



CO₂ Hydrogenation on Metal-Organic Frameworks-Based Catalysts: A Mini Review

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Conversion of carbon dioxide (CO₂) into value-added fuels and chemicals can not only reduce the emission amount of CO₂ in the atmosphere and alleviate the greenhouse effect but also realize carbon recycling. Through hydrogenation with renewable hydrogen (H₂), CO₂ can be transformed into various hydrocarbons and oxygenates, including methanol, ethanol, methane and light olefins, etc. Recently, metal-organic frameworks (MOFs) have attracted extensive attention in the fields of adsorption, gas separation, and catalysis due to their high surface area, abundant metal sites, and tunable metal-support interface interaction. In CO₂ hydrogenation, MOFs are regarded as important supports or sacrificed precursors for the preparation of high-efficient catalysts, which can uniformly disperse metal nanoparticles (NPs) and enhance the interaction between metal and support to prevent sintering and aggregation of active metal species. This work summarizes the recent process on hydrogenation of CO₂ to methanol, methane and other C₂₊ products over various MOFs-based catalysts, and it will provide some clues for the design of MOFs materials in energy-efficient conversion and utilization.

Keywords: MOFs, CO₂ hydrogenation, methanol, methane, C₂₊ Products

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INTRODUCTION

Due to the rapid consumption of fossil resources, e.g., coal, petroleum, and natural gas, a large number of CO₂ have been released into the atmosphere (Song, 2006). From 2006 to 2021, the global CO₂ concentration in the atmosphere has been elevated from 381 to 415 ppm (NOAA, 2022). The massive emission of CO₂ has brought serious environmental problems, such as global climate change and ocean acidification (Valles-Regino et al., 2015). Hence, reduction of CO₂ amount and mitigation of greenhouse effect are the major challenges faced by the whole human society.

Regardless of this, CO₂ is an important C1 platform molecule. Conversion of CO₂ through sustainable catalytic processes into valuable chemicals and clean fuels is a promising way for CO₂ utilization which could promote a circular carbon economy (Srinivas et al., 2014; Didas et al., 2015; Porosoff et al., 2016; Rafiee et al., 2018). CO₂ conversion can be achieved by electro-catalysis, photo-catalysis, and thermal-catalysis processes. Electro-catalysis or photo-catalysis from clean and renewable electrical or solar energy is regarded as an important route for CO₂ reduction reaction (CO₂ RR). Through the rational design of high efficient catalysts, these reactions can be performed under relatively mild conditions that considerably decrease the energy consumption (Liu et al., 2012; Handoko et al., 2013; Jhong et al., 2013; Wang et al., 2015; Perathoner and Centi, 2019; Wang J.-J. et al., 2021; Zhang et al., 2021; Zhang et al., 2022a). Nevertheless, the electro-catalysis or photo-catalysis for CO₂ conversion is time or geographically dependent, which, thus, decreases their

economic viability. Compared to the former two manners, the thermal catalytic conversion of CO₂ shows higher efficiency and it is more potential for industrial application. Since the CO₂ molecule is thermodynamically stable and kinetically inert, the activation of the C=O bond in CO₂ needs to overcome a high energy barrier. Renewable hydrogen (H₂) generated from photolysis or electrolysis of water has high energy density and it can effectively reduce CO₂. Thus, hydrogenation of CO₂ into high-value hydrocarbons and oxygenates, including methane (CH₄), methanol (CH₃OH), ethanol (C₂H₅OH), and light olefins (C₂=C₄), has received increasing research interest (Sha et al., 2020).

The catalytic system for CO₂ hydrogenation mainly consists of metal sites and support, including metal oxide/carbide, zeolite, graphene, and so on. Coperet and co-workers prepared zirconia-supported copper nanoparticles (NPs), which showed methanol selectivity of 75% (Larmier et al., 2017). Encapsulation of Cu NPs in Beta zeolite elevates ethanol selectivity and space-time yield (STY) to ~ 100% and 398 mg g_{cat}⁻¹ h⁻¹ (Ding et al., 2020). Highly selective conversion of CO₂ into light olefins, aromatics, gasolines, and diesel was also achieved over metal oxides/zeolites bifunctional catalysts (Gao et al., 2017; Wang Y. et al., 2018; Zhou et al., 2019; Wang S. et al., 2020; Wei et al., 2021; Zhang et al., 2022b; Wang et al., 2022). In general, improvement of metal site dispersion and modulation of metal-support interaction can increase CO₂ conversion and product selectivity.

In recent years, metal-organic frameworks (MOFs) have been considered important host materials in adsorption, gas separation and catalysis processes, due to their large surface area, abundant metal sites, and three-dimensional (3D) porous structure (Kumar et al., 2017; Guntern et al., 2021). MOFs are composed of metal-oxygen clusters serving as secondary building units (SBUs) that are connected by the organic ligands (Ranocchiarri and Bokhoven, 2011; Chavan et al., 2012). The cages and the missing linker defects in MOFs are ideal places for confining ultra-small metal NPs, thus, inhibiting the sintering and aggregation of active sites (An et al., 2017; Zhao et al., 2018; Abdel-Mageed et al., 2019; Hu et al., 2019; Zhu et al., 2020; Yu et al., 2021). The metal-support interaction can be adjusted by controlling the pyrolysis of nodes and linkers in MOFs (Furukawa et al., 2010; Abdel-Mageed et al., 2019; Wang, 2022). This work gives a short review about the recent progress on the application of MOFs-based catalysts in CO₂ hydrogenation to methanol, methane, and some C₂₊ products. Synthesis and structural regulation of MOFs materials have been reviewed in many other literatures (Eddaoudi et al., 2002; Cavka et al., 2008; Wang C. et al., 2018; Usman et al., 2021).

CO₂ Hydrogenation to Methanol

Methanol is an important platform compound in the chemical industry, and it can be transformed into commodity olefins, aromatics, formaldehyde, and longer-chain alcohols (Liu et al., 2018; Yarulina et al., 2018). Considering the unique features role of methanol in energy conversion, a concept of “methanol economy” was proposed by Olah and co-workers (Goepfert et al., 2014). Hydrogenation of CO₂ to methanol is described as the following Equation 1



Although CO₂ hydrogenation to methanol is exothermic, the activation of O=C=O bond requires to overcome a high energy barrier that makes operating temperature generally as high as 240–300°C (Murthy et al., 2021). An increase in reaction temperature not only accelerates competitive reverse water-gas shift (RWGS) reaction (Equation 2) and produces more CO but also induces sintering and aggregation of active metal NPs.



One efficient method to improve the sintering resistance of active metal species is the enhancement of metal-support interface interaction through confining ultrasmall metal NPs within the pores or cages of MOFs. Yaghi and co-workers prepared the catalyst with the single Cu nanocrystal encapsulated in the cage of UiO-66 (Cu@UiO-66); Cu@UiO-66 shows 100% methanol selectivity, and 8 times higher yield than Cu/ZnO/Al₂O₃ in CO₂ hydrogenation (Rungtaweeworant et al., 2016). It suggests that the strong interaction between Cu nanocrystal and Zr-based SBUs of UiO-66 effectively stabilizes Cu active sites. Anchoring Cu NPs into the missing-linker defects of UiO-66 considerably enhances the interaction of metallic Cu with Zr₆O₈ nodes of UiO-66. It is found that the isolated Cu can only produce CO via RWGS reaction, whereas Cu NPs anchored on the Zr₆O₈ nodes generates larger numbers of Cu-O-Zr interface sites that show higher activity for methanol synthesis (Figure 1A) (Zhu et al., 2020). An and co-workers reported that the organic coordinating groups in MOFs play a vital role in stabilizing metal NPs (An et al., 2017). The ultra-small Cu/ZnO_x NPs are *in situ* generated through the reduction of frameworks Cu²⁺ and Zn²⁺ ions in Zr₆ clusters of UiO-bpy (2,2-bipyridine) MOF (Figure 1B). The strong interaction between Cu/ZnO_x NPs and bpy moieties in MOFs prevents the phase separation of Cu/ZnO_x. Thus, the prepared Cu/ZnO_x@MOFs catalyst shows methanol selectivity of 100% in CO₂ hydrogenation, with the STY as high as 2.59 g_{MeOH} kg_{Cu}⁻¹ h⁻¹. It should be noticed that although these MOF catalysts have been widely used in CO₂ hydrogenation, they usually need to be carried out at a relatively low temperature, because of their low thermal/hydrothermal stability. It is found that the organic ligands in MOF decompose easily at the high reaction temperature, causing the collapse of the pore structure and the decrease of catalytic activity.

Another way to enhance the metal-support interaction is to pyrolyze the metal-loaded MOF precursors in an inert atmosphere. Liu and co-workers fabricated a stable Cu@ZrO_x catalyst via *in situ* treatment of Cu/UiO-66 in H₂ flow at different temperatures (Liu et al., 2019). Cu@ZrO_x possesses abundant Cu-ZrO_x interfaces and a stable 3D ZrO_x framework that leads to the formation of more Cu⁺ species on the surface of ZrO₂. As a result, CO₂ hydrogenation to methanol is significantly improved via forming more formate and methoxy intermediates. An inverse ZnO/Cu catalyst with closer proximity to ZnO-Cu interface was prepared by Hu and co-workers through directly calcining Cu@ZIF-8 (Hu et al., 2019). It is shown that the small ZnO NPs on the surface of Cu promote the formation of methanol in CO₂ hydrogenation. HKUST-1 was used as the Cu source to

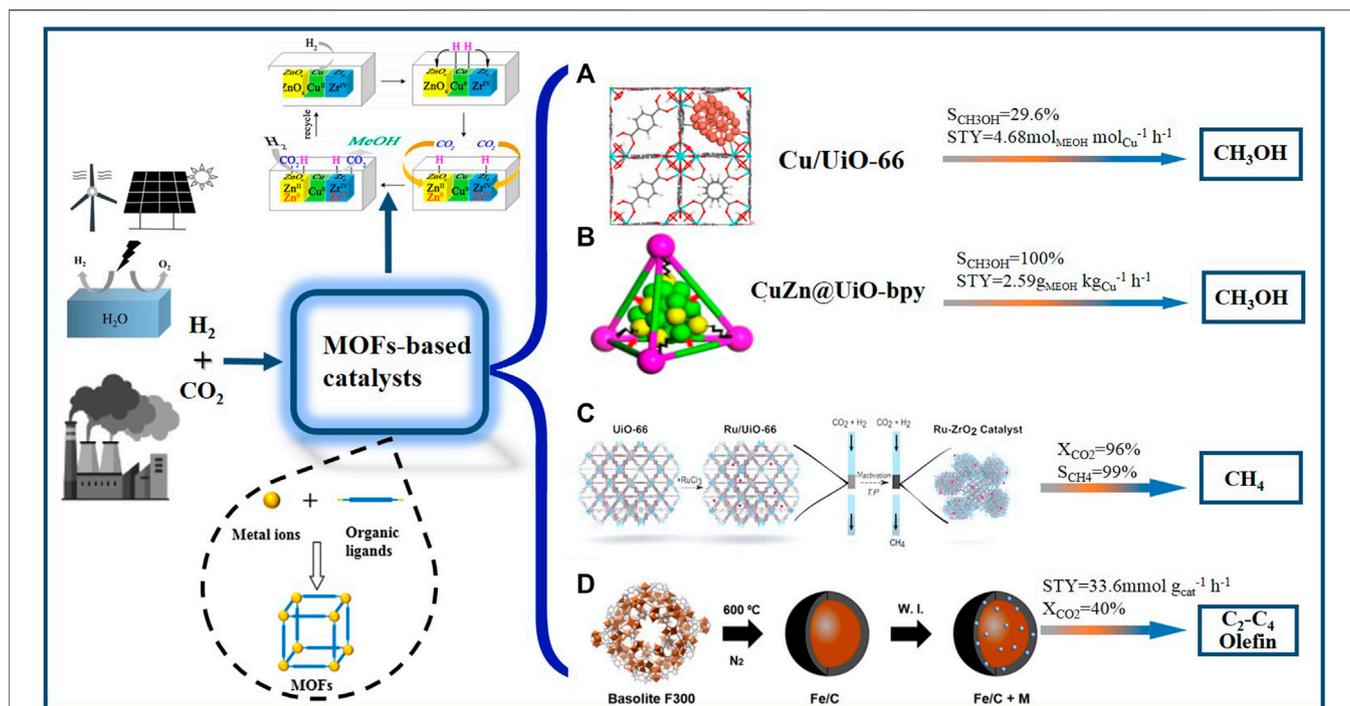


FIGURE 1 | CO₂ hydrogenation over various MOFs-based catalysts. **(A)** Interface bonding of sub-nanometer Cu clusters with Zr₆O₈ nodes over Cu/UIO-66 and its catalytic results in CO₂ hydrogenation to methanol. Reproduced with permission from Zhu et al. (2020). Copyright 2020 Springer Nature. **(B)** The Cu/ZnO NPs embedded UiO-bpy and its catalytic results in CO₂ hydrogenation to methanol. Reproduced with permission from An et al. (2017). Copyright 2017 American Chemical Society. **(C)** Structural evolution in the decomposition process of Ru/UIO-66 and its catalytic results obtained material for CO₂ hydrogenation to CH₄. Reproduced with permission from Lippi et al. (2017). Copyright 2017 Royal Society of Chemistry. **(D)** Fe/C-K catalyst fabricated through decomposition of Basolite F300 MOF and its catalytic results obtained material for CO₂ hydrogenation to CH₄. Reproduced with permission from Ramirez et al. (2018). Copyright 2018 American Chemical Society.

prepare the ZrO₂@HKUST-1 core-shell precursor via one-step hydrothermal method. Upon calcination and reduction, the Cu nanoclusters are highly dispersed on ZrO₂, forming strong Cu-ZrO₂ interface interaction. This nano Cu-ZrO₂ catalyst gives a methanol space-time yield (STY) of about 5.2 times higher than that of the sample obtained by the traditional impregnation method (Yu et al., 2021).

Besides Cu-based catalysts, other metals-loaded MOFs have been developed for CO₂ hydrogenation to methanol. Yin and co-workers embedded ultrasmall Pd crystals into ZIF-8 and further pyrolyzed them into PdZn alloy after calcination under airflow (Yin et al., 2018). The strong interface interaction between PdZn and ZnO not only prevents the aggregation of metal sites but also leads to the formation of more oxygen defects, thereby enhancing catalytic activity and stability of PdZn catalyst in CO₂ hydrogenation to methanol. Co₃O₄ coated by amorphous In₂O₃ shell was synthesized through decomposition of In-modified ZIF-67(Co) (Pustovarenko et al., 2020). Co₃O₄/In₂O₃ core-shell catalyst exhibits a maximum methanol STY of 0.65 g_{MeOH} g_{cat}⁻¹ h⁻¹ over 100 h time on stream. Olsbye and co-workers (Gutterød et al., 2019) encapsulated Pt NPs into the octahedral cavity of UiO-67. The Pt-embedded UiO-67 produces more methanol but less methane in CO₂ hydrogenation than the Pt/C, Pt/SiO₂ and Pt/Al₂O₃ at 170°C and 1–8 bar. It is shown that the interface between Pt NPs and linker-deficient Zr₆O₈ nodes is

the main site for methanol formation. A decrease in missing-linker defects lowered the methanol formation rate (Gutterød et al., 2020). Introduction of H₂O is beneficial to increase in methanol selectivity, due to the facilitation of methanol desorption. The catalytic results of some MOFs-based catalysts in CO₂ hydrogenation to methanol are summarized in **Table 1**.

CO₂ Hydrogenation to Methane

Methane (CH₄) is the main component of natural gas and it is also an important building block in the chemical industry, and can be further transformed into downstream products such as ethyne and ammonia (Bai et al., 2008; Sha et al., 2020). Hydrogenation of CO₂ to CH₄ provides an alternative solution to alleviated methane market shortage (Qin et al., 2017). Although CO₂ methanation is a strongly exothermic reaction (Equation 3), it is always operated at high temperatures because of the kinetic limitation.



Supported ruthenium (Ru), rhodium (Rh), nickel (Ni), and cobalt (Co) catalysts are commonly used, as their high activity in CO₂ hydrogenation. Strong metal-support interaction (SMSI) improves the dispersion of metal species and the stability of catalyst. Using SMSI to mediate the catalytic behavior of supported metal species is of significance in CO₂

TABLE 1 | Summary performance of catalysts for CO₂ hydrogenation reaction.

Catalysts	Main Product	H ₂ /CO ₂ Ratio	T (°C)	P (MPa)	Loading (Wt%)	X _{CO₂} (%)	Selectivity (%)	STY (g kg _{cat} ⁻¹ h ⁻¹)	TOS (h)	Ref
Cu-UiO-66	Methanol	3:1	175	1	1.0	1	100	—	—	Rungtaweeworanit et al. (2016)
Cu/UiO-66	Methanol	3:1	250	3.2	1.4	—	29.6	679.76	50	Zhu et al. (2020)
Cu@3D-ZrOx	Methanol	3:1	260	4.5	12.4	13.1	78.8	796	105	Liu et al. (2019)
Cu/ZnO _x @UiO-66	Methanol	3:1	250	4	5.9	4.3	87	28.3	100	Yang et al. (2021)
Cu/ZnO _x @UiO-bpy	Methanol	3:1	250	4	6.9	3.3	100	37.5	100	An et al. (2017)
Cu-ZrO ₂ (ZrO ₂ @HKUST-1)	Methanol	3:1	220	3	11	6.8	64.4	287.9	16	Yu et al. (2021)
ZnO/Cu(Cu@ZIF-8)	Methanol	3:1	260	4.5	57.6	—	—	933	76	Hu et al. (2019)
PdZn (Cu@ZIF-8)	Methanol	3:1	270	4.5	—	14	55	650	50	Yin et al. (2018)
In ₂ O ₃ /Co ₃ O ₄ (In@ZIF-67)	Methanol	3:1	300	5	—	—	87	650	100	Pustovarenko et al. (2020)
Ni@MIL-101	Methane	8:1	320	0.1	10	56.4	91.6	—	10	Mihet et al. (2019)
Ni@MOF-5	Methane	4:1	320	0.1	10	75.1	100	—	100	Zhen et al. (2015)
Ni@UiO-66	Methane	3:1	300	—	20	57.6	100	—	100	Zhao et al. (2018)
Ru@UiO-66	Methane	4:1	350	0.5	1.0	96	99	—	—	Lippi et al. (2017)
K-CuZnAl + Na-Fe@C	Ethanol	3:1	350	5	—	39.2	35	—	50	Wang Y. et al., 2021
Fe/C-K (Basolite F300)	Olefins	3:1	320	3	—	40	~40	—	50	Ramirez et al. (2018)

hydrogenation. MOFs are believed as promising supports or sacrificed templates, as they can promote active metal species dispersion and enhance the metal-support interaction.

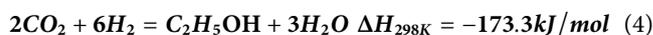
Mihet and co-workers encapsulated Ni into MIL-101 (Ni@MIL-101) using the impregnation method. The high surface area (2,497 m² g⁻¹) and pore volume (1.75 cm³ g⁻¹) of Ni@MIL-101 make the Ni particles highly dispersed in MIL-101 which enhances the adsorption and activation of CO₂. With such a catalyst, CO₂ conversion reaches 56.4%, with CH₄ selectivity of 91.6% at 320°C and gas hourly space velocity (GHSV) of 4,650 ml g⁻¹ h⁻¹ (Mihet et al., 2019). Ni@MOF-5 shows higher Ni dispersion due to a larger surface area (2,961 m² g⁻¹) and thus resulting in higher CO₂ conversion and CH₄ selectivity of 75.1 and ~100% respectively at 300°C, 1 atm and GHSV of 2000 ml g⁻¹ h⁻¹ (Zhen et al., 2015). In addition, the metal-support interaction is also enhanced by anchoring Ni on MOFs. Zhao and co-workers prepared a series of UiO-66-supported Ni-based catalysts using impregnation and reduction methods (Zhao et al., 2018). Encapsulation of ultrasmall Ni particles in UiO-66 can increase the interface interaction of Ni with UiO-66 support, which, hence, inhibits the sintering of Ni species. The prepared 20%Ni@UiO-66 exhibits CO₂ conversion of 57.6% and CH₄ selectivity of 100% in CO₂ hydrogenation. Interestingly, no significant deactivation was observed even after a reaction of 100 h.

Lippi and co-workers investigated the structural evolution in the decomposition process of metal-loaded MOFs (Lippi et al., 2017; Lippi et al., 2021). The 3D framework of Ru-impregnated UiO-66 (Ru/UiO-66) gradually collapsed under CO₂ methanation conditions to form amorphous C and Zr containing phase structure, which is then transformed into tetragonal ZrO₂(t) and finally into more stable monoclinic ZrO₂(m) (Figure 1C). The structure and morphology of catalyst can be precisely controlled by altering the treatment conditions during MOFs decomposition. The Ru/ZrO₂(m) is a highly active and stable CO₂ methanation catalyst and it gives the

CO₂ conversion of 96% and CH₄ selectivity of 99% at 350°C and 5 bar. The catalytic results of reported MOFs-based catalysts for CO₂ hydrogenation to CH₄ was shown in Table 1.

CO₂ Hydrogenation to C₂₊ Products

Conversion of CO₂ to C₂₊ products, such as alcohol, olefins and aromatics, is highly desirable but remains a greater challenge than to C1 compounds due to the high C-C coupling barrier (Guo et al., 2018; Wei et al., 2021). Although CO₂ hydrogenation to ethanol, light olefin, or aromatic is exothermic (Equations 4–6), relatively high temperature and pressure are always necessary for the activation of CO₂ molecules.



Recently, some researchers suggested that direct pyrolysis of metal-loaded MOFs in an inert atmosphere can generate various metal-carbides, in which the metal NPs are closely confined in the carbon porous materials to achieve strong metal-support interaction and avoid aggregation of active sites. Tsubaki and co-workers designed the K-CuZnAl and Na-Fe@C composite catalyst. This catalyst enhances the ethanol selectivity as high as 35.0% and CO₂ conversion of 39.2%, at 350°C and 5.0 MPa in CO₂ hydrogenation (Wang Y. et al., 2021). The K-CuZnAl activates CO₂ to form methanol and CO, and Na-Fe@C promotes the C-C coupling, with Na-Fe@C obtained from the pyrolysis of Fe-based MOFs under N₂ flow. The carbon matrix effectively prevents Fe sintering and achieves the uniform dispersion of Fe active sites.

The hydrogenation of CO₂ to olefins is a potential way of achieving a sustainable carbon cycle. It is generally performed via a two-step process on Fe-based catalysts: CO₂ is firstly converted to CO via RWGS reaction, and then CO is hydrogenated to olefins via Fischer-Tropsch synthesis (FTS) reaction (Yang et al.,

2017; De et al., 2020). Ramirez and co-workers prepared the Fe/C-K catalyst through the decomposition of Basolite F300 MOF under N₂ atmosphere (Ramirez et al., 2018). It shows good catalytic performance for CO₂ hydrogenation to olefins; CO₂ conversion and C₂⁺-C₄⁺ STY reach 40% and 33.6 mmol g_{cat}⁻¹ h⁻¹ at 320°C and 3 MPa (Figure 1D). The uniform distribution of Fe active sites is considered effectively promote RWGS and FTS reactions.

Similarly, Li and co-workers fabricated ZnZrO_x@C catalyst with three-dimensional (3D) hierarchical structure through carbonization of Zn-modified UiO-66 (Wang Y. et al., 2020). The introduction of Zn into the synthesis gel of UiO-66 induces the formation of more defects due to the substitution of Zn for Zr. Upon coupling with H-ZSM-5 zeolite, it affords the selectivity of aromatics in hydrocarbons as high as 73.1%, CH₄ is decreased to 3.4%. Compared with possesses traditional ZnZrO_x oxides, ZnZrO_x@C catalyst formed by the carbonization of defective MOFs owns richer surface vacancies, and hence, shows higher CO/CO₂ conversion due to their strong adsorption. In addition, the 3D hierarchical carbon framework structure facilitates the diffusion of products, thus, avoiding secondary reactions and elevating the proportion of benzene, toluene, and xylene (BTX) in aromatics.

DISCUSSION

Metal-organic frameworks (MOFs) are burgeoning porous materials and they are widely used in adsorption, separation, and catalysis processes due to their unique pore structure, versatile compositions, and large surface area. The cages and the missing-linker defects in MOFs provide ideal places for encapsulating or anchoring metal nanoparticles, thereby preventing the sintering and aggregation of active sites. Nevertheless, MOFs are also important sacrificed templates for the preparation of high-efficient metal oxides or carbides. Some MOFs derived metal@C were designed, and exhibited high

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catalytic performance in CO₂ hydrogenation to methanol, methane, and other C₂⁺ products, due to high dispersion of active sites and strong metal-support interaction.

Despite that MOFs as supports or catalysts have received extensive attention and they show superior catalytic activity and product selectivity in CO₂ hydrogenation, however, the much lower thermal and hydrothermal stability of MOFs than SiO₂, Al₂O₃, and zeolites limits the applications in many industrial processes. This is because the organic ligands are nearly impossible to resist high temperature or their facile pyrolysis character. Nevertheless, there are potential candidates for preparing highly dispersed oxide-supported metal catalysts with strong metal-support interaction.

AUTHOR CONTRIBUTIONS

QZ: conceptualization, writing—original draft; SW: conceptualization, funding acquisition, writing—review and editing; MD: conceptualization, funding acquisition; WF: supervision, conceptualization, funding acquisition, writing—review and editing.

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