

Progress in MOF-based catalyst design and reaction mechanisms for CO₂ hydrogenation to methanol

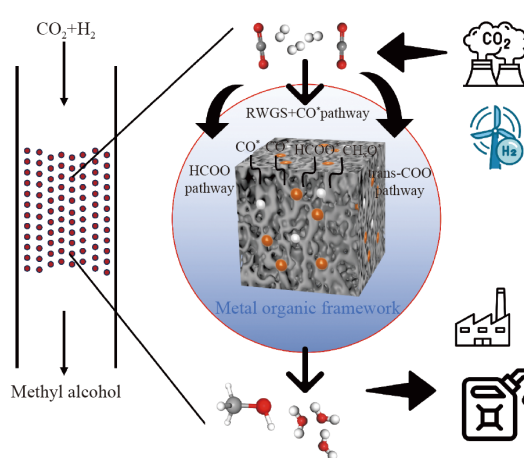
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Abstract: Against the backdrop of escalating global climate change and energy crises, the resource utilization of carbon dioxide (CO₂), a major greenhouse gas, has become a crucial pathway for achieving carbon peaking and carbon neutrality goals. The hydrogenation of CO₂ to methanol not only enables carbon sequestration and recycling, but also provides a route to produce high value-added fuels and basic chemical feedstocks, holding significant environmental and economic potential. However, this conversion process is thermodynamically and kinetically limited, and traditional catalyst systems (e.g., Cu/ZnO/Al₂O₃) exhibit inadequate activity, selectivity, and stability under mild conditions. Therefore, the development of novel high-performance catalysts with precisely tunable structures and functionalities is imperative. Metal-organic frameworks (MOFs), as crystalline porous materials with high surface area, tunable pore structures, and diverse metal-ligand compositions, have the great potential in CO₂ hydrogenation catalysis. Their structural design flexibility allows for the construction of well-dispersed active sites, tailored electronic environments, and enhanced metal-support interactions. This review systematically summarizes the recent advances in MOF-based and MOF-derived catalysts for CO₂ hydrogenation to methanol, focusing on four design strategies: (1) spatial confinement and *in situ* construction, (2) defect engineering and ion-exchange, (3) bimetallic synergy and hybrid structure design, and (4) MOF-derived nanomaterial synthesis. These approaches significantly improve CO₂ conversion and methanol selectivity by optimizing metal dispersion, interfacial structures, and reaction pathways. The reaction mechanism is further explored by focusing on the three main reaction pathways: the formate pathway (HCOO*), the RWGS (Reverse Water Gas Shift reaction) + CO* hydrogenation pathway, and the trans-COOH pathway. *In situ* spectroscopic studies and density functional theory (DFT) calculations elucidate the formation and transformation of key intermediates, as well as the roles of active sites, metal-support interfaces, oxygen vacancies, and promoters. Additionally, representative catalytic performance data for MOF-based systems are compiled and compared, demonstrating their advantages over traditional catalysts in terms of CO₂ conversion, methanol selectivity, and space-time yield. Future perspectives for MOF-based CO₂ hydrogenation catalysts will prioritize two main directions: structural design and mechanistic understanding. The precise construction of active sites through multi-metallic synergy, defect engineering, and interfacial electronic modulation should be made to enhance catalyst selectivity and stability. In addition, advanced *in situ* characterization techniques combined with theoretical modeling are essential to unravel the detailed reaction mechanisms and intermediate behaviors, thereby guiding rational catalyst design. Moreover, to enable industrial application, challenges related to thermal/hydrothermal stability, catalyst recyclability, and cost-effective large-scale synthesis must be addressed. The development of green, scalable preparation methods and the integration of MOF catalysts into practical reaction systems (e.g., flow reactors) will be crucial for bridging the gap between laboratory research and commercial



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deployment. Ultimately, multi-scale structure-performance optimization and catalytic system integration will be vital for accelerating the industrialization of MOF-based CO₂-to-methanol technologies.

Key words: CO₂ hydrogenation; metal-organic frameworks (MOFs); catalyst design; reaction mechanism; methanol

As the increasingly serious global energy crisis and environmental problems, the resource utilization of carbon dioxide (CO₂), one of the major greenhouse gases, has become an important research direction for achieving the carbon neutrality goal^[1–3]. The hydrogenation reduction of CO₂ to alcohols (such as methanol, ethanol, propanol, etc.) can not only effectively store and recycle carbon resources, but also produce high-value chemicals and clean fuels^[4–6]. Among these alcohols, methanol has attracted significant research interest, due to its high energy density, excellent storage and transportation performance, and wide application^[7–9].

The hydrogenation of CO₂ to methanol is subject to both thermodynamic and kinetic constraints^[10–12]. Therefore, developing suitable catalysts is critical to improving reaction rate and product selectivity^[13–14]. Conventional metal oxide catalysts, such as Cu/ZnO/Al₂O₃, have been widely used in the industrial methanol synthesis, but their coking resistance and catalytic activity still need to be improved^[15–17]. Metal-organic framework (MOF) materials are a class of three-dimensional porous crystal materials assembled from metal ions (or clusters) and organic ligands via coordination bonds^[18–20]. MOFs have shown excellent potential in catalysis due to their high specific surface area^[21–23], tunable pore structure, diverse metal nodes and organic ligands. These features provide structural flexibility and designability, allowing for catalyst design through strategies such as constructing interface structures and regulating the catalytic microenvironment. In the CO₂ hydrogenation to methanol reactions, MOFs can not only serve as excellent carrier materials, but also be transformed into multifunctional composite catalysts through pyrolysis or chemical modification, thereby regulating the reaction pathways and enhancing methanol selectivity^[24–25]. A recent review by Zhang et al.^[26] has carefully discussed the preparation process of copper active sites on traditional carriers, the effect of copper particle size on catalytic performance, and the evaluation of physicochemical properties and catalytic activity under the synergy of additives and carriers. By contrast, this review will focus on the design strategies of MOFs and their derivatives in CO₂ hydrogenation to methanol, including confined construction, defect engineering, metal synergy and derivative synthesis. On this basis, it will provide deep analyses involving the specific interfacial electron regulation, confinement effect and intermediate stability mechanisms of MOFs, and the industrial scalability, regenerability and economy of MOF catalysts will be systematically analyzed for the first time.

This review will systematically summarize the recent research progress of MOFs and their derived catalysts in the CO₂ hydrogenation to methanol, focusing on catalyst design

strategies, catalytic reaction mechanisms, key factors influencing catalytic performance, and future development directions. By integrating typical research cases, an in-depth analysis of the structural advantages of MOFs in this reaction system aims to provide theoretical basis and technical guidance for the development of novel and efficient CO₂ conversion catalysts.

1 Design strategy of CO₂ hydrogenation to methanol catalyst based on MOFs materials

MOF materials can precisely construct catalytic active centers by regulating the metal nodes, organic ligands, pore structure, or post-treatment via controlled crystal growth, thus showing unique advantages in CO₂ hydrogenation to methanol. According to the different catalyst construction methods, current design strategies for MOF-based and derived catalysts mainly include: confined structures and *in situ* construction, defect engineering and ion exchange, metal synergy and hybridization design, as well as MOF-derived material synthesis and template method.

1.1 Confined structures and *in situ* construction methods

To enhance the activity and selectivity of MOF-based catalysts for CO₂ hydrogenation to methanol, a variety of confined structures and *in situ* construction methods have proposed in recent years. The former confines metal nanoparticles within the MOF framework, while the latter can utilize the structural properties of the MOF to enable *in situ* generation and dispersion of metal components. These not only effectively regulate the metal particle size and the metal dispersion, but also strengthen the interaction between the metal and the carrier, significantly improving catalytic performance^[27–28].

In CO₂ hydrogenation to methanol, MOFs can act not only as porous carrier materials, but also be transformed into multifunctional composite catalysts through pyrolysis or chemical modification to regulate the reaction pathways and improve methanol selectivity^[29]. The reaction was carried out at 175 °C, 1 MPa, and the Cu₃UiO-66 showed the highest methanol formation rate (TOF = 3.7×10^3 s⁻¹) and 100% methanol selectivity, significantly superior to the compared Cu/ZrO₂, Cu/UiO-66, Cu/ZnO/Al₂O₃ catalyst systems. This study provides the first insight into the role of MOF-derived Secondary Building units (SBU) in the formation of strong metal-support interactions over copper particles, thereby laying the foundation for the development of MOF-based catalysts with high selectivity and efficiency.

Tshuma et al.^[30] synthesized CuZn bimetallic modified

MOFs by the acid-etching and self-assembly method. Using a zeolitic imidazolate framework-8 (ZIF-8) as the zinc source, copper ions (Cu^{2+}) were first introduced to induce acid etching, leading to the formation of CuZn-BTC complexes. Subsequently, the obtained CuZn-BTC complexes underwent solvothermal synthesis, calcination, and reduction treatments in sequence, ultimately yielding CuZn-based catalysts (as shown in Figure 1).

The CuZn-BTC catalyst retains the morphology of the MOF precursor while providing uniform metal dispersion and a smaller particle size, outperforming catalysts prepared by traditional coprecipitation method. In the CO_2 hydrogenation to methanol reaction, a CO_2 conversion rate of 20.8% and a CH_3OH selectivity of 91.2% were achieved at 240°C, 3.0 MPa, GHSV (Gas Hourly Space Velocity) = 6000 mL/(g·h). The methanol selectivity remained stable at 89%–94% within the temperature range of 220–260 °C. Furthermore, during a 275 h continuous test, both CO_2 conversion rate and methanol selectivity decreased by no more than 4%, demonstrating excellent long-term operational stability^[30].

The PdZn alloy catalyst derived from the PD-@zeolite-imidazole framework (ZIF-8) developed by Yazhi Yin et al.^[31] demonstrated the great potential of confined structures and *in situ* construction methods in catalyst design. By confining Pd nanoparticles within the pore structure of ZIF-8, the researchers effectively avoided particle aggregation. Subsequent *in situ* pyrolysis generated ZnO with a high specific surface area and abundant surface defects, facilitating the uniform dispersion of Pd. In addition, the strong metal-support interaction formed between Pd and ZnO further optimized the electronic properties and reactivity of the catalyst. Under the optimized reaction conditions, the PdZn catalyst exhibited an extremely high methanol yield of 0.65 $\text{g}_{\text{MeOH}}/(\text{kg}\cdot\text{h})$ and a turnover frequency (TOF) of 972 h^{-1} , significantly exceeding traditional Pd-based catalysts^[31].



Fig. 1 Schematic diagram of the formation mechanism of CuZn-BTC prepared using ZIF-8 as the sacrificial template^[30] (with permission from RSC Publications)

1.2 Defect engineering and ion exchange strategies

Metal-organic framework (MOF) materials can be designed to generate unsaturated coordination sites via crystal defect engineering. This process can introduce structural defects into the MOF framework, which not only serve as anchoring sites for metal species in the active center, but also facilitate the construction of stable and highly dispersed active centers^[32–33].

Marcos et al.^[34] constructed a defect-rich UiO-66 support and loaded copper (5%, 10%, and 20%) on the defect sites by impregnation to enhance metal-support interaction. This study found that the defect sites improved Cu dispersion, significantly boosting the CO_2 conversion and methanol yield. Specifically, under reaction conditions of 250 °C and 3 MPa, the Cu/MOF catalyst with a 20% loading showed the best methanol generation and CO_2 conversion. The methanol space-time yield was up to 2.59 $\text{g}_{\text{MeOH}}/(\text{kg}\cdot\text{h})$, which was three times higher than that of the traditional commercial Cu/ZnO/ Al_2O_3 catalyst. In addition, the catalyst demonstrated 100% methanol selectivity and excellent stability, maintaining consistent performance over 275 h in continuous reactions.

Zhu et al.^[35] constructed a Cu/UiO-66-A catalyst based on a Zr-O-Cu bridging structure. A hydrothermal ion-exchange strategy was used to control the defect site concentration in UiO-66, selectively anchoring Cu^{2+} to the hydroxyl site of the Zr_6 metal cluster. The methanol generation rate of this catalyst was up to 4.7 $\text{mol}_{\text{MeOH}}/(\text{mol}\cdot\text{h})$ at 250 °C and 3.2 MPa, much higher than that of conventional Cu/ZrO₂ catalysts. DFT calculations and experimental analyses further demonstrated that, within the structure of UiO-66, the absence of ligands led to the formation of coordination defects at the Zr metal nodes. Through the hydrothermal ion-exchange process, Cu^{2+} anchored at the hydroxyl sites of the Zr metal clusters and formed the Zr-O-Cu bridging structure. They served as key active sites due to strong CO_2 adsorption capability, which was the essential source of the high catalyst activity (as shown in Figure 2). In the Cu/UiO-66 catalyst system, the Zr-O-Cu interface significantly enhanced CO_2 adsorption capacity and catalytic activity via multiple coordination modes, such as bidentate and tridentate bridging. These structures and calculations provide a theoretical foundation for the efficiency of Cu/UiO-66 catalysts in CO_2 conversion.

1.3 Metal synergy and hybrid design

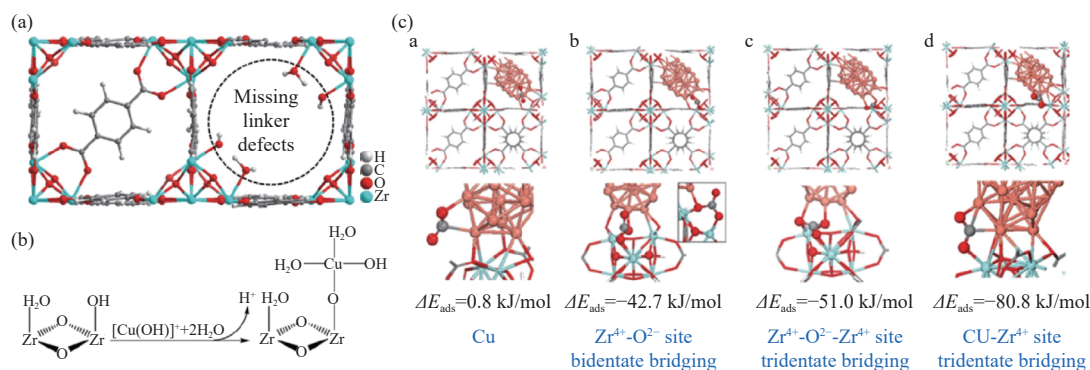
The introduction of a second metal can regulate the electronic structure, oxygen vacancy distribution and reaction pathways of the principal metal, thereby achieving synergistic catalysis^[36–37]. In the complex reaction system of CO_2 hydrogenation to methanol, a single metal often fails to simultaneously meet the synergy requirements of multiple reaction steps. By constructing bimetallic or multimetallic

systems, different metals can play complementary roles during the reaction, thereby enhancing the overall catalyst performance. Specifically, the second metal not only improves the dispersion of the metal components and prevents agglomeration, but also forms new interface structures between metal-metal or metal-support as the active reaction centers. In addition, electron transfer from the second metal can modulate the electron density of the principal metal, optimizing its ability to adsorb and desorb reaction intermediates. Meanwhile, certain metals are conducive to the formation of oxygen vacancies, thereby promoting CO₂ activation and H₂ dissociation. As a result, bimetallic catalysts often exhibit superior catalytic performance in terms of activity, selectivity, and stability compared to the single-metal systems.

Mitsuka et al.^[38] prepared Cu-ZnO/amUiO-66 composite catalysts by uniformly distributing Cu-ZnO nanocomposites in an amorphous UiO-66 framework (amUiO-66) through spray drying. This catalyst exhibited three times higher activity and 1.5 times higher methanol yield in CO₂ hydrogenation to methanol compared to crystalline UiO-66.

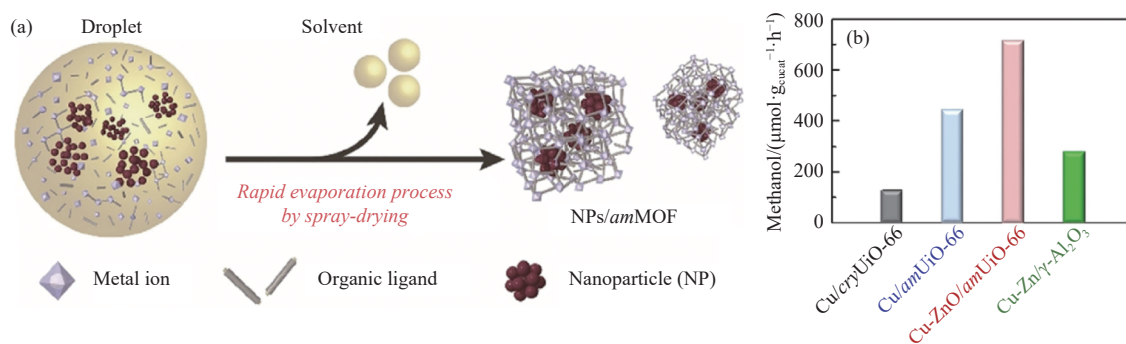
It verified the positive role of metal synergy and the disordered MOF structure in improving catalytic performance. Figure 3 shows the spray-drying preparation process of Cu/amUiO-66 and Cu-ZnO/amUiO-66 catalysts. The rapid evaporation process during spray drying enabled the uniform distribution of metal ions, ligands and nanoparticles in the amorphous UiO-66 framework, greatly enhancing the activity of the catalyst. Figure 3(b) compares the methanol synthesis performance of different catalysts, including Cu/cryUiO-66, Cu/amUiO-66, Cu-ZnO/ γ -Al₂O₃ and Cu-ZnO/amUiO-66, in CO₂ hydrogenation. The results demonstrated that the Cu-ZnO/amUiO-66 catalyst exhibited the highest methanol production, further verifying the synergistic enhancement arising from metal cooperation and MOF structural design.

Zhang et al.^[39] synthesized a CuO-ZnO@ZIF-8 catalyst with a “flower-like” structure, which exhibited a significantly higher surface oxygen vacancy concentration than that of the CuO-ZnO prepared by coprecipitation. At 200 °C, this catalyst achieved a CO₂ conversion rate of 14.64% and a methanol selectivity of 93.41%.



(a): A linker missing in the UiO-66 structure is replaced by two –OH/OH₂ species, which are active for ion exchange to deposit metal onto the Zr₆ nodes of the MOF. (b): Possible reaction for Cu deposition (ion exchange) in aqueous solution. (c): Adsorption energies (ΔE_{ads} in kJ/mol) of CO₂ at the Cu/UiO-66-a interface, including a: Cu only sites, b: Zr⁴⁺-O²⁻ sites on the Zr₆O₈ nodes in a bidentate bridging mode, c: Zr⁴⁺-O²⁻-Zr⁴⁺ sites on the Zr₆O₈ nodes in a tridentate bridging mode, and d: Cu-Zr⁴⁺ interfacial sites.

Fig. 2 Structure of Cu/UiO-66 catalyst and its influence on CO₂ conversion^[35]
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(a): Cu/amUiO-66 and Cu-ZnO/amUiO-66 synthesized by the spray-drying method for highly enhanced catalytic activity of CO₂ hydrogenation for methanol synthesis; (b): The amount of methanol synthesized from CO₂ and H₂ by Cu/cryUiO-66, Cu/amUiO-66, Cu-ZnO/ γ -Al₂O₃, and Cu-ZnO/amUiO-66 catalysts.

Fig. 3 Schematic illustration of the spray-drying synthesis of Cu/amUiO-66 and Cu-ZnO/amUiO-66 catalysts^[38]
(with permission from Wiley Publications)

As a carrier, ZIF-8 not only provides stable structural framework, but also optimizes metal dispersion through its unique pore structure and surface functional groups, promoting metal-metal synergy. In particular, the framework of ZIF-8 provides a favorable environment for the formation of oxygen vacancies, effectively enhances the adsorption of CO_2 and H^* species, reduces the energy barriers for intermediate formation, and further strengthens the interaction between Cu and ZnO, thereby significantly improving the catalytic performance.

Zhang et al.^[40] loaded ZnO onto Zr-based MOFs to prepare ZnO/Zr₁₂-bpdc catalysts for CO_2 hydrogenation to methanol. The Zr-based MOFs contain $\text{Zr}_{12}(\text{m}_2\text{-OH})_8(\text{m-OH})_6$ clusters, linked by linear biphenyl phthalates (bpdc). The resulting ZnO/Zr₁₂-bpdc catalyst showed a methanol space-time yield (STY) of up to 0.11 $\text{g}_{\text{MeOH}}/(\text{kg}\cdot\text{h})$ at 250 °C and 4 MPa, with methanol selectivity over 95%. In this system, the interfacial contact between ZnO and Zr₁₂ clusters in the MOFs replaced the traditional ZnO/ZrO₂ interfacial structure. The presence of Zr₁₂ clusters provides abundant metal-metal and metal-carrier interactions, offering a more stable and active reaction environment for ZnO. These clusters not only aid in dispersion and stabilization of ZnO, but also likely optimize the active sites of ZnO during the catalytic process through electron transfer and surface structure regulation, thereby enhancing both methanol STY and selectivity of methanol.

Duma et al.^[41] used Cu-ZnO catalysts loaded on aluminum fumarate metal-organic frameworks (AlFum MOF) for CO_2 hydrogenation to methanol. Both Cu and Zn active sites were uniform dispersion. Characterization by scanning electron microscopy (SEM), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), and transmission electron microscopy (TEM) confirmed that the support morphology was retained after the metal loading. The unique pore structure of AlFum MOF, effectively restricted the agglomeration of metal particles and maintained their homogeneous dispersion, thereby significantly enhancing the catalytic activity. With increasing Cu and Zn loading, the CO_2 conversion rate rose from 10.8% to 45.6%, and the methanol yield increased from 34.4 to 56.5 $\text{g}_{\text{MeOH}}/(\text{kg}\cdot\text{h})$. The high activity of AlFum MOF-supported catalysts underscores the promising application of MOFs as supports in thermocatalytic conversions.

1.4 Strategies for constructing MOF-derived materials

MOF-derived catalysts are currently an effective strategy for preparing novel heterogeneous catalysts. Through pyrolysis and *in situ* transformation of MOF materials, the catalysts with highly dispersed metal centers, high specific surface area, and active interfaces can be prepared. The synergistic effect of these advantages can optimize the electronic structure of the catalysts, significantly enhancing their reactivity and selectivity^[42–44].

The Gascon team prepared an $\text{In}_2\text{O}_3@\text{Co}_3\text{O}_4$ core-shell composite catalyst by the stepwise oxidation-pyrolysis strategy of In/Co-ZIF-67. During the reaction, the catalyst underwent structural evolution from Co_3O_4 and amorphous In_2O_3 shell to $\text{Co}_3\text{InC}_{0.75}$, a structural recombination process that contributed to increasing methanol yield and selectivity. In CO_2 hydrogenation to methanol, the catalyst achieved a methanol selectivity of 87%, and a methanol yield of up to 0.65 $\text{g}_{\text{MeOH}}/(\text{g}\cdot\text{h})$, while maintaining stable performance over 100 h of continuous operation. This study showed that the structural regulation in MOF-derived catalyst contributes to optimizing methanol yield and selectivity^[45].

Yu et al.^[46] prepared highly dispersed Cu-ZrO₂ catalysts using ZrO₂@HKUST-1 as a precursor by calcination reduction. The MOF-derived highly dispersed Cu nanoclusters not only act as efficient active centers, but also increase the proportion of Cu-ZrO interface. Density functional theory (DFT) calculations indicated that CO_2 can be activated at the Cu-ZrO₂ interface, thereby promoting the CO_2 hydrogenation. This catalyst demonstrated an excellent methanol generation selectivity in CO_2 hydrogenation, with a space-time yield 5.2 times higher than that of the conventional catalyst.

San et al.^[47] prepared a highly dispersed Cu/graphene catalyst using a “template genetic inheritance” (TGI) method. It introduced MOF precursors into the interlayer of graphene sheets, highly ordered and uniform dispersion of Cu particles upon MOF skeleton collapse. Graphene not only provides abundant Cu anchoring sites, but also acts as a carbon source for the *in situ* reduction of CuO. This catalyst achieved a CO_2 conversion rate of over 22% and a methanol selectivity.

Qi et al.^[48] constructed the CuZn-BTC precursor via a one-pot method, and subsequently prepared a Cu-ZnO/ Al_2O_3 catalyst through calcination. This catalyst had highly dispersed Cu and ZnO centers, along with abundant Cu-ZnO interfaces, which enhanced the adsorption and activation of CO_2 and H_2 , thereby improving both methanol selectivity and catalytic activity (as shown in Figure 4).

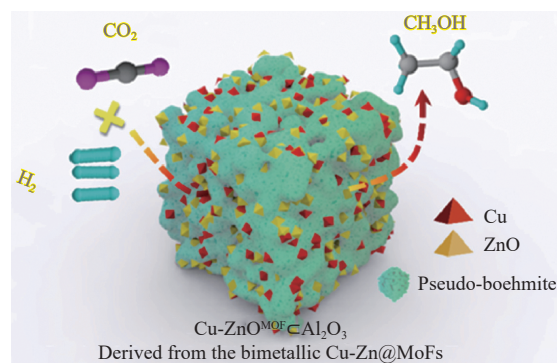


Fig. 4 Schematic diagram of the structure and reaction process of the Cu-ZnO/ Al_2O_3 catalyst derived from bimetallic Cu-Zn@MOFs^[48] (with permission from Elsevier)

The catalyst exhibited 86.9% methanol selectivity and 407.2 g_{MeOH}/(kg·h) space-time yield (STY) at 240 °C, 3.0 MPa, with a CO₂ conversion rate of 9.1%, significantly superior to those of the traditional Cu-ZnO^{NO₃}/Al₂O₃ catalyst (methanol selectivity = 79.6%, STY = 209.0 g_{MeOH}/(kg·h), CO₂ conversion rate = 5.1%).

Cai et al.^[49] successfully synthesized a Pd@In₂O₃ catalyst using TCPP(Pd)@MIL-68(In) as a sacrificial template, as shown in Figure 5. First, Pd²⁺ ions were introduced into the MIL-68([In(OH)BDC]_n), followed by coordination of TCPP(Pd) with the MOF template and subsequent pyrolysis to obtain the Pd@In₂O₃ catalyst. The catalyst had a methanol space-time yield (STY) of 81.1 g_{MeOH}/(g·h), a CO₂ conversion rate of 80%, and a methanol selectivity of 81% at 295 °C and 3 MPa (Figures 5(b) and 5(c)). The catalyst also exhibited stable performance over 50 h of continuous operation (Figure 5(d)), indicating excellent durability. It was shown that the reduction degree of the metal center can be modulated through the electron interaction between Pd and In₂O₃, thereby optimizing methanol selectivity.

In addition, using MOFs as precursors can effectively improve the metal-oxide interface on the catalyst. Wu et al.^[50] systematically compared the structural properties of MOF-derived Cu-Zn-Zr catalysts and their performance in CO₂ hydrogenation to methanol. The results showed that the catalyst structure and composition are closely related to the topology of the MOF precursors. While the number of surface Cu sites is positively correlated with the CO₂ hydrogenation activity, the Cu coordination environment in the MOF precursors affects the product distribution of the derived catalysts. The CZZ-HN catalyst had a significantly higher (STY_{CH₃OH} and TOF_{CH₃OH}) than the co-precipitated CZZ-CP, due to an enhanced metal-oxide interface. The study validated the effectiveness of the MOF-derived

catalysts in optimizing the metal-oxide interfaces, and provided valuable insights for the rational design of high-performance catalysts.

Under different catalyst design strategies, the performance of MOF-derived catalysts in CO₂ hydrogenation of to methanol exhibits clear correlations with catalyst composition, reaction temperature, pressure, space velocity (GHSV), and H₂/CO₂ ratio on CO₂ conversion rate and methanol selectivity. First, regarding catalyst composition, Cu-Zn series catalysts, such as CuO-ZnO@ZIF-8 (sample 1), ZnO/Zr₁₂-bpdc (sample 2), CuZnO-MOF-74-350 (sample 13), and Cu/ZnO (sample 21), typically exhibit excellent methanol selectivity (≥ 80%) under conditions of 190–260 °C and 3–4 MPa, while CO₂ conversion rates are mostly range between 5% and 20%. For example, CuO-ZnO@ZIF-8 achieved a CO₂ conversion rate of 14.6% and methanol selectivity of up to 93.4% at 200 °C, 2.0 MPa, GHSV = 2400 h⁻¹^[39]; When the pressure rose to 4 MPa, the selectivity of ZnO/Zr₁₂-bpdc increased further to 95.0%, but the conversion rate was only 7.5%^[40]. These results suggest that, by optimizing the Zn/Cu ratio and carrier pore structure, conversion efficiency can be improved while maintaining high selectivity.

At the same time, In-based and Pd-In-based catalysts also demonstrated promising performance. For instance, Pd@In₂O₃ (sample 7) achieved 8.0% CO₂ conversion rate and 81.0% methanol selectivity at 295 °C, 3.0 MPa, GHSV = 19200 h⁻¹, while In₂O₃@ZrO₂ (sample 17) maintained similar conversion and selectivity levels under comparable conditions^[49]. These catalysts typically operate at higher temperatures (≈290–300 °C) and pressures of 3–5 MPa, indicating In₂O₃ and ZrO₂ components significantly promote CO₂ adsorption and activation, and thus maintain high methanol selectivity at higher temperatures.

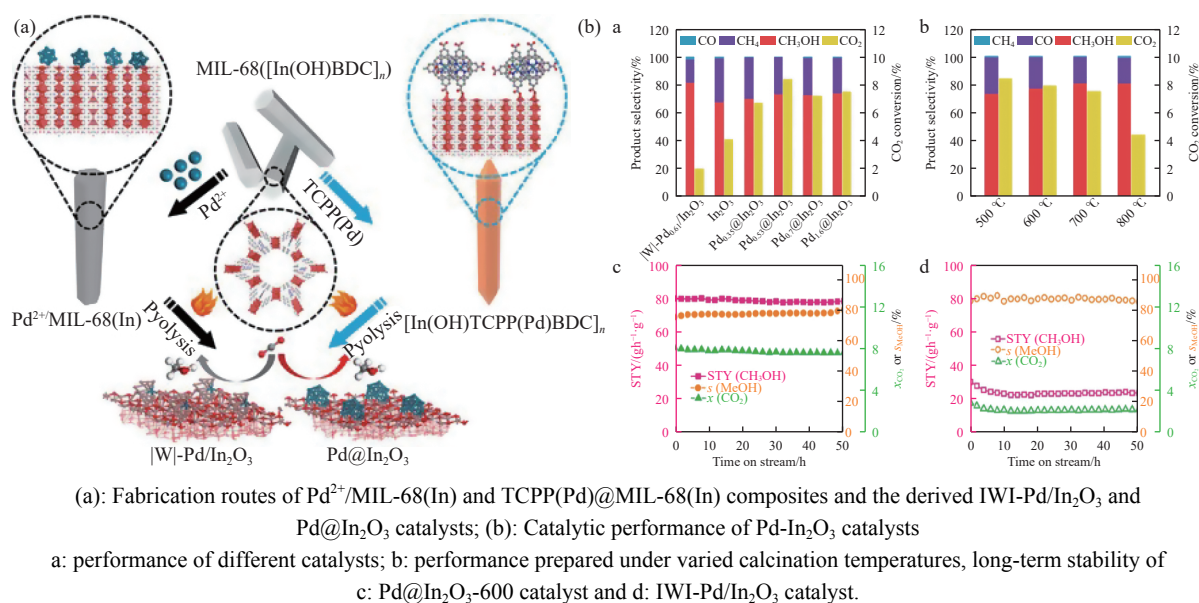


Fig. 5 Process and performance of synthesizing Pd@In₂O₃ catalyst using TCPP(Pd)@MIL-68(In) template^[49] (with permission from ACS Publications)

In contrast, multi-metal/C-N-doped catalysts synthesized from MOF precursors or C-N networks, such as 15Cu/6.4ZnO/AlFum MOF (sample 3), Mo-Co-C-N (sample 11), and In-Co-Zn /C-N (sample 16), have a unique advantage in improving conversion rates. For instance, 15Cu/6.4ZnO/AlFum MOF attained a CO₂ conversion as high as 45.6% at 230 °C, 5.0 MPa, GHSV = 10,000 h⁻¹, though the methanol selectivity was only 6.86%^[41]. Although multi-metal synergy can enhance catalytic activity, imprecise control over metal ratios and interactions may promote side reactions, highlighting the need to balance conversion and selectivity through precise interfacial and electronic structure design.

The reaction conditions also critically influence catalytic performance. Overall, the increasing temperature enhances CO₂ conversion rate, but when the temperature exceeds 300 °C, methanol selectivity decreases markedly. For example, Cr₂O₃/C-500-500 (sample 9) exhibited only 29.9% selectivity at 350 °C^[51]. The optimal temperature range typically lay between 220–260 °C, which guarantees a moderately high CO₂ conversion rate (10%–20%) and maintains a high selectivity (≥70%). In terms of pressure, raising from 2.0 to 5.0 MPa can increase CO₂ conversion rate by about 2–3 times, whereas methanol selectivity remains largely unchanged or even decrease slightly.

Although high pressure promotes CO₂ adsorption and hydrogenation active site formation, it may also enhance side reactions such as methanation. Space velocity is another key factor for balancing conversion rate and selectivity. At low GHSV (< 6000 h⁻¹), the conversion rate of CO₂ is higher. By contrast, When GHSV is over 15000 h⁻¹, selectivity remains stable despite a drop in conversion rate. Regarding the H₂/CO₂ ratio, most studies employed 3:1, with only a few exceptions using 4:1, such as In-Co-Zn/C-N and H-MoS₂ /ZnS (sample 10), which increased CO₂ conversion to 9.0% under higher hydrogen supply but reduced methanol selectivity to 67.3%^[52].

Based on the above analysis of methanol performance in Table 1^[39–41,45,47–65], future catalyst design should focus on the following aspects: first, making full use of MOF precursors (e.g., ZIF-8, MOF-74) to construct highly dispersed Cu-Zn active sites, and to systematically optimize the Cu/Zn ratio and pore structure under conditions of 220–240 °C and 3–4 MPa; second, taking advantage of the interfacial synergy between In₂O₃ and metal oxides such as Pd, Co or ZrO₂ to enhance CO₂ adsorption and activation through electronic regulation; third, carefully introducing carbon-nitrogen doping or carbon coating strategies to enhance thermal stability and anti-deactivation, while avoiding the formation of excessive ineffective phases.

Table 1 Summary table of typical catalysts for hydrogenation of CO₂ to alcohol and their reaction conditions and catalytic performance

Number	Catalyst	Temperature /°C	Pressure /MPa	GHSV /(mL·g ⁻¹ ·h ⁻¹)	H ₂ /CO ₂	CO ₂ conversion rate/%	CH ₃ OH selectivity/%	References
1	CuOZnO@ZIF-8	200	2.0	2400	3	14.6	93.4	[39]
2	ZnO/Zr ₁₂ -bpdc	250	4.0	4800	3	7.5	95.0	[40]
3	15Cu/6.4ZnO/AlFum MOF	230	5.0	10000	3	45.6	6.86	[41]
4	3In@4Co(20)	300	5.0	15600	4	20.5	87.0	[45]
5	12%Cu-ZrO ₂ -1-3	220	3.0	15000	3	6.8	64.4	[47]
6	Cu-ZnO MOF c Al ₂ O ₃	240	3.0	14400	3	9.1	86.9	[48]
7	Pd@In ₂ O ₃	295	3.0	19200	3	8.0	81.0	[49]
8	Cu/ZnO/ZrO ₂ -HN	260	4.0	5400	3	material 22	material 40	[50]
9	Cr ₂ O ₃ /C-500-500	350	3.0	1200	3	16.8	29.9	[51]
10	h-MoS ₂ /ZnS	260	5.0	15000	4	9.0	67.3	[52]
11	Mo-Co (2:1)-C-N (800)	275	2.0	6000	3	9.2	58.4	[53]
12	Cu@ZrO ₂	220	3.0	15600	3	5.0	85.0	[54]
13	CuZnO-MOF-74-350	190	4.0	4000	3	7.5	80.0	[55]
14	Cu/ZnOx/ZrO ₂	260	4.0	12000	3	18.7	52.0	[56]
15	Cu@ZrO ₂ -U	260	3.0	2400	3	12.1	70.5	[57]
16	InCoZn/CN	300	2.0	6000	3	7.0	77.0	[58]
17	In ₂ O ₃ @ZrO ₂	290	3.0	12000	3	10.4	84.6	[59]
18	Cu/ZnOx@UiO-66	250	4.0	12000	3	3.5	86.0	[60]
19	ZnO/Cu	260	4.5	21600	3	23	56	[61]
20	Cu/ZnOx/ZrO ₂	260	4.0	12000	3	18.7	52	[62]
21	Cu/ZnO	250	4.0	1500	3	20.9	58.2	[63]
22	Cu/ZrO ₂	280	4.5	21600	3	11.1	68.4	[64]
23	ZnO-ZrO ₂	320	3.0	18000	3	5.7	70	[65]

Combined with *in situ* characterization techniques and high-throughput screening, these strategies are expected to achieve a dual breakthrough in CO₂ conversion rate and methanol yield while maintaining high selectivity.

1.5 Summary

In CO₂ hydrogenation to methanol, MOFs and their derivatives offer considerable advantages for catalyst design and optimization, due to their ability for preparing highly dispersed catalysts with controllable components. In recent years, through precise design and effective regulation of MOF precursors, the active centers and catalytic performance of MOFs and derived catalysts have been effectively optimized. Current design strategies for MOF-based catalysts can be classified into confined structure and *in situ* construction, defect engineering and ion exchange, metal synergy and hybridization design, and MOF-derived material construction strategies.

Firstly, confined structure and *in situ* construction achieves *in situ* transformation of metal centers by confining metal nanoparticles within the MOF framework. This method not only effectively improves the dispersion of metal particles, but also strengthens metal-support interactions, thereby significantly enhancing the catalytic activity and selectivity. Secondly, defect engineering and ion exchange strategies provide anchoring sites for metal centers by introducing and modulating defect sites in the MOF material. Defects, such as oxygen vacancies, can effectively anchor metal particles, improving the metal dispersion and metal-carrier interaction. Compared to *in situ* confined construction, defect engineering optimizes the electronic environment of metals by adjusting defect density and type, which can significantly enhance catalytic activity. On this basis, the ion-exchange strategy further enhances metal dispersion and catalyst stability by introducing different metal ions. In terms of metal synergy and hybrid design, the introduction of a second metal to construct bimetallic or multi-metallic systems leverages synergistic effects between different metals, which enhances activity, selectivity and stability of the catalyst. The MOF-derived material construction strategy involves pyrolysis or chemical transformation of MOFs to promote synergistic catalytic effect between highly dispersed metal centers and active interfaces, improved overall catalytic performance.

The catalysts prepared via the above strategies have exhibited high activity, favorable selectivity, and robust stability in CO₂ hydrogenation to methanol. It provides important theoretical support and practical guidance for future catalyst design and application. MOF-derived materials and bimetallic catalytic systems show considerable potential for practical implementation., and future should focus on further optimizing catalyst structure and performance to promote the commercial application of CO₂ hydrogenation to methanol technology.

2 Research on the reaction mechanism of CO₂ hydrogenation to methanol

2.1 Reaction mechanism

The reaction mechanism of CO₂ hydrogenation to methanol is complex, involving multiple reaction pathways and key intermediates^[66]. Based on existing experimental and theoretical studies, three typical pathways have been identified: the formate pathway (HCOO* pathway), the reverse water-gas shift followed by CO hydrogenation (RWGS + CO* hydrogenation) pathway, and trans-COOH pathway.

The formate pathway is currently the most widely recognized dominant route. In this pathway, CO₂ is initially activated to form a HCOO* intermediate, followed by a series of continuous hydrogenation reactions to form intermediate products, such as H₂COOH*, HCOOH*, CHO*, ultimately yielding methanol (CH₃OH)^[67]. Theoretical studies suggest that the highest occupied molecular orbital (HOMO, 1πg) electron of the CO₂ molecule is concentrated on the oxygen atoms, while the lowest unoccupied molecular orbital (LUMO, 2πu) electron is located on the carbon atom. As a result, the oxygen atom acts as a Lewis base and tends to combine with a proton to form the COOH* intermediate, whereas the carbon atom, as a Lewis acid, is more receptive to nucleophilic attack by hydride to form HCOO*.

Based on theoretical models and *in situ* characterization studies, this pathway has been validated in copper-based catalytic systems. For example, Zhao et al.^[68] studied the reaction mechanism of CO₂ hydrogenation to methanol on a Cu(III) catalytic surface through theoretical calculations and proposed a typical formate pathway sequence (CO₂* → ·HCOO* → ·H₂COOH* → HCOOH* → CHO* → CHO* → CH₃OH*). The reaction energy barrier curve was plotted at 499 K (as shown in Figure 6), with different colored regions corresponding to energy changes at each reaction stage. The trend of reaction energy barrier illustrates the formation and transformation of different intermediates. This reaction pathway research provides critical insights for CO₂ utilization and conversion.

The second reaction pathway is the RWGS + CO* hydrogenation pathway. In this route, CO₂ first undergoes a reverse water-gas shift (RWGS) reaction to form the HCOO* intermediate, followed by the C–O bond cleavage to generate the CO* intermediate. Finally, CO* undergoes a hydrogenation reaction to produce methanol. This pathway shows strong reactivity at high temperatures or on metal/oxide interface catalysts. Studies have shown that it can also dominate on certain catalyst surfaces with strong CO* adsorption and activation capabilities, such as PdZn alloys or Cu/ZnO_x systems. For example, researchers coated Pd nanoparticles in a ZIF-8 shell and interfaced them with ZnO nanorods to produce PdZn alloy^[31].

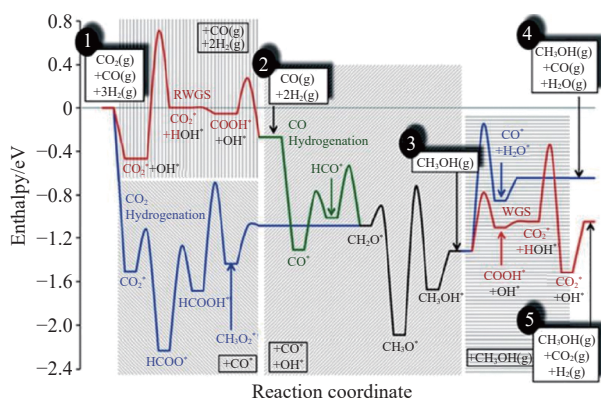


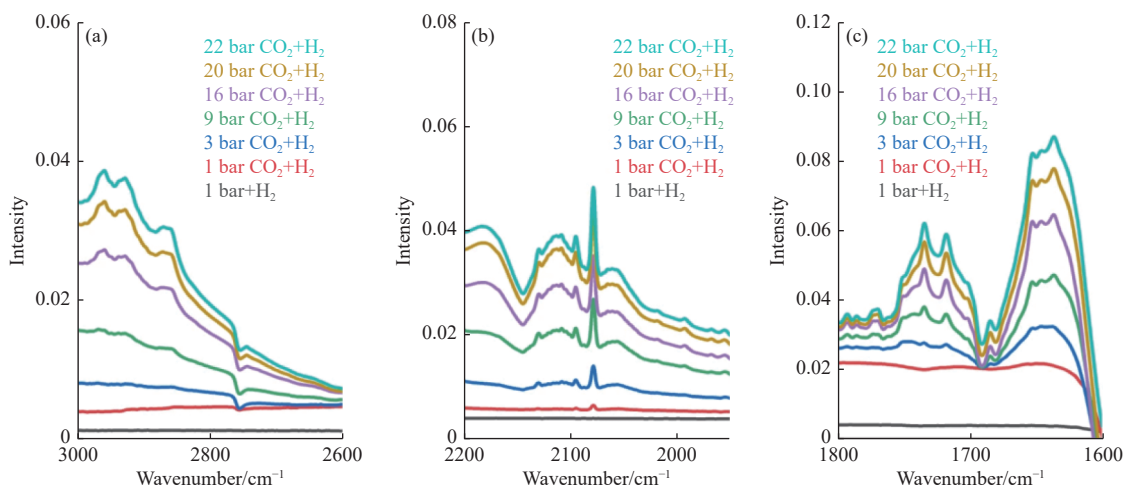
Fig. 6 Reaction energy barrier variation curve for CO_2 hydrogenation to methanol^[68]
(with permission from RSC Publications)

Experimental results showed that, when catalyzing CO_2 hydrogenation to methanol at 523–563K, 4.5 MPa, the PdZn alloy achieved a methanol selectivity of 66%–78%, and the turnover frequency (TOF) could reach up to 972 h^{-1} . On this basis, Theoretical calculations suggest that the Pd-Zn surface selectively generates the HCOO^* intermediate and reduces the d -band of Pd below the Fermi level through electron-charging, thereby enhancing the H_2 dissociation capacity and CO_2 adsorption capacities. It can further promote the generation of methanol through the CO^* intermediate.

Zhu et al.^[35] introduced Cu into UiO-66 by ion exchange and reduced the Cu^{2+} to metallic Cu particles. Fourier transform infrared spectroscopy (DRIFTS) and density functional theory (DFT) calculations were employed to investigate the adsorption behavior and reaction mechanism of CO_2 over Cu/UiO-66 derived catalysts. The study showed that during the CO_2 hydrogenation process, CO_2 molecules first adsorbed on the catalyst surface to form

carbonate/bicarbonate intermediates, and then gradually hydrogenated to form intermediates such as formic acid and methoxy, finally converting into methanol. Figure 7 shows the changes in infrared spectra of adsorbed species and reaction products on the catalyst surface during the CO_2 hydrogenation reaction under different CO_2 pressures. As the increase of CO_2 pressure from 1 to 22 bar, distinct intensity changes were shown in different wavenumber regions, which were closely related to the formation of intermediate and final product during CO_2 hydrogenation. These variations support the CO_2 hydrogenation reaction pathway on Cu/UiO-66 catalyst as mentioned by Zhu et al.^[35]. Gaseous CO was observed by DRIFTS, and CO adsorbed at different Cu sites distinct features in different spectral regions. This further confirms the presence of two major reaction pathways on the Cu/UiO-66 catalyst, namely, the formate pathway and the RWGS + CO^* hydrogenation pathway. At higher CO_2 pressures, the formation of carbonate/bicarbonate intermediates on the catalyst surface becomes more pronounced, suggesting that CO_2 molecules first adsorb on the catalyst surface, and then are gradually hydrogenated to form intermediates such as formic acid and methoxy, eventually converting into methanol.

An et al.^[69] employed the DRIFTS to analyze the role of the metal/oxide interface activity in smaller Cu/ZnO_x nanoparticles within the CuZn@UiO-bpy catalyst on the reaction performance. The DRIFTS results showed multiple negative peaks in the $1400\text{--}750 \text{ cm}^{-1}$ region. It belonged to carbonate and bicarbonate species, revealing CO_2 chemical adsorption and conversion at the metal/oxide interface. The results showed that the metal/oxide interface plays a key role in the formation and stabilization of critical reaction intermediates in catalytic CO_2 hydrogenation.



(a): range of $3200\text{--}2600 \text{ cm}^{-1}$ showing the formation of methoxy groups; (b): range of $2200\text{--}1950 \text{ cm}^{-1}$ showing CO species adsorbed on various types of Cu sites; (c): range of $1800\text{--}1600 \text{ cm}^{-1}$ showing the formation of bicarbonate/carbonate species.

Fig. 7 Changes in infrared spectra of CO_2 hydrogenation reaction catalyzed by Cu/UiO-66 under different CO_2 pressures^[35]
(with permission from Nature Publishing Group Publications)

In the synergistic reaction pathway, the RWGS + CO hydrogenation pathway is particularly crucial: CO₂ first undergoes RWGS at the Cu-ZnO_x interface to form the CO intermediate, and then the CO* molecule is rapidly hydrogenated to a series of intermediates such as H₂CO*, HCO*, CHO*, and finally to methanol (CH₃OH). The ultrafine particle size and MOF confinement effect give the interface with an extremely high CO* adsorption density and a lowered activation energy, accelerating the generation and continuous hydrogenation of CO*. At the same time, the high-density Cu-ZnO_x interface effectively inhibits CO* re-desorption of to CO or over-hydrogenation to methane, thus achieving nearly 100% methanol selectivity and excellent catalytic activity.

The third reaction pathway is the trans-COOH pathway, in which CO₂ reacts in the presence of water to form a COOH* intermediate, followed by hydrogenation to some intermediates such as COHOH*, H₂COH*, and HCOH*, ultimately producing methanol. Although this pathway is less studied, it highlights the synergistic role of water in the CO₂ hydrogenation and points out the influence of water on selectivity and reaction rate. Studies have shown that formate adsorbed on copper catalysts surface is a major intermediate in low-temperature methanol synthesis, but it cannot be converted to methanol through pure hydrogen or hydrogen-water mixtures^[70]. However, formate does produce methanol in the presence of hydrogen and water, suggesting that the involvement of water plays an important role in increasing methanol yield. Figure 8 shows the different intermediates and reaction pathways in CO₂ hydrogenation. In the trans-carboxyl pathway, hydrogen atoms react with CO or CO₂ to form formate and carboxyl intermediates. CO₂ is first hydrogenated to formate, and then, in the presence of water, the carboxyl intermediate is further hydrogenated to methanol.

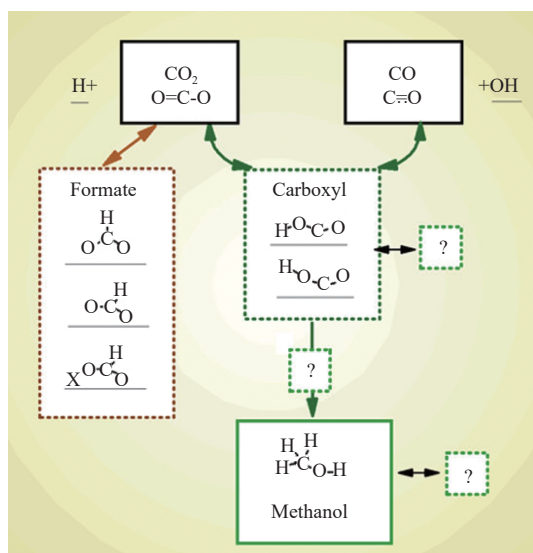


Fig. 8 Intermediates and reaction pathway of CO₂ hydrogenation via the trans-COOH route (trans-COOH pathway) (with permission from ACS Publications)^[70]

These intermediates and reaction steps are consistent with the previously described trans-carboxyl pathway, further verifying the synergistic role of water in the CO₂ hydrogenation, especially in modulating reaction selectivity and rate. For example, Gutterød et al.^[71] directly captured the COOH adsorption peak at 1725 cm⁻¹ by *in situ* DRIFTS, followed by CHO* and HCOH* peaks at 1545 and 1380 cm⁻¹, respectively. Combined with DFT calculations, it was found that the presence of water reduced the overall energy barrier of this pathway by approximately 10 kJ/mol compared to the HCOO* pathway, resulting in up to 85% methanol selectivity and excellent catalytic activity at 473 K (199.85 °C).

2.2 Key influence factors

CO₂ hydrogenation is a complex multi-step process involving CO₂ activation, H₂ dissociation, formation and transformation of intermediates, and product desorption. Catalyst design and optimization are crucial in steering these reactions. In particular, MOF-based catalysts offer significant advantages due to their unique structural properties, tunable metal centers and high specific surface area. It can significantly improve the activity and selectivity by precisely regulating active sites on catalyst. In CO₂ hydrogenation, MOF catalysts mainly increase methanol production efficiency by modulating CO₂ activation reaction, facilitating interfacial electron effects, and suppressing side reactions. The following sections will explore these mechanisms and their specific roles in MOFs-based catalysts, respectively.

2.2.1 CO₂ activation and intermediate control

The role of the catalyst extends beyond mere adsorption of CO₂ to include precise management of reaction intermediates. Owing to their tunable structural design, MOFs-based catalyst can effectively activate the CO₂ molecules and stabilize key intermediates by regulating the coordination environment between the metal center and the carrier. Specifically, the electron density and geometry of the metal centers play a decisive role in the adsorption and transformation of CO₂, thereby determining the overall reaction efficiency and selectivity.

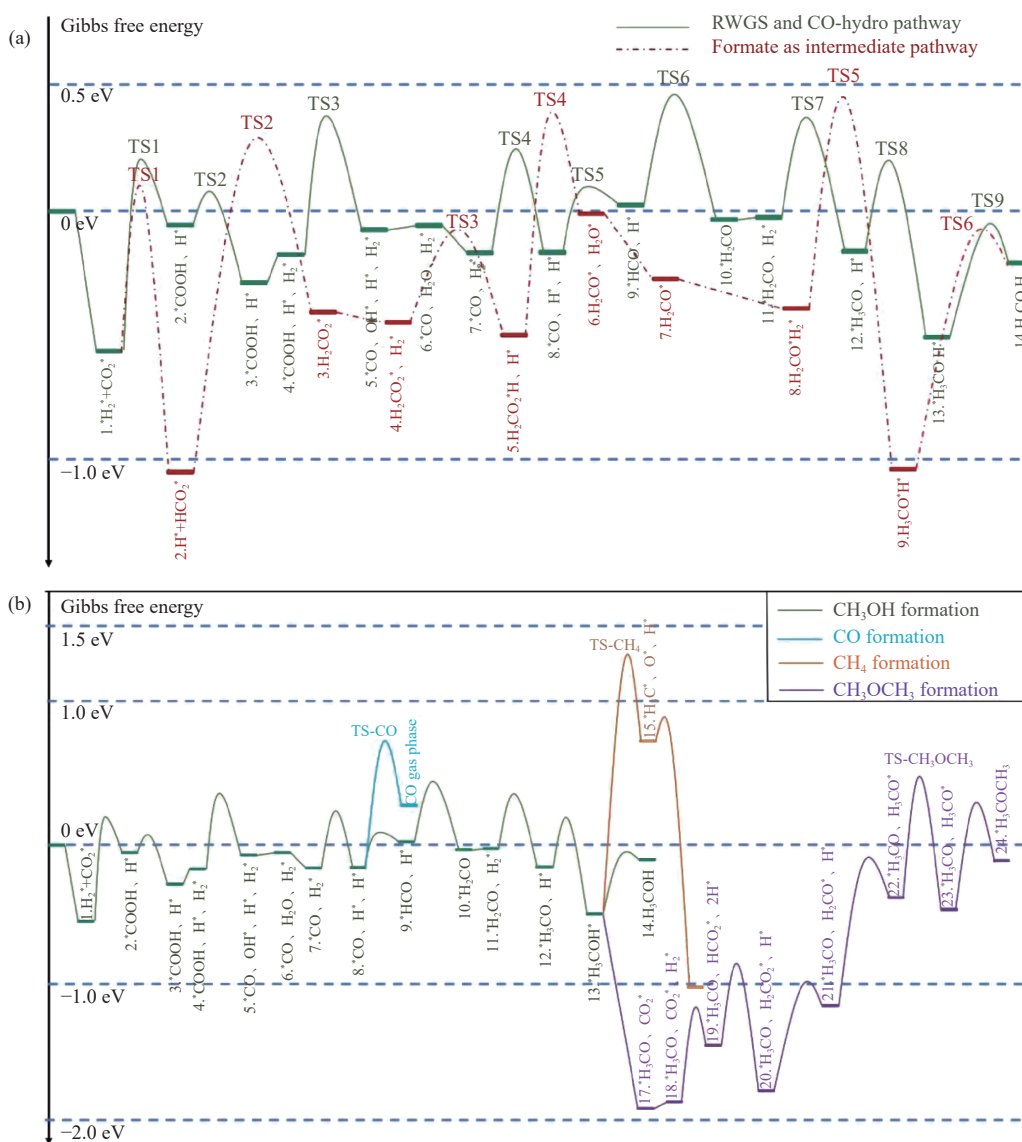
Zhu et al.^[35] conducted a systematic study of Cu/Uio-66-a. It was found that the Zr-O-Cu interface not only provided Cu⁰/Cu⁺ active centers, but also promoted a bridge adsorption mode for CO₂ through Zr₆ nodes, effectively stabilizing CO₂ molecules and facilitating their transition to HCOO*. This tailored metal-carrier interaction highlights the crucial role of MOFs catalysts in CO₂ activation. DFT calculations further revealed that the interface significantly enhanced the adsorption strength of CO₂, thereby reducing the initial activation energy of the reaction. Through such precise interface engineering, MOF-based catalysts were able to optimize CO₂ conversion pathway, showing

excellent activity in generating key intermediates such as HCOO*.

Yu et al.^[46] prepared a Cu-ZrO₂ interface catalysts by pyrolyzing ZrO₂@HKUST-1, which strengthened metal-support interaction and enhanced the activation ability of CO₂. Their findings indicated that the Cu⁰-ZrO₂ interface is not only conducive to the activation of CO₂, but also stabilized key intermediates such as HCOO* and CH₃O*, providing favorable conditions for high methanol selectivity. This interface modulation strategy significantly improves the efficiency of CO₂ hydrogenation. Figures 9(a) and 9(b) show the Gibbs free energy changes along CO₂ hydrogenation reactions. In Figure 9(a), the initial energy barrier of CO₂ adsorption is 1.4 eV (TS1). Then, CO₂ is converted to different intermediates (e.g., HCOOH*,

HCO*) through multiple transition states (TS1 to TS9), with energy barrier changes ranging from 0.6 to 1.0 eV.

In particular, the energy barrier variations from TS2 to TS3 is about 0.9 eV, and those from TS5 to TS6 is 0.7 eV. In Figure 9(b), the energy profile for methanol formation remains relatively flat, peaking at 1.4 eV after TS-CH₄. By contrast the pathway for CO generation shows a lower energy barrier (0.6 eV, TS-CO). The methane (CH₄) pathway shows a low energy barrier of 1.2 eV (TS-CH₄), while ethanol (CH₃OCH₃) has the highest generation energy barrier, reaching 1.8 eV. Overall, the optimization of the Cu-ZrO₂ interface significantly lowers the energy barrier for CO₂ conversion, especially in the formation of HCOO* and CH₃O*, thereby enhancing selectivity and reaction efficiency.



(a): Energy evolution from CO₂ adsorption to various intermediates (e.g., HCOOH, HCO) and transition states (TS1-TS9); (b): Reaction pathways for methanol (CH₃OH), carbon monoxide (CO), methane (CH₄), and dimethyl ether (CH₃OCH₃), highlighting the critical role of the Cu-ZrO₂ interface in CO₂ conversion.

Fig. 9 Gibbs free energy changes for CO₂ hydrogenation^[46]
(with permission from Elsevier)

2.2.2 Interface electronic effects and synergy mechanisms

An important feature of MOFs-based catalysts in CO₂ hydrogenation is the easy regulation of electronic effects at the metal-support interface. By modulating the electronic properties of this catalyst interface, the CO₂ activation and intermediate stability can be improved. Interfacial electron migration not only enhances CO₂ adsorption, but also stabilizes key intermediates such as HCOO* and CH₃O*, thereby increasing the methanol production rate.

Cui et al.^[59] constructed In₂O₃@ZrO₂ heterostructured catalysts by the pyrolysis of MIL-68@UiO-66. It was found that interfacial electron migration could significantly enhance catalytic performance. Specifically, electrons migrate from ZrO₂ to In₂O₃, enhancing the reduction of HCOO* and CH₃O* generation. This electron regulation mechanism highlights the crucial role of MOFs-based catalysts in achieving interface optimization, electron modulation, and intermediate transformation. X-ray photoelectron spectroscopy (XPS) analysis revealed that the C 1s peak shift of the In₂O₃@ZrO₂ catalyst before and after reaction, indicating a change in the electronic environment. Further investigation revealed that the strong interaction between In₂O₃ and ZrO₂, along with thermal effects, jointly regulated the interfacial electron migration process. This electron transfer mechanism promotes the dissociation of H₂ and accelerates the hydrogenation reaction of HCOO* and CH₃O* species, ultimately enhancing the synthesis efficiency of methanol.

The optimization of electron density at metal centers in MOFs and the metal-carrier synergy significantly affected the catalyst activity and selectivity. For example, the Cu_xZnO-MOF-74-350 catalyst synthesized by Han et al.^[72] features a Cu-ZnO interface by adjusting the Cu/Zn ratio, significantly enhancing the adsorption and activation capabilities of H₂ and CO₂. Characterization results indicated that the catalyst promoted high methanol selectivity by stabilizing the Cu⁰/Cu⁺ valence state. The Cu_xZnO-MOF-74-350 catalyst demonstrated approximately 80% methanol selectivity at a 7.5% CO₂ conversion rate, with a catalytic stability for up to 100 h at 190 °C and 4.0 MPa. The excellent performance is mainly due to the Cu-ZnO interface, which is conducive to CO₂ adsorption and stabilizes key intermediates such as HCOO*, thereby enhancing methanol selectivity. This study showed that interface optimization in MOFs can effectively enhance catalyst performance to accelerate CO₂ hydrogenation to methanol.

2.2.3 Side reaction inhibition and additive effects

Structural defects in catalysts (e.g., oxygen vacancies) and the introduction of additives can effectively suppress side reactions, including the formation of CO and CH₄. In CO₂ hydrogenation, water molecules not only promote the desorption of methanol, but also inhibit the formation of by-

products. The introduction of defect sites and additives further enhance CO₂ activation, optimize reaction pathways, and finally improve the selectivity of methanol.

Gutterød et al.^[71] found that water molecules play a dual role in CO₂ hydrogenation, which can promote methanol desorption and inhibit CH₄ formation. Water promotes the formation of C–O bonds through hydrogen bonding with intermediates, thereby enhancing the selectivity of methanol. The pore structure and surface defects (e.g., oxygen vacancies) in MOFs-based catalysts provide an effective reaction environment for water molecules, further enhancing catalytic performance. As illustrated in Figure 10, the transformation and energy changes of each intermediate in the reaction pathways. The energy changes involve −7.2 kJ/mol for the conversion from 1 to 4^{Me}, −40.2 kJ/mol for the conversion from 5^{MeMe} to 2^{MeMe}, −20.7 kJ/mol for the conversion from 4^{Me} to 3^{Me}, and −38.7 kJ/mol for the conversion from 3^{Me} to 2^{MeH}. The energy profile indicates that water plays a facilitating role in the reactions, especially in the conversion step from 1 to 4^H, where the energy changes to 6.8 kcal/mol. In the conversion from 5^{Me} to 3^{Me}, the synergistic effect between water and methanol further enhanced reaction efficiency. By analyzing the reaction pathways and energy changes, the study revealed that water increases the methanol selectivity of by altering intermediate stability and suppress the occurrence of side reactions. These results suggest that water not only promotes methanol formation in the catalytic process, but also inhibits the formation pathway of CH₄ to a certain extent.

In the CuO-ZnO@ZIF-8 catalyst constructed by Zhang et al.^[39], a high concentration of oxygen vacancies was found to significantly enhance the synergistic adsorption of H* and CO₂, thereby accelerating intermediate formation and improving the selectivity of methanol. These structural defects provide abundant active sites in MOFs-based catalysts and help to reduce by-product generations. The introduction of such defects into MOFs increases the reaction rate.

Similarly, the MOF-808-Zn catalyst enhances the efficiency and selectivity of CO₂ hydrogenation by optimizing the metal-carrier interface and defect sites^[73]. Specifically, Zn²⁺ ions are introduced into the Zr₆(μ₃-O)₄(μ₃-OH)₄ nodes of the MOF-808 through post-synthetic methods. In this process, ligands are removed through mild thermal treatment to generate open Zr⁴⁺ sites. In terms of defect sites, the structure of MOF-808-Zn catalyst enhances catalytic effect by introducing oxygen vacancies and open metal sites. Oxygen vacancies exemplified by Zn²⁺-O-Zr⁴⁺ coordination environments not only provide additional active sites, but also stabilize key intermediates. The open Zr⁴⁺ sites further enhance the adsorption and activation of CO₂ molecules. By optimizing these defect sites, the MOF-808-Zn catalyst can effectively suppress side reactions such as the formation of CH₄, thereby enhancing the selectivity of methanol. As shown in Figure 11, the Zn²⁺-O-Zr⁴⁺ sites in MOF-808-Zn act synergistically to promote the adsorption and conversion of CO₂, ultimately generating methanol.

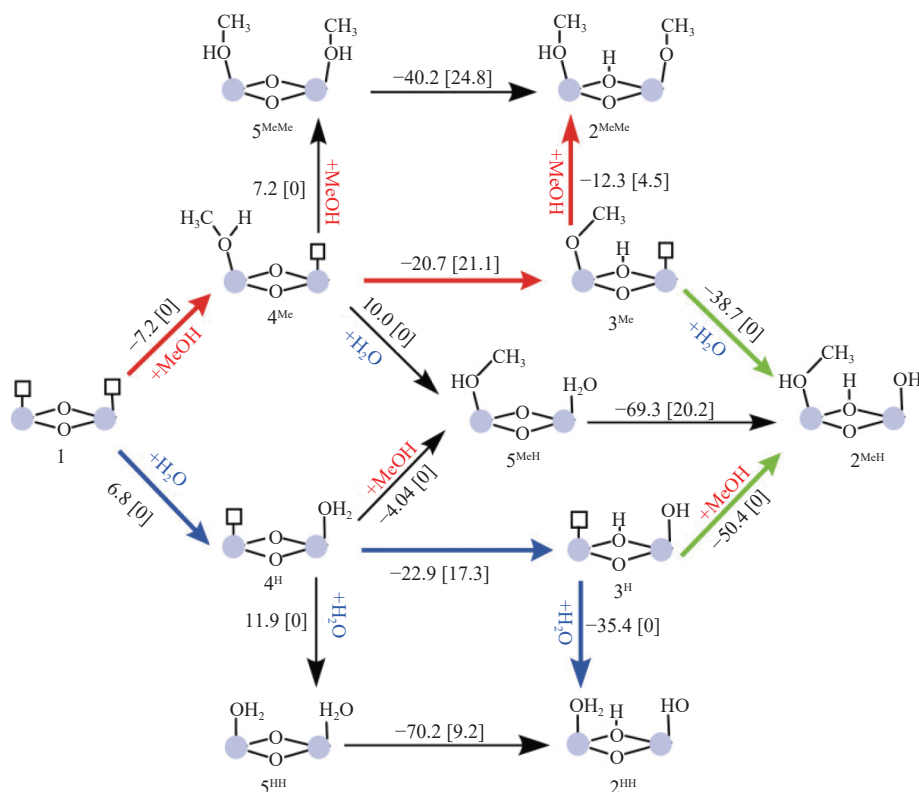


Fig. 10 Reaction pathways and energy profiles for CO₂ hydrogenation, showing intermediate transformations and their interactions with methanol (MeOH) and water (H₂O)^[71]
(with permission from ACS Publications)

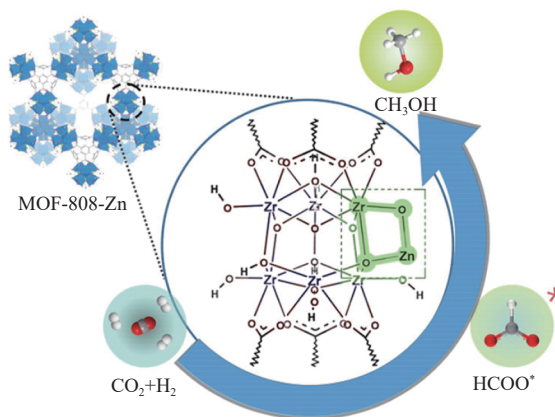


Fig. 11 Structure of MOF-808-Zn and the reaction mechanism for CO₂ hydrogenation to methanol^[73]
(with permission from ACS Publications)

Beyond the intrinsic reaction pathways, studies have found that the microstructure of catalyst has a significant influence on the reaction mechanism. For example, oxygen defect sites at the interface between Pd-Zn alloys and ZnO have been shown to facilitate the adsorption and transformation of oxygen-anchored intermediates such as HCOO*^[74]. In addition, both Pd-Zn alloy composition ratios and particle size significantly affect catalytic activity, exhibiting typical “volcano behavior”. The ZIF-8 coating can both increase oxygen defects on the ZnO surface and control the size of Pd nanoparticles to form a highly active

sub-nano Pd-Zn alloy. However, an excessively thick ZIF-8 shell impedes Pd-Zn alloy formation and weakens interfacial interaction, which is detrimental to methanol production. Therefore, ZIF-8 shell thickness control and interface optimization have become important means to enhance catalytic performance.

In summary, CO₂ hydrogenation to methanol involves multiple reaction pathways and multi-step hydrogenation processes.

The microstructure of the catalyst and its surface electronic properties play a core role in determining pathway selectivity and catalytic activity. By carefully regulating catalyst particle size, interface structure, oxygen defect concentration, and multiphase synergy mechanism, it is possible to achieve precise control over CO₂ hydrogenation reaction pathway, thereby improving methanol selectivity and yield.

3 Summaries and prospects

MOFs and their derived catalysts show great potential in CO₂ hydrogenation to methanol. By adopting design strategies such as *in situ* confinement, defect engineering, and metal-interface synergy, MOFs can effectively optimize metal dispersion, improve metal-carrier interaction, and construct stable catalytic active centers. As a result, the activity, selectivity, and stability of catalysts are significantly enhanced. In particular, the structural

adjustability of MOFs enables them to exhibit excellent catalytic performance under different reaction conditions.

The reaction mechanism for CO₂ hydrogenation to methanol primarily proceeds three pathways: formate pathway (HCOO*), RWGS + CO* hydrogenation pathway and trans-carboxyl pathway. The formate pathway is generally dominant, though the specific pathway can vary depending on the catalyst and reaction conditions. The performance of MOF-based catalysts depends not only on their structural design, but also on factors such as metal-carrier interface effects, electronic effects, defect structures, and additives. The optimization of metal-carrier interface can effectively enhance CO₂ activation ability, the regulation of electronic effect helps stabilize key intermediate, and the introduction of defect sites and additives improves methanol selectivity and suppresses side reactions.

With a deeper understanding of the MOFs catalyst, future research will mainly focus on the following areas to further enhance its application potential in the CO₂ hydrogenation to methanol reaction.

(1) Catalyst design and structural regulation will be the focus of future research. By optimizing the metal center, carrier interface, and pore structure design of MOF-based catalysts, the adsorption capacity of CO₂ and the stability of intermediates can be optimized, thereby improving the selectivity and efficiency of the reaction.

(2) Exploring multi-metal synergistic effects will be another important direction for improving catalyst performance. By designing bimetallic or multi-metallic systems and optimizing the electronic effects and synergies between metals, the activity and selectivity of catalysts can be effectively enhanced.

(3) Elucidating reaction mechanisms and catalytic pathways is essential for further catalyst improvement. Future research should focus on analyzing the mechanisms of action of metal-carrier interfaces, oxygen vacancies, and defects, clarifying the dominant factors of each reaction pathway on different catalysts, and providing a theoretical basis for the optimal design of catalysts.

(4) The stability and recyclability of catalysts remain key challenges in the industrial application of MOFs-based catalysts. Future research should aim to enhance the thermal stability and pressure resistance of catalysts, explore catalyst regeneration and recycling protocols to ensure the excellent catalyst lifetime.

(5) Although MOF catalysts have shown excellent performance at the laboratory scale, their translation into efficient systems for industrial production remains challenging. Future research must balance production costs, recovery efficiency, and performance under real industrial environments for large-scale applications.

Declaration of Competing Interest

The authors declare no conflict of interest.

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基于 MOFs 材料的 CO₂ 加氢制甲醇催化剂设计和反应机理研究进展

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摘 要: CO₂ 加氢制甲醇是实现碳资源循环利用和“碳中和”目标的重要路径之一。本文综述了金属有机框架材料(Metal organic Frameworks, MOFs)及其衍生物在该反应体系中的研究进展,从催化剂设计策略、反应机理以及催化性能关键影响因素等角度探讨了 MOFs 及其衍生物在 CO₂ 加氢制甲醇中的优势。本工作首先从设计策略方面综述了提升金属分散度、调控界面结构、构建协同活性中心和稳定结构等因素对催化性能的影响;其次,在反应机制层面总结了 CO₂ 加氢制甲醇主要加氢路径及催化剂选择不同反应路径的主导机制;随后,讨论了催化性能的关键影响因素,及各因素调节对 CO₂ 活化、中间体稳定性及副反应抑制的影响规律;最后,本文结合典型研究案例,对 MOFs 基催化剂催化 CO₂ 加氢制甲醇的主要挑战及未来在催化剂构筑中的研究趋势进行展望。

关键词: CO₂ 加氢;金属有机框架(MOFs);催化剂设计;反应机理;甲醇

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