2 support further inhibiting the CO_2 hydrogenation. In addition, it was found that the $\text{In}_{13}/\text{CeO}_2$ catalyst could be regenerated by washing the catalyst with Ar to a certain extent. However, repeated reaction-regeneration cycles showed that the conversion continued to decline after regeneration and was even lower in the following cycles. In summary, the adsorption of water for $\text{In}_{13}/\text{CeO}_2$ can recover some activity due to the partial reversibility, while it is irreversible for the structural change leading to sustaining deactivation. For comparison, $\text{In}_{13}/\text{ZrO}_2$ showed an excellent stability under the reaction conditions. Monoclinic ZrO_2 as a support can greatly improve the activity of In_2O_3 for CO_2 hydrogenation to methanol. Javier and Cecilia et al. [30] recently investigated electron, geometric, and interfacial phenomena, and the special role of Zr as a carrier in the catalytic hydrogenation of CO_2 to methanol. According to the kinetic analysis, monoclinic ZrO_2 -based catalysts can activate reactants

better than Al_2O_3 or CeO_2 oxide-supported In_2O_3 , possibly due to the superior nature of oxygen vacancy on the carrier In_2O_3 and the direct contribution of ZrO_2 to CO_2 activation through its oxygen vacancy.

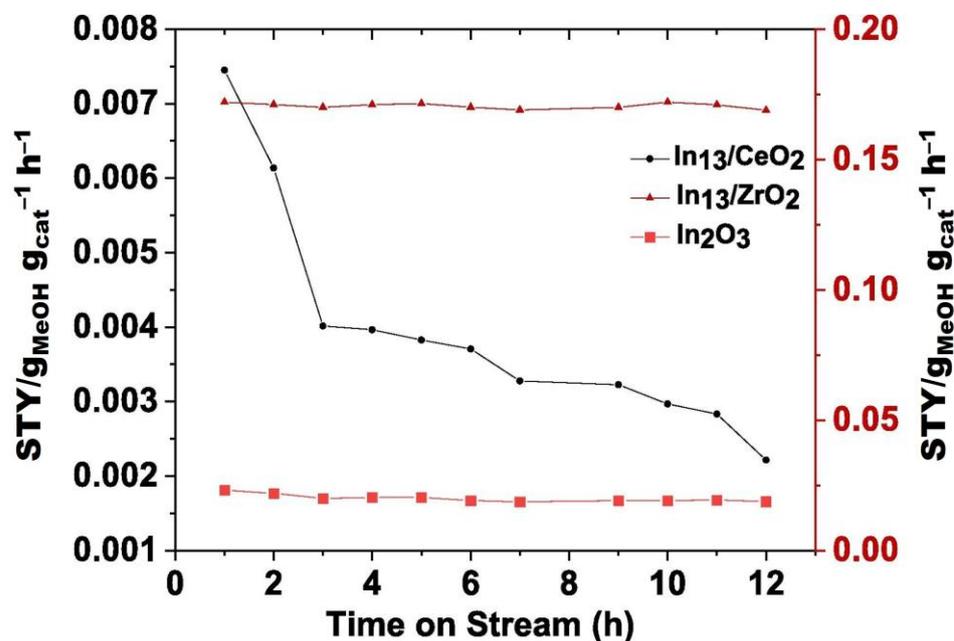


Figure 5. Evolution of the methanol STY with time on stream (TOS) over $\text{In}_{13}/\text{ZrO}_2$ and $\text{In}_{13}/\text{CeO}_2$ [19].

3.3. Bimetallic Catalysts

Bimetallic catalysts have unique electronic effects due to their unique chemical composition and geometric configuration, which can regulate the electronic, geometric, and chemical properties of their active components, thereby enhancing catalytic performance. Because of this, bimetallic catalysts have been widely used in CO_2 hydrogenation to methanol in recent years, and catalysts with high catalytic activity and methanol selectivity can be obtained by adjusting the composition ratio and grain size of the two metal elements.

The metal Cu is widely used in the hydrogenation of CO_2 to methanol, and Cu-containing bimetallic catalysts have been widely studied in recent years. For example, Xu et al. [91] compared the catalytic performances and surface properties of Cu-Pd bimetallic catalysts ($\text{Cu}/\text{Pd} = 33.5$) over different supports (SiO_2 , CeO_2 , TiO_2 , and ZrO_2) and explored the effect of the reduction temperature on the catalytic performances. The results showed that the catalytic performances of SiO_2 and ZrO_2 -loaded catalysts were more noticeably influenced by the reduction in temperature compared to the CeO_2 and TiO_2 -loaded catalysts. This can be attributed to the varying degrees of interaction between Pd and Cu caused by the support and reduction in temperature. Lin et al. [92] prepared TiO_2 - CeO_2 and TiO_2 - ZrO_2 binary supports using the precipitation method in different ratios and then loaded Pd and Cu impregnated on the binary supports to form bimetallic catalysts. It was found that the production and selectivity of methanol were improved by the binary supports catalysts compared with the single support catalysts. This is probably because the surface area of the binary supports was significantly increased, which enhanced both the dispersion of the metal phase and gas adsorption. Meanwhile, the presence of more oxygen vacancies in the binary supports also promoted CO_2 conversion. In addition, the binary carriers improved the CO_2 adsorption behavior of weakly bonded species, which contributed to improving catalytic performances. Compared to the Ti-Ce binary support, the Ti-Zr binary support showed a greater improvement in the adsorption characteristics of weakly bonded CO_2 and the moderately strong metal-support interaction (SMSI) effects. The methanol generation rate of Pd-Cu/ $\text{Ti}_{0.1}\text{Zr}_{0.9}\text{O}_2$ bimetallic catalyst reached

$0.62 \mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{s}^{-1}$. Han et al. [93] prepared Cu/ZnO catalysts with abundant Cu-ZnO interface using Cu-Zn bimetallic organic frameworks (MOFs) template strategy (χ represents the Cu/Zn ratios), named ($\text{Cu}_\chi\text{ZnO-MOF-74-350}$), which exhibited high methanol selectivity of 80% and long-term durability of 100 h under the condition of 190 °C and 4.0 MPa (Figure 6). The good catalytic performances were mainly due to the abundant Cu-ZnO interface, which facilitates the adsorption of CO_2 and the formation of intermediates. Yu et al. [94] prepared Cu-Zn catalysts coated with UiO-66 using the deposition-precipitation method. The results showed that the Cu-Zn@UiO-66 catalysts with a Cu-Zn loading of 35 wt% and a Cu/Zn molar ratio of 2.5 had excellent catalytic activity. The catalyst had a maximum methanol yield of 9.1% at 240 °C and good reaction stability after a time on stream of 100 h due to the ultra-small nanoparticles (NP) confined in UiO-66 and the abundant Cu/ZnO $_\chi$ interface leading to the enhancement of synergistic effect of Cu and ZnO, which promotes the conversion of CO_2 and the formation of methanol. In recent studies, Ni and In-based catalysts have also been used to form bimetallic oxide catalysts with Cu, both of which exhibit excellent catalytic performances. Wang et al. [95] studied the effect of Cu-Ni loading on different graphites (GO, rGO, NGO) for the synthesis of methanol from CO_2 hydrogenation. The results showed that the CuNi-rGO catalyst showed 7.87% CO_2 conversion and 98.7% methanol selectivity at 498 K and 4.0 MPa. This was attributed to the promotion of Cu^{2+} reduced by Ni and the strong chemisorption activation of CO_2 caused by the CuNi-rGO catalyst. Shi et al. [96] prepared bimetallic catalysts with different Cu and In ratios via the co-precipitation method. When the molar ratio of Cu to In was 1:2, the catalysts exhibited the excellent performance due to the high dispersion and the improvement of synergistic effect of active sites. Under the condition of 260 °C, 3.0 MPa, and $7500 \text{ mL}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$, the catalyst obtained CO_2 conversion of 10.3%, CH_3OH selectivity of 86.2%, and CH_3OH STY of $0.190 \text{ g}_{\text{MeOH}}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$.

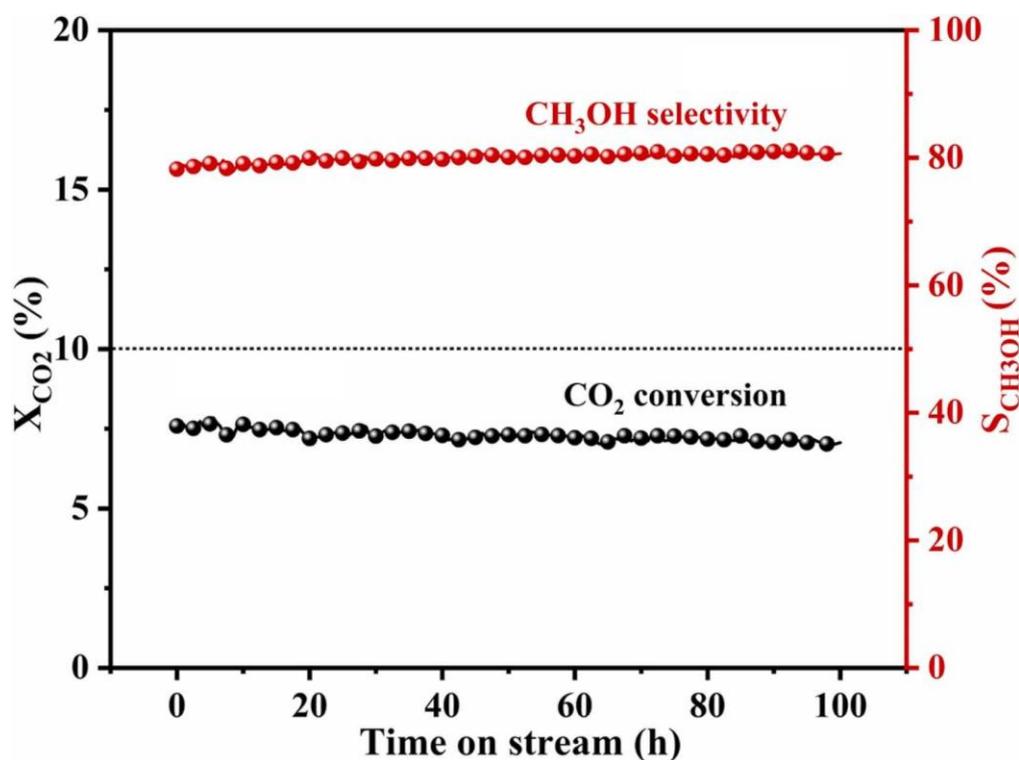


Figure 6. Catalytic stability on-stream test of the continuous catalytic process over CuZnO-MOF-74-350 with $\text{V}_{\text{H}_2}/\text{CO}_2 = 3/1$, $P = 4.0 \text{ MPa}$, $T = 190 \text{ }^\circ\text{C}$, and $\text{WHSV} = 4000 \text{ mL}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ [93].

In bimetallic catalysts with Ni as the main active component, the electronic structure of the Ni atom is changed by the neighboring metal atoms, resulting in unique activity for methanol production. Studt et al. [97] synthesized and tested a series of catalysts with

different Ni-Ga ratios (including Ni-rich sites and Ga-rich sites), and the results showed that Ni₅Ga₃ was particularly active and selective. Notably, they had superior methanol production due to their better ability to reduce the RWGS activity in favor of methanol production compared with the conventional Cu/ZnO/Al₂O₃ catalyst. Rasteiro et al. [98] prepared Ni₅Ga₃ catalysts with SiO₂, ZrO₂, and CeO₂ as supports using the incipient wetness impregnation method. Among these three catalysts, the Ni₅Ga₃ catalyst supported by CeO₂ was poisoned at the active site due to excessive adsorption of intermediates at the alloy-carrier interface, which resulted in the failure of intermediates to hydrogenate to methanol. The Ni₅Ga₃ catalyst supported by SiO₂ had a poor affinity to adsorb CO₂, which limited the methanol production through the alloy surface route. In contrast, the interface of the Ni₅Ga₃ catalyst supported by ZrO₂ contributed to forming the stable intermediates and promoting hydrogen overflow, thus exhibiting the most excellent catalytic activity. This study illustrates the importance of alloy-support synergy. Otherwise, Duyar et al. [99] introduced a third metal (Au, Cu, Co) as a promoter in Ni-Ga/SiO₂, which enhanced the activity of CO₂ hydrogenation to methanol by weakening the interaction between the surface and the adsorbate with Au and Cu compared to Ni₅Ga₃/SiO₂. The experimental results showed that the activity of Au-Ni-Ga increased by nearly four times, and Cu-Ni-Ga showed the highest specific activity among the three catalysts.

Pd is also often used as a bimetallic catalyst with other metals such as In, Zn, and Ga for CO₂ hydrogenation to methanol. The formation of the bimetallic system facilitates the overflow of H₂ to the active site, which reacts with the adsorbed CO₂ and promotes methanol production. Therefore, the Pd-M (In, Zn, Ga) bimetallic system has great potential for CO₂ hydrogenation to methanol. As seen in the work of Ojelade's team [100], they conducted a comparative study of PdZn/CeO₂ catalysts with different Pd/Zn composition ratios for methanol synthesis. When the Pd/Zn molar ratio was close to 1, the PdZn alloy phase on the CeO₂ support was maximum, and the methanol STY maximum was 0.114 g_{MeOH}·g_{cat}⁻¹·h⁻¹. Yin et al. [101] studied PdZn alloy catalysts prepared from Pd@ZIF-8 precursors, which exhibited excellent methanol STY up to 0.65 g_{MeOH}·g_{cat}⁻¹·h⁻¹ and TOF of 972 h⁻¹. This may be attributed to the SMSI effects between Pd and ZnO support, which are facilitated by the sub-nano-Pd being confined within the ZIF-8 pore structure. Snider et al. [102] synthesized InPd/SiO₂ catalysts with different In/Pd ratios using the incipient wetness impregnation method. The catalysts showed the highest activity at 4 MPa and 300 °C when the molar ratio of In to Pd was 2:1. More specifically, the methanol selectivity and yield were 61% and 0.588 g_{MeOH}·g_{cat}⁻¹·h⁻¹, respectively. Experimental results and DFT calculations indicated that the synergistic interaction between bimetallic In-Pd particles enriched with In on the surface of In₂O₃ enhances the reaction activity. Tian et al. [103] used TCPP(Pd)@MIL-68(In) as a sacrificial template to synthesize the loaded Pd@In₂O₃ catalysts, and the obtained catalysts showed a high 81.1 g_{MeOH}·g_{Pd}⁻¹·h⁻¹ within 50 h STY and 81% methanol selectivity at 295 °C and 3.0 MPa. DFT calculations showed that the InPd clusters over-reduced In₂O₃, which was detrimental to the improvement of the catalytic activity for methanol production by regulating the electronic interactions between Pd and In₂O₃. Collins et al. [104] prepared GaPd bimetallic catalysts by loading different ratios of Ga and Pd atoms (2,4,8 atom/atom) on SiO₂. The results showed that the turnover frequency to methanol based on surface palladium was 200-folds higher than that of the monometallic Pd/SiO₂ catalyst, because the apparent activation energy of methanol synthesis on the surface palladium is much lower than that on the monometallic Pd/SiO₂ catalyst. The characterization results showed that Pd₂Ga bimetallic particles play a significant role in dissociating H₂ and providing hydrogen atoms to Ga₂O₃ in the reaction. Close contact between Pd₂Ga and Ga₂O₃ may be the key to optimizing the performances of the bifunctional mechanism. A new Rh-In bimetallic catalyst was first reported by Li et al. [105]. They prepared a series of Rh-containing catalysts with different In/Al compositions using the wet-impregnation method. The result indicated that the optimal ratio of In to Al was 1, and the methanol yield was 0.001 g_{MeOH}·g_{cat}⁻¹·h⁻¹. The catalysts were characterized by their ability to maintain high H₂ conversion in H₂-deficient feed gas

and inhibit the RWGS reaction. Geng et al. [106] prepared SiO₂-loaded In-Ru bimetallic catalysts and investigated the promotion of In on Ru in CO₂ hydrogenation to methanol. The catalyst achieved 85% methanol selectivity without methane at 240 °C and 3.4 MPa. It enhanced the charge transfer from the surface to the formic acid state, stabilized the formic acid and methoxy on the surface, and inhibited H₂ activation and the conversion of CO hydrogenation to CH₄ and the violent decomposition of methanol on Ru to CO.

3.4. Solid Solution Catalysts

In addition to the catalysts mentioned above, solid solution catalysts have a broad application prospect for the hydrogenation of CO₂ to methanol [10]. For example, Li et al. [107] prepared a series of Ga-promoted ZnZrO_x solid solution catalysts to improve the methanol activity and keep high methanol selectivity. They found that when Ga content varied from 0 to 10% (the mole fraction of Ga in the total metal molar content), the CO₂ conversion fluctuated between 7.7 and 8.8%, while the methanol selectivity remained unchanged (87.5% vs. 87.4%) at 320 °C. The introduction of Ga in the ZnZrO_x solid solution catalyst improved the adsorption and activation ability of the catalyst for H₂ and CO₂ and promoted the hydrogenation of HCOO* to CH₃O* (Figure 7). Li's team also prepared ZnO-ZrO₂ solid solution catalysts with ordered mesoporous structure using the evaporation-induced self-assembly (EISA) method and compared them with the catalysts prepared using the co-precipitation method [108]. The results showed that the methanol producing rate of 20% ZnO-ZrO₂ catalyst synthesized using the EISA method was 0.707 g_{MeOH}·g_{cat}⁻¹·h⁻¹, which was 1.35 times that of the co-precipitation catalyst at 320 °C and 5.5 MPa. This is mainly because the EISA catalyst has a larger specific surface area and more active sites for adsorbing CO₂ and H₂. The preparation method mainly dissolves the triblock copolymer P123 in ethanol and adds n-butanol zirconium and ZnCl₂. After stirring overnight, the solvent is evaporated to form a gel and then calcined. The surface of the calcined catalyst needs to be washed with water and ethanol, respectively, and finally dried.

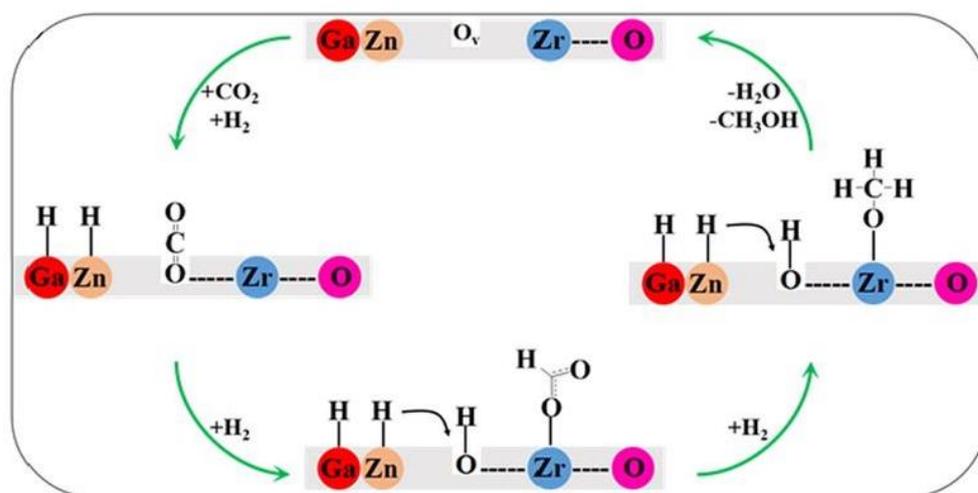


Figure 7. Proposed reaction mechanism for CO₂ hydrogenation to methanol over 5% GaZnZrO_x catalyst [107].

Furthermore, Tada et al. [109] explored the effect of Zn content on the hydrogenation of CO₂ to methanol over Zn_xZr_{1-x}O_{2-x} catalyst and ensured the structure of active sites through theoretical calculation and experiment. When Zn content was low, the Zn_xZr_{1-x}O_{2-x} catalyst was mainly composed of Zn clusters (i.e., isolated [ZnO_a] clusters and [ZnO_c] oligomers), which meant the formation of Zn-O-Zr sites with specific activity for CO₂ hydrogenation to methanol. However, the excessive addition of Zn can result in the aggregation of ZnO clusters and the domain formation of ZrO₂ and ZnO phases. Similarly, Huang et al. [110] synthesized a series of ZnO-ZrO₂ composite oxides via the co-deposited method and overall studied their

phase structural evolution and catalytic properties in the CO₂ hydrogenation reaction. It was found that with the increase in Zr content, the phase structure of ZnO-ZrO₂ composite oxides evolved from the mixture of hexagonal ZnO phase and Zn-doped ZrO₂ solid solution phases to pure Zn-doped ZrO₂ solid solution phase, which showed high selectivity for the formation of CH₃OH. Wang et al. [111] prepared a Cu/CeZrO_x solid solution catalyst using the microimpingement flow reactor with ultrasound, which had a better micro-mixing efficiency compared with the conventional batch method (Figure 8). Under reaction conditions of 240 °C, 3 MPa, 30,000 mL·g_{cat}⁻¹·h⁻¹, the Cu/CeZrO_x solid solution catalyst exhibited methanol selectivity of 55.3% and STY of 0.222 g_{MeOH}·g_{cat}⁻¹·h⁻¹ at CO₂ conversion of 4.67%, which was higher than other traditional Cu-based catalysts [112–114]. This was ascribed to the synergistic interaction between the oxygen vacancies and a higher proportion of Cu⁺.

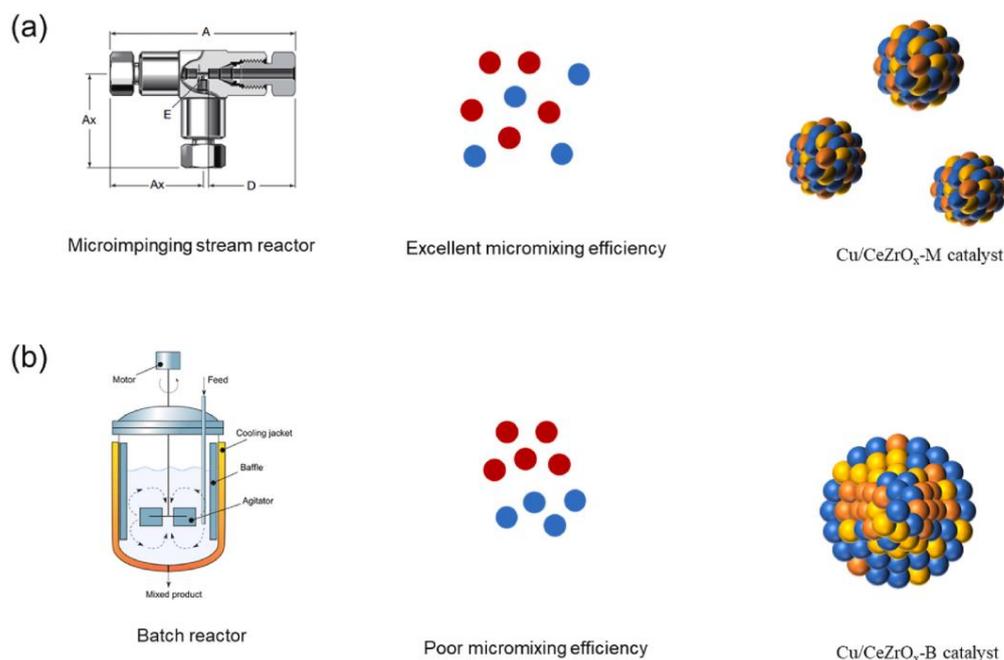


Figure 8. (a) Cu/CeZrO_x-M prepared via the new microimpinging stream reactor coupled with ultrasound, (b) 960 Cu/CeZrO_x-B catalysts prepared via the conventional batch method [111].

3.5. Other Catalysts

Recently, some other catalysts have been widely studied as well. For example, Li et al. [115] synthesized a Mo-Co-C-N catalyst with a ZIF-67 precursor under reaction conditions of 2 MPa, 6000 mL·g_{cat}⁻¹·h⁻¹, and 275 °C, and the CO₂ conversion, methanol selectivity, and STY reached 9.2%, 58.4%, and 0.106 g_{MeOH}·g_{cat}⁻¹·h⁻¹, respectively. This is mainly because the addition of N provided abundant oxygen vacancies, facilitating the dissociation and adsorption of CO₂ and further increasing methanol selectivity [116]. Zeng et al. [117] developed boxlike assemblages of quasi-single-layer MoS₂ nanosheets, which were edge-blocked by ZnS crystallites (denoted as h-MoS₂/ZnS) via a MOF-engaged method. Under reaction conditions of 260 °C, 5 MPa, and 15,000 mL·g_{cat}⁻¹·h⁻¹, the h-MoS₂/ZnS catalyst can achieve STY_{MeOH} of 0.93 g_{MeOH}·g_{cat}⁻¹·h⁻¹, CO₂ conversion of 9.0%, and methanol selectivity of 67.3%. Li et al. [118] reported a novel Cd/TiO₂ catalyst, with methanol selectivity of 81%, CO₂ conversion of 15.8%, and little CH₄ selectivity. The unique electronic properties of Cd clusters on the TiO₂ substrates were the main reason for the high selectivity of CO₂ hydrogenation to methanol through the HCOO* pathway at the interface catalytic site.

4. Mechanism Studies

For CO₂ hydrogenation to methanol, various metal-based catalysts have been studied, and Cu-based catalysts are widely employed because of their higher catalytic activity as well as better selectivity to methanol. However, the active center and the underlying catalytic mechanism are still inconclusive. It is generally recognized that metallic Cu is the active phase, which mainly includes three types of recognized active sites: the interface of Cu and ZnO, Cu⁰, and Cu⁺ species. Many researchers have proposed various mechanisms of CO₂ hydrogenation to methanol over Cu-based catalysts using experiments and DFT calculation methods. Three main mechanisms have been put forward based on the nuance of interface models and chosen pathways, namely the formate (HCOO*) mechanism, the RWGS + CO-Hydro mechanism, and the trans-COOH mechanism [119]. In the following content, we mainly focus on the recent theoretical advances in reaction pathways of the three mechanisms on Cu-based catalysts and their extension to other catalyst systems for guiding the design of efficient catalysts.

4.1. The HCOO Mechanism and *r*-HCOO Mechanism

The majority of researchers prefer that the most possible pathway for CO₂ hydrogenation to methanol is the HCOO mechanism, in which formate (HCOO*) is the key intermediate formed by CO₂ reacting with preadsorbed surface atomic H via either an Eley-Rideal (ER) [120,121] or Langmuir–Hinshelwood (LH) mechanism [33,122]. HCOO is then hydrogenated to dioxymethylene (*HCOOH), followed by further hydrogenation to *H₂COOH. The obtained *H₂COOH is cleaved to formaldehyde (*H₂CO) which is further hydrogenated to methoxy (*H₃CO) and methanol (*H₃COH) [123].

Yang et al. [120] explored the possible reaction pathway for CO₂ hydrogenation to methanol on Cu (111) and Cu nanoparticle surfaces through a combination of experimental and theoretical methods. DFT calculations show that the hydrogenation of CO₂ on the Cu surface is carried out by formate intermediates, and the overall reaction rate is limited by the hydrogenation of formate and dioxymethylene. However, CO hydrogenation was easy to be hindered, which was mainly because CO tended to be converted to formyl, and the obtained formyl is unstable and preferred to dissociate into CO and H atoms on Cu. Sun et al. [60] proposed a possible reaction mechanism of CO₂ hydrogenation to methanol, which followed the formate pathway on the dual active sites of CuZn₁₀Zr through in situ diffuse reflectance infrared Fourier transform spectra. The exposed Cu⁰ took to participate in the H₂ activation, while on the Cu⁺ species, the intermediate of formate from the CO₂ and H₂ co-adsorption was more inclined to produce methanol rather than other by-products, improving the methanol selectivity. Qu et al. [124] explored the SMSI between Cu and ZnAl₂O₄ spinel and found that the spinel catalyst had a double H₂ activation center. The interstitial H atoms in the spinel promoted the conversion of CO₂ to formate species, while the H₂ dissociated by Cu could accelerate the formation of methanol from formate. Wang et al. [125] investigated the effects of transition metal doping on CO₂ hydrogenation on Cu (211) surfaces using the DFT method and found that the doping of Rh, Ni, Co, and Ru can promote CO₂ hydrogenation to COOH. Studies have also found that the hydrogenation of HCOO*/H₂COO* is assumed to be the rate-controlling step in the CO₂ hydrogenation to methanol process for the formate-intermediated route [126]. Han et al. [74] studied the mechanistic pathway of CO₂ hydrogenation to methanol over hollow Cu@ZrO₂ catalysts using in situ FTIR tests. The results revealed that methanol formation followed the formate-intermediated pathway, and the synergistic effect between Cu and ZrO₂ at the interface was crucial in the reaction mechanism.

In addition, the H atoms spilled over to the support surface at the metal–support interface region, participated in the formation of the carbonaceous intermediate species, and were finally converted to HCOO*, CH₂O*, CH₃O*, and CH₃OH. Liu et al. [127] systematically explored three possible paths of CO₂ hydrogenation to methanol over a single-atom Zr-doped Cu-based catalyst from the kinetic and thermodynamic aspects of each elementary reaction by the DFT method (Figure 9). The results showed that methanol

was produced by the HCOO pathway, which involved the intermediates of bi-HCOO*, HCOOH*, H₂COO*, H₂COOH*, H₂CO*, and H₃CO*. In addition, the H₂COO*, H₂CO*, and H₃CO* hydrogenation were proven to be the rate-limiting steps. Liu et al. [89] studied the pathway of methanol synthesis on Pt/In₂O₃ catalysts with ZrO₂ addition through theoretical calculations and found that CO₂ activated at the In-Ov-Zr site tends to form methanol through the formate pathway. They also calculated the Gibbs free energy of CO adsorption on the catalyst model with or without ZrO₂ by DFT, and the results showed that the Gibbs free energy of CO adsorption on the model with ZrO₂ was lower. This is mainly because the addition of ZrO₂ significantly reduced the interaction between CO and Pt sites, making it easier for CO to desorb from Pt sites to the gas phase under reaction conditions and inhibiting the poisoning of CO on Pt sites. Wang et al. [128] found that both Cu/ZnO and trace Au-added Cu/ZnO catalysts were carried out in the formate path in the methanol synthesis reaction through in situ DRIFTS characterization and DFT calculations. The metal–oxide interface with oxygen vacancy modification is considered as the active site, and the introduction of Au produces more active sites, which promotes the activation of CO₂ and the modulation of intermediate species, thereby significantly improving the catalytic performance of methanol synthesis.

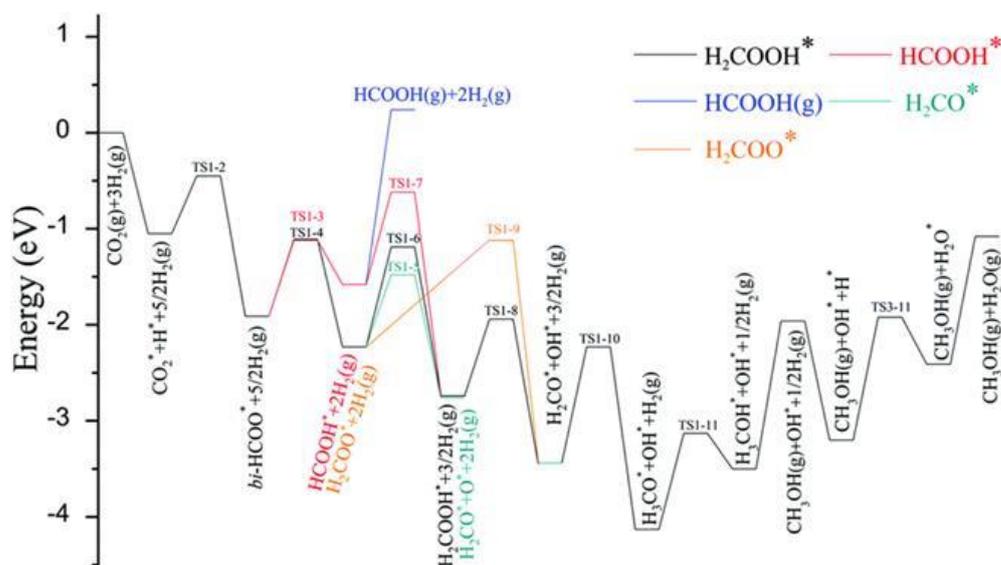


Figure 9. Potential energy profiles of the HCOO pathway in the process of methanol synthesis from CO₂ hydrogenation on the Zr1–Cu surface [128].

In addition to the aforementioned traditional formate pathway, a revised formate (r-HCOO) pathway has been proposed. In the work of Grabow et al. [129], the partial species proposed in previous mechanisms were considered. Meanwhile, the new intermediates such as HCOOH* and CH₃O₂* were also involved. It was found that the CH₂O, HCOOH, and HCOOCH₃ were determined to be crucial byproducts through an extensive set of periodic, self-consistent DFT calculations. Moreover, the DFT results showed that the HCOO* can be converted to HCOOH* preferentially, rather than H₂CO₂*, as suggested in previous mechanisms. HCOOH* was then further hydrogenated to form CH₃O₂*, which then transformed into CH₂O* by cracking its OH group. CH₃O* was the final intermediate before the formation of CH₃OH*. Recently, Chen et al. [130] also found that the optimal mechanism on the W-doped Rh (111) surface for CO₂ hydrogenation to methanol was the r-HCOO pathway. Liu et al. [31] systematically studied the mechanisms and kinetics of CO₂ hydrogenation over a series of MOF-808-coated single-atom metal catalysts via DFT calculation methods. Two plausible CO₂ hydrogenation pathways on CuII-MOF-808 catalysts were studied, namely formate path and carboxyl path. As a result, the formate pathway was more favorable, and the conversion of H₂COOH* to H₂CO* was the key step from the kinetic perspective over CuII-MOF-808 (Figure 10). The study of Li et al. [131]

showed that H_2 dissociation on the ZrO_2 sample needed to overcome the high activation energy, which was the rate-determining step of the reaction. While the introduction of Zn in the $ZnZrO_x$ catalyst promoted the heterolytic dissociation of H_2 , making the dissociation of H_2COOH^* the rate-determining step of the reaction, the Zn-O-Zr asymmetric sites on $ZnZrO_x$ catalyst showed a synergistic effect at the atomic level, which promoted the synthesis of methanol.

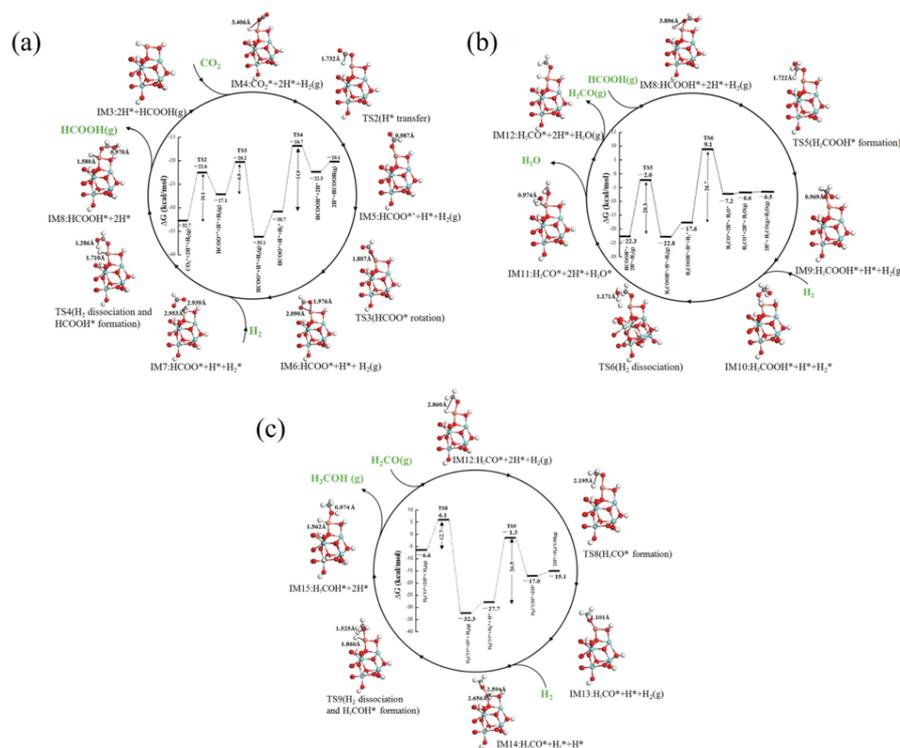


Figure 10. Gibbs free energy profile for CO_2 hydrogenation to (a) $HCOOH$, (b) H_2CO , and (c) H_3COH over Cu^{II} -MOF-808, respectively [31].

4.2. The RWGS + CO-Hydro Mechanism

For the RWGS + CO-Hydro pathway, CO_2 is hydrogenated to form the CO^* intermediate, followed by CO hydrogenation to methanol with HCO (formyl), H_2CO (formaldehyde), and H_3CO (methoxy) intermediates. The RWGS + CO-Hydro mechanism has been suggested for Cu-based systems and bimetallic catalysts [7,124]. Zhang et al. [75] designed $Cu^+/CeZrO_x$ interfaces by employing a series of ceria-zirconia solid solution catalysts with different Ce/Zr ratios to form a $Cu^+-Ov-Ce^{3+}$ structure in which Cu^+ atoms were combined with the oxygen vacancies of Ce. The in situ DRIFTS results showed that the oxygen vacancies in the solid solutions can not only effectively assist the CO_2 activation, modulate the electronic state of copper, and promote the formation of $Cu^+/CeZrO_x$ interfaces, but also contribute to stabilizing the key *CO intermediate compound to inhibit its desorption and facilitate its further hydrogenation to methanol through the RWGS + CO-Hydro pathway. Rasteiro et al. [132] found that the reaction pathway on the Ni-Ga alloy involved both the RWGS + CO-Hydro and formate routes employing DRIFTS analyses, as confirmed by the presence of formate, methoxy, and CO intermediates. Yang et al. [133] considered both the formate pathway and the RWGS + CO-Hydro route to investigate the CO_2 hydrogenation process on metal-doped Cu (111) surfaces using DFT calculations and Kinetic Monte Carlo (KMC) simulations. The calculation results indicated that the addition of Pd, Rh, Pt, and Ni can promote the formation of methanol on Cu (111). Meanwhile, the conversion of CO and HCO to CH_3OH through the RWGS + CO-Hydro pathway was found to be much faster than that via the formate pathway. Liu et al. [134] employed the DFT calculation to study the reaction energy and activation barriers of all elementary steps involved in

three possible hydrogenation mechanisms (Figure 11a). The calculated results indicated that the activation barrier of the rate-determining step of the RWGS + CO-Hydro mechanism was the lowest, which can be completed through the $\text{CO}_2^* \rightarrow \text{trans-COOH}^* \rightarrow \text{cis-COOH}^* \rightarrow \text{CO}^* \rightarrow \text{HCO}^* \rightarrow \text{HCOH}^* \rightarrow \text{H}_2\text{COH}^* \rightarrow \text{CH}_3\text{OH}^*$ pathway (Figure 11b). Ou et al. [135] also found that methanol was generated over Pd/TiO₂ catalyst following the RWGS + CO-Hydro pathway rather than the formate pathway due to its lower activation barrier. Sun et al. [136] found through in situ DRIFTS experiments that Cu⁺ species in Cu/SiO₂ catalysts prepared using the FSP method can inhibit the desorption of CO* by stabilizing CO* intermediates and further promote the hydrogenation of CO* to CH₃OH, promoting the RWGS + CO-hydro pathway.

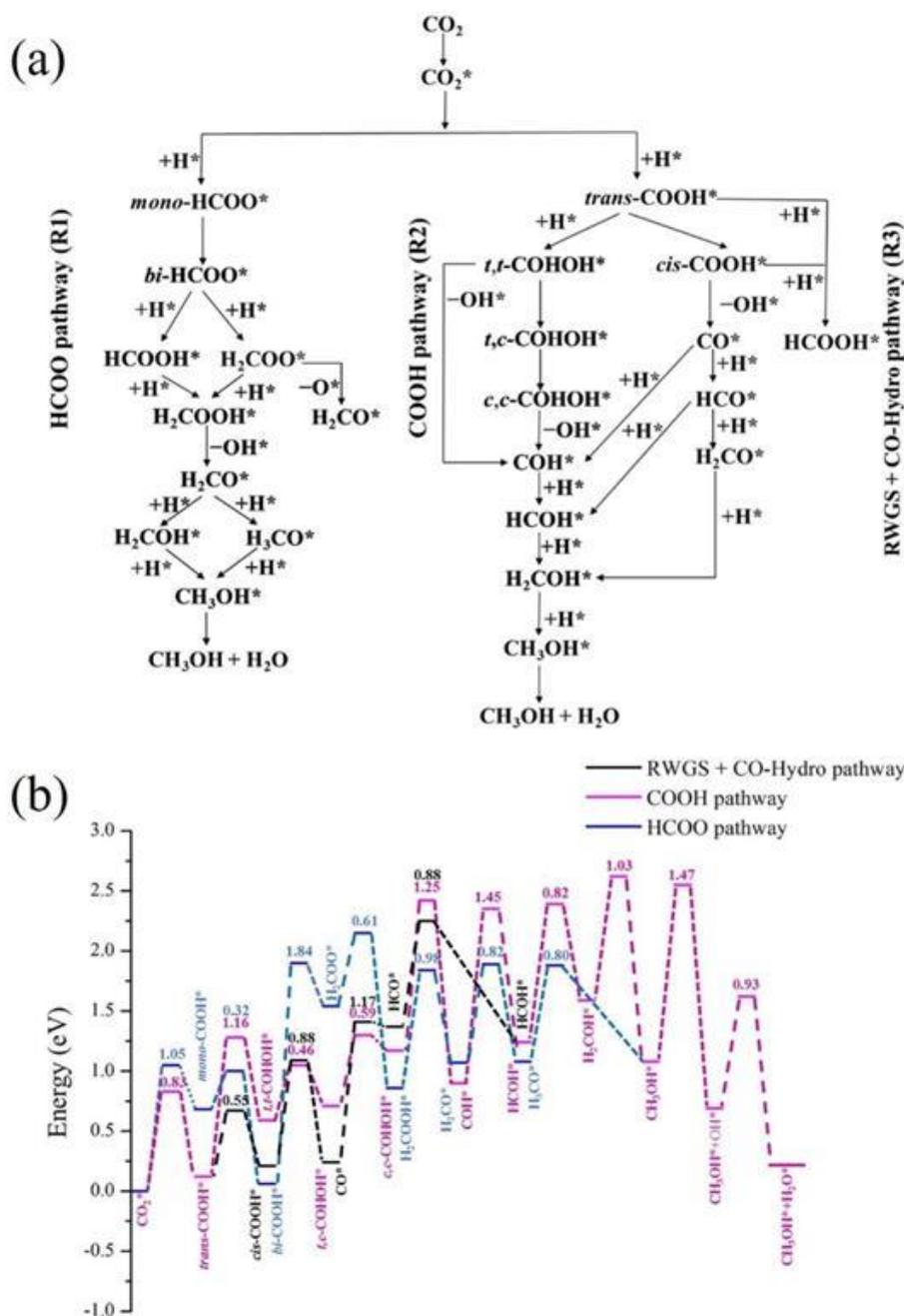


Figure 11. (a) Reaction networks for CO₂ hydrogenation to CH₃OH on the Cu@Pd core-shell surface. (b) Potential energy profiles of the HCOO pathway, the COOH pathway, and the RWGS + CO-Hydro pathway [134].

4.3. The Trans-COOH Mechanism

The earliest study of the trans-COOH mechanism with the hydrocarboxyl (COOH*) species as the first hydrogenated species was proposed by Zhao and co-workers [137] on the basis of the experiment of Yang et al. [138]. They found that in the presence of H₂O, the hydrogenation of CO₂ to produce hydrocarboxyl (trans-COOH) is kinetically more favorable than formate via a unique hydrogen transfer mechanism (Figure 12). The obtained trans-COOH was then converted to hydroxymethylidyne (COH) via dihydroxycarbene (COHOH) intermediates and then continuously hydrogenated for three steps to form hydroxymethylene (HCOH), hydroxymethyl (H₂COH), and methanol, respectively.

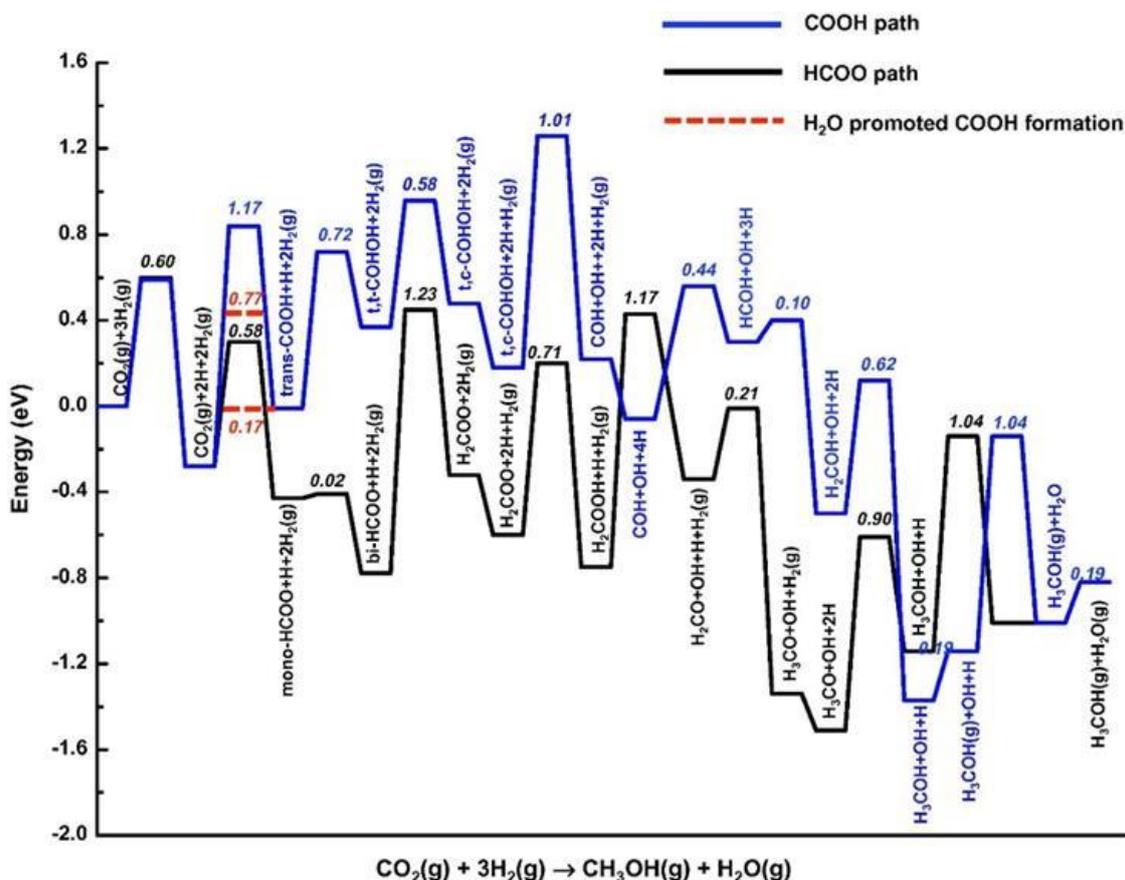


Figure 12. Potential energy surfaces for CO₂ hydrogenation to methanol on Cu (1 1 1) via the formate and hydrocarboxyl mechanisms [137].

In addition, Tang et al. [33] discussed three possible reaction pathways of CO₂ hydrogenation to CH₃OH on Ga₃Ni₅ (221) surfaces based on formate (HCOO), hydrocarboxyl (COOH) formations, and RWGS reaction with CO hydrogenation through DFT calculations. It was found that the reduction of CO₂ to CH₃OH was more likely to occur completely through the LH mechanism, and trans-COOH was proved to be the most favorable pathway. Similarly, Liu et al. [34] also considered the three possible reaction pathways according to DFT calculations to explore the reaction mechanisms on PdCu₃ (111) surface. The results showed that the CO₂ hydrogenation to CH₃OH preferred to occur via the COOH pathway. The adsorbed CO₂ reacted with H atoms to form COOH*, which was further hydrogenated to produce COHOH* and hydroxymethylidyne. And methanol was formed by the HCOH and H₂COH intermediates.

5. Summary and Outlook

The combination of CO₂ and renewable H₂ can be used to synthesize valuable methanol, which is not only conducive to mitigating carbon emissions but also bene-

ficial to achieving the artificial carbon cycle. In this work, we summed up the advances in studies of reaction thermodynamics, catalyst development, and mechanism study for the hydrogenation of CO₂ to methanol. In terms of reaction thermodynamics, the low-temperature and high-pressure operating conditions are proven to be favorable. In terms of catalyst development, we mainly review the research progress of Cu-based catalysts, In₂O₃-based catalysts, bimetallic catalysts, solid solution catalysts, and other novel catalysts. For Cu-based catalysts, the suitable supports, promoters, and preparation methods contribute to improving the number or activity of active sites to enhance the H₂ adsorption and the CO₂ activation and promote the formation of methanol. For In₂O₃-based catalysts, several strategies are employed to improve the catalytic performances. More specifically, the introduction of metal promoters can promote H₂ activation and oxygen vacancy formation. The oxide support is used to improve the dispersion of the active component and prevent the active component from sintering as well. For the bimetallic catalysts, the second metal can not only inhibit the aggregation of active species but also regulate the electronic structure around the active components. For the solid solution catalysts, their application further improves the thermal stability and structural performances of traditional catalysts. In addition, the catalytic performances of novel catalysts (e.g., MoS₂, MOFs, and Cd/TiO₂) are briefly introduced. In terms of the mechanism study, we summarized three possible reaction pathways, namely the formate (HCOO*) mechanism, the RWGS + CO-Hydro mechanism, and the trans-COOH mechanism, and reviewed their recent theoretical advances on Cu-based catalysts and their extension to other catalytic systems.

As an important carbon-neutral technology, CO₂ hydrogenation to methanol has shown great promise for industrial application. In order to further improve its process performances and technical competitiveness, it is crucial to design efficient catalysts, explore reaction mechanisms, and conduct deep kinetic study and reactor design. From the perspective of the catalyst design, increasing the dispersion and the exposed surface of Cu, regulating the interaction between Cu and ZnO, and balancing the surface H/C ratio of active sites are the main focus of future research. From the perspective of the reaction mechanisms, exploring the role of the active site and investigating the factors of the rate-determining steps through in situ catalyst characterization techniques and theoretical simulation calculations can further guide the rational design of efficient catalysts. In addition, the reaction kinetics of the CO₂ and CO hydrogenation involved in the methanol synthesis process is the foundation for the subsequent reactor design and optimization of reactors, which provides constructive suggestions for large-scale industrial applications.

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