

REVIEW

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rsc.li/materials-advancesDirect CO₂ to methanol reduction on Zr₆-MOF based composite catalysts: a critical review†Elif Tezel,‡ Dag Kristian Sannes,‡ Stian Svelle, Petra Ágota Szilágyi * and
Unni Olsbye *

The pressing problem of climate change on account of anthropogenic greenhouse-gas emissions underlines the necessity for carbon capture and utilisation technologies. Several heterogeneous catalyst systems allowing the conversion of waste CO₂ into desirable products, such as methanol, have emerged as promising and potentially viable solutions to this perennial problem. In particular, composite catalysts based on hexanuclear zirconium metal-organic framework matrices have shown much promise in the direct conversion of CO₂ into value-added and useful products. Herein, we critically review the literature in this area and relate differences in composition, defect chemistry, and structural characteristics, their reaction conditions with their performance and stability in the thermocatalytic hydrogenation of CO₂ to methanol, on the basis of both experimental and theoretical studies. We also highlight the obstacles in directly comparing the performance of these systems for CO₂ hydrogenation and suggest potential solutions and opportunities for further advancement.

Introduction

Climate change is arguably the most pressing emergency humanity faces. There is a scientific and increasingly societal consensus that it is caused by the emission of greenhouse

gases, chiefly but not exclusively carbon-dioxide, which is by large a consequence of anthropogenic activities such as transport, construction, heating, *etc.*¹ While it is clear that there is an urgent need to decarbonise industries and shift the energy paradigm to renewables, in order to avoid a full-scale climate catastrophe, it is becoming evident that solutions must be found to also remove greenhouse gases from the atmosphere.

Two distinct methodologies tackle the reduction of atmospheric carbon-dioxide levels: carbon capture and sequestration (CCS) and carbon capture and utilisation (CCU).^{2–9} Both of the methodologies rely on removing CO₂ from the emitter initially,

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e.g. nascent carbon dioxide from flue gas, or, in a more challenging approach, directly from the atmosphere by various CO₂ capture materials, mainly aqueous solutions of amino alcohols such as monoethanolamine (MEA) and diethanolamine (DEA). However, they differ in the way they handle carbon dioxide post-capture; CCS is aimed at storing it in the long term either in cavities or in rocks, while CCU aims at transforming CO₂ into more reduced forms of carbon, ideally into value-added substances including methanol and formic acid, through chemical reactions. While it is evident that all technologies able to definitively remove CO₂ from the atmosphere must be applied in the short-to-medium term to combat the adverse effects of climate change, CCU offers a more economically viable solution to the paradigm as it ultimately aims at yielding commercialisable products with potential application as fuels or platform chemicals, i.e., the approach offers a way to tackle climate change simultaneously, and the energy crisis or a path to sustainable feedstock sourcing.

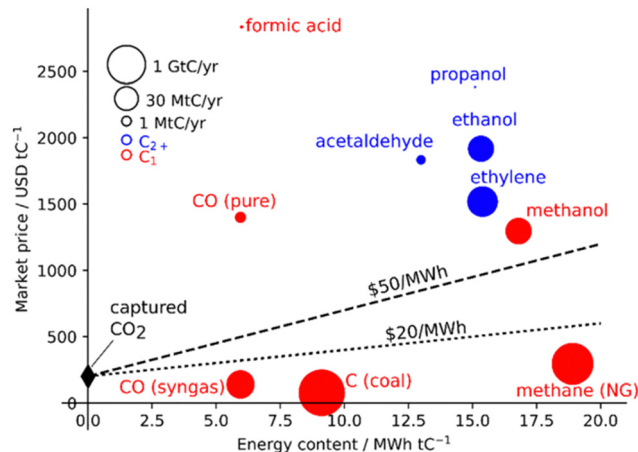


Fig. 1 Market price of CO₂ conversion products per energy content. Lines represent minimum energy and CO₂ costs. Capital costs are not considered. Reprinted with permission from ref. 14. Copyright 2019 American Chemical Society (<https://pubs.acs.org/doi/10.1021/acs.chemrev.8b00705>).



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He combines kinetic, quantum chemical, and operando studies to investigate individual reaction steps and deactivation phenomena occurring within the catalyst crystals or bodies.



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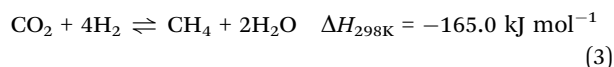
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Unni Olsbye obtained an MSc in Industrial Chemistry at NTNU, Norway, in 1987, and a PhD in Organic Chemistry at the University of Oslo (UiO), Norway, in 1991. She worked at SINTEF and Nordox Industrier before returning to UiO as associate professor in 2001. She was promoted to full professor in 2002. Her research group focuses on catalysis for sustainable valorization of light molecules (C₁–C₃), mainly using zeolite- and metal organic

framework-based catalysts. Experimental studies of kinetic and mechanistic consequences of single material parameter variation are used as a guiding tool for catalyst design.



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CO_2 and H_2 have various pathways for the direct hydrogenation of CO_2 , and in eqn (1)–(3), some key reactions at the standard operating conditions are shown with their corresponding free enthalpy at 298 K.^{52,53} Reaction (1) shows the enthalpy for the reverse water gas shift (RWGS), (2) methanol formation and, (3) CO_2 methanation (Sabatier's reaction). Comparing the enthalpy of CO_2 methanation and methanol formation, it becomes clear that methanol is not the thermodynamically preferred product, and excellent catalyst design is necessary to suppress methane formation and provide high selectivity toward methanol production. Generally, Cu and Ag catalysts produce mainly methanol, while Ni and Ru catalysts are typically active for the methanation reaction. Pd, Pt, Rh, Mo, and Au-based catalysts frequently produce both methanol and methane simultaneously.⁵⁴

We used the Factsage software⁵⁵ to calculate the equilibrium conversion of CO_2 in the 170–300 °C temperature range and a pressure range of 1–50 bars with H_2/CO_2 ratio of 3 : 1, which are the typical conditions used for catalytic testing in literature and are similar to conditions used in industry.⁵⁶ The conversion of CO_2 and product selectivity were calculated according to eqn (4) and (5). Methanol formation is an exothermic reaction with an $\Delta H_{298\text{K}} = -49.5 \text{ kJ mol}^{-1}$ (eqn (2)); hence, according to Le Chatelier's principle, the forward reaction is favoured at low temperatures (Fig. 2). Low temperatures provide the additional benefit of suppressing the competing RWGS, which reduces the partial pressure of CO_2 and affects the equilibrium by producing water.

Conversion of CO_2 :

$$X_{\text{CO}_2}(\%) = \frac{\Sigma \text{Products}}{\Sigma \text{Products} + \text{CO}_2} \times 100 \quad (4)$$

Selectivity to carbon-containing species (CO and methanol):

$$S_{\text{Product}_i}(\%) = \frac{\text{Products}_i}{\Sigma \text{Products}} \times 100 \quad (5)$$

However, when the temperature is decreased, so is the formation rate of methanol. Therefore, a compromise must be made between operating at low temperatures for high selectivity and high temperatures for increased rates. As the formation of methanol requires four molecules to react, while only two product molecules are formed, high pressures push the equilibrium towards product formation, increasing both the selectivity to methanol and the conversion of CO_2 .

CO_2 to methanol reduction mechanism

In order to create highly active and selective catalysts enabling CO_2 utilisation, it is crucial to comprehend the mechanism underlying the conversion of CO_2 into methanol.⁵⁷ Two primary routes have been proposed for CO_2 hydrogenation to methanol (Fig. 3). The first route proceeds *via* the hydrogenation of a surface CO species formed by direct C–O bond cleavage of CO_2 or from a carboxyl intermediate. The second pathway proceeds through surface formate species formed from hydrogenation of adsorbed CO_2 and is often referred to as the formate pathway. The preferred route depends on the catalyst and which intermediates are stabilised on the specific surface. The formate pathway is the prominent mechanism on the Cu/ZnO catalyst; in contrast, on Cu/CeO₂, Cu/TiO₂ and Cu/ZrO₂, the primary mechanism for methanol formation is through hydrogenation of a surface CO intermediate. This is because surface formate species are too strongly adsorbed on these catalysts, effectively poisoning the catalyst surface and suppressing the subsequent hydrogenation. To improve both the activity and selectivity of the catalysts, promoters are often employed, which essentially fine-tune the intermediates' adsorption energies to reduce kinetic barriers and facilitate effective catalytic pathways.⁵⁸

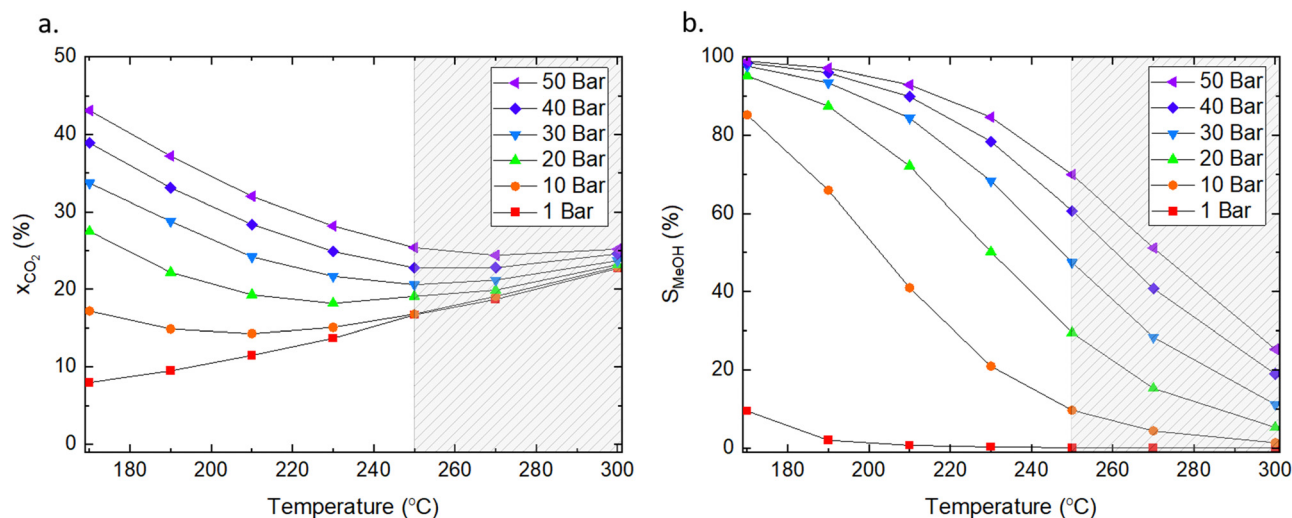


Fig. 2 Influence of pressure and temperature on (a) equilibrium conversion of CO_2 and (b) selectivity toward methanol at equilibrium. The dashed area indicates the temperature range typically applied for CO_2 hydrogenation to methanol in industry. The ratio of H_2/CO_2 was 3 : 1, and methane was excluded from the calculations. Factsage was used for the analyses.⁵⁵



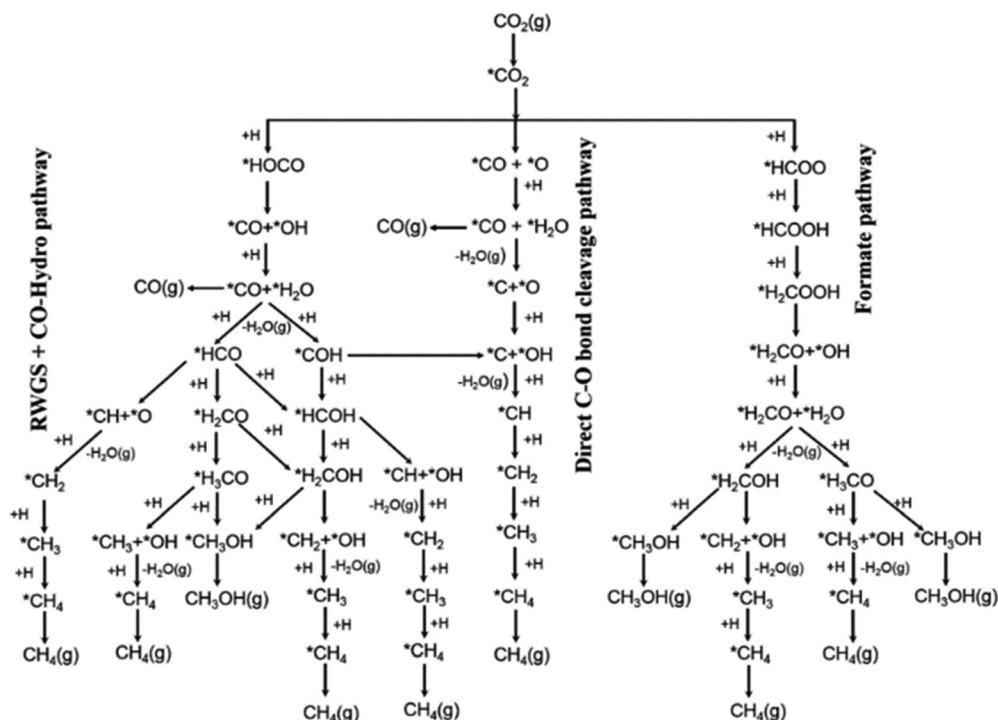


Fig. 3 Possible reaction pathways of CO₂ hydrogenation to CO, CH₃OH, and CH₄. *(X) indicates adsorbed species. Reprinted with permission from ref. 57. Copyright 2017 American Chemical Society (<https://pubs.acs.org/doi/10.1021/jacs.7b05362>).

Among the most studied systems for direct CO₂ reduction to methanol is copper supported on Al₂O₃ and ZrO₂ combined with a vast range of promoters such as Zn, Zr, Ce, Al, and Si.^{59–61} Cu supported on Al₂O₃ with ZnO as a promoter is often denoted as Cu/ZnO/Al₂O₃ and has been commercialised on the industrial scale since the 1960s and is therefore often used as a benchmark catalyst for CO₂ hydrogenation.⁵⁶

Experimentally it was found that Cu⁰ is part of the active sites in Cu/ZnO/Al₂O₃ for methanol formation, and the performance of the catalyst is linearly dependent on the surface area of the copper nanoparticles (NPs).^{62–64} The active site for methanol formation has been investigated using density functional theory, and it was found that open Cu surfaces (*e.g.* Cu(110) and Cu(100)) partially covered by oxygen are active for CO₂ hydrogenation to methanol.⁶⁵ It has been shown that the methanol synthesis rate over Cu(100) was roughly 30 times faster than on the Cu(110) surface, suggesting that the facets of Cu affect the catalyst's performance. Other theoretical studies have also shown that other facets of Cu may be active for methanol formation. For instance, the stepped Cu(533) surface enhanced the activity compared to the flat Cu(111) surface. Similarly, the step sites on the Cu(997) are more reactive than the terrace sites on Cu(111) for Cu/Zn catalysts.^{66,67}

The size of the Cu NPs is also vital for the activity of the materials. It has been found for Cu NPs smaller than 8 nm, that the turnover frequency (TOF) decreases proportionally with decreasing size. The exact nature of this structure sensitivity for small Cu NPs is unknown but it could be explained by either the stabilisation of a larger fraction of step sites or the removal of unsaturated Cu sites for NPs of Cu above 8 nm.²⁵ Another

study showed that the methanol formation rates, normalised by surface copper species, are constant for Cu/ZnO catalysts with Cu NPs varying from 8.5 to 37.3 nm. It was found that the formation of CO is favoured as the size of the Cu NPs is decreased, illustrating that CO₂ conversion is site-selective and the selectivity of the materials may be tuned in favour of methanol by increasing the size of the Cu NPs.⁶⁸

The role of ZnO is still heavily debated, and not all the mechanistic steps are well understood.⁶⁴ As with many promoters, ZnO acts as a spacer for the Cu NPs, which improves the dispersion and stability of the material.⁶⁹ Control experiments on pure Cu and Zn catalysts compared to Cu/Zn catalysts show that there is a synergetic interaction between the two.⁶⁶ DFT calculations performed on a stepped Cu(211) surface partly substituted with Zn atoms showed that Zn increased the adsorption of key intermediates of methanol production and decreased the kinetic barriers, leading to an increase in the rate of methanol formation. Some experimental studies suggest that Zn may migrate to the Cu NPs during reduction, creating active Cu/Zn sites. Cu/Zn active sites were postulated after observing an increase in active sites by increasing the reduction temperature. SMSI have been observed for the Cu/ZnO system using vibrational spectroscopy, thermal desorption of probe molecules and observing the wetting behaviour of Cu/ZnO model systems. Ambient pressure X-ray photoemission spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM) show the presence of a 1 nm thick layer of ZnO_x on a few of the Cu NPs in the Cu/ZnO/Al₂O₃ catalyst.^{64,70–72} The graphite-like ZnO_x layer might facilitate the substitution of Cu atoms on the surface of the Cu NPs. Other studies have

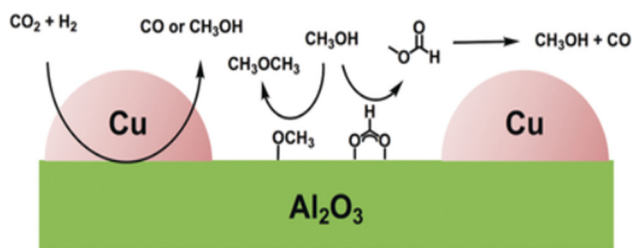


Fig. 4 CO₂ hydrogenation on Cu/Al₂O₃. Used with permission of Angewandte Chemie International Edition, from CO₂ Hydrogenation on Cu/Al₂O₃: role of the metal/support interface in driving activity and selectivity of a Bifunctional Catalyst, Lam *et al.*, 2019, **58**, 39 permission conveyed through Copyright Clearance Center, Inc.

reported that the ZnO_x layer is active for methanol formation. A core-shell Cu/Zn alloy with a ZnO_x outer shell was prepared by elaborate synthesis and post-synthesis procedures. The active site was found at the ZnO_x outer shell, and 100% methanol selectivity was observed.⁷³ Other studies have suggested that the role of ZnO is to act as a hydrogen reservoir for spillover hydrogen, which may help to keep the surface species of the copper NPs hydrogenated.⁷⁴

Al₂O₃ is the commercially used support for the Cu/ZnO system resulting in a catalyst displaying high activity, high product selectivity and low cost. The support material act as a stabilising oxide that increases catalyst stability and maintains the dispersion of Cu and ZnO NPs.⁷⁵ The acidic sites on the Al₂O₃ surface are strong enough to adsorb both methoxy and formate species which can react with methanol, by dehydrating it and form either dimethyl ether (DME) or methyl formate, the latter may decompose to methanol and CO, providing an additional source of CO (Fig. 4).^{76,77} Cu/ZnO/ZrO₂ has gained increasing interest in the research community for its higher catalytic activity than Cu/ZnO/Al₂O₃ and is one of the state-of-

the-art catalysts from a research viewpoint.⁷⁸ The increased activity arising from the application of ZrO₂ compared to other support materials may be attributed to its capability to enhance the Cu and ZnO dispersion, *i.e.* to increase the surface area of the NPs and modify the surface of the copper.⁷⁹ In addition, ZrO₂ is less hydrophilic than Al₂O₃, which facilitates the desorption of water formed in the course of the reaction, thereby enhancing both the conversion of CO₂ and selectivity to methanol by thermodynamically promoting methanol formation.^{80,81} Studies of the binary systems of Cu/ZnO and Cu/ZrO₂ have been investigated in great depth to gain improved insight into the ternary system. It is generally accepted that the binary Cu/ZnO catalyst has higher activity for CO₂ hydrogenation, while Cu/ZrO₂ shows a higher selectivity to methanol. The ternary system offers a higher yield of methanol than either of the binary systems, although at the expense of a decreased selectivity (Fig. 5). Additional promoters, *e.g.* Ga₂O₃ and Y₂O₃, may increase the activity of the ternary catalyst Cu/ZnO/ZrO₂ by increasing Cu dispersion.⁶³

The average lifetime of the Cu/ZnO/Al₂O₃ catalyst under standard operating conditions in industry is typically 2–4 years and a decrease in catalyst activity is observed during this time.⁵⁶ The sintering of either the Cu or ZnO NPs and the oxidation of Cu cause the catalyst deactivation predominantly.⁸² Studies on the deactivation suggest that sintering of the Cu NPs does not change the nature of the active sites, as seen by a constant activation energy for methanol formation during deactivation, suggesting the loss of activity is caused by the loss of active sites.⁸³ Experimental studies have shown that after prolonged exposure to the reaction conditions (700 hours), the space-time yield of methanol is reduced by 34.5% over the Cu/Zn/Al₂O₃ catalyst.⁸⁴ The study reported an increase in the size of ZnO NPs, but no significant change in the Cu NPs, likely due to the low reaction temperature of 200 °C. Two separate studies found that the deactivation of the catalyst is promoted by the presence of water formed by the RWGS

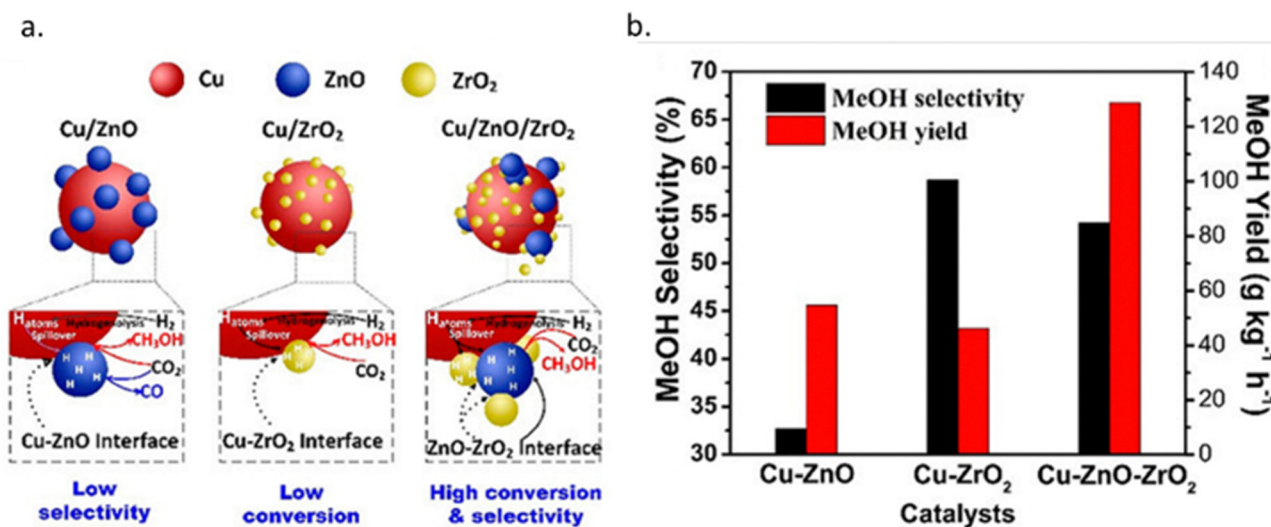


Fig. 5 (a) Schematic diagram of the CO₂ hydrogenation process over Cu–ZnO, Cu–ZrO₂ and Cu–ZnO–ZrO₂ catalysts. (b) Methanol yields and methanol selectivity of Cu–ZnO, Cu–ZrO₂ and Cu–ZnO–ZrO₂ catalysts. Reprinted with permission from ref. 78. Copyright 2019 American Chemical Society (<https://pubs.acs.org/doi/full/10.1021/acscatal.9b01943>).



reaction. The size of the NPs in one of these studies, after catalytic testing for 48 hours at 240 °C and 50 bar with varying quantities of water, is shown in Fig. 6, clearly showing an increase in NP size with an increasing quantity of water.^{83,85}

XPS results have also shown that the loss of activity of the material may be due to Cu oxidising to Cu²⁺ during the reaction. The oxidative nature of CO₂ and *in situ* formed water is likely the reason for the oxidation of Cu.⁸⁴ These results imply that strong interactions with the support for all constituents are essential for high stability of the catalyst.

MOFs as support materials may provide a satisfactory solution to the problems highlighted above. MOFs are highly crystalline materials, allowing for excellent control of the active sites. Even though MOFs are a relatively new group of hybrid materials, numerous structures have been reported with a large variety of inorganic cations, clusters, and organic linker molecules. The effect of various support materials with an extensive range of chemical properties may be investigated, and the catalyst's active sites may be fine-tuned. The agglomeration of the active species on nonporous supports is the primary deactivation mechanism and MOFs may hinder agglomeration by trapping the NPs inside the framework. The size of NPs may be carefully tuned by changing the size of the pores of the material by changing the length and size of the linker. If the active specie is also grafted inside the framework, it is possible to fine-tune the interaction between the active specie and the support, which could both further hinder agglomeration and hinder oxidation or reduction of the active specie by changing the nature of the framework. However, the pore sizes of MOFs are substantially smaller than the optimum size of the Cu NPs of 8 nm, which may limit the activity of the catalysts. Defects inherent to the MOFs framework, which are described later, may provide effective tools for accommodating the formation of larger NPs.

Finally, MOFs have been shown to be highly tuneable in terms of their hydrophilicity, which may be of relevance in affecting both catalyst stability and selectivity, as has been previously

suggested in a bid of rationalising the different behaviours of various oxide supports. For the above-mentioned reasons, it is apparent that MOF-based supports have highly desirable and unique properties when it comes to providing a highly active and selective catalyst for direct CO₂-to-methanol reduction.

Experimental catalytic performance trends and mechanistic insights for Zr₆ MOF-based catalyst

Zr₆-based MOF structures and incorporated metal particles have been successfully studied as composite catalysts for CO₂ hydrogenation to methanol in the literature.^{37–46,86–88} Each study has numerous variables in terms of structural, compositional, and reaction parameters aimed to effectively improve the dispersion of catalytic sites and the adsorption and activation of CO₂ for efficient catalysis of CO₂ hydrogenation at lower temperatures. Furthermore, the inorganic nodes of MOFs may provide Lewis and Brønsted acid sites, which can contribute to activating CO₂ or stabilising certain intermediates. Besides, different catalytic sites can be incorporated into MOFs, and the coordination environment can be adjusted, such as to control the CO₂ hydrogenation to value-added products. Even though there is a strong interplay between these parameters and the catalyst performance, determining the optimum catalyst remains a challenge due to the inconsistency of test conditions. Below, we discuss in detail the effects of these parameters on the performance of composite Zr₆-based MOF catalysts. Firstly, we review the impact of the structural and compositional variations in the catalyst support and active sites on the catalytic performance. Then we analyse the effects of reaction conditions, including temperature, pressure, and space velocity.

Structural and compositional variables-performance relations

The aim of this section is to provide insight into the effects of different structural components of multicomponent systems on the performance of catalysts for CO₂ hydrogenation to methanol. The structural properties of MOFs, the nature of the metal active sites, and metal-support interactions are evaluated. Zr-based MOFs, specifically UiO-66, UiO-67, and MOF-808 have differences, including synthesis procedure, linker composition, and presence of non-structural sites. The principle of isoreticularity can be used to design isotopological frameworks with varying pore sizes by using linkers with the same connectivity but different lengths, such as seen for UiO-66 and UiO-67. UiO-66 (Fig. 7a) and UiO-67 (Fig. 7b) consist of 12-connected Zr₆(μ³-O)₄(μ³-OH)₄ clusters which are interconnected by BDC and BPDC linkers, respectively. Even though MOF-808 (Fig. 7c) shares the same Zr₆ inorganic node, as UiO-66/67, its crystal structure differs since only six tritopic linkers (BTC) are coordinated to each node, or secondary building unit (SBU). In this topology, charge compensation is provided by an additional six monotopic ligands, which are easily exchangeable.⁸⁹ Also, various synthesis methods have been reported in the literature, and studies show significant effects of the type of modulator on

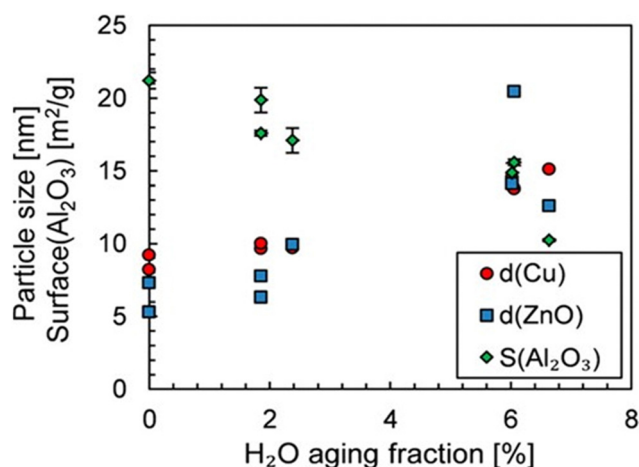
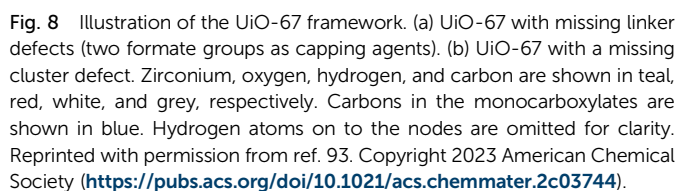


Fig. 6 Influence of H₂O volume fraction on the Cu and ZnO particle size and Al₂O₃ surface. The aging period was 48 hours. Reprinted with permission from ref. 85. Copyright 2019 American Chemical Society (<https://pubs.acs.org/doi/full/10.1021/acs.iecr.9b01898>).





Defects in MOFs could be defined as sites that locally break the periodic arrangement of atoms or ions of the static crystalline parent framework due to missing or dislocated atoms or ions.⁹¹ Even though various types of defects have been reported, two types of defects exist most commonly: missing linker (Fig. 8a) and missing cluster defects (Fig. 8b). Missing linker defects are formed when linkers are replaced by monodentate capping agents. Typically, these capping agents are monocarboxylates called modulators, which are added during the synthesis to assist the MOF self-assembly into crystallites.⁹² Similarly, missing cluster defects are formed when a cluster is removed from the framework; this kind of defect results in a relatively large cavity in the structure. While the presence of the cluster defects has been reported in UiO-66 MOF, the linker defects have been investigated in both UiO-66 and UiO-67.^{90,93–96} The linker defects typically stem from the incomplete ligand exchange reaction between the linker and modulator. The non-defective UiO66/67 MOFs contain a 1 : 1 ratio between Zr and the linker; however, the ratio was observed to be less than one for materials with missing linker defects. The defect quantity is increased in the UiO-66/67 because of the strong interaction between Zr^{4+} and carboxylate, which slows down the linker exchange reaction. Missing cluster defects and missing linker defects could affect the properties of the material, including surface area, pore volume, mechanical stability, and thermal



stability. Besides, the cluster defects could have an influence on the performance of the catalysts due to diminished Lewis acid sites. The synthesis parameters to influence the concentration of missing linker- and cluster-defects in MOFs are discussed in detail below. Shearer *et al.* have previously reported an extensive study on synthesis conditions leading to missing linker defects in UiO-66. They found that the missing-linker defect concentration could be reduced by either increasing the synthesis temperature or increasing the linker-to-zirconium ratio, and, additionally, it has been found that increasing the synthesis time leads to a less defective material.^{90,97} The reduction of missing linker defects when alternating these synthesis variables is attributed to increasing the rate of the exchange reaction between the linker and the modulator, thereby increasing the probability of linkers coordinating with the zirconium nodes and providing more time for self-assembly, respectively. Kaur *et al.* published an extensive study on the synthesis of UiO-67, including the effect of changing the solvent dimethylformamide (DMF) to Zr ratio. The study showed that missing linker defects were far more prominent for samples synthesised in dilute (DMF:Zr ratio of 300:1) rather than in concentrated reaction mixtures (DMF to Zr ratio of 50:1).⁹⁸ In addition, due to the tridentate nature of BTC in MOF-808, it is possible to further increase the missing linker defects by changing the tridentate linker with a bidentate linker such as isophthalic acid.⁹⁹ The effect of synthesis parameters on the formation of missing cluster defects is less readily available; however, it has been found that the synthesis of UiO-66 using a large amount of modulator, especially with a low pK_a value, induces missing cluster defects. Clearly, the synthesis conditions play an essential role in tuning missing linker and missing cluster defects.⁹⁰

The specific surface areas of ideal Zr₆-MOFs with UiO-66 and UiO-67 topologies are around 1187 and 3000, respectively, according to Brunauer-Emmett-Teller (BET) theory.³² Missing clusters tend to yield higher BET; in contrast missing linker defects result in lower specific surface areas,⁹⁰ while functionalised linkers⁸⁹ may also impact the BET values. Reported literature values are in the following range: UiO-66 (1100–1600 m² g⁻¹) and UiO-67 (2100–2700 m² g⁻¹). For MOF-808, specific surface areas in the range of 1200–2300 m² g⁻¹ have been reported, depending on the capping agent on the uncoordinated Zr sites.⁸⁵ Among materials reported as CO₂ hydrogenation catalysts in the literature, we note that metal incorporation alters the BET area (Fig. 9). The effect was particularly strong for the incorporation of Cu and Zn in UiO-67, while the incorporation of Pt on UiO-67 had only a small impact on specific surface area (Fig. 9). A significant decrease in the BET surface area indicates that the structural integrity of the MOF has not been preserved, which may affect the accessibility of active sites. No direct correlation is observable between the specific surface area of the MOF support and the catalysts' CO₂ conversion performance (Fig. 9). The reason may be several convoluted factors influencing the results, *e.g.*; the location of the metal particles in relation to the MOF matrix may be widely different, as both particle size and SMSI can be potentially affected. It stands to reason that when the surface area is low

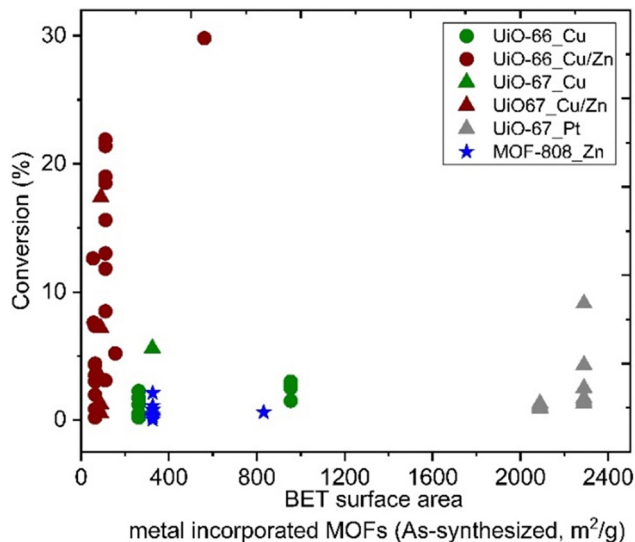


Fig. 9 Catalytic conversion versus BET surface area of metal incorporated MOFs.

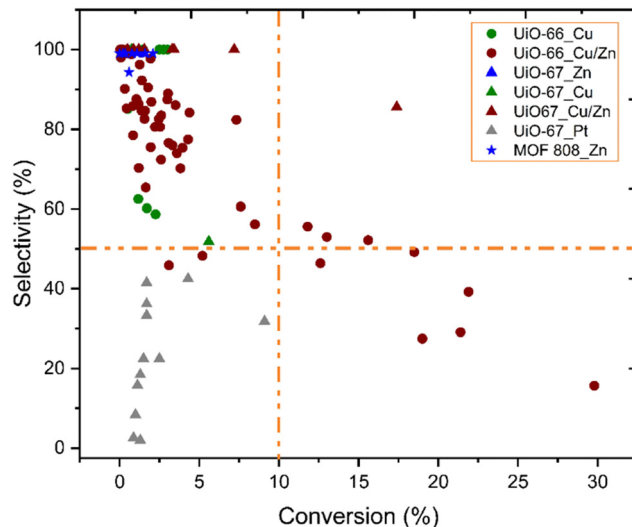


Fig. 10 Selectivity toward methanol versus conversion of CO₂. While different symbols represent various metal–organic frameworks, different colours represent various incorporated metal active sites.^{37–46} Orange dashed lines represent 10% conversion and 50% selectivity and have been included to guide the eyes.

but tangible catalyst activity has been observed, the metal particles would likely be deposited onto the surface of the (partially) collapsed or otherwise altered MOF particles, which then effectively act as a conventional support surface.

Fig. 10 shows the correlation between the performance of catalysts for CO₂ hydrogenation to methanol and catalyst composition, *i.e.*; MOF topology and active metal guest. While UiO-66 structures with Cu or Cu/Zn active sites have been most commonly studied, UiO-67 structures have also been reported with Pt, Cu/Zn, and Zn active sites. Besides, the MOF-808 structure was only investigated with Zn active sites. Higher conversions (>10%) have been overwhelmingly achieved with the UiO-66 topology and uniquely with Cu/Zn active components. Although general trends are hard to pinpoint, we note the lack of well-established studies with numerous variations on reaction conditions, inherently making the comparison challenging.

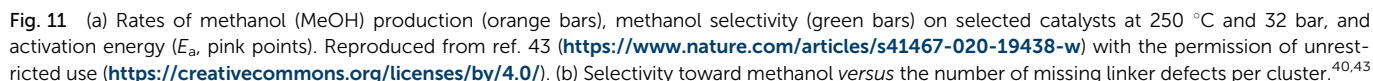
In the following, we will first discuss contributions where the MOF structure of Cu containing MOFs was preserved,^{42,43} and then proceed to studies where the MOF structure collapsed. Finally, we will discuss the performance of Zn-MOF and Pt-MOFs.^{37,45,46} The catalytic properties for CO₂-to-methanol are strongly correlated with the characteristics of the metal oxide-metal interfaces.⁴² MOF-based composite catalysts incorporated with Cu have been commonly investigated because of the presumed strong interaction between Cu and metal nodes of MOFs. Rungtaweeworant *et al.* investigated the support effects on Cu-based catalysts for CO₂ hydrogenation to methanol over different support materials, including UiO-66, and reported that Cu particles encapsulated into UiO-66 (Cu@UiO-66) show 100% selectivity towards methanol in the 175 °C to 250 °C temperature range and at 10 bar, while the MOF structure was preserved.⁴² In this study, the MOF was grown around Cu NPs. Interestingly, XPS data indicated a lower oxidation state of Zr after incorporation of Cu, suggesting SMSI between Cu and Zr₆ SBUs. The

authors concluded that the high yield and selectivity toward methanol stem from Cu–ZrO₂ interfaces in the Cu@UiO-66 since the oxidised form of Cu may stabilise the formate intermediates while the metallic Cu activates the hydrogenation through hydrogen dissociation.

To shed light on how Cu–ZrO₂ interfaces influence methanol production, Zhu *et al.* modified UiO-66 by creating missing linker defects (Fig. 8b), which could increase the abundance of Cu–ZrO₂ interfaces. A direct correlation between the activity and selectivity of the catalysts and the quantity of Cu–ZrO₂ interfaces was demonstrated.⁴³ The nature of the Cu–ZrO₂ interaction was investigated qualitatively and quantitatively, using two samples denoted Cu/UiO-66-a and Cu/UiO-66-b. The location and nature of the Cu particles in Cu/UiO-66-a and Cu/UiO-66-b were characterised using Cu K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The results indicated that while 30% of the Cu atoms in Cu/UiO-66-a (1.4 wt% Cu) were bonded to ZrO₂ nodes, thereby creating Cu–ZrO₂ interfaces, the presence of Cu–ZrO₂ interfaces in Cu/UiO-66-b (1.8 wt% Cu) was suggested to be too low to contribute to the X-ray absorption spectra (XAS). On the other hand, the particle size of metallic Cu was almost identical for both samples. The significantly better performance of Cu/UiO-66-a compared with Cu/UiO-66-b (Fig. 11a) was suggested to highlight the importance of Cu–ZrO₂ interface sites for methanol production through CO₂ hydrogenation.

Even though the previous study highlighted the importance of missing linker defects of UiO-66 on the activity of catalysts, the optimum amount of defect concentration has yet to be investigated. In another example, Ye *et al.* theoretically examined the quantitative influences of missing-linker defects on the activation of H₂ and CO₂ for hydrogenation of CO₂ to methanol





Also, some studies investigated the effects of the particle size of metal sites in MOF-based composite catalysts on CO₂ hydrogenation to methanol, which could have significant effects on the performance of the catalyst.^{38,40,42–44} For example, Yang *et al.* synthesised ultra-small Cu/ZnO_x nanoparticles within 1.2–2 nm in UiO-66 *via* the double solvent method for CO₂-to-methanol hydrogenation to overcome the agglomeration of metal particles and phase separation between Cu and ZnO_x at the high reaction temperatures, and consequently resulting in improved stability during the reaction.⁴⁴ The reported Cu particle size for MOF-based composite catalysts containing Cu or Cu/Zn at different reaction temperatures is displayed in Fig. 13. Although a clear trend in the effect of the varying Cu size on CO₂ conversion is not apparent in Fig. 13a, we would like to point out that the size of Cu particles for most catalysts that provided conversion over 10% was 4 nm. Furthermore, 2 nm is the most common particle size for Cu in MOF-based composite catalysts that exhibited selectivity toward methanol

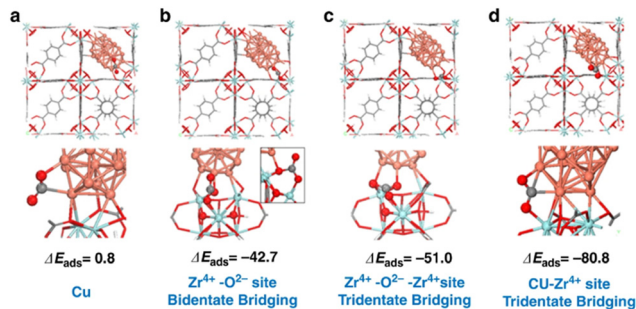


Fig. 12 Adsorption energies (ΔE_{ads} in kJ mol^{-1}) of CO_2 at the Cu/Uio-66 interface (a) Cu only sites, (b) $\text{Zr}^{4+}\text{-O}^{2-}$ sites in a bidentate bridging mode, (c) $\text{Zr}^{4+}\text{-O}^{2-}\text{-Zr}^{4+}$ sites in a tridentate bridging mode, and (d) Cu- Zr^{4+} (ZrO_2) interfacial sites. Reproduced from ref. 43 (<https://www.nature.com/articles/s41467-020-19438-w>) with the permission of unrestricted use (<https://creativecommons.org/licenses/by/4.0/>).

over 50% (Fig. 13b). It should be noted that the latter size corresponds well with the pore size of the Uio-67 framework, indicating that the catalyst particles were embedded in the pores of the supporting framework, at least prior to the catalyst testing. We already noted that the size of the Cu NPs on Al_2O_3 was crucial for the catalyst activity for methanol production, and a decrease in the size of Cu NPs smaller than 8 nm decreased the turnover frequency (TOF),²⁵ thereby supporting our findings. Even though the confinement effects increased the activity of the catalysts, decreasing the size of metal NPs could cause adverse effects on the activity.^{38,41}

The particle size of the Cu particles could be varied by different parameters, including Cu loading. XANES and EXAFS analyses revealed that low loading (0.04 wt% Cu) of Cu in Cu/Uio-66 only yielded atomically dispersed Cu on the Zr nodes in Cu/Uio-66, whereas higher Cu loading (7.6 wt% Cu) led to the formation of metallic Cu nanoparticles mainly with a small proportion of Cu- ZrO_2 interfaces only.⁴³ In addition, when the size of the Cu NPs was increased by further increasing the Cu loading, a decrease in methanol yield was observed.

The influence of Cu loading on the particle size of Cu is reported in Fig. 14a. No direct correlation is observed between the size of Cu metal and Cu loading for the catalysts containing only Cu active sites. On the other hand, an increase in Cu loading increases the size of Cu particles for the catalysts containing Cu and Zn (Fig. 14a-inset). Regardless of the effect on the metal particle size, the extent of guest loading itself could affect the performance since an increase in loading could increase the number of active sites, however, there are no obvious trends between Cu metal loading and conversion or selectivity (Fig. 14b and c, respectively).

In summary, our critical literature analysis shows that catalyst particles may be active when embedded in the pores of MOFs or otherwise encapsulated therein, even though this size regime is well below what is considered optimal – for Cu the least.²⁵ In fact, small, 2 nm-sized nanoparticles have demonstrated the highest methanol selectivity, which suggests some degree of contribution from the MOF host. To further evaluate this, we continue our discussion with the possibility for MOF-metal SMSI and its impact on the direct hydrogenation of CO_2 to methanol.

Zhang *et al.* investigated the construction of $\text{Zn}^{2+}\text{-O-Zr}^{4+}$ motifs in MOF-808 to gain better insights into the structural requirement for CO_2 hydrogenation to methanol.³⁷ The $\text{Zn}^{2+}\text{-O-Zr}^{4+}$ active sites on the Zr_6 nodes were formed *in situ* after exchanging the $\mu^3\text{-OH}$ proton with ZnEt_2 . The MOF-808-Zn catalyst exhibited over 99% selectivity towards methanol at 250 °C, the yield was stable for 100 hours, and the activity of the catalyst did not decrease during the reuse of MOF-808-Zn for a second time. No structural change and aggregation of Zn was observed according to powder diffraction (PXRD) patterns and transmission electron microscopy (TEM) images. In addition, XAS results supported the presence of $\text{Zn}^{2+}\text{-O-Zr}^{4+}$ centres, and hydrogen isotope scrambling showed H_2 scission, presumably by the Zn^{2+} centres. Furthermore, they suggested that open Zr^{4+} sites were critical for methanol production, as this was not observed on Zn^{2+} centres supported on Zr nodes of

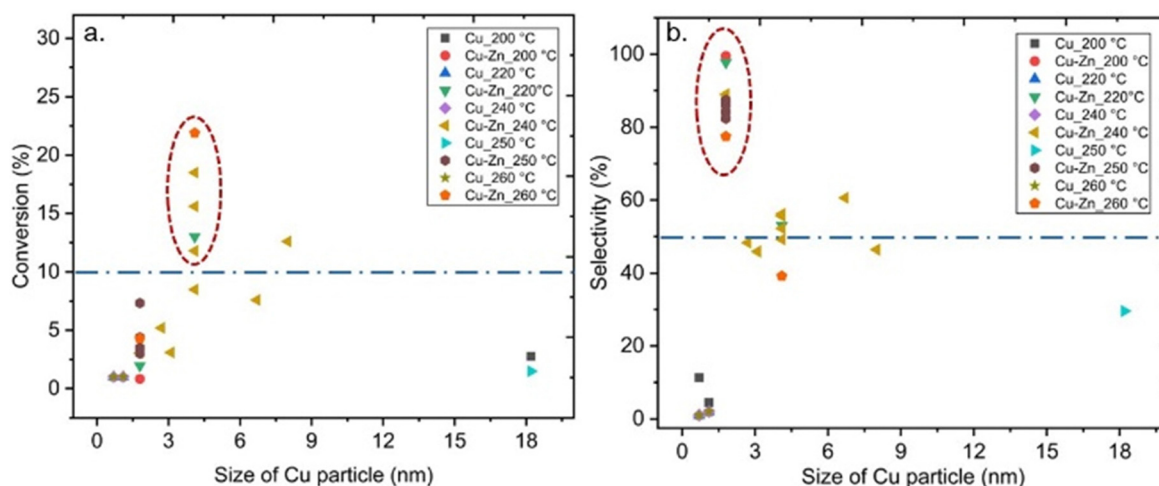
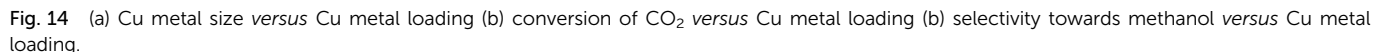


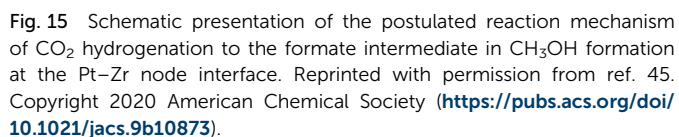
Fig. 13 (a) Conversion of CO_2 versus size of Cu particle. (b) Selectivity towards methanol versus size of Cu particle. Blue dashed lines represent 10% conversion and 50% selectivity.



Lastly, Gutterød *et al.* studied Pt NPs embedded inside UiO-67 with mixed linkers of BDC and BPDC. They reported 13% and 40% selectivity toward methanol at the mild reaction conditions of 170 °C and 8 or 30 bar, respectively.^{45,46} The Pt NPs are believed to be decorated by Zr clusters close to the Pt, which are partially or fully detached from the framework during the growth of the Pt NP. The synergy between the Pt NPs and the unsaturated Zr nodes is key to producing methanol, as demonstrated by combining coupling Steady-State Isotope Transient Kinetic Analysis (SSITKA) and *operando* IR analysis with DFT calculations. The proposed mechanism for CO₂ hydrogenation to methanol occurs through the formate pathway at the interface of a zirconia node with a missing linker defect concentration of 0.4 per cluster, providing the necessary unsaturated sites, and the platinum NPs. Firstly, CO₂ is adsorbed on the zirconium cluster near the Pt NPs, which adsorb and dissociate hydrogen molecules. Then, the hydride transfers to the CO₂ molecule, forming a formate specie, which coordinates in a bidentate manner after removing the hydroxyl

In summary, methanol formation has occurred on Cu, Cu/Zn, Zn, and Pt metal containing Zr₆-MOFs. The role of the metal is to dissociate H₂, while the subsequent H transfer to CO₂ and consequent H₂CO₂ intermediate formation takes place on the open Zr sites. Considering that the integrity of the MOF structure does not appear to be the limiting factor, as a significant decrease in surface area⁴¹ and linker functionalisation⁴⁰ did not drastically affect the activity of the catalysts, it is hypothesised that it is the metal guest-ZrO₂ interface, which is the key site for the reaction to occur.

In addition to the nature of the catalysts discussed above, the reaction conditions, specifically the reaction temperature and pressure, play crucial roles in the methanol production from CO₂ hydrogenation. According to the literature data on Zr₆ MOF-based composite catalysts, the trends between reaction conditions (temperature and pressure) on CO₂ conversion and selectivity toward methanol are reported in Fig. 16. Overall, there is a significant divergence in the reaction conditions reported, including but not restricted to the applied reaction temperatures and pressures varying from 170 °C to 300 °C and from 1 to 40 bar, respectively. In general, an increase in reaction temperature increases the reaction rate and thus conversion. On the other hand, CO₂ hydrogenation to methanol is an exothermic reaction and thermodynamically favourable at lower temperatures. However, lower reaction temperatures would not be sufficient to overcome the activation barrier for the reaction. The experimental results show that over 10% conversion of CO₂ could be achieved above 240 °C (Fig. 16a).



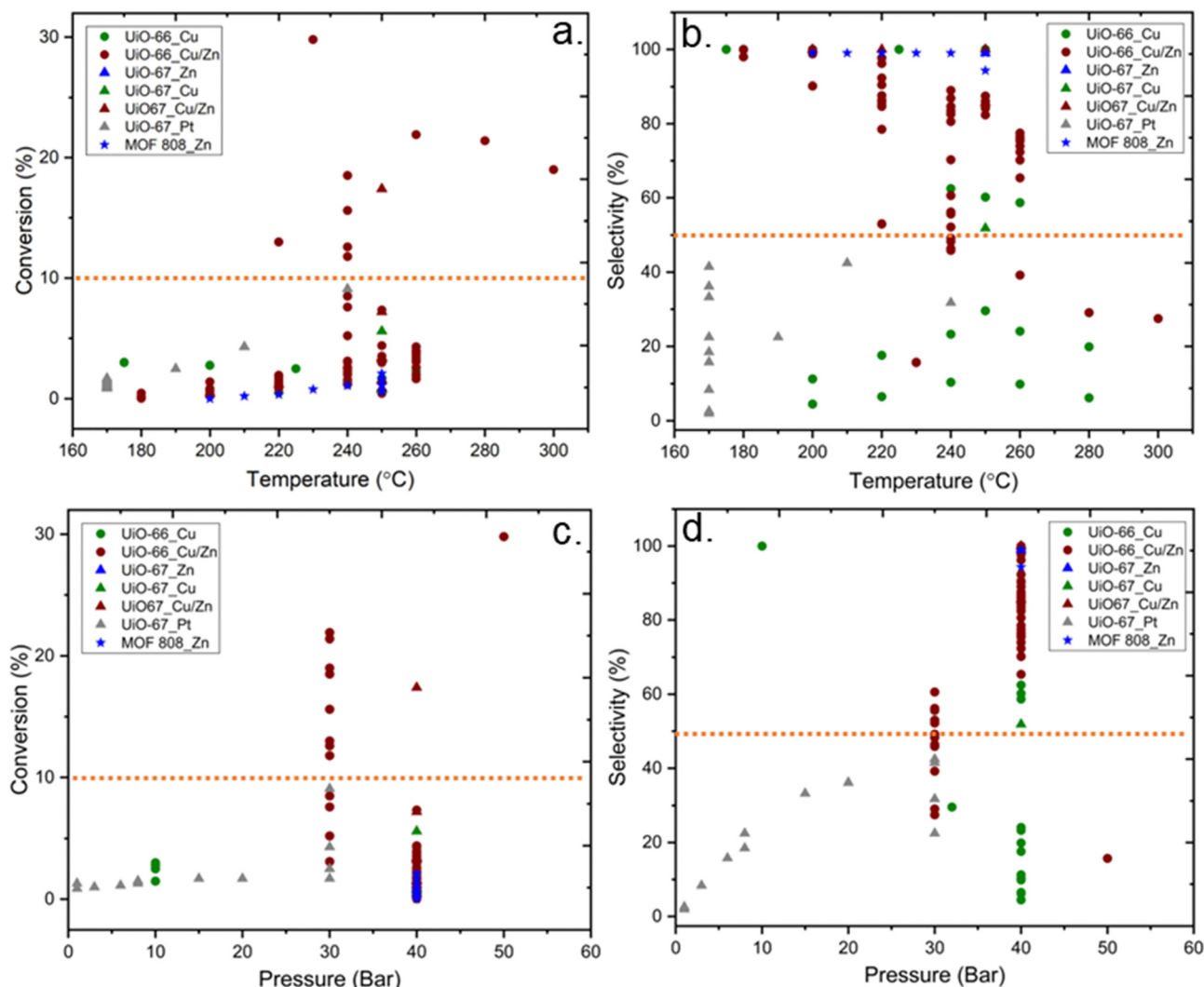


Fig. 16 The effects of temperature and pressure on the performance (a) conversion versus temperature (b) selectivity toward methanol versus temperature (c) conversion versus pressure (d) selectivity toward methanol versus pressure. Orange dashed lines represent 50% selectivity toward methanol and 10% conversion.

Even though the 10% conversion of CO₂ at 240 °C is below the thermodynamic limitations, which is approximately 20% at 30 bar, it is well above the average of the reported conversions using Zr₆-MOF-based catalysts. On the other hand, no common trend is observed for selectivity to methanol (Fig. 16b) as a function of temperature, even though it is expected that higher reaction temperatures could have adverse effects on the selectivity from thermodynamics considerations. Although theoretical thermodynamic calculations could provide information regarding the optimum reaction temperature, the fact that the optimum reaction parameters also depend on the type of catalytic system used needs to be considered. The methanol production from the hydrogenation of CO₂ is favourable at high pressures, in accordance with Le Chatelier's principle (eqn (2)). According to previous experimental data, the conversion of CO₂ is above 10% at pressures over 30 bar (Fig. 16c), and the selectivity towards methanol is below 50% under 30 bar, except for one data point, which showed 100% selectivity at 10 bar by

using Cu NPs encapsulated into UiO-66 as catalyst (Fig. 16d). These trends indicated that pressure plays a vital role for methanol production.

It has been reported that in addition to the reaction temperature and pressure, space velocity of reactant feed also has an impact on the conversion and product selectivity; however, the lack of information, including reactor dimensions, catalyst mass and flow rate, does not allow proper performance comparison among the reported studies. A table containing the type of MOF structure, active metals, and reaction conditions is provided in the ESI.†

Summary and outlook

In this review, we summarise the effects of structural properties and reaction parameters on CO₂ hydrogenation to methanol using Zr₆-based MOF structures with incorporated metal



One thing that has been laid bare through our critical review of previous literature is the lack of standardised methodologies enabling the comparison of data reported by various groups. This not only makes writing a review difficult, but it also hinders developing an in-depth understanding of the performance of catalysts, and, thus ultimately, to optimise catalysts for the direct CO₂-to-methanol conversion. For this reason, we suggest some practices for data acquisition and reporting, both on the materials and testing conditions, post-synthesis, during operation, and post-mortem, to improve the comparability of test results.

In summary, we believe that following the above basic principles in terms of catalyst characterisation and catalyst testing would contribute significantly to developing insights into the structure–composition–performance relationships, which is arguably the best way to enable the rational design

of more efficient catalysts. In addition, our analysis of the available literature also highlights that Zr₆-based frameworks are desirable support materials of catalysts for the direct CO₂-to-methanol conversion.

Author contributions

E. T. and D. S. contributed equally to writing the original draft. P. A. S., S. S. and U. O. all contributed to reviewing & editing, and conceptualising the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

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References

- 1 S. Bilgen, *Renewable Sustainable Energy Rev.*, 2014, **38**, 890–902.
- 2 M. Bui, C. S. Adjiman, A. Bardow, E. J. Anthony, A. Boston, S. Brown, P. S. Fennell, S. Fuss, A. Galindo, L. A. Hackett, J. P. Hallett, H. J. Herzog, G. Jackson, J. Kemper, S. Krevor, G. C. Maitland, M. Matuszewski, I. S. Metcalfe, C. Petit, G. Puxty, J. Reimer, D. M. Reiner, E. S. Rubin, S. A. Scott, N. Shah, B. Smit, J. P. M. Trusler, P. Webley, J. Wilcox and N. Mac Dowell, *Energy Environ. Sci.*, 2018, **11**, 1062–1176.
- 3 H.-J. Ho, A. Iizuka and E. Shibata, *Ind. Eng. Chem. Res.*, 2019, **58**, 8941–8954.
- 4 W. Gao, S. Liang, R. Wang, Q. Jiang, Y. Zhang, Q. Zheng, B. Xie, C. Y. Toe, X. Zhu, J. Wang, L. Huang, Y. Gao, Z. Wang, C. Jo, Q. Wang, L. Wang, Y. Liu, B. Louis, J. Scott, A.-C. Roger, R. Amal, H. He and S.-E. Park, *Chem. Soc. Rev.*, 2020, **49**, 8584–8686.
- 5 S. Chu, *Science*, 2009, **325**, 1599.
- 6 B. L. Salvi and S. Jindal, *SN Appl. Sci.*, 2019, **1**, 885.
- 7 S. Kar, A. Goepfert and G. K. S. Prakash, *Acc. Chem. Res.*, 2019, **52**, 2892–2903.
- 8 A.-H. Liu, R. Ma, C. Song, Z.-Z. Yang, A. Yu, Y. Cai, L.-N. He, Y.-N. Zhao, B. Yu and Q.-W. Song, *Angew. Chem., Int. Ed.*, 2012, **51**, 11306–11310.
- 9 Z.-Z. Yang, L.-N. He, Y.-N. Zhao, B. Li and B. Yu, *Energy Environ. Sci.*, 2011, **4**, 3971–3975.
- 10 G. Wang, J. Chen, Y. Ding, P. Cai, L. Yi, Y. Li, C. Tu, Y. Hou, Z. Wen and L. Dai, *Chem. Soc. Rev.*, 2021, **50**, 4993–5061.
- 11 B. Hu, C. Guild and S. L. Suib, *J. CO₂ Util.*, 2013, **1**, 18–27.
- 12 A. Galadima and O. Muraza, *Renewable Sustainable Energy Rev.*, 2019, **115**, 109333.
- 13 W. Zhang, Z. Jin and Z. Chen, *Adv. Sci.*, 2022, **9**, 2105204.
- 14 S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Nørskov, T. F. Jaramillo and I. Chorkendorff, *Chem. Rev.*, 2019, **119**, 7610–7672.
- 15 G. A. Olah, A. Goepfert and G. K. S. Prakash, *Beyond Oil and Gas: The Methanol Economy*, 2009, pp. 233–278, DOI: [10.1002/9783527627806.ch12](https://doi.org/10.1002/9783527627806.ch12).
- 16 A. Corma and H. Garcia, *J. Catal.*, 2013, **308**, 168–175.
- 17 S. Perathoner and G. Centi, *ChemSusChem*, 2014, **7**, 1274–1282.
- 18 G. Leonzio, *J. CO₂ Util.*, 2018, **27**, 326–354.
- 19 F. Zaera, *Coord. Chem. Rev.*, 2021, **448**, 214179.
- 20 S. Zhang, Z. Wu, X. Liu, K. Hua, Z. Shao, B. Wei, C. Huang, H. Wang and Y. Sun, *Top. Catal.*, 2021, **64**, 371–394.
- 21 I. Ganesh, *Renewable Sustainable Energy Rev.*, 2014, **31**, 221–257.
- 22 J. Zhong, X. Yang, Z. Wu, B. Liang, Y. Huang and T. Zhang, *Chem. Soc. Rev.*, 2020, **49**, 1385–1413.
- 23 W. Wang, S. Wang, X. Ma and J. Gong, *Chem. Soc. Rev.*, 2011, **40**, 3703–3727.
- 24 X. Jiang, X. Nie, X. Guo, C. Song and J. G. Chen, *Chem. Rev.*, 2020, **120**, 7984–8034.
- 25 R. van den Berg, G. Prieto, G. Korpershoek, L. I. van der Wal, A. J. van Bunningen, S. Lægsgaard-Jørgensen, P. E. de Jongh and K. P. de Jong, *Nat. Commun.*, 2016, **7**, 13057.
- 26 X. Yang, X. Ma, X. Yu and M. Ge, *Appl. Catal., B*, 2020, **263**, 118355.
- 27 F. Wang, J. Jiang and B. Wang, *Catalysts*, 2019, **9**, 477.
- 28 X.-J. Kong and J.-R. Li, *Engineering*, 2021, **7**, 1115–1139.
- 29 L. Feng, K.-Y. Wang, X.-L. Lv, T.-H. Yan and H.-C. Zhou, *Natl. Sci. Rev.*, 2019, **7**, 1743–1758.
- 30 M. Li, D. Li, M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2014, **114**, 1343–1370.
- 31 S. M. Moosavi, A. Nandy, K. M. Jablonka, D. Ongari, J. P. Janet, P. G. Boyd, Y. Lee, B. Smit and H. J. Kulik, *Nat. Commun.*, 2020, **11**, 4068.
- 32 J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850–13851.
- 33 H. Furukawa, F. Gándara, Y.-B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson and O. M. Yaghi, *J. Am. Chem. Soc.*, 2014, **136**, 4369–4381.
- 34 R. J. Marshall, Y. Kalinovsky, S. L. Griffin, C. Wilson, B. A. Blight and R. S. Forgan, *J. Am. Chem. Soc.*, 2017, **139**, 6253–6260.
- 35 H. Wu, Y. S. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim and W. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 10525–10532.
- 36 M. J. Cliffe, W. Wan, X. Zou, P. A. Chater, A. K. Kleppe, M. G. Tucker, H. Wilhelm, N. P. Funnell, F.-X. Coudert and A. L. Goodwin, *Nat. Commun.*, 2014, **5**, 4176.
- 37 J. Zhang, B. An, Z. Li, Y. Cao, Y. Dai, W. Wang, L. Zeng, W. Lin and C. Wang, *J. Am. Chem. Soc.*, 2021, **143**, 8829–8837.



- 38 B. An, J. Zhang, K. Cheng, P. Ji, C. Wang and W. Lin, *J. Am. Chem. Soc.*, 2017, **139**, 3834–3840.
- 39 Z. G. Duma, X. Dyosiba, J. Moma, H. W. Langmi, B. Louis, K. Parkhomenko and N. M. Musyoka, *Catalysts*, 2022, **12**, 401.
- 40 C. E. Pompe and P. Á. Szilágyi, *Faraday Discuss.*, 2021, **231**, 371–383.
- 41 J. Yu, G. Chen, Q. Guo, X. Guo, P. Da Costa and D. Mao, *Fuel*, 2022, **324**, 124694.
- 42 B. Rungtaweeworani, J. Baek, J. R. Araujo, B. S. Archanjo, K. M. Choi, O. M. Yaghi and G. A. Somorjai, *Nano Lett.*, 2016, **16**, 7645–7649.
- 43 Y. Zhu, J. Zheng, J. Ye, Y. Cui, K. Koh, L. Kovarik, D. M. Camaioni, J. L. Fulton, D. G. Truhlar, M. Neurock, C. J. Cramer, O. Y. Gutiérrez and J. A. Lercher, *Nat. Commun.*, 2020, **11**, 5849.
- 44 Y. Yang, Y. Xu, H. Ding, D. Yang, E. Cheng, Y. Hao, H. Wang, Y. Hong, Y. Su, Y. Wang, L. Peng and J. Li, *Catal. Sci. Technol.*, 2021, **11**, 4367–4375.
- 45 E. S. Gutterød, A. Lazzarini, T. Fjermestad, G. Kaur, M. Manzoli, S. Bordiga, S. Svelle, K. P. Lillerud, E. Skúlason, S. Øien-Ødegard, A. Nova and U. Olsbye, *J. Am. Chem. Soc.*, 2020, **142**, 999–1009.
- 46 E. S. Gutterød, S. H. Pulumati, G. Kaur, A. Lazzarini, B. G. Solemsli, A. E. Gunnæs, C. Ahoba-Sam, M. E. Kalyva, J. A. Sannes, S. Svelle, E. Skúlason, A. Nova and U. Olsbye, *J. Am. Chem. Soc.*, 2020, **142**, 17105–17118.
- 47 T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
- 48 J. Ma, N. Sun, X. Zhang, N. Zhao, F. Xiao, W. Wei and Y. Sun, *Catal. Today*, 2009, **148**, 221–231.
- 49 A. M. El-Zeftawy, *J. King Saud Univ., Eng. Sci.*, 1995, **7**, 209–254.
- 50 G. A. Olah, *Angew. Chem., Int. Ed.*, 2005, **44**, 2636–2639.
- 51 A. J. Shih, M. C. O. Monteiro, F. Dattila, D. Pavesi, M. Philips, A. H. M. da Silva, R. E. Vos, K. Ojha, S. Park, O. van der Heijden, G. Marcandalli, A. Goyal, M. Villalba, X. Chen, G. T. K. K. Gunasooriya, I. McCrum, R. Mom, N. López and M. T. M. Koper, *Nat. Rev. Methods Primers*, 2022, **2**, 84.
- 52 K. Stangeland, H. Li and Z. Yu, *Ind. Eng. Chem. Res.*, 2018, **57**, 4081–4094.
- 53 J. Gao, Y. Wang, Y. Ping, D. Hu, G. Xu, F. Gu and F. Su, *RSC Adv.*, 2012, **2**, 2358–2368.
- 54 J. Wambach, A. Baiker and A. Wokaun, *Phys. Chem. Chem. Phys.*, 1999, **1**, 5071–5080.
- 55 C. W. Bale, E. Bélisle, P. Chartrand, S. A. Decterov, G. Eriksson, A. E. Gheribi, K. Hack, I. H. Jung, Y. B. Kang, J. Melançon, A. D. Pelton, S. Petersen, C. Robelin, J. Sangster, P. Spencer and M.-A. Van Ende, *FactSage Thermochemical Software and Databases*, 2010–2016, Calphad, 2016, vol. 54, pp. 35–53, <https://www.factsage.com>.
- 56 J. Sehested, *J. Catal.*, 2019, **371**, 368–375.
- 57 S. Kattel, P. Liu and J. G. Chen, *J. Am. Chem. Soc.*, 2017, **139**, 9739–9754.
- 58 N. A. Sholeha, H. Holilah, H. Bahruji, A. Ayub, N. Widiastuti, R. Ediaty, A. A. Jalil, M. Ulfa, N. Masruchin, R. E. Nugraha and D. Prasetyoko, *S. Afr. J. Chem. Eng.*, 2023, **44**, 14–30.
- 59 W. J. Lee, A. Bordoloi, J. Patel and T. Bhatelia, *Catal. Today*, 2020, **343**, 183–190.
- 60 P. Gao, F. Li, N. Zhao, F. Xiao, W. Wei, L. Zhong and Y. Sun, *Appl. Catal., A*, 2013, **468**, 442–452.
- 61 L. Zhang, Y. Zhang and S. Chen, *Appl. Catal., A*, 2012, **415–416**, 118–123.
- 62 M. Behrens and R. Schlögl, *Z. Anorg. Allg. Chem.*, 2013, **639**, 2683–2695.
- 63 S. Natesakhawat, J. W. Lekse, J. P. Baltrus, P. R. Ohodnicki, Jr., B. H. Howard, X. Deng and C. Matranga, *ACS Catal.*, 2012, **2**, 1667–1676.
- 64 V. D. B. C. Dasireddy and B. Likozar, *Renewable Energy*, 2019, **140**, 452–460.
- 65 L. C. Grabow and M. Mavrikakis, *ACS Catal.*, 2011, **1**, 365–384.
- 66 T. Koitaya, S. Yamamoto, Y. Shiozawa, Y. Yoshikura, M. Hasegawa, J. Tang, K. Takeuchi, K. Mukai, S. Yoshimoto, I. Matsuda and J. Yoshinobu, *ACS Catal.*, 2019, **9**, 4539–4550.
- 67 D. Kopač, B. Likozar and M. Huš, *Appl. Surf. Sci.*, 2019, **497**, 143783.
- 68 A. Karelovic and P. Ruiz, *Catal. Sci. Technol.*, 2015, **5**, 869–881.
- 69 F. Zhang, X. Xu, Z. Qiu, B. Feng, Y. Liu, A. Xing and M. Fan, *Green Energy Environ.*, 2022, **7**, 772–781.
- 70 R. Naumann d'Alnoncourt, X. Xia, J. Strunk, E. Löffler, O. Hinrichsen and M. Muhler, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1525–1538.
- 71 J. D. Grunwaldt, A. M. Molenbroek, N. Y. Topsøe, H. Topsøe and B. S. Clausen, *J. Catal.*, 2000, **194**, 452–460.
- 72 M. Behrens, F. Studt, I. Kasatkin, S. Köhl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B.-L. Knief, M. Tovar, R. W. Fischer, J. K. Nørskov and R. Schlögl, *Science*, 2012, **336**, 893–897.
- 73 Y. Choi, K. Futagami, T. Fujitani and J. Nakamura, *Appl. Catal., A*, 2001, **208**, 163–167.
- 74 H. Y. Chen, S. P. Lau, L. Chen, J. Lin, C. H. A. Huan, K. L. Tan and J. S. Pan, *Appl. Surf. Sci.*, 1999, **152**, 193–199.
- 75 K. Xiao, Q. Wang, X. Qi and L. Zhong, *Catal. Lett.*, 2017, **147**, 1581–1591.
- 76 R. S. Schifano and R. P. Merrill, *J. Phys. Chem.*, 1993, **97**, 6425–6435.
- 77 E. Lam, J. J. Corral-Pérez, K. Larmier, G. Noh, P. Wolf, A. Comas-Vives, A. Urakawa and C. Copéret, *Angew. Chem., Int. Ed.*, 2019, **58**, 13989–13996.
- 78 K. Li and J. G. Chen, *ACS Catal.*, 2019, **9**, 7840–7861.
- 79 H. Li, L. Wang, X. Gao and F.-S. Xiao, *Ind. Eng. Chem. Res.*, 2022, **61**, 10446–10454.
- 80 I. U. Din, M. S. Shaharun, M. A. Alotaibi, A. I. Alharthi and A. Naeem, *J. CO₂ Util.*, 2019, **34**, 20–33.
- 81 F. Arena, K. Barbera, G. Italiano, G. Bonura, L. Spadaro and F. Frusteri, *J. Catal.*, 2007, **249**, 185–194.
- 82 S. Kuld, M. Thorhauge, H. Falsig, C. F. Elkjær, S. Helveg, I. Chorkendorff and J. Sehested, *Science*, 2016, **352**, 969–974.



- 83 M. B. Fichtl, D. Schlereth, N. Jacobsen, I. Kasatkin, J. Schumann, M. Behrens, R. Schlögl and O. Hinrichsen, *Appl. Catal., A*, 2015, **502**, 262–270.
- 84 B. Liang, J. Ma, X. Su, C. Yang, H. Duan, H. Zhou, S. Deng, L. Li and Y. Huang, *Ind. Eng. Chem. Res.*, 2019, **58**, 9030–9037.
- 85 A. Prašnikar, A. Pavličič, F. Ruiz-Zepeda, J. Kovač and B. Likozar, *Ind. Eng. Chem. Res.*, 2019, **58**, 13021–13029.
- 86 G. Chen, J. Yu, G. Li, X. Zheng, H. Mao and D. Mao, *Int. J. Hydrogen Energy*, 2023, **48**, 2605–2616.
- 87 J. Ye, M. Neurock and D. G. Truhlar, *J. Phys. Chem. C*, 2022, **126**, 13157–13167.
- 88 E. S. Gutterød, S. Øien-Ødegaard, K. Bossers, A.-E. Nieuwelink, M. Manzoli, L. Braglia, A. Lazzarini, E. Borfecchia, S. Ahmadigoltapeh, B. Bouchevreau, B. T. Lønstad-Bleken, R. Henry, C. Lamberti, S. Bordiga, B. M. Weckhuysen, K. P. Lillerud and U. Olsbye, *Ind. Eng. Chem. Res.*, 2017, **56**, 13206–13218.
- 89 E. Aunan, C. W. Affolter, U. Olsbye and K. P. Lillerud, *Chem. Mater.*, 2021, **33**, 1471–1476.
- 90 G. C. Shearer, S. Chavan, S. Bordiga, S. Svelle, U. Olsbye and K. P. Lillerud, *Chem. Mater.*, 2016, **28**, 3749–3761.
- 91 O. Halbherr and R. A. Fischer, Defects and Disorders in MOF, *The Chemistry of Metal–Organic Frameworks*, 2016, pp. 795–822, DOI: [10.1002/9783527693078.ch26](https://doi.org/10.1002/9783527693078.ch26).
- 92 A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chem. – Eur. J.*, 2011, **17**, 6643–6651.
- 93 D. K. Sannes, S. Øien-Ødegaard, E. Aunan, A. Nova and U. Olsbye, *Chem. Mater.*, 2023, **35**, 3793–3800.
- 94 X. Feng, J. Hajek, H. S. Jena, G. Wang, S. K. P. Veerapandian, R. Morent, N. De Geyter, K. Leyssens, A. E. J. Hoffman, V. Meynen, C. Marquez, D. E. De Vos, V. Van Speybroeck, K. Leus and P. Van Der Voort, *J. Am. Chem. Soc.*, 2020, **142**, 3174–3183.
- 95 P. Chammingkwan, G. Y. Shangkm, L. T. T. Mai, P. Mohan, A. Thakur, T. Wada and T. Taniike, *RSC Adv.*, 2020, **10**, 28180–28185.
- 96 Y. Feng, Q. Chen, M. Jiang and J. Yao, *Ind. Eng. Chem. Res.*, 2019, **58**, 17646–17659.
- 97 G. C. Shearer, S. Chavan, J. Ethiraj, J. G. Vitillo, S. Svelle, U. Olsbye, C. Lamberti, S. Bordiga and K. P. Lillerud, *Chem. Mater.*, 2014, **26**, 4068–4071.
- 98 G. Kaur, S. Øien-Ødegaard, A. Lazzarini, S. M. Chavan, S. Bordiga, K. P. Lillerud and U. Olsbye, *Cryst. Growth Des.*, 2019, **19**, 4246–4251.
- 99 H. H. Mautschke, F. Drache, I. Senkovska, S. Kaskel and F. X. Llabrés i Xamena, *Catal. Sci. Technol.*, 2018, **8**, 3610–3616.
- 100 K. Hemmer, M. Cokoja and R. A. Fischer, *ChemCatChem*, 2021, **13**, 1683–1691.

