

Review

Catalytic Hydrogenation of Carbon Dioxide to Methanol on MOF-Confined Metal Nanoparticles: A Review

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Abstract

High energy demand due to boosted economic growth has led to heavy consumption of fossil fuels, thus causing massive emissions of carbon dioxide (CO₂) in the air. A promising solution to reduce carbon emissions is to convert CO₂ into methanol (CH₃OH), which requires high-performance catalysts. Metal nanoparticles have been in the spotlight due to their under-coordinated active sites. Nonetheless, conventional catalytic substrates have emerged with a decline in catalytic performance due to agglomeration of MNPs. Metal–organic frameworks (MOFs) have been acknowledged as alternative platforms to preclude aggregation of MNPs by encapsulation. This review introduces conventional heterogeneous catalysts on CO₂ hydrogenation to CH₃OH as the first endeavor, then summarizes recent progress of MNPs@MOFs on the same reaction, and, finally, points out the problems that remain unsolved.

Keywords: metal–organic frameworks; MOF-confined metal nanoparticles; CO₂ hydrogenation; methanol; encapsulation; synergy effects



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1. Introduction

The growing population and modern living standards have resulted in a rapid growth of energy demand. Since the industrial revolution in the late 1700s, energy consumption has heavily relied on the combustion of carbon-based fossil fuels and thus continually increased the atmospheric CO₂ concentration [1], reaching 412 ppm in 2020 [2]. This has caused serious global warming and environmental problems [3]; consequently, there has been an urgent need to reduce carbon footprint. One solution is carbon capture and storage (CCS), and the other is carbon capture and utilization (CCU). CCS, as it is named, is composed of three main stages: (i) CO₂ capture; (ii) transportation; and (iii) permanent CO₂ storage by injecting into a ground or ocean [4]. CCU has gained more and more attention due to the mitigation of carbon emissions by making high-value-added chemical products [5]. Relying on well-understood technological components, CCS appears to be a mature and readily deployable solution towards carbon reduction [6]. Nevertheless, it is limited by cost-intensive operation [7] (e.g., requirement of high energy input for CO₂ separation) and CO₂ transportation [8]. With respect to CCS, among all potential products by CO₂ hydrogenation, methanol (CH₃OH) is highly attractive as it is a potential clean-burning fuel for automobiles [9,10]. Under this background, high-performance catalysts for such CO₂ conversion have been targeted.

Because of the stable C=O bond [11], CO₂ hydrogenation to CH₃OH is particularly challenging [12], attracting global effort to develop advanced catalysts for CO₂ activation and selective conversion towards the products. In contrast to the development of heterogeneous catalysts, there is a narrow portfolio towards homogeneous catalysis of CH₃OH synthesis via CO₂ hydrogenation [13]. The major challenges include formate species blocking the active site towards further hydrogenation [14], lengthy catalyst synthesis [15], catalyst incompatibility towards any additive, reaction pH, side products such as CO [16], energy-intensive operation, catalyst deactivation during recycling [17], etc., thus resulting in very limited choices of applicable molecular catalysts. Conversely, heterogeneous catalysts, which are commonly MNP (metal nanoparticle)-based catalysts, are expected to overcome these challenges and present a commercial-scale CH₃OH production. Hereby, it still stands at a prominent position in the research trend. In thermal catalysis, which is more advantageous than electrocatalysis and photocatalysis in terms of kinetics and industry-scaled production [18–20], harsh operating conditions are often applied for efficient cleavage of a stable C=O bond [21–23]. Nevertheless, deactivation might emerge on conventional heterogeneous catalysts due to the rapid crystallization of nano-sized particles, with the intention of minimizing their surface energy [24]. This is particularly severe under high-temperature operation due to a drastic increment of chemical potential for MNPs, driving them to evolve toward an equilibrium shape mainly through coalescence and/or Ostwald ripening [25]. Coalescence is the migration of particles across a surface in a Brownian motion, while Ostwald ripening is the unleashing of individual atoms from particles followed by surface diffusion. These homeless particles or atoms will be prone to merge into a large nanoparticle for lowering chemical potential and finally approaching an equilibrium state [26,27]. Apparently, the formation of large nanoparticles is accompanied by a notable decrement in exposed surfaces and active sites, resulting in a remarkable decline in catalytic performance [28]. The presence of water accelerates sintering [29,30], due to which most catalysts may be stranded in the sintering event for CH₃OH synthesis because of the concomitant water byproduct. In addition, the active sites of conventional catalysts can be occupied by undesired adsorbates as they are fully exposed to reactants in an open space, thus leading to lower product selectivity by side reactions [31].

To address these challenges, a core-shell strategy has been proposed [32]. The shell is of vital importance as it can provide high shape-selectivity catalysis by stopping the consecutive reaction due to limited space for reaction, allowing efficient transfer of size-selective molecules toward active sites [33], and acting as the capsule to stabilize MNPs in curbing their agglomeration—a hallmark of a core-shell catalyst [34]. In respect to this, metal–organic frameworks (MOFs), featured with highly tunable porosity and tailorable chemistry [35], have been recognized as an ideal platform for encapsulation of MNPs [36]. Herein, this review aims to provide a solid introduction to conventional support-based and MOFs-encapsulated MNPs for CO₂ hydrogenation to methanol. Finally, suggestions for directions of future work on CO₂-to-methanol conversion by MOF-based confined MNPs will be given.

2. Conventional Support-Based MNPs

The conventional heterogeneous catalysts are commonly metal nanoparticles (MNPs) supported by metal-oxide-based substrates, which can maximize the usage of under-coordinated active sites of MNPs by strong metal-support interactions (SMSI) and enhance their CO₂ hydrogenation performance by synergistic effects [37]. Four main categories are introduced in this section: they are Cu-based catalysts, noble-metal-based catalysts, bimetallic catalysts, and metal oxide complexes.

2.1. Cu-Based Catalysts

Cu catalysts alone cannot provide high selectivity and catalytic activity to CH₃OH synthesis [38,39], thus requiring an appropriate support to stabilize its active sites and tune its activity to advance catalytic performance [11]. The development of Cu-based catalysts for CH₃OH synthesis dates back to 1905 when Paul Sabatier and Jean-Baptiste Senderens reported their discovery of Cu for effective CH₃OH decomposition [40]. This discovery encouraged a number of pioneering research studies to look into how catalysts could promote effective CH₃OH decomposition by assuming equally effective CH₃OH formation over them under different operating conditions [40]. In 1921, George Patart filed the first patent for a Cu-based catalyst for CH₃OH synthesis [41], but its vulnerability to sulfur poisoning made it unattractive for commercialization. In 1963, Phineas Davies and Frederick Snowdon from Imperial Chemical Industries (ICI) patented a metal oxide (copper, zinc, and chromium) composite for CH₃OH production at 30–120 atm [42]. It enabled the production of CH₃OH in high quantities without the need for high pressure. Based on the finding that substitution of alumina by chromium oxide could prolong the catalyst life, John Thomas Gallagher and John Michell Kidd [43] revised the patent in 1965 and developed Cu/ZnO/Al₂O₃, a highly selective catalyst that reigned supreme in the following CH₃OH industry. Since then, the investigation of Cu-ZnO-based catalysts has dominated this topic, resulting in tremendous publications [44]. Until now, the conventional Cu/ZnO/Al₂O₃ catalyst remains prominent for the CH₃OH industry owing to its low monetary price and high activity at mild operating conditions [44,45].

Although the incorporation of an Al promoter elevates CO₂ hydrogenation performance for CH₃OH synthesis [46], its strong hydrophilic character appears to be an issue during operation. For instance, the high production of water can induce a rapid particle sintering followed by a subsequent loss of active sites, finally leading to the deactivation of the catalyst [47]. In an attempt to address the issue, less hydrophilic promoters like ZrO₂ have been proposed, which was confirmed by Arena et al. [48]. They performed a series of activity tests for Cu-ZnO/ZrO₂ and commercial Cu-ZnO/Al₂O₃ at 160–260 °C and 1.0–3.0 MPa, revealing that enhanced CH₃OH formation is essentially due to the less hydrophilic character of ZrO₂. Nevertheless, this is not the only promotional effect gifted by ZrO₂, under which stronger Cu-support interaction and improved Cu dispersion were also introduced with lower Cu coordination and increased Cu-O distance in contrast to the Cu/ZnO catalyst [49]. In addition, ZrO₂ can improve Cu/Zn dispersion and Cu redox ability [46,50–52], plus bringing a strong modification on textural and chemical effects as well as adsorption properties [53,54]. As a result of multi-fold modifications by ZrO₂, the ternary catalyst Cu/ZnO/ZrO₂ can pose a much higher activity and selectivity towards CH₃OH synthesis relative to conventional Cu/ZnO/Al₂O₃ catalysts [55].

Cu-ZnO/ZrO₂ ternary catalyst shows competitive activity with the commercial catalyst. Nevertheless, introducing additional promoters, such as SiO₂, Ga₂O₃, and TiO₂, can revamp Cu-ZnO/ZrO₂ into a more powerful and active catalyst [56–58]. For example, Sloczynski et al. [59] prepared a series of oxide additives of B, Ga, In, Gd, Y, Mn, and Mg on their promotional effects for Cu/ZnO/ZrO₂. They found that the additives have a significant impact on textural and structural properties in terms of copper dispersion, ZrO₂ loading, and hydrophobic character, and thus improved CH₃OH yield, with Ga₂O₃ as the best among them. Phongamwong et al. [60] studied the activity of a series of CuO-ZnO-ZrO₂-SiO₂ in variation of 0–5% wt silica content, using the reverse co-precipitation method. The result showed that the addition of 1 wt% silica could outperform the silica-free system by an increase of 26% in CH₃OH synthesis activity at 20 bar and 240 °C, based on which silica was believed to increase the exposed area of copper catalysts and surface basicity of parent catalysts.

2.2. Noble Metal and Bimetallic Catalysts

Other than Cu-based catalysts, Pd is often considered the second option to catalyze CO₂ hydrogenation to CH₃OH. Similarly, supports and promoters hold the key to CH₃OH production as Pd sites promote CO formation, and it alone cannot stabilize the formate intermediate long enough to be converted into CH₃OH, instead being decomposed into CO and H₂O via RWGS reaction [61]. Despite 90% CO selectivity detected upon pure Pd, the addition of ZnO could form a bimetallic PdZn alloy, which acted as an active phase towards selective CH₃OH production [61]. As a result, 11% CO₂ conversion and 60% CH₃OH selectivity were achieved at 250 °C and 20 bar. As revealed, PdZn alloy can passivate the Pd surface and strengthen the adsorption of formate species. Additionally, ZnO and Pd played their own roles with ZnO for CO₂ adsorption and Pd in H₂ dissociation, and such co-operation efficiently furnished this bifunctional catalyst [61].

In addition to ZnO, Ga₂O₃ is the other solid support pairing properly with Pd NPs [62]. The Pd/Ga₂O₃ catalyst involving active Pdⁿ⁺ (0 < n < 2) sites could afford CO₂ conversion of 19.6% with CH₃OH yield in 10.1%, where the operating pressure and temperature are 5.0 MPa and 523 K, respectively [63]. The authors reckoned that Ga_xO_y support generated an optimal amount of partially oxidized Pd species upon the catalyst surface; hence, Pd/Ga₂O₃ was endowed with the best activity in contrast to other Pd/metal oxides [63]. However, CH₃OH selectivity is an issue in this case due to the in-parallel RWGS reaction leading to undesired CO. Interestingly, other study showed a suppressing effect on CO by Pd/SiO₂. It enlightened the use of Ga₂O₃ as a promoter to Pd/SiO₂, aiming for amelioration of CH₃OH selectivity, overall showing a 500-fold increase in CH₃OH production rate than the parent catalyst Pd/SiO₂, where TOR (10^{−3} s^{−1}) is 0.002 [64].

Au is scarcely studied since its bulk phase shows inertness in catalyzing hydrogenation, but it can become active when it is deposited as a nanoparticle on metal oxide support. For instance, the study by Yang et al. [65] demonstrated the activity of Au/CeO_x/TiO₂ on CO₂ abstraction and hydrogenation at low pressure, in which CO and CH₃OH production was promoted together with enhanced CH₃OH selectivity by a small coverage of CeO_x. Behm group [66] carried out a systematic study on different metal oxide supports (TiO₂, Al₂O₃, ZnO, and ZrO₂) for Au NPs at moderate operating conditions (5 bar pressure and 220–240 °C) and achieved the best CH₃OH selectivity (i.e., 83.3% approximately) with ZnO support. Proceeding to the study of Au particle size effect over Au/ZnO, they disclosed that small-sized Au catalysts could result in a positive impact on CH₃OH formation rate while imposing an adverse effect on CH₃OH selectivity due to competitive CO production.

Given the above description for synergistic catalysis by PdZn and CuZn active sites, bimetallic systems have also been widely investigated for CH₃OH production. For instance, Song et al. [67] reported a sequence of novel silica-supported Pd_xCu_{1−x} (where x is within the range of 0.25–0.34) bimetallic catalysts, achieving a maximum rate of CH₃OH production at x = 0.34. Such a bimetallic promotional effect was rationalized as the coexistence of PdCu and PdCu₃ alloy phases, which delivered higher hydrogen absorption capacity. They subsequently extrapolated the optimal atomic ratio widely (2.4–18.7%) for the same catalyst and revealed that Pd-Cu(2.4)/SiO₂ produced 1.6 times more CH₃OH than commercial Cu-ZnO-Al₂O₃. Nevertheless, competitive CO production outpaced CH₃OH, thus leading to regrettably low CH₃OH selectivity [68]. In addition, Jaramilo's group [69] synthesized silica-supported In-Pd bimetallic catalyst with In:Pd molar ratios varying by 1:0, 1:1, 2:1, and 0:1. Thanks to the In-Pd alloy phase and its synergy with indium oxide, all bimetallic samples outperformed individual metals in terms of CO₂ conversion and CH₃OH selectivity. Among them, In:Pd(2:1)/SiO₂ won the championship by achieving the highest production (5.1 μmol/g_{InPdS}) and selectivity (61%) of CH₃OH (Table 1). Similar enhancement was

observed at the In-Ni/SiO₂ system, indicating a translatable promotion mechanism on these alloy/oxide systems.

Table 1. CH₃OH selectivity and activity of studied samples under 573 K, 40 bar [69].

Sample	CH ₃ OH Selectivity (%)	CH ₃ OH Activity (g _{methanol} g _{cat} ^{−1} h ^{−1})
In ₂ O ₃ /SiO ₂	24	0.104
In:Pd(2:1)/SiO ₂	61	0.588
In:Pd(1:1)/SiO ₂	42	0.507
In:Pd(1:2)/SiO ₂	23	0.334
Pd/SiO ₂	4	0.046

2.3. Metal Oxide Catalysts

Aside from metal-based catalysts, metal oxides have emerged as promising catalysts in CH₃OH synthesis. For example, binary metal oxides ZnO-ZrO₂ showed good stability and activity by achieving >10% CO₂ conversion along with approximately 90% selectivity at 320 °C and 5 MPa after 500 h reaction [70]. Similarly, MZrO_x (M = Cd, Ga) could deliver 4.3–12.4% and 80% for CO₂ conversion and CH₃OH selectivity, respectively, apparently performing better than individual oxides [71]. In both cases, the synergy between catalytic components is the main driving force for such amelioration of catalytic activity.

Indium oxide has been recognized and highlighted for its 100% CH₃OH selectivity, but was limited by low CO₂ conversion [72], which has motivated tremendous work to improve it. Javier's group [73] demonstrated an enhancement with combined In₂O₃/ZrO₂, highlighting the key role of ZrO₂ to increase active sites. Witton et al. [74] proposed an investigation of the promotional effect of Ga_xIn_{2-x}O₃ by varying the Ga/In ratio, with Ga_{0.4}In_{1.6}O₃ giving the highest hydrogenation efficiency and CH₃OH yield increasing from 1.1% (In₂O₃) to 2.4% at 340 °C and from 0.48% (In₂O₃) to 1.14% at 360 °C. Such enhancement was attributed to stronger adsorption of reaction intermediates by the catalyst. Pd-doping is also an available solution to enhance the catalytic property of In₂O₃ since the former is favorable for H₂ split, a friendly H atom supplier as noted above [75].

3. MOF-Encapsulated MNPs

Since the work in 1995 by Yaghi [76], metal–organic frameworks (MOFs) as three-dimensional porous coordination polymers have rapidly grown their influence in the fields of chemistry and material science. The same group in 1999 developed [Zn₄O(tpa)₃]n (tpa = terephthalic acid), also called MOF-5, as one of the most well-known and studied MOFs [77]. In reticular chemistry, three core elements are required for the design of MOFs: building blocks, targeted nets, and iso-reticular chemistry [78]. Building blocks can be mainly denoted as secondary building units (SBUs) and organic linkers [79]. Topological nets are generally purposed to show the basic architectures of MOFs, by using dot-line expression to impart the spatial distribution of building blocks (e.g., Zr-MOFs shown in Figure 1) [80]. They usually serve as the basis and first phase for MOF design and construction. Under this scheme, iso-reticular chemistry can guide the regulation of chemical or physical properties through smart selection and combinations of building blocks while maintaining the underlying topology, making them desirable for broad applications under various environmental conditions [81]. In short, MOFs have been recognized as ultra-porous hybrid crystalline materials in which secondary building units are assembled by polydentate linkers (usually carboxylate, sulfonate, or phosphonate), integrating into well-defined networks.

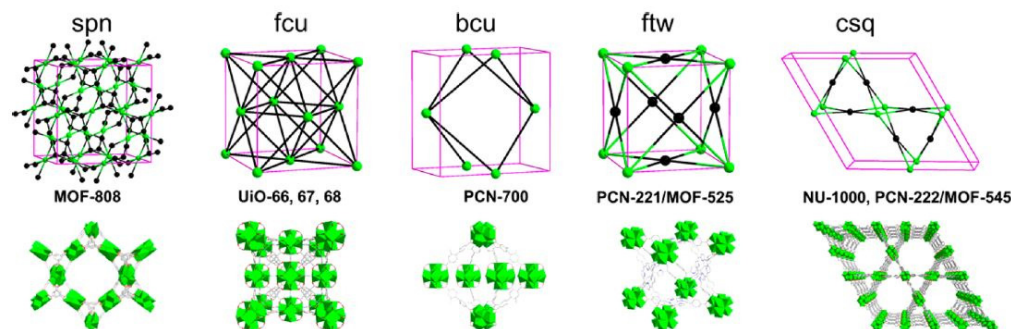


Figure 1. Schematic presentation of selected Zr-MOF topological nets, where spn, fcu, bcu, ftw, and csq represent the topology of sodalite, face-centered cubic, body-centered cubic, Fluorite, and cubic square net, respectively [82]. (Copyright © 2016 American Chemical Society).

3.1. Structural Characteristics

The growing popularity of MOFs is mainly attributed to their high porosities and large pore volumes and surface areas, which provide the basis for various functions. Currently, most well-developed MOFs are microporous in nature as they have shown superior performance on gas adsorption; however, they are limited in emerging applications, such as drug delivery and catalysis, with strong demand to host large objects and to provide efficient molecular diffusion. Under this context, MOFs with large pores are requested, which can be easily decorated with different functional groups and provide large confined spaces, ideally dispersing and protecting active NPs. Stemming from the size of NPs and the nature of targeted reactions, proper MOF confinement can considerably improve the activity in various nanocatalysis [83]. This background highlights the importance of urgent development of mesoporous and macroporous MOFs [84], which is approachable through elongating the length of organic linkers [85].

3.2. MOF Stability

As the framework of active MNPs, MOF stability is of vital importance to all research objects as it can determine their lifespans for technical implementation, which is essentially determined by the strength of metal–ligand bonds [86–88]. On the ground of Pearson’s hard and soft acids and bases (HSAB) principle, a strong metal–ligand bond can only be derived by hard acid–hard base or soft acid–soft base combination, while alternative options (e.g., hard acids and soft bases, or soft acids and hard bases) will lead to a fragile and vulnerable interaction [89]. Thence, MOFs synthesized by high-valency metals and carboxylate-based ligands exhibit outstanding stability in water and acidic solutions. The mechanism behind this is that the substitution of carboxylate-based ligands by water molecules [90,91] or the replacement of hard acid metal ions and hard-base ligands by protons and hydroxides through hydrolysis [92] becomes difficult in water solution or water vapor (Figure 2). Likewise, in an acidic solution, the proton is not strong enough to compete with the high-valent metal ion for chemically bonding with carboxylate linkers. Unfortunately, such MOFs are vulnerable to basic solutions. On the contrary, MOFs in soft-acid–base combination (lowly valent metal with azolate-based ligands) are effective on base and water resistance but weaker on combating acidic corrosion [89].

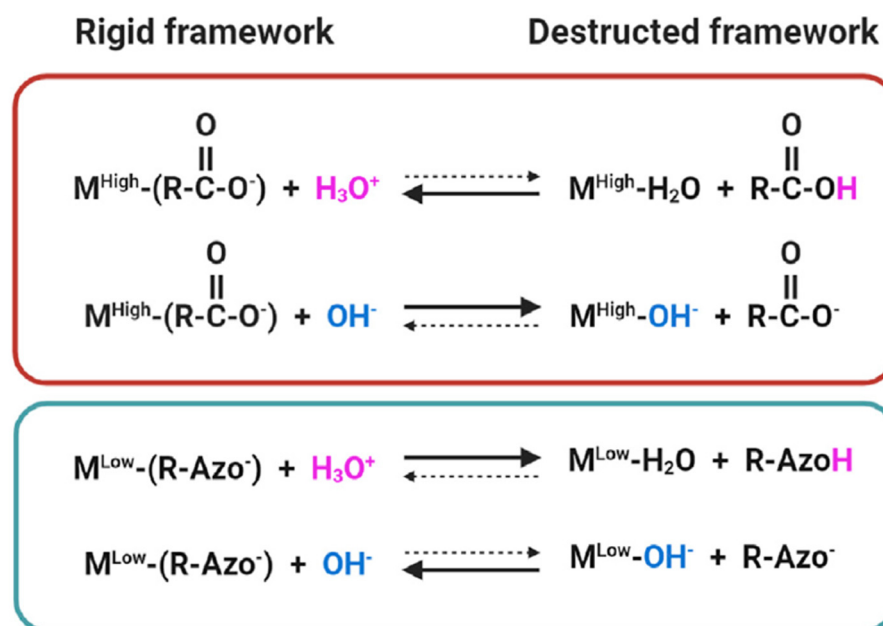


Figure 2. Metal–ligand substitution reactions between MOFs and protons/hydroxides. M^{high} and M^{low} denote high- and low-valence metal nodes, respectively. Solid arrows represent a more favored process, and dashed arrows represent a less favored process [93]. (Copyright © 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany).

HSAB theory can guide researchers to obtain MOFs with high chemical and water stability by enhancing the node-linker bond strength. MIL-101-Cr, as a chromium terephthalate-based material, is a result of applying hard-acid-base theory. It showcases its chemical and water stability by staying intact for 5 days in acidic solution [94] and for months in a moist condition [95]. A strong metal-ligand bond is indeed conducive to MOF thermal stability. Nevertheless, it alone cannot firmly protect MOF intactness under harsh conditions. MIL-101-Cr was reported to decompose at 275 °C, attesting its relatively poor thermal stability even though its inorganic bricks are tightly bound by the linkers [96].

Connectivity [93], referring to the number of SBUs in connection with a single ligand and the number of ligands in connection with SBUs, is proposed as another key factor for thermal stability [84]. Taking UiO-66 as an example, its SBU is an octahedral cluster with six vertices occupied by Zr^{4+} and eight triangular faces covered by four $\mu_3\text{-O}$ and $\mu_3\text{-OH}$ respectively [97]. Unlike MIL-101-Cr, which is constructed from 6-connected $[\text{Cr}_3(\mu_3\text{-O})\text{OH}(\text{H}_2\text{O})_2(\text{COO})_3]$ clusters and linear dicarboxylate linkers, UiO-66 has 12 organic linkers bridging to each of its SBUs, generating six more coordination bonds than MIL-101-Cr (Figure 3) [98]. Due to such higher connectivity, the thermal decomposition temperature for UiO-66 is significantly increased up to 540 °C [99].

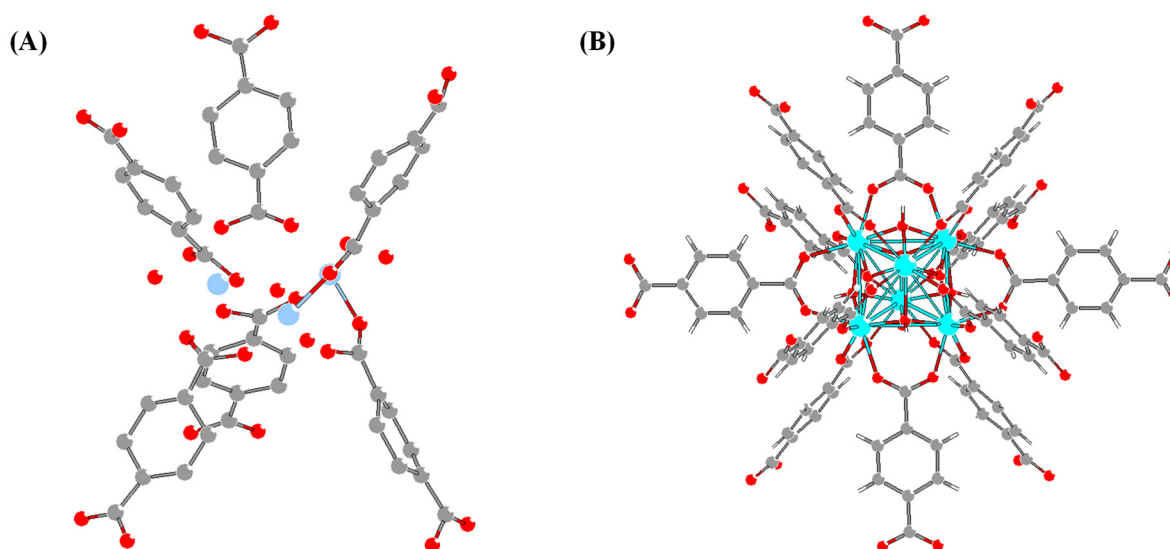


Figure 3. Secondary building unit of (A) MIL-101-Cr (in linkage of 6 organic linkers) and (B) UiO-66 (in linkage of 12 organic linkers), where C, O, Cr, Zr, and H are grey, red, blue, light turquoise, and white atoms, respectively.

The high porosity and surface area are prominent features of MOFs, making them desirable for adsorption and other applications. However, it is indicative of many void spaces inside the structure and might lead to poor sustainability when MOFs are exposed to a pressured or vacuum environment [100]. Most MOFs can only withstand shear stress under 1 GPa, exhibiting their vulnerability in response to mechanical loading. However, UiO-type MOFs are a counterexample, as evidenced by the large shear modulus of UiO-66(Zr) and UiO-66(Hf) with an order of magnitude higher than that of other MOFs and similar to zeolites [101]. Such extraordinary mechanical stability is, ascribed to strong metal–ligand bonds and high connectivity, critical to host MNPs with long-term durability in harsh catalysis, as demonstrated below.

3.3. Case Studies

To the best of our knowledge, Yaghi et al. [102] were the first group to commence on CH_3OH synthesis by CO_2 reduction using MOF-encapsulated MNPs. They examined Cu@UiO-66 performance by comparing it with a series of catalysts, including Cu/UiO-66, Cu/ZnO/ Al_2O_3 , and Cu/ ZrO_2 . Among these candidates, Cu@UiO-66 was found to steadily produce the highest output of CH_3OH with 100% selectivity. The rationale behind this was more intimate interactions between the Cu surface and Zr oxide SBU, generating more Cu active sites for CO_2 conversion. High CH_3OH selectivity on Cu@UiO-66 was attributed to its intrinsic catalytic nature, meaning that the catalyst itself was disfavoured for CO production. The authors also found that Zr- and Zn-oxides were the main promoters for the Cu catalyst, thus improving CH_3OH yield. Interestingly, this agrees with the findings discovered by Lercher et al. and Castaño et al. [103,104], where Cu–O–Zr and Zn–O–Cu interfaces are the smallest part of active sites responsible for improved activities of CO_2 activation, thus increasing its conversion rate to CH_3OH . In contrast to intact UiO-66 applied in Yaghi et al.’s work [102], Lercher et al. [103] entrapped Cu nanoparticles using defective UiO-66 instead. They assessed its catalytic performance at 523 K and 32 bar and found three times higher than their reference samples (i.e., Cu/ ZrO_2 and Cu/ZnO/ Al_2O_3) due to its sufficiently small metallic Cu nanoparticles in the framework and large fractions of Cu–O–Zr interfacial sites. Castaño et al. [104] studied the reaction on ZIF-8-encapsulated 14-nm Cu NPs, which was 2-fold higher methanol productivity than the commercial Cu–Zn–Al catalyst and remarkably stable for over 150 h at reaction conditions (i.e., 500 MPa and

523 K). The supplemented DFT calculations further revealed inhibition of RWGS reaction on Cu@ZIF-8 and stronger adsorption of CO₂ on the Cu-O-Zn interface than both Zn-O and bare Cu sites, thus making a very selective CO₂-to-CH₃OH conversion (>90%).

Pioneering work by Yaghi et al., [102] has also been supported by Wang and his co-workers [105], who successfully embedded Cu/ZnO nanocatalysts inside UiO-bpy for CO₂ hydrogenation. The catalyst proved its splendid stability by diminishing less than 10% catalytic activity during 100 h on stream. At 250 °C and 4 MPa (CO₂/H₂ = 1:3), it exhibited 100% CH₃OH selectivity and STY of 0.0809 mmol_{MeOH}·g_{Cu}^{−1}h^{−1}, higher than 54.8% and 0.0259 mmol_{MeOH}·g_{Cu}^{−1}h^{−1} for Cu/ZnO/Al₂O₃, and 51.9% and 0.00406 mmol_{MeOH}·g_{Cu}^{−1}h^{−1} for Cu@UiO-bpy. Such performance was attributed to the synergism of Cu, ZnO, and Zr₆ SBUs; moreover, they reported the importance of the chemical environment for particle confinement by evaluating the catalytic performance between Cu/ZnO_x@UiO-bpy and CuZn@MIL-253-Al.

Different from narrow windows with a smaller cage in UiO-bpy, which could vastly suppress Cu agglomeration by strong NP/SBU interactions and steric hindrance, MIL-253-Al possessed a larger cavity and relatively expanded window size. Thereby, Cu nanoparticles in MIL-253-Al could grow into a larger size and even extend to the external surface of the MOF, resulting in only one-third CH₃OH yield of Cu/ZnO_x@UiO-bpy. The encapsulation of nanoparticles in MOFs is usually realized by the “ship-in-a-bottle” approach involving impregnation, coprecipitation, and deposition-precipitation [106]. However, it is rather challenging to precisely control the loading composition of active nanoparticles inside MOF cages since the precursors might precipitate on the external surface of MOFs, forming aggregated counterparts [107]. While using the traditional impregnation approach for preparing Cu/ZnO_x@UiO-66, Li et al. [108] reported a similar issue and found an easy separation between Zn and Cu phases. Thereby, they proposed an otherwise double solvent method to overcome the synthesis hurdle. No agglomeration of metal particles and phase separation was observed while synthesizing Cu/ZnO_x@UiO-66. The confinement effect endowed a catalyst with a stable hydrogenation process over a period of 100 h stream. The highly dispersed Cu/ZnO in UiO-66 cages, and appreciable interpenetration of Cu and ZnO_x phases presented a rich Cu-ZnO_x-Zr node interface, which enabled high CH₃OH activity with STY of 39.7 mmol_{MeOH}·g_{Cu}^{−1}h^{−1} and 86.1% selectivity, higher than 7.19 mmol_{MeOH}·g_{Cu}^{−1}h^{−1} and 47.2% for Cu/ZnO/Al₂O₃ under exactly the same reaction conditions as performed by Wang et al. [105].

In addition to the Cu catalyst, Pd is the second most examined due to excellent hydrogen splitting capability; however, pure Pd favors CO production from CO₂ hydrogenation, thus delivering poor selectivity of CH₃OH. Alloying Pd with Zn can make the catalyst reversely favorable for CH₃OH synthesis—an amelioration of CH₃OH selectivity [109]. In 2019, Tsang et al. [110] developed an efficient PdZn alloy catalyst by depositing Pd nanoparticles on oxygen-defective ZnO nanorods coated by ZIF-8. The increase in ZIF-8 thickness could bring higher CO₂ adsorption capacity owing to the concomitant increment in oxygen defects on ZnO; however, it discouraged the formation of PdZn alloy due to the spatial isolation effect. To obtain the optimum thickness of ZIF-8 jacket, a volcano-shaped correlation between CH₃OH activity and etching time over Pd-ZnO@ZIF-8 was hence developed. Under the reaction condition of 563 K and 4.5 MPa (CO₂/H₂ = 1:3), CH₃OH productivity reached a maximum (STY = 19.8 g g_{Pd}^{−1} h^{−1}) when the etching time was 1 h. The authors extrapolated that there should be a trade-off between the PdZn phase and surface oxygen defects for CH₃OH synthesis; thus, they proposed a synergistic catalysis mechanism for the fabrication of high-performance Pd-ZnO catalysts.

CH₃OH is generally produced via two pathways from CO₂ hydrogenation, including (i) CO formation from CO₂ by reversed-water-gas-shift (RWGS) reaction, which can

further be hydrogenated into CH_3OH , and (ii) formate pathway [111,112], in which HCOO is recognized as the key intermediate and further hydrogenated into methoxy and CH_3OH [113,114]. Similar to a Pd catalyst, Pt alone shows high activity for RWSG reaction, resulting in the inhibition of CH_3OH synthesis due to intense competition with CO formation [111,114,115]. Though CH_3OH can be synthesized from syngas, the presence of CO_2 adversely affects the synthesis rate and might result in more unconverted CO gas retained upon the catalyst surface [116]. High CO production is not favored for CH_3OH selectivity and is detrimental to active metal sites by poisoning [117]. Therefore, the key to selective CH_3OH production is to avoid the RWSG pathway and stabilize HCOO^* species.

To stabilize HCOO^* species, UiO-series MOFs with abundant Zr oxides as Lewis acid sites have been explored, intending for further hydrogenation towards CH_3OH [118]. Thermodynamically, low-temperature operation can help shift the equilibrium towards CH_3OH production, hence probably preventing it from undergoing RWSG. Olsbye et al. [119] prepared a mixed-ligand-UiO-67-encapsulated Pt catalyst (UiO-67-Pt) and assessed its CO_2 hydrogenation performance at 170 °C and 8 bar ($\text{CO}_2/\text{H}_2 = 1:3$). The CH_3OH STY over UiO-67-Pt approached $0.072 \text{ mmol}_{\text{MeOH}} \cdot \text{g}_{\text{Cu}}^{-1} \text{h}^{-1}$ with a selectivity of 13% and outperformed UiO-67(LD)-Pt, a less defective UiO-67-encapsulated Pt catalyst with CH_3OH STY $0.0216 \text{ mmol}_{\text{MeOH}} \cdot \text{g}_{\text{Cu}}^{-1} \text{h}^{-1}$ and selectivity of 7%. It is believed that the success originates from the unsaturated Zr sites serving as key participants for the catalytic promotion. They not only synergized with Pt nanoparticles to form rich Pt-Zr interfaces, which were accountable for CH_3OH production, but also held HCOO species tightly for further hydrogenation into CH_3OH (Figure 4). Thereby, UiO-67-Pt with $660 \mu\text{mol} \cdot \text{g}^{-1}$ unsaturated Zr sites could deliver higher productivity of CH_3OH than UiO-67(LD)-Pt with solely $70 \mu\text{mol} \cdot \text{g}^{-1}$. It is also fascinating to note that the addition of water could further enhance CH_3OH selectivity by promoting CH_3OH desorption from Zr sites while inhibiting methane formation [120].

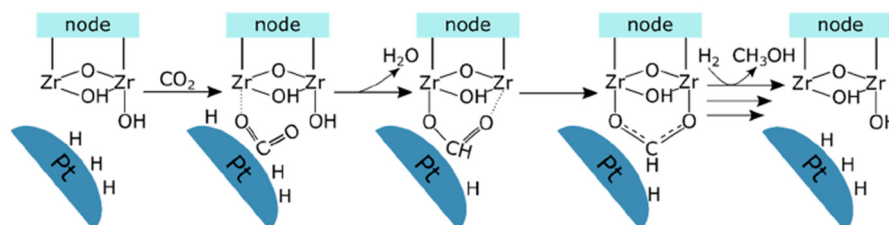


Figure 4. Schematic presentation of the reaction mechanism of CO_2 hydrogenation to HCOO intermediate in CH_3OH formation at the Pt-Zr node interface [120] (Copyright © 2019 American Chemical Society).

Thus far, the major active sites of MNPs@MOFs, in accordance with published works above, are the interfacial sites between MNPs and metal nodes of MOFs, where synergistic catalysis is presented, as reported by other reviews [121–123]. Nevertheless, supplemented DFT calculations merely focus on CO_2 activation. It remains unclear how synergism works along with each reaction step for thermal CO_2 -to- CH_3OH conversion. By the rough comparison from Table 2, the catalytic activities might be impacted by the factors that need to be verified by further research, as follows:

- Support effect, as implied by catalytic activities between $\text{Cu}/\text{ZnO}@ \text{UiO-66}$ and $\text{Cu}/\text{Zn}@ \text{UiO-bpy}$.
- Reaction conditions (i.e., pressure and temperature), as indicated by performance between $\text{Cu}@ \text{UiO-66}$ and $\text{Cu}@ \text{def-UiO-66}$, despite better CO_2 activation on $\text{Cu}@ \text{def-UiO-66}$, as the defected Zr node generates more interfacial sites.
- NP, $\text{Pd-ZnO}@ \text{ZIF-8}$ shows significantly higher methanol productivity in contrast to $\text{Cu}@ \text{ZIF-8}$.

Table 2. MOF-confined NPs for hydrogenation of CO₂ to CH₃OH, where T, P, S_{methanol}, and STY are denoted to be temperature, pressure, methanol selectivity, and space time yield of CH₃OH, respectively.

Catalyst	NP, wt%	T, K	P, bar	X CO ₂ , %	S _{methanol} , %	STY, $\frac{\text{g}_{\text{methanol}}}{\text{g}_{\text{cat}}^{-1} \text{ h}^{-1}}$	Ref.
Cu@UiO-66	1.0	448	10	10.2	100.0	0.042	[102]
Cu@ZIF-8	12.1	523	50	10.2	98.0	0.27	[104]
Cu@def-UiO-66	1.4	523	32	<5.0	29.6	0.033	[103]
Cu/ZnO@UiO-bpy	6.9	523	40	10.2	98.0	0.018	[105]
Cu/ZnO@UiO-66	6.65	523	40	7.33	86.1	0.320	[108]
Pd-ZnO@ZIF-8	3.0	563	45	3.5	78.0	0.594	[110]
Pt@UiO-67	2.5	443	8	50.0	13.0	0.0192	[119,120]

4. Future Outlook

As summary, MOFs can be facilely tailored to meet the following requirements: (i) survive at hydrothermal conditions and withstand mechanical forces—outstanding robustness; (ii) have highly disperse active NPs in the pores of MOFs due to high porosity and surface area; (iii) offer selective-size molecules with access to active sites by shuffling off those irrelevant to desired reactions—molecular-sieving effect due to pre-selected pore matrix; (iv) inhibit the agglomeration of active NPs by encapsulation—pore confinement effect; (v) exhibit higher catalytic performance than individual counterparts by synergizing with active NPs—high catalytic activity, etc. Therefore, MOFs can act as eligible shells for cores (active metal NPs), and MNPs@MOF are promising for effective and stable CO₂ hydrogenation to CH₃OH. Despite tremendous efforts by the researchers on progressing developments of MNPs@MOF on CH₃OH production, the interpretation of confinement effect by MOFs as well as the reaction mechanism at a molecular level is less than well understood for MNPs@MOF composites, the synthesis of catalysts is cost-ineffective, and the product selectivity, including the yield rate, is far from the industrial level. Therefore, more extensive efforts are needed to overcome these challenges.

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