available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Metal-organic frameworks MOF-808-X as highly efficient catalysts for direct synthesis of dimethyl carbonate from CO₂ and methanol

Keng Xuan ^{a,b}, Yanfeng Pu ^a, Feng Li ^a, Jing Luo ^{a,b}, Ning Zhao ^{a,*}, Fukui Xiao ^{a,#}^a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, Shanxi, China^b University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 8 November 2018

Accepted 26 December 2018

Published 5 April 2019

Keywords:

Metal-organic frameworks

MOF-808

Micropore size

Carbon dioxide utilization

Dimethyl carbonate

ABSTRACT

A series of metal-organic frameworks MOF-808-X (6-connected) were synthesized by regulating the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/1,3,5\text{-benzenetricarboxylic acid (BTC)}$ molar ratio (X) and tested for the direct synthesis of dimethyl carbonate (DMC) from CO_2 and CH_3OH with 1,1,1-trimethoxymethane (TMM) as a dehydrating agent. The effect of the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{BTC}$ molar ratio on the physicochemical properties and catalytic performance of MOF-808-X was investigated. Results showed that a proper $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{BTC}$ molar ratio during MOF-808-X synthesis was fairly important to reduce the redundant BTC or zirconium clusters trapped in the micropores of MOF-808-X. MOF-808-4, with almost no redundant BTC or zirconium clusters trapped in the micropores, exhibited the largest surface area, micropore size, and the number of acidic-basic sites, and consequently showed the best activity among all MOF-808-X, with the highest DMC yield of 21.5% under the optimal reaction conditions. Moreover, benefiting from the larger micropore size, MOF-808-4 outperformed our previously reported UiO-66-24 (12-connected), which had even more acidic-basic sites and larger surface area than MOF-808-4, mainly because the larger micropore size of MOF-808-4 provided higher accessibility for the reactant to the active sites located in the micropores. Furthermore, a possible reaction mechanism over MOF-808-4 was proposed based on the *in situ* FT-IR results. The effects of different reaction parameters on DMC formation and the reusability of MOF-808-X were also studied.

© 2019, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Dimethyl carbonate (DMC) is an environmentally benign chemical compound with versatile chemical properties and is widely used in many fields. For example, DMC can be used as a green solvent, electrolyte in lithium ion batteries, and an alternative to some toxic substances such as phosgene, dimethyl

sulphate, and alkyl halide used in carbonylation and methylation reactions. DMC can also be used as a fuel additive owing to its high oxygen content and octane value [1–3]. Several pathways for DMC synthesis, including phosgene (COCl_2) methanolysis, propylene carbonate transesterification, urea methanolysis, oxidative carbonylation of CH_3OH , electrosynthesis, and direct synthesis of DMC from CO_2 and CH_3OH have been

* Corresponding author. Tel: +86-351-4041153; Fax: +86-351-4046129; E-mail: zhaoning@sxicc.ac.cn

Corresponding author. Tel: +86-351-4041153; Fax: +86-351-4046129; E-mail: xiaofk@sxicc.ac.cn

This work was financially supported by the Natural Science Foundation of Shanxi Province, China (201601D102006), the Science Foundation for Young Scientists of Shanxi Province, China (201701D221052), the National Natural Science Foundation of China (21776294), the Key Science and Technology Program of Shanxi Province, China (MD2014-09, MD2014-10), and the Independent Research Project of the State Key Laboratory of Coal Conversion (2018BWZ002).

DOI: S1872-2067(19)63291-2 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 40, No. 4, April 2019

developed. Among these, the direct synthesis of DMC from CO₂ and CH₃OH is considered as the most environment-friendly pathway due to the avoidance of highly toxic reagents such as COCl₂ and CO, the high atom utilization (83%), and the direct utilization of greenhouse gas CO₂ [2,4–7].

For the synthesis of DMC from CH₃OH and CO₂, many catalysts have been developed. Among the reported heterogeneous catalysts such as ZrO₂ [8–10], CeO₂ [11,12], Ce_xZr_{1-x}O₂ [13], Fe_xZr_{1-x}O_y [14], ZrO₂/SBA-15 [15], Al₂O₃/CeO₂ [16], Ce_xZr_{1-x}O₂/grapheme [17], [EMIM]Br/Ce_{0.5}Zr_{0.5}O₂ [18], and Cu-Ni/ZrO₂ [19]. Zr-based metal oxide catalysts have attracted much attention owing to their excellent stability as well as high selectivity towards DMC. However, low surface area and undeveloped porosity of the Zr-based metal oxide catalysts may limit their activity because the bulk phase of the catalyst is inaccessible and ineffective, and the number of active sites exposed on the external surface of the catalyst are insufficient [20].

Metal organic frameworks (MOFs), a class of crystalline porous materials constructed from various organic ligands and metal nodes, are promising in heterogeneous catalysis owing to their large surface area, highly developed porosity, as well as a large number of accessible active sites in the coordination-unsaturated metal nodes [21–23]. To address the disadvantages of Zr-based metal oxide catalyst for the first time, we have previously employed trifluoroacetic acid (TFA)-modulated Zr-based metal-organic frameworks UiO-66-X as the catalysts for the direct synthesis of DMC from CO₂ and CH₃OH, where X refers to the molar equivalents of TFA modulator relative to the organic linker (terephthalic acid, BDC) used in UiO-66-X synthesis. Results suggested that catalyst UiO-66-24 showed the best catalytic activity with a DMC formation rate of 0.17 mmol g-cat⁻¹ h⁻¹ in the absence of a dehydrating agent. This rate is much higher than that of ZrO₂ (0.03 mmol g-cat⁻¹ h⁻¹). Through characterization, it was found that UiO-66-24 could not only provide higher surface area (>1479 m² g⁻¹) and highly developed pore structure, but also could provide a larger number of acidic sites (hydroxyl and coordinately unsaturated Zr⁴⁺ sites) and basic sites (coordinately unsaturated O sites) when compared to that by ZrO₂, and endowed it with a higher catalytic activity [24]. Although UiO-66-24 was a promising catalyst for the synthesis of DMC from CH₃OH and CO₂, its micropores with a diameter < 1.2 nm might be too small for the reaction between two CH₃OH molecules and one CO₂ molecule (accumulation diameter of two CH₃OH and one CO₂ molecules is about 1.3 nm), indicating that the active sites located in these micropores could not be utilized for the reaction [24–26]. Therefore, in order to allow the contact of the reactants with as many active sites as possible, exploration of other Zr-based MOFs with sufficient active sites and larger pore sizes may be an effective strategy for the direct synthesis of DMC from CO₂ and methanol.

To date, several Zr-based MOFs with different connectivities, including UiO-66 (with 12-connected Zr₆ nodes), NU-1000 (with 8-connected Zr₆ nodes), and MOF-808 (with 6-connected Zr₆ nodes), have been reported [22,23,27]. It was suggested that the Zr-based MOFs with lower connectivity could not only

provide sufficient active sites, but also larger pore sizes for the catalytic reaction [22,23]. Therefore, we hypothesized that MOF-808, which possesses the lowest connectivity, may be a promising candidate for the direct synthesis of DMC from CO₂ and methanol.

Hence, in this work, a series of MOF-808-X catalysts with different metal/ligand molar ratios (molar ratio of ZrOCl₂·8H₂O/BTC from 0.5 to 5) were synthesized and used as catalysts for the direct synthesis of DMC from CO₂ and CH₃OH in the presence of TMM as a dehydrating agent (Eqs. 1 and 2) [18]. The effects of ZrOCl₂·8H₂O/BTC molar ratio on the physicochemical properties and catalytic activities of MOF-808-X were investigated by XRD, TEM, N₂-physisorption, TGA, FT-IR, NH₃-TPD, and CO₂-TPD techniques. The relationship between the activities and physicochemical properties (especially the acid-base property and the micropore size) of MOF-808-X was clarified. In addition, *in situ* FT-IR spectroscopy was used to unravel the reaction mechanism over MOF-808-4. Finally, the effects of different reaction parameters on DMC formation and the reusability of MOF-808-X were also studied.

2. Experimental

2.1. Materials

Zirconium chloride (ZrCl₄, 98%), zirconium oxychloride octahydrate (ZrOCl₂·8H₂O, 98%), terephthalic acid (BDC, 99%), 1,3,5-benzenetricarboxylic (BTC, 99%), and 1,1,1-trimethoxymethane (TMM, 99.5%) were purchased from Aladdin Industrial Inc. (Shanghai, China). *N,N*-dimethylformamide (DMF, 98%), CH₃OH (99.8%), benzene (99%), and dimethyl carbonate (DMC, 99%) were obtained from Tianli Chemical Co. (Tianjin, China). Carbon dioxide (CO₂, 99.9%), ammonia (NH₃, 99.9%), and argon (Ar, 99.99%) were purchased from Yihong Gas Industrial Co. (Taiyuan, China). All chemicals were commercially available and used without further purification except for methanol, which was treated with activated 4 Å zeolite to remove water.

2.2. Catalyst preparation

MOF-808-X were synthesized by adjusting the molar ratio of metal to ligand following the method reported by Li et al. [28], with some modifications (Scheme 1). Typically, a predetermined amount of ZrOCl₂·8H₂O (1.90, 2.58, 5.16, 7.74, 10.32, and 12.91 g corresponding to 4, 8, 16, 24, 32, and 40 mmol, respectively) and 1.68 g (8 mmol) of BTC (the molar ratios of ZrOCl₂·8H₂O/BTC corresponding to 0.5, 1, 2, 3, 4, and 5, respectively) were dissolved in DMF/formic acid (200 mL/200 mL) mixture with magnetic stirring until a clear solution was obtained. Then the solution was transferred into a 1000 mL glass flask and heated at 130 °C while continuously stirring for 4 h. After naturally cooling to room temperature, the white precipitate was collected by centrifugation and washed with fresh

Scheme 1. Synthesis of MOF-808-X.

DMF three times, followed by double extraction with 200 mL of DMF for 12 h to remove the unreacted BTC. Thereafter, to remove the DMF molecules trapped inside the pores of the product, CH_3OH was used instead of DMF and the same procedure as that of BTC removal was followed. Finally, all the purified catalysts were dried at 80 °C under vacuum for 12 h and the as-prepared catalysts are denoted as MOF-808-X ($\text{X} = 0.5, 1, 2, 3, 4, 5$), where X represents the molar ratio of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{BTC}$.

2.3. Catalytic characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer operated at 40 kV and 40 mA with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) over the 2θ range of 2° – 90° and a scanning speed of 2° min^{-1} .

The morphologies of MOF-808-X were observed with a high resolution transmission electron microscope (HRTEM, JEM-2010, JEOL, Japan) at an accelerating voltage of 200 kV.

Nitrogen sorption-desorption isotherms were measured at -196°C on a Micromeritics Tristar ASAP 2020 instrument. Prior to the measurement, all the samples were degassed under vacuum at 150 °C for 12 h. Specific surface areas of the samples were calculated using the Brunauer-Emmett-Teller (BET) equation, and pore size distributions were obtained using the Original Density Functional Theory (ODFT) method.

Thermogravimetric analysis (TGA) was carried out to estimate the composition of MOF-808-X by using a NETZSCH thermogravimetric analyzer with a heating rate of 2°C min^{-1} from room temperature to 800 °C in air.

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus 470 FT-IR spectrometer fitted with a transmission attachment to further study the compositions of MOF-808-X.

NH_3 -temperature-programmed desorption (NH_3 -TPD) and CO_2 -temperature-programmed desorption (CO_2 -TPD) were conducted to investigate the acid-base properties of the catalysts. Prior to adsorption, the samples (30 mg, 20–40 mesh) were pretreated with argon (40 mL min^{-1}) at 150 °C for 3 h. Adsorption process was performed in NH_3 or CO_2 (40 mL min^{-1}) for 1 h at room temperature. The physisorbed NH_3 or CO_2 was then flushed with argon at room temperature for 1 h. Thereafter, the desorption process was conducted from room temperature to 700 °C with a heating rate of $10^\circ\text{C min}^{-1}$ under argon flow (40

mL min^{-1}), and the desorbed NH_3 and CO_2 were continuously monitored using a BALZERS Q-Mass spectrometer with the mass signals of $m/e = 17$ and 44, respectively.

The possibly leached Zr^{4+} was determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Thermo iCAP6300, Thermo Fisher, USA).

2.4. Catalytic reaction

The direct synthesis of DMC from CO_2 and CH_3OH in the presence of TMM as the dehydrating agent was carried out in an 80 mL Teflon-lined stainless-steel autoclave equipped with a magnetic stirrer, heating jacket and a thermocouple. Typically, 0.5 g of the catalyst (activated at 150 °C for 12 h under vacuum before use) was introduced into the autoclave. Then a mixture of CH_3OH (200 mmol) and TMM (20 to 140 mmol) was added into the reactor. After that, the autoclave was purged with CO_2 until the desired pressure was reached. After reacting for a specific amount of time, the reactor was immediately cooled by ice-water bath and depressurized. The reaction mixture in liquid and gas phases were analyzed using a gas chromatograph (GC) equipped with a capillary column SHIMADZU CBP/20 and a flame ionization detector (FID). For all the reactions, DMC was only detected in the liquid phase and no other by-products were detected in both liquid and gas phases. Therefore, the DMC selectivity was considered to be 100%. The amount of DMC formed was determined by the internal method with benzene as the internal standard. The DMC yield and its formation rate were calculated from Eqs. 3 and 4, respectively. The turnover frequency (TOF) based on the amount of metal in various catalysts was calculated from Eq. 5.

$$\text{DMC yield} = \frac{\text{Amount of DMC formed (mmol)} \times 2}{\text{Amount of } \text{CH}_3\text{OH added (mmol)}} \quad (\text{Eq. 3})$$

$$\text{DMC formation rate} = \frac{\text{Amount of DMC formed (mmol)}}{\text{Reaction time (h)} \times \text{Amount of catalyst (g)}} \quad (\text{Eq. 4})$$

$$\text{TOF} = \frac{\text{Amount of DMC formed (mmol)}}{\text{Amount of metal in catalyst (mmol g-cat}^{-1}\text{)} \times \text{Reaction time (h)}} \quad (\text{Eq. 5})$$

2.5. Reaction mechanism investigation

The reaction mechanism for the direct synthesis of DMC from CH_3OH and CO_2 was investigated using the *in situ* FT-IR spectroscopy. Approximately 15 mg of MOF-808-4 was pressed into a self-supporting thin wafer with a diameter of 1 cm, which was loaded into an *in situ* FT-IR apparatus equipped with CaF_2 windows and connected to a vacuum system. Prior to CH_3OH adsorption, the catalyst disk was degassed at 150 °C until no further change in the spectra was observed. After degassing, CH_3OH adsorption over the catalyst disk was carried out at 140 °C for an assigned time. Then, CO_2 was introduced into the system to study the CO_2 adsorption. A Nicolet Nexus 470 FT-IR spectrometer with a resolution of 4 cm^{-1} was used for recording the spectra in the range of 1000 to 4000 cm^{-1} .

3. Results and discussion

3.1. Structural and textural properties of MOF-808-X

The structural properties of MOF-808-X were studied by XRD and TEM. It can be seen from Fig. 1a that the XRD patterns of all the catalysts synthesized using different molar ratios of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{BTC}$ matched well with the reported MOF-808 [22,28], demonstrating the successful synthesis of MOF-808-X catalysts. Based on the peak width of $2\theta = 4.4^\circ$ and the Scherrer equation, the crystallite sizes of MOF-808-X were calculated to be 19, 22, 26, 53, 60, and 31 nm, respectively. The particle size variation trend reflected by XRD was in good accordance with the results of TEM (Fig. 1b–g). In addition, with the molar ratio of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{BTC}$ increasing from 0.5 to 4, the peak intensity of the XRD patterns increased and the morphology of MOF-808-X gradually changed from inter-grown irregular particles for MOF-808-0.5, MOF-808-1, and MOF-808-2 to octahedral for MOF-808-3 and MOF-808-4, indicating the increased crystallinity of MOF-808-X. However, as the molar ratio of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{BTC}$ was further increased to 5, the crystallinity decreased. The low crystallinity of MOF-808-0.5, MOF-808-1, and MOF-808-2 compared to MOF-808-3 and MOF-808-4 is probably attributed to the disturbance by BTC trapped in the pores of MOF-808, since the molar ratios of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{BTC}$ for MOF-808-0.5, -1, and -2 synthesis were lower than that for the perfect MOF-808 synthesis (molar ratio of

$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{BTC} = 3$), i.e. BTC was redundant for the construction of perfect MOF-808. The low crystallinity of MOF-808-5 might be due to the disturbance of zirconium clusters trapped in the pores of MOF-808-5, since $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ is redundant for the perfect MOF-808 construction [29,30]. From the XRD and TEM results, it can be concluded that the crystallinity of MOF-808-X is highly dependent on the molar ratio of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{BTC}$, and that MOF-808-4 exhibits the best crystallinity.

N_2 adsorption-desorption was performed to investigate the effect of the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{BTC}$ molar ratio on the textural properties of MOF-808-X. N_2 adsorption isotherms presented in Fig. 2a show that MOF-808-0.5, -1, and -2 exhibit type IV isotherms with H3 hysteresis loops, while MOF-808-3, -4, and -5 show type I isotherm. This indicates that MOF-808-0.5, -1, and -2 possess micropores and mesopores/macropores, while the pore structures of MOF-808-3, -4, and -5 predominantly consisted of micropores, as reflected by their pore size distributions (Fig. 2b). The mesopores/macropores with diameters in the range of 6–130 nm in MOF-808-0.5, -1, and -2, reflected by pore size distribution, are probably formed by the accumulation of particles, since the pores in this diameter range were not observed in the TEM images (insertion of Figures 1b–d). Typically, the characteristic micropore size of perfect MOF-808 was 1.8 nm [22,23]. However, from the results in Fig. 2b, it can

Fig. 1. (a) XRD patterns of MOF-808-X, and TEM images of (b) MOF-808-0.5, (c) MOF-808-1, (d) MOF-808-2, (e) MOF-808-3, (f) MOF-808-4, and (g) MOF-808-5.

Fig. 2. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of various catalysts.

Table 1
Textural properties of various catalysts.

Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Average pore size (nm)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	
			Total (V_{p})	Micropore (V_{micro})
MOF-808-0.5	1142	5.5	1.59	0.34
MOF-808-1	1155	5.2	1.47	0.35
MOF-808-2	1290	3.5	1.18	0.42
MOF-808-3	1311	2.1	0.70	0.47
MOF-808-4	1373	2.0	0.63	0.51
MOF-808-5	665	2.0	0.33	0.23
UiO-66-24 [24]	1479	1.8	0.68	0.48

be noted that the micropores in MOF-808-0.5, -1, and -2 were mainly centered at 1.2 and 1.8 nm. The pore with 1.2 nm size was probably derived from the trapping of BTC molecules in the micropores with the diameter of 1.8 nm, since BTC for MOF-808-0.5, -1, and -2 synthesis was redundant for the perfect MOF-808 construction [29,30]. As can be seen in Fig. 2b, with the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /BTC molar ratio gradually increasing from 0.5 to 4, the number of the micropores centered at 1.2 nm decreased and finally disappeared for MOF-808-3 and MOF-808-4. Accordingly, the number of micropores centered at 1.8 nm increased, indicating the decrease of BTC trapped in the micropores, which probably accounts for the increase of the BET surface area (S_{BET}) (from $1142 \text{ m}^2 \text{g}^{-1}$ to $1373 \text{ m}^2 \text{g}^{-1}$), micropore volume (V_{micro}) (from $0.34 \text{ cm}^3 \text{g}^{-1}$ to $0.51 \text{ cm}^3 \text{g}^{-1}$), and the micropore size of MOF-808-X, as displayed in Table 1 and Fig. 2b. However, as the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /BTC molar ratio further increased to 5, the S_{BET}

and the micropore volume dramatically decreased, which might be due to the trapped zirconium clusters in the micropores of MOF-808-5, since $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ is redundant for the perfect MOF-808 construction [29,31].

By comparison with our previously reported UiO-66-24 ($1479 \text{ m}^2 \text{g}^{-1}$) [24], it is noted that the S_{BET} values of MOF-808-X were lower, but the average pore sizes were larger (Table 1 and Fig. 2b). As is well-known, although a higher surface area could provide more active sites for the catalytic reaction, a larger pore size was also desired to provide high accessibility of the active sites for the reactant.

3.2. Composition of MOF-808-X

TGA/DTG and FT-IR were applied to investigate the effect of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /BTC molar ratio on the compositions of MOF-808-X. TGA/DTG profiles presented in Fig. 3 show that a minor mass-loss below 200°C was observed due to the desorption of water and CH_3OH . Then, a moderate weight-loss from 200 – 350°C was found resulting from the decomposition of HCOOH coordinated with Zr_6 nodes. When the temperature was further raised to 350 – 650°C , a sharp weight loss occurred due to the combustion of BTC coordinated with Zr_6 nodes. Then BTC was completely burned out above 650°C , with ZrO_2 left as the only residue [21,32,33].

Based on the weight loss at 200 – 650°C , the number of coordinated HCOOH molecules, BTC linkers, and Zr_6 nodes in one MOF-808-X unit can be calculated and the chemical formula of MOF-808-X could be determined in accordance with the method reported by Shearer et al. [21,33] (Table 2). As can be seen

Fig. 3. TGA/DTG profiles of (a) MOF-808-0.5, (b) MOF-808-1, (c) MOF-808-2, (d) MOF-808-3, (e) MOF-808-4, and (f) MOF-808-5.

Table 2

Composition and acid-base properties of various catalysts.

Catalyst	Composition		Acid-base properties (mmol g-cat ⁻¹)		
	Chemical formula	Linker/Zr ₆	Number of acidic sites	Number of basic sites	Total
MOF-808-0.5	[Zr ₆ O ₄ (OH) ₄] (BTC) _{2.5} (HCOO) _{3.7}	2.5	2.8	1.2	4.0
MOF-808-1	[Zr ₆ O ₄ (OH) ₄] (BTC) _{2.2} (HCOO) _{3.5}	2.2	3.3	1.7	5.0
MOF-808-2	[Zr ₆ O ₄ (OH) ₄] (BTC) _{2.1} (HCOO) _{4.2}	2.1	3.6	2.2	5.8
MOF-808-3	[Zr ₆ O ₄ (OH) ₄] (BTC) _{1.7} (HCOO) _{5.3}	1.7	4.8	2.9	7.7
MOF-808-4	[Zr ₆ O ₄ (OH) ₄] (BTC) _{1.5} (HCOO) _{3.5}	1.5	5.2	3.1	8.3
MOF-808-5	[Zr ₆ O ₄ (OH) ₄] (BTC) _{1.1} (HCOO) _{3.8}	1.1	3.5	2.0	5.5
Perfect MOF-808	[Zr ₆ O ₄ (OH) ₄] (BTC) _{2.0} (HCOO) _{6.0}	2.0	—	—	—
UiO-66-24 [24]	[Zr ₆ O ₄ (OH) ₄] (BDC) _{4.0} (CF ₃ COO) _{1.7}	4.0	4.6	5.2	9.8

from Table 2, with the increasing ZrOCl₂·8H₂O/BTC molar ratio, the molar ratio of linker/Zr₆ gradually decreased from 2.5 for MOF-808-0.5 to 1.1 for MOF-808-5, which is also reflected in the FT-IR spectra of MOF-808-X (Fig. 4), i.e. as the ZrOCl₂·8H₂O/BTC molar ratio increased, the bands at 1617, 1572, 1385, and 760 cm⁻¹ belonging to BTC (labeled with blue arrow) decreased [29,34], and the bands at 714 and 660 cm⁻¹ attributed to Zr–O bond in Zr₆ nodes (labeled with purple arrow) increased [35], further indicating the decrease in linker/Zr₆ node molar ratio. In addition, it is noted from Table 2 that higher linker/Zr₆ molar ratios were observed in MOF-808-0.5, -1, and -2 when compared to that in the perfect MOF-808 (linker/Zr₆ molar ratio = 2.0), indicating the presence of unreacted BTC trapped in MOF-808-X, which was in good agreement with the N₂ adsorption-desorption results. The bands at 1715 cm⁻¹ corresponding to the uncoordinated –COOH of free BTC in the FT-IR spectra of MOF-808-0.5, -1, and -2 also demonstrated the presence of unreacted BTC trapped in these samples [29,36]. In contrast, for MOF-808-3, -4, and -5, since BTC was insufficient for the construction of perfect MOF-808, the linker/Zr₆ node molar ratio (< 2.0) was lower than that in perfect MOF-808, indicating that almost no BTC was trapped in the micropores of MOF-808-3, -4, and -5. Therefore, the dramatic decrease in S_{BET} and the micropore volumes of MOF-808-5 could be attributed to the trapped zirconium clusters in the micropores.

To summarize, the N₂ adsorption-desorption, TGA/DTG, and

Fig. 4. FT-IR spectra of MOF-808-X.

FT-IR results indicated that with the ZrOCl₂·8H₂O/BTC molar ratio increasing from 0.5 to 4, the amount of BTC trapped in the micropores of MOF-808-X decreased, leading to the increased surface area and micropore size. Accordingly, the molar ratio of linker/Zr₆ node of MOF-808-X decreased, i.e. the number of Zr₆ nodes per unit weight of catalyst for the direct synthesis of DMC from CO₂ and CH₃OH increased. However, further increasing the ZrOCl₂·8H₂O/BTC molar ratio to 5 resulted in the presence of redundant zirconium clusters trapped in the micropores and the significant decrease of BET surface area and micropore volume of MOF-808-5. It should be noted that although unreacted BTC or the redundant zirconium clusters in MOF-808-X could be partly removed by DMF washing, BTC or redundant zirconium clusters trapped in the micropores of MOF-808-5 were difficult to be completely removed [37]. Therefore, the results implied that a proper molar ratio of ZrOCl₂·8H₂O/BTC was fairly important to reduce the redundant BTC or zirconium clusters trapped in the micropores of MOF-808-X. Additionally, it was noted from TGA profile that the weight of residual ZrO₂ in MOF-808-X (50%~64%) was higher than that in UiO-66-24 (41%) [24], suggesting that MOF-808-X could provide more Zr₆ nodes than UiO-66-24 for this reaction.

3.3. Acid-base properties of MOF-808-X

It was earlier reported that the acid-base properties are crucial for the direct synthesis of DMC from CO₂ and CH₃OH [9,14,38]. Thus, NH₃-TPD and CO₂-TPD were carried out to detect the acid and base properties, respectively, of MOF-808-X. For the NH₃-TPD profiles of MOF-808-X (Fig. 5a), NH₃ desorption peaks below 250 °C were observed, which can be attributed to the weak to moderate acidic sites related to the hydroxyl (Brönsted acidic site) and the exposed Zr⁴⁺ (Lewis acidic acid) in Zr₆ nodes [24,27,39,40]. Unfortunately, due to the perturbation of BTC and HCOOH ligands, the Brönsted and Lewis acidic sites in MOF-808-X were not identified by pyridine FT-IR (Fig. S2). Based on the area of the NH₃ desorption profiles, the corresponding number of acidic sites in MOF-808-X is calculated and listed in Table 2. It is found that as the molar ratio of ZrOCl₂·8H₂O/BTC increased, the number of acidic sites significantly increased from 2.8 mmol g-cat⁻¹ for MOF-808-0.5 to 5.2 mmol g-cat⁻¹ for MOF-808-4. As indicated by the TGA/DTG

Fig. 5. (a) NH_3 -TPD and (b) CO_2 -TPD profiles of MOF-808-X.

results, the increased number of acidic sites is probably due to the increased number of Zr_6 nodes in MOF-808-X [22,23,27]. However, as the molar ratio of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /BTC further increased to 5, the number of acidic sites decreased to 3.5 mmol g-cat⁻¹, even though MOF-808-5 contained more Zr as indicated by the TGA/DTG results. This is probably because the redundant zirconium clusters trapped in the micropores decreased the specific surface area of MOF-808-5, which in turn inhibited the exposure of the acidic sites.

In the CO_2 -TPD profiles of MOF-808-X (Fig. 5b), three peaks can be identified. The peak located at 25 to 200 °C can be attributed to CO_2 desorbed from the weak and moderately basic sites related to unsaturated O^{2-} anion of Zr-O-Zr or Zr-O- in Zr_6 nodes [41–44]. The peaks located at 200 to 350 °C and 350 to 650 °C can be assigned to CO_2 released from the decomposition of HCOOH and BTC linker, respectively, as confirmed by the results of TGA/DTG and the control test in which a similar peak was observed in the TPD profile of MOF-808-4 without CO_2 adsorption (Fig. S3). Based on the area of CO_2 desorption peaks between 25 to 200 °C, the number of basic sites in MOF-808-X is calculated and listed in Table 2. It is found that the number of basic sites in MOF-808-X increased as the $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /BTC molar ratio increased from 0.5 to 4, which might be due to the increased number of Zr_6 nodes in MOF-808-X, as indicated by TGA/DTG [22,23,27]. As the molar ratio of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /BTC further increased to 5, the number of basic sites decreased to 2.0 mmol g-cat⁻¹ due to the decrease in specific surface area that inhibited the exposure of the basic sites.

When compared to our previously reported UiO-66-24 [24], although MOF-808-X contains more Zr_6 nodes and the connectivity of Zr_6 nodes is lower, the number of acidic-basic sites in it is lower (Table 2), which might result from the partial coordination of formate ions (HCOO^-) to the unconnected sites of Zr_6 nodes in MOF-808-X, as shown in Scheme 1 [22].

3.4. Catalytic performance

3.4.1. Catalytic activity tests

Catalytic activities of MOF-808-X for the direct synthesis of DMC from CO_2 and CH_3OH were evaluated by batch reaction

and the results are summarized in Table 3. It is well known that the synthesis of DMC from CO_2 and CH_3OH was limited by a thermodynamic equilibrium [45,46]. Therefore, trimethoxymethane (TMM) was used as the dehydrating agent to shift the reaction towards the direction of DMC formation by the removal of by-product, water [6,47]. As illustrated in Table 3, the addition of TMM significantly increased the DMC yield from 0.12 % (Entry 7) to 3.28 % (Entry 5) over MOF-808-4. As the formation of DMC from TMM and CO_2 (Eq. 6) is also thermodynamically favorable [18], a control test without CH_3OH was carried out to check whether DMC could be formed from the reaction of TMM and CO_2 . The result shows that only 0.35% (Entry 8) of DMC was formed from the reaction of TMM and CO_2 , indicating that TMM worked as a dehydrating agent instead of a reactant, which was in agreement with the results of Zhang et al. [18] and Saha et al. [17]. The effect of MOF-808-X catalyst on the dehydrating process (Eq. 2) was also investigated. The result indicated that the reaction rate between TMM and H_2O without the catalyst was almost identical to that in the

Table 3

Catalytic activity of various catalysts.

Entry	Catalyst	CH_3OH (mmol)	TMM (mmol)	DMC yield (%)	DMC formation rate (mmol g-cat ⁻¹ h ⁻¹)	TOF (h ⁻¹)
1	MOF-808-0.5	200	100	1.50	0.75	0.18
2	MOF-808-1	200	100	2.10	1.05	0.24
3	MOF-808-2	200	100	2.80	1.40	0.32
4	MOF-808-3	200	100	3.16	1.58	0.33
5	MOF-808-4	200	100	3.28	1.64	0.34
6	MOF-808-5	200	100	2.44	1.22	0.23
7	MOF-808-4	200	0	0.12	0.06	0.01
8	MOF-808-4	0	100	0.35 ^a	0.17	0.04
9	UiO-66-24	200	100	2.14	1.07	0.31
10	ZrO_2 ^b	200	100	0.82	0.41	0.05
11	CeO_2 ^b	200	100	0.88	0.44	0.08
12	None	200	100	0	0	–

Reaction conditions: 140 °C; 4 h; CO_2 pressure: 12 MPa; catalyst weight: 0.5 g; reactor volume: 80 mL.

^a DMC yield for the reaction between CO_2 and TMM is defined as $Y_{\text{DMC}} = \text{Amount of DMC formed (mmol)} / \text{Amount of TMM added (mmol)} \times 100\%$.

^b Preparation method, XRD patterns, and SEM images of ZrO_2 and CeO_2 are presented in Supporting Information (S1).

presence of MOF-808-X, indicating the negligible effect of MOF-808-X in the dehydrating process. Additionally, it should be noted that although TMM promoted the reaction through water removal, the reaction did not occur in the absence of catalyst (Entry 12), confirming that the reaction between CO₂ and CH₃OH proceeded catalytically.

To compare the catalytic activities of MOF-808-X, the DMC formation rates as well as the turnover frequencies (TOFs), which represent the number of DMC molecules formed based on the amount of metal present in various catalysts (the amount of metal in various catalysts is presented in Table S1), were calculated at a reaction time of 4 h, when the reaction was within kinetic region (Fig. 8d). As illustrated in Table 3, when the molar ratio of ZrOCl₂·8H₂O/BTC gradually increased from 0.5 to 4, the DMC formation rate gradually increased from 0.75 mmol g-cat⁻¹ h⁻¹ for MOF-808-0.5 (Entry 1) to 1.64 mmol g-cat⁻¹ h⁻¹ for MOF-808-4 (Entry 5), while the TOF gradually increased from 0.18 h⁻¹ to 0.34 h⁻¹. As the molar ratio of ZrOCl₂·8H₂O/BTC further increased to 5, the DMC formation rate and TOF decreased to 1.22 mmol g-cat⁻¹ h⁻¹ and 0.23 h⁻¹, respectively (Entry 6).

According to the reported mechanism for DMC synthesis, both the acidic and basic sites play important roles in the reaction of CO₂ and methanol; CH₃OH is activated to methyl species and methoxy species on the acidic and basic sites, respectively. Methoxy carbonate anion is then formed by the reaction of methoxy species with CO₂ adsorbed on the basic sites. Methoxy carbonate anion further reacts with methyl cation to produce DMC [9,38,48]. Therefore, the catalytic activity of MOF-808-X is probably highly dependent on the number of acidic and basic sites. The relationship between the number of acidic and basic sites and the DMC formation rates over MOF-808-X are presented in Fig. 6. It could be clearly seen that the DMC formation rates were basically in accordance with the order of the number of acidic and basic sites on MOF-808-X, and MOF-808-4, with the largest number of acidic and basic sites, exhibited the best activity, indicating that the higher number of acidic and basic sites are favorable for enhancing the catalytic performance, which is consistent with our previous results [14,15,24] and those reported by Tomishige et al. [9] and Lee et al. [49–51].

In addition, from the N₂ adsorption-desorption results, it is

found that as the ZrOCl₂·8H₂O/BTC molar ratio increased from 0.5 to 4, BTC trapped in the micropores decreased. Consequently, the volume of micropores with a diameter of 1.8 nm and the average micropore size of MOF-808-X increased, which may be favorable for the enhancement of the catalytic activity of MOF-808-X since larger micropore size could provide higher accessibility for the reactant to the active sites located in the micropores [14,43,52]. However, for MOF-808-5, the average pore size of which was similar to MOF-808-4, the activity was lower than that of MOF-808-4. This is probably because the redundant zirconium clusters trapped in the micropores of MOF-808-5 dramatically decreased its specific surface area and thus inhibited the exposure of the acidic-basic sites.

Considering that the structure of MOF-808-X with lower crystallinity might not be stable during the reaction, the catalytic activity of MOF-808-X may be affected. Hence, all the MOF-808-X catalysts, after activity assessment, were recycled and characterized by XRD. Results show that the structures of all the MOF-808-X after reacting for 4 h were well retained (Fig. S4), indicating that the different activities of MOF-808-X were mainly because of the variation in their physiochemical properties resulting from the ZrOCl₂·8H₂O/BTC regulation.

Furthermore, the best performed MOF-808-4 catalyst was compared with our previously reported Zr-based MOF catalyst UiO-66-24 under the same reaction conditions [24]. It is noted that UiO-66-24 with higher surface area and larger number of acidic-basic sites showed a lower catalytic activity when compared to MOF-808-4, probably due to the presence of smaller micropores in UiO-66-24, which make the surface area and active sites not fully utilizable in the reaction. This strongly suggests that in spite of the lower surface area and the less number of active sites, the larger micropore size plays an important role in determining the higher catalytic activity of MOF-808-4.

The activity of MOF-808-4 was also compared with monolithic ZrO₂ and spindle-like CeO₂ with cubic fluorite structure, since the monolithic ZrO₂ [10] and spindle-like CeO₂ [12] catalysts showed superior activity among metal oxide catalysts. However, the activity of monolithic ZrO₂ and spindle-like CeO₂ prepared in this work (detailed synthetic procedures and characterization are presented in S1 in Supporting Information) was much lower than that of MOF-808-4 (Entries 9 and 10). These results allow us to conclude that MOF-808-4 could be a good candidate for the direct synthesis of DMC from

Fig. 6. Relationship between the DMC formation rate and (a) the number of acidic sites, (b) the number of basic sites, and (c) the total number of acidic and basic sites.

CO₂ and CH₃OH.

3.4.2. Possible reaction mechanism

The possible reaction mechanism for DMC synthesis over MOF-808-4 was investigated by *in situ* FT-IR spectroscopy (Fig. 7). Prior to CH₃OH adsorption, MOF-808-4 catalyst was activated at 150 °C under vacuum until the spectra remained almost identical. As seen in Fig. 7a, the bands at 2931, 2820, 1142, and 1037 cm⁻¹ appeared and increased after the exposure to CH₃OH at 140 °C. The bands at 2931 and 2820 cm⁻¹ are associated with C–H stretching vibrations of terminal (t–OCH₃, i.e. Zr–OCH₃) and bridged (b–OCH₃, i.e. Zr–(OCH₃)–Zr) methoxy species, respectively. The bands at 1142 and 1037 cm⁻¹ can be assigned to the C–O bending vibrations of terminal (Zr–OCH₃) and bridged (Zr–(OCH₃)–Zr) methoxy species [10,38,48,53,54], respectively.

After introducing CO₂ to the CH₃OH-pre-adsorbed MOF-808-4, the intensity of the bands related to Zr–OCH₃ and Zr–(OCH₃)–Zr gradually decreased (Fig. 7b). The decrease in intensity of Zr–OCH₃ probably resulted from the insertion of CO₂ into Zr–OCH₃ resulting in the formation of intermediate Zr–OCOOCH₃, while the decrease in intensity of Zr–(OCH₃)–Zr is probably due to the reaction between Zr–OCOOCH₃ and the methyl group in Zr–(O–CH₃)–Zr to form DMC [11,16,38]. Unfortunately, the evolution of the bands corresponding to the possible intermediates Zr–OCOOCH₃ located between 1000–2000 cm⁻¹ [38,48,53] were not identified due to the perturbation of BTC and HCOOH ligands in the FT-IR spectra (Fig. S5).

Based on the results of *in situ* FT-IR, a possible reaction mechanism over MOF-808-4 is inferred as follows (Scheme 2). (1) Adsorbed CH₃OH initially bonds to the Lewis acidic sites (exposed Zr⁴⁺) of Zr₆ node in MOF-808-4 to form Zr–OCH₃ and releases H atom. The H atom then reacts rapidly with the terminal hydroxyl (Zr–OH) to form H₂O. The generated H₂O could coordinate with the exposed Zr⁴⁺ to form Zr–OH₂, as indicated by the increase in intensity of the hydroxyl group of Zr₆ node (broad band at 3700–3500 cm⁻¹) during CH₃OH adsorption (Fig. S5a) [32]. In the actual reaction, the formed water could be removed by reacting with TMM (Eq. 6). In addition, CH₃OH can also be activated into methyl cation (CH₃⁺) by the acidic sites (Zr⁴⁺) of Zr₆ node, the formed CH₃⁺ could be then adsorbed on the basic site (unsaturated O²⁻ in Zr–O–Zr or Zr–O⁻) of Zr₆ node to form the bridged methoxy (Zr–(OCH₃)–Zr). Accordingly, the hydroxyl dissociated from CH₃OH could adsorb on the acidic site (exposed Zr⁴⁺) to form the terminal hydroxyl (Zr–OH). (2) Upon exposure to CO₂, the adsorbed CO₂ on the basic sites of Zr₆ nodes in MOF-808-4 inserts into Zr–OCH₃ to form the intermediate Zr–OCOOCH₃. (3) Finally, the generated Zr–OCOOCH₃ reacts with CH₃⁺ released from Zr–(OCH₃)–Zr to form DMC.

It should be noted that CO₂ may also first interact with the catalyst in the DMC formation procedure. According to the reaction mechanism reported by Bell et al. [38] and Inumaru et al. [10], CO₂ can be activated into a bidentate bicarbonate species (b–HCO₃–Zr) and a bidentate carbonate species (b–CO₃–Zr). The b–HCO₃–Zr is active which could react with CH₃OH to form methyl carbonate intermediate. However, formation of the methyl

Fig. 7. *In situ* FT-IR spectra of (a) CH₃OH adsorption on MOF-808-4, and (b) CO₂ adsorption on CH₃OH-pre-adsorbed MOF-808-4.

Scheme 2. Proposed reaction mechanism for the direct synthesis of DMC from CO_2 and CH_3OH over MOF-808-4.

carbonate intermediate from this pathway is much slower than that formed from the reaction of t-Zr-OCH_3 with CO_2 . Therefore, it could be speculated that DMC was mainly produced by the reaction between methyl carbonate, which is formed from the reaction of t-Zr-OCH_3 with CO_2 , and CH_3^+ , as shown in Scheme 2.

On investigating the reaction mechanism, it is found that both the acidic sites (exposed Zr^{4+} and terminal hydroxyl) and the basic sites (unsaturated O^{2-} in Zr-O-Zr and Zr-O^-) in Zr_6 clusters of MOF-808-4 play important roles in promoting the reaction, which indicates that more number of acidic and basic sites are beneficial for enhancing the catalytic activity of MOF-808-X.

In addition, it was suggested that the formation of CH_3^+ was the rate-determining step in DMC synthesis [38,48,49]. According to the mechanism of reaction over ZrO_2 reported by Bell et al. [38], when CO_2 is introduced to methanol-pre-adsorbed ZrO_2 , the decrease in intensity of the C–O bending vibrations in the bridged methoxy ($\text{Zr-(OCH}_3\text{)-Zr}$) (1032 cm^{-1}) is much slower than that in the terminal methoxy (Zr-OCH_3) (1157 cm^{-1}), suggesting that the reaction between Zr-OCH_3 and CO_2 to form Zr-OCOOCH_3 occurred rapidly, while the cleavage of C–O bond in $\text{Zr-(OCH}_3\text{)-Zr}$ to form CH_3^+ was relatively slower, which limits the reaction between CH_3^+ and Zr-OCOOCH_3 for the formation of DMC. However, in the case of

MOF-808-4, it is worth noting from Fig. 7a that the decrease in the intensity of C–O bending vibrations in $\text{Zr-(OCH}_3\text{)-Zr}$ (1037 cm^{-1}) was more pronounced than that in ZrO_2 reported by Bell et al. [38], indicating that the C–O bond of $\text{Zr-(OCH}_3\text{)-Zr}$ over MOF-808-4 could be rapidly cleaved to form CH_3^+ , which could then react with the generated intermediate Zr-OCOOCH_3 to form DMC [11,38,48]. The rapid cleavage of C–O bond in the bridged methoxy ($\text{Zr-(OCH}_3\text{)-Zr}$) over MOF-808-4 compared to that over ZrO_2 is probably attributed to the neighboring acidic-basic sites in Zr_6 nodes of MOF-808-4 [9,38] (six Zr atoms of Zr_6 node are arrayed as an octahedron in which the acidic-basic sites, including the Lewis acidic sites (exposed Zr^{4+}), basic sites (unsaturated O^{2-} in Zr-O-Zr or Zr-O^-), and terminal hydroxyl are adjacent to each other [55,56], see Scheme 2). Tomishige et al. [9] and Bell et al. [38] revealed that the neighboring acidic sites (exposed Zr^{4+} and hydroxyl) and basic sites (unsaturated O^{2-} in Zr-O-Zr or Zr-O^-) in ZrO_2 are favorable for the cleavage of C–O bond in $\text{Zr-(OCH}_3\text{)-Zr}$ to form CH_3^+ and the bonding of CH_3^+ with the methyl carbonate species to form DMC. Gates et al. [55] also found that the Zr-based MOF catalyst UiO-66 shows much higher activity than ZrO_2 in the reaction of ethanol dehydration to ether, since the larger number of the neighboring acidic-basic sites in the highly dispersed Zr_6 nodes of UiO-66 allows a rapid bonding of ethanol with ethoxy adsorbed on the neighboring sites of Zr_6 nodes, facilitating the bimolecular ether

formation. Therefore, it is reasonable to infer that the neighboring acidic-basic sites in Zr_6 nodes of MOF-808-4 may also allow catalytic bonding of CH_3^+ (arising from C–O bond cleavage of $Zr-(OCH_3)-Zr$) with the neighboring $Zr-OCOOCH_3$ on Zr_6 nodes, thereby leading to the rapid formation of DMC [9,55]. Based on the results discussed above, we suppose that the rapid cleavage of C–O bond in the bridged methoxy ($Zr-(OCH_3)-Zr$) to form CH_3^+ (the rate-determining step in DMC synthesis) may be another important factor contributing to the high activity of MOF-808-4.

3.4.3. Effects of reaction parameters on DMC yield

MOF-808-4 was used to gain further insights into the effects of reaction parameters, including the reaction temperature, reaction pressure, amount of TMM, and reaction time on the DMC yield (Fig. 8). Experimental results show that the optimal reaction conditions for DMC synthesis from CO_2 and CH_3OH were: reaction temperature of 140 °C, CO_2 pressure of 12 MPa, TMM amount of 100 mmol, and reaction time of 48 h, under which, the highest DMC yield of 21.5% was obtained (Fig. 8d). DMC yield obtained under the optimal reaction conditions over MOF-808-4 was compared with that over several other catalysts developed in recent years (Table 4). It was found that the optimal DMC yield over MOF-808-4 was higher or comparable to that obtained using the same/similar dehydrating agent such as DMP, TMM, and butylene oxide (Entries 1 to 6), indicating that MOF-808-4 could be an efficient catalyst for the direct synthesis of DMC from CO_2 and CH_3OH . However, it should be noted that the optimal DMC yield over MOF-808-4 was lower

than that over CeO_2 , with 2-cyanopyridine as the dehydrating agent (Entry 7), reported by Tomishige et al. [11]. Thus, we suppose that 2-cyanopyridine might be a better dehydrating agent in the reaction. Hence, the formation of DMC over MOF-808-4 by using 2-cyanopyridine as the dehydrating agent was also carried out, but the DMC yield achieved over MOF-808-4 (34.3%, Entry 9) was still lower than that over CeO_2 (97%, Entry 7) [11]. This is probably because MOF-808-4 showed no catalytic activity in the reaction between H_2O and TMM or 2-cyanopyridine, while CeO_2 can not only catalyze the reaction between CO_2 and methanol, but also can show high catalytic activity in the hydration of 2-cyanopyridine, which could further accelerate the formation of DMC [11,57].

In order to study the possible contribution of homogeneous catalytic reaction due to active species leaching, MOF-808-4 was removed from the reaction medium by filtration after reacting for 4 h. It was found that only 1.3% of Zr^{4+} was leached from MOF-808-4 in the filtrate, as confirmed by ICP-OES. In addition, no further increase in the DMC yield in the filtrate was observed after the catalyst removal (Fig. 8d), indicating that the reaction was catalyzed heterogeneously.

3.4.4. Reusability

The reusability of MOF-808-X was tested under the optimum reaction conditions. After each reaction, the catalyst was collected by centrifugation and washed with CH_3OH , followed by drying at 150 °C for 12 h. As illustrated in Fig. S6A, although the reusability of all the MOF-808-X was not good, MOF-808-3 and -4 exhibited a relatively better reusability. To understand

Fig. 8. Dependence of DMC yield on (a) the reaction temperature at 12 MPa, 100 mmol TMM, and 24 h, (b) the reaction pressure at 140 °C, 100 mmol TMM, and 24 h, (c) the amount of TMM at 140 °C, 12 MPa, and 24 h, and (d) the reaction time at 140 °C, 12 MPa, and 100 mmol TMM.

Table 4

Comparison of the DMC yield over MOF-808-4 with that reported in the literature.

Entry	Catalyst	Dehydrating agent	P_{CO_2} (MPa)	T (°C)	T (h)	DMC yield (%)	Ref.
1	$\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$	DMP ^a	200 mmol	120	140	7.2	[13]
2	$\text{Bu}_2\text{Sn}(\text{OMe})$	DMP ^a	200 mmol	180	24	9.4	[51]
3	$\text{ZrO}_2\text{-MgO}$	Butylene oxide	9	150	8	6.2	[58]
4	$\text{ZrO}_2\text{-KCl-MgO}$	Butylene oxide	4	150	8	7.2	[47]
5	$\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{Graphene}$	TMM	12	110	16	23.2	[17]
6	$\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	TMM	12	140	34	10.4	[18]
7	CeO_2	2-cyanopyridine	16	120	16	97.0	[11]
8	MOF-808-4	TMM	12	140	48	21.5	This work
9	MOF-808-4	2-cyanopyridine	12	140	48	34.3	This work

^a DMP: Dimethoxymethane.

the reason, all the recycled MOF-808-X catalysts were characterized by XRD. As can be seen in Fig. S6B, after cycle 1, the structures of MOF-808-3 and -4 were retained, but the intensity of the characteristic peaks slightly decreased, which might account for the slight decrease in the DMC yield over MOF-808-3 and -4 in cycle 2. However, for MOF-808-0.5, -1, -2, and 5, the DMC yield over these catalysts dramatically decreased after cycle 1, which was probably due to a severe collapse of the frame structure as indicated by the XRD patterns that show a dramatic decrease in the intensity of the characteristic peaks of these samples. The relatively better reusability of MOF-808-3 and -4 could be attributed to their good crystallinity, since the frame structure of MOF catalyst with better crystallinity could be retained better during the reaction [59,60]. Although the reusability of MOF-808-X was far from that required for practical applications, the high activity of MOF-808-4 in cycle 1 and the relationship between the stability and crystallinity of MOF-808-X provide us a direction for the future development of more efficient and stable MOF-based catalysts for DMC synthesis from CO_2 and methanol.

4. Conclusions

In summary, MOF-808-X (6-connected) have been proven to be effective for the direct synthesis of DMC from CO_2 and CH_3OH , with TMM as the dehydrating agent. The $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}/\text{BTC}$ molar ratio has significant effect on the physicochemical properties and catalytic performances of MOF-808-X. By regulating the molar ratio of $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}/\text{BTC}$ for MOF-808-X synthesis, the amount of the redundant BTC or zirconium clusters trapped in the micropores can be reduced. As a result, MOF-808-4, with almost no redundant BTC or zirconium clusters trapped in the micropores, exhibited the largest micropore size, surface area, and the number of acidic-basic sites. Consequently, MOF-808-4 showed the best activity among MOF-808-X, with the highest DMC yield of 21.5% under the optimum reaction conditions. However, its comparison with UiO-66-24 (12-connected) indicated that despite MOF-808-4 had lower surface area and fewer acidic-basic sites than UiO-66-24, it had lower connectivity that provided larger micropore size for the higher accessibility of the active sites located in the micropores to the reactants, leading to the higher activity of MOF-808-4 over UiO-66-24. This indicates that in addition to surface area and the number of active sites, the mi-

cropore size also has a significant effect on the improvement of the catalytic activity. Furthermore, mechanistic studies suggested that the rapid formation of CH_3^+ (rate-determining step in DMC synthesis) over MOF-808-4 also contributes to its high activity. Reusability tests showed that although all the MOF-808-X catalysts were not satisfactory, those with good crystallinity were relative more stable. Hence, more efforts are required to explore other efficient and stable MOF catalysts for DMC synthesis from CO_2 and CH_3OH in the future studies.

References

- [1] G. Fiorani, A. Perosa, M. Selva, *Green Chem.*, **2018**, 20, 288–322.
- [2] S. Huang, B. Yan, S. Wang, X. Ma, *Chem. Soc. Rev.*, **2015**, 44, 3079–3116.
- [3] S. Pan, L. Zheng, R. Nie, S. Xia, P. Chen, Z. Hou, *Chin. J. Catal.*, **2012**, 33, 1772–1777.
- [4] D. Delledonne, F. Rivetti, U. Romano, *Appl. Catal. A*, **2001**, 221, 241–251.
- [5] Y. Cao, H. Cheng, L. Ma, F. Liu, Z. Liu, *Catal. Surv. Asia*, **2012**, 16, 138–147.
- [6] M. Honda, M. Tamura, Y. Nakagawa, K. Tomishige, *Catal. Sci. Technol.*, **2014**, 4, 2830.
- [7] Y. Liao, F. Li, X. Dai, N. Zhao, F. Xiao, *Chin. J. Catal.*, **2017**, 38, 1860–1869.
- [8] K. Tomishige, T. Sakaihorii, Y. Ikeda, K. Fujimoto, *Catal. Lett.* **1999**, 58, 225–229.
- [9] K. Tomishige, Y. Ikeda, T. Sakaihorii, K. Fujimoto, *J. Catal.*, **2000**, 192, 355–362.
- [10] T. Akune, Y. Morita, S. Shirakawa, K. Katagiri, K. Inumaru, *Langmuir*, **2018**, 34, 23–29.
- [11] M. Honda, M. Tamura, Y. Nakagawa, K. Nakao, K. Suzuki, K. Tomishige, *J. Catal.*, **2014**, 318, 95–107.
- [12] S. Wang, L. Zhao, W. Wang, Y. Zhao, G. Zhang, X. Ma, J. Gong, *Nanoscale*, **2013**, 5, 5582–5588.
- [13] K. Tomishige, K. Kunitomi, *Appl. Catal. A*, **2002**, 237, 103–109.
- [14] A. Li, Y. Pu, F. Li, J. Luo, N. Zhao, F. Xiao, *J. CO₂ Utiliz.*, **2017**, 19, 33–39.
- [15] Y. Pu, K. Xuan, F. Wang, A. Li, N. Zhao, F. Xiao, *RSC Adv.*, **2018**, 8, 27216–27226.
- [16] M. Aresta, A. Dibenedetto, C. Pastore, A. Angelini, B. Aresta, I. Pápai, *J. Catal.*, **2010**, 269, 44–52.
- [17] R. Saada, S. Kellici, T. Heil, D. Morgan, B. Saha, *Appl. Catal. B*, **2015**, 168–169, 353–362.
- [18] Z. Zhang, Z. Liu, J. Lu, Z.-T. Liu, *Ind. Eng. Chem. Res.*, **2011**, 50, 1981–1988.
- [19] O. Arbeláez, A. Orrego, F. Bustamante, A. L. Villa, *Catal. Lett.*, **2016**,

Graphical Abstract

Chin. J. Catal., 2019, 40: 553–566 doi: S1872-2067(19)63291-2

Metal-organic frameworks MOF-808-X as highly efficient catalysts for direct synthesis of dimethyl carbonate from CO₂ and methanol

Keng Xuan, Yanfeng Pu, Feng Li, Jing Luo, Ning Zhao *, Fukui Xiao *

Institute of Coal Chemistry, Chinese Academy of Sciences; University of Chinese Academy of Sciences

Metal-organic framework catalysts MOF-808-X were highly active for the direct synthesis of dimethyl carbonate (DMC) from CO₂ and CH₃OH. The effects of the ZrOCl₂·8H₂O/1,3,5-benzenetricarboxylic acid (BTC) molar ratio on the physicochemical properties and catalytic activities of MOF-808-X were clarified.

- 146, 725–733.
- [20] A. H. Tamboli, A. A. Chaugule, H. Kim, *Chem. Eng. J.*, **2017**, 323, 530–544.
 - [21] G. C. Shearer, S. Chavan, S. Bordiga, S. Svelle, U. Olsbye, K. P. Lillerud, *Chem. Mater.*, **2016**, 28, 3749–3761.
 - [22] S. Y. Moon, Y. Liu, J. T. Hupp, O. K. Farha, *Angew. Chem. Int. Ed.*, **2015**, 54, 6795–6799.
 - [23] Y. Liu, R. C. Klet, J. T. Hupp, O. Farha, *Chem. Commun.*, **2016**, 52, 7806–7809.
 - [24] K. Xuan, Y. Pu, F. Li, A. Li, J. Luo, L. Li, F. Wang, N. Zhao, F. Xiao, *J. CO₂ Utiliz.*, **2018**, 27, 272–282.
 - [25] M. Saito, T. Toyao, K. Ueda, T. Kamegawa, Y. Horiuchi, M. Mat-suoka, *Dalton Trans.*, **2013**, 42, 9444–9447.
 - [26] R. S. Mehare, S. P. Ranganath, V. Chaturvedi, M. V. Badiger, M. V. Shelke, *Energy Fuels*, **2018**, 32, 908–915.
 - [27] C. Ardila-Suárez, S. Perez-Beltran, G. Ramírez-Caballero, P. B. Balbuena, *Catal. Sci. Technol.*, **2018**, 8, 847–857.
 - [28] Z. Q. Li, J. C. Yang, K. W. Sui, N. Yin, *Mater. Lett.*, **2015**, 160, 412–414.
 - [29] Y. Peng, H. Huang, Y. Zhang, C. Kang, S. Chen, L. Song, D. Liu, C. Zhong, *Nat. Commun.*, **2018**, 9, 187.
 - [30] G. Cai, H. Jiang, *Angew. Chem. Int. Ed.*, **2017**, 56, 563–567.
 - [31] L. H. Wee, F. Bonino, C. Lamberti, S. Bordiga, J. A. Martens, *Green Chem.*, **2014**, 16, 1351–1357.
 - [32] H. Furukawa, F. Gandara, Y. B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson, O. M. Yaghi, *J. Am. Chem. Soc.*, **2014**, 136, 4369–4381.
 - [33] G. C. Shearer, S. Chavan, J. Ethiraj, J. G. Vitillo, S. Svelle, U. Olsbye, C. Lamberti, S. Bordiga, K. P. Lillerud, *Chem. Mater.*, **2014**, 26, 4068–4071.
 - [34] S. Hinokuma, G. Wiker, T. Suganuma, A. Bansode, D. Stoian, S. Caminero Huertas, S. Molina, A. Shafir, M. Rønning, W. van Beek, A. Urakawa, *Eur. J. Inorg. Chem.*, **2018**, 2018, 1847–1853.
 - [35] H. Ranjan Sahu, G. Ranga Rao, *Bull. Mater. Sci.*, **2000**, 23, 349–354.
 - [36] Y. Wang, L. Li, P. Dai, L. Yan, L. Cao, X. Gu, X. Zhao, *J. Mater. Chem. A*, **2017**, 5, 22372–22379.
 - [37] D.Y. Hong, Y. K. Hwang, C. Serre, G. Férey, J. S. Chang, *Adv. Funct. Mater.*, **2009**, 19, 1537–1552.
 - [38] K. T. Jung, A. T. Bell, *J. Catal.*, **2001**, 204, 339–347.
 - [39] F. Vermoortele, B. Bueken, G. Le Bars, B. Van de Voorde, M. Vandichel, K. Houthoofd, A. Vimont, M. Daturi, M. Waroquier, V. Van Speybroeck, C. Kirschhock, D. E. De Vos, *J. Am. Chem. Soc.*, **2013**, 135, 11465–11468.
 - [40] R. C. Klet, Y. Liu, T. C. Wang, J. T. Hupp, O. K. Farha, *J. Mater. Chem. A*, **2016**, 4, 1479–1485.
 - [41] S. Øien, D. Wragg, H. Reinsch, S. Svelle, S. Bordiga, C. Lamberti, K. P. Lillerud, *Cryst. Growth Des.*, **2014**, 14, 5370–5372.
 - [42] P. He, J. Xu, V. V. Tersikh, A. Sutrisno, H. Y. Nie, Y. Huang, *J. Phys. Chem. C*, **2013**, 117, 16953–16960.
 - [43] P. Gao, F. Li, H. Zhan, N. Zhao, F. Xiao, W. Wei, L. Zhong, H. Wang, Y. Sun, *J. Catal.*, **2013**, 298, 51–60.
 - [44] N. D. Didier Tichit, Bernard Coq, Robert Durand, *Chem. Mater.*, **2002**, 14, 1530–1538.
 - [45] F. Bustamante, A. F. Orrego, S. Villegas, A. L. Villa, *Ind. Eng. Chem. Res.*, **2012**, 51, 8945–8956.
 - [46] B. Y. Yu, M. K. Chen, I. L. Chien, *Ind. Eng. Chem. Res.*, **2018**, 57, 639–652.
 - [47] V. Eta, P. Mäki-Arvela, A. R. Leino, K. Kordas, T. Salmi, D. Yu. Murzin, J. P. Mikkola, *Ind. Eng. Chem. Res.*, **2010**, 49, 9609–9617.
 - [48] Y. Ikeda, M. Asadullah, K. Fujimoto, K. Tomishige, *J. Phys. Chem. B*, **2001**, 105, 10653–10658.
 - [49] H. J. Lee, S. Park, J. C. Jung, I. K. Song, *Korean J. Chem. Eng.*, **2011**, 28, 1518–1522.
 - [50] H. J. Lee, W. Joe, I. K. Song, *Korean J. Chem. Eng.*, **2011**, 29, 317–322.
 - [51] H. J. Lee, W. Joe, J. C. Jung, I. K. Song, *Korean J. Chem. Eng.*, **2012**, 29, 1019–1024.
 - [52] H. Li, X. Jiao, L. Li, N. Zhao, F. Xiao, W. Wei, Y. Sun, B. Zhang, *Catal. Sci. Technol.*, **2015**, 5, 989–1005.

- [53] L. Chen, S. Wang, J. Zhou, Y. Shen, Y. Zhao, X. Ma, *RSC Adv.*, **2014**, 4, 30968–30975.
- [54] D. Yang, V. Bernales, T. Islamoglu, O. K. Farha, J. T. Hupp, C. J. Cramer, L. Gagliardi, B. C. Gates, *J. Am. Chem. Soc.*, **2016**, 138, 15189–15196.
- [55] D. Yang, M. A. Ortuno, V. Bernales, C. J. Cramer, L. Gagliardi, B. C. Gates, *J. Am. Chem. Soc.*, **2018**, 140, 3751–3759.
- [56] Y. Bai, Y. Dou, L. H. Xie, W. Rutledge, J. R. Li, H. C. Zhou, *Chem. Soc. Rev.*, **2016**, 45, 2327–2367.
- [57] M. Honda, M. Tamura, Y. Nakagawa, S. Sonehara, K. Suzuki, K. Fujimoto, K. Tomishige, *ChemSusChem*, **2013**, 6, 1341–1344.
- [58] V. Eta, P. Mäki-Arvela, J. Wärnå, T. Salmi, J. P. Mikkola, D. Y. Murzin, *Appl. Catal. A*, **2011**, 404, 39–46.
- [59] A. J. Howarth, Y. Liu, P. Li, Z. Li, T. C. Wang, J. T. Hupp, O. K. Farha, *Nat. Rev. Mater.*, **2016**, 1, 15018.
- [60] M. Lin Foo, S. Horike, T. Fukushima, Y. Hijikata, Y. Kubota, M. Takata, S. Kitagawa, *Dalton Trans.*, **2012**, 41, 13791–13794.

金属有机框架MOF-808-X高效催化CO₂和甲醇直接合成碳酸二甲酯

宣 铿^{a,b}, 蒲彦锋^a, 李 枫^a, 雒 京^{a,b}, 赵 宁^{a,*}, 肖福魁^{a,#}

^a中国科学院山西煤炭化学研究所煤转化国家重点实验室, 山西太原030001

^b中国科学院大学, 北京100049

摘要: 碳酸二甲酯(DMC)是一种重要的绿色无毒化工原料, 其分子结构中含有甲基、甲氧基和羰基等官能团. DMC既可以替代卤代甲烷和硫酸二甲酯用作甲基化试剂, 替代剧毒的光气用作羰基化试剂, 也可以与醇类、酯类及氨基醇类进行酯交换反应用于合成树脂和精细化学品. 此外, DMC因具有相容性好、含氧量高和饱和蒸气压低等特点, 还可用作低毒溶剂和燃油添加剂. 目前, 已报道的DMC合成方法主要包括光气法、甲醇氧化羰基化法、酯交换法、尿素醇解法和直接合成法. 其中, 以CO₂和甲醇为原料直接合成DMC的方法受到广泛关注. 该方法不仅具有原料价格低廉、工艺简单、原子经济性高的优点, 还可以将温室气体CO₂资源化利用, 有望成为未来生产DMC的一条全新的高效途径. 目前, 用于该反应的催化剂研究主要集中在金属氧化物和改性金属氧化物上, 这些催化剂存在比表面积较小、活性位点数量不足以及活性不高的缺点.

本文针对传统金属氧化物的缺点, 合成了一系列锆基金属有机框架催化剂MOF-808-X (X为ZrOCl₂·8H₂O/均苯三甲酯(BTC)的摩尔比), 并将其用于催化CO₂和甲醇合成DMC, 系统考察了MOF-808-X合成过程中ZrOCl₂·8H₂O/BTC摩尔比对MOF-808-X催化剂组成、比表面积、孔道结构以及酸碱位点数量的影响, 探讨了MOF-808-X催化剂物化性质与其催化性能之间的关系. 结果表明, 通过调控ZrOCl₂·8H₂O/BTC摩尔比, 可以减少堵塞在MOF-808-X微孔中未反应的配体BTC或氧化锆原子簇的量, 提高MOF-808-X的比表面积、微孔孔径以及酸碱位点数量, 从而显著提升MOF-808-X催化剂的催化活性. 当ZrOCl₂·8H₂O/BTC摩尔比=4时, MOF-808-4催化剂具有最大的比表面积、最大的微孔孔径和最多的酸碱位点, 因而表现出最高的催化活性. 与我们之前报道的UiO-6-24相比, 虽然MOF-808-4的比表面积和酸碱位点数更小, 但由于MOF-808-4具有更大的微孔孔径(1.8 nm), 其微孔内的活性位点具有更高的催化效率, MOF-808-4表现出了更高的催化活性. 原位红外光谱结果表明, 酸性位点活化甲醇生成甲基阳离子的过程是该反应的速率控制步骤, 由于MOF-808-4中Zr₆原子簇上酸碱位点相互邻近, 吸附在相邻碱性位点上的中间产物羰基甲氧基可以与酸性位点上的甲基阳离子迅速反应, 促进甲基阳离子和DMC的生成, 从而进一步提高MOF-808-4的催化活性. 此外, 催化剂重复利用实验结果表明, MOF-808-X催化剂结晶度越好, 催化剂重复利用性能越好. MOF-808-X催化剂在CO₂和甲醇直接合成DMC反应中的成功应用可为开发用于该反应的高效非均相催化剂提供新的思路.

关键词: 金属有机框架; MOF-808; 微孔孔径; 二氧化碳; 甲醇; 碳酸二甲酯

收稿日期: 2018-11-08. 接受日期: 2018-12-26. 出版日期: 2019-04-05.

*通讯联系人. 电话: (0351)4041153; 传真: (0351)4046129; 电子信箱: zhaoning@sxicc.ac.cn

#通讯联系人. 电话: (0351)4041153; 传真: (0351)4046129; 电子信箱: xiaofk@sxicc.ac.cn

基金来源: 山西省自然科学基金(201601D102006); 山西省青年科学基金(201701D221052); 国家自然科学基金(21776294); 山西省重点科技攻关项目(MD2014-09, MD2014-10); 煤转化国家重点实验室自主研究课题(2018BWZ002).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).