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Article (Special Column on the 15th International Conference on Carbon Dioxide Utilization (ICCDU XV))

Cycloaddition of CO₂ and propylene oxide by using *M*(HBTC)(4,4'-bipy)·3DMF (*M* = Ni, Co, Zn) metal-organic frameworks

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ARTICLE INFO

Article history:

Received 25 November 2017

Accepted 25 December 2017

Published 5 August 2018

Keywords:

M(HBTC)(4,4'-bipy)·3DMF (*M* = Ni, Co, Zn)

Microwave method

Carbon dioxide

Epoxide

Cyclic carbonate

ABSTRACT

Three pillar-layered metal-organic frameworks (MOFs) based on *M*(HBTC)(4,4'-bipy)·3DMF (*M* = Ni, Co, and Zn; HBTC = 1,3,5-benzenetricarboxylic acid, 4,4'-bipy = 4,4'-bipyridine) were synthesized using a solvothermal method. Zn(HBTC)(4,4'-bipy)·3DMF was synthesized for the first time using both a solvothermal and microwave method, and subsequently characterized by various physicochemical methods. The structure of *M*(HBTC)(4,4'-bipy)·3DMF consisted of honeycomb grid layers of M²⁺ ions and BTC units, which were further linked by the 4,4'-bipy pillars to form a three-dimensional highly porous framework. All the MOFs displayed excellent synergistic catalytic properties with alkyl ammonium halides (TBAX) in the solventless fixation of CO₂ with epoxides to produce cyclic carbonates. The catalytic activities of these MOFs followed the trend Zn > Co > Ni, which was explained by the acid-base bifunctional properties. The microwave-synthesized Zn(HBTC)(4,4'-bipy)·3DMF material exhibited physical, chemical, and catalytic properties that were similar to those of the catalyst obtained using a conventional solvothermal synthesis. The scope of various parameters, including recyclability, was studied, and a plausible reaction mechanism was suggested.

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1. Introduction

Technological advancements and revolutions in industry have been fueling rapid changes in the human lifestyle. To provide human amenities at affordable costs, carbon-based resources have been exploited as energy sources (e.g., coal, oil, gas) or in the production of textiles, dyes, coatings, and plastics. Even though the formation of CO₂ as a byproduct may appear safe in such cases, the atmospheric level of CO₂ has reached a record high level [1–4]. Alarming levels of this greenhouse gas have led to increased global warming. Geological sequestration techniques could be used to address CO₂ emissions temporarily.

Dematerialization or rematerialization of CO₂ emission is also being implemented at the government level. Recently, trans-materialization, the strategy of changing waste CO₂ to a potential C1 resource material is receiving increased research attention. The capture, storage, or fixation of CO₂ has been performed using functional or porous materials [5–8].

Among the various routes to cyclic carbonates, the catalyzed cycloaddition of epoxides with CO₂ is popular; the carbonates produced can be used either as electrolytes in lithium-ion batteries or as intermediates in the synthesis of acyclic carbonates, ethylene glycol, polymers, and pharmaceuticals [9–15]. Various inorganic and organic-based catalysts have been employed for

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This work was supported by Korea Electric Power Corporation and National Research Foundation of Korea (2016-R1D1A1B-03931325).

DOI: 10.1016/S1872-2067(17)63005-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 8, August 2018

the process, but most of them suffer from various drawbacks such as harsh reaction conditions, low turnover, or difficulties in catalyst recyclability [16–23]. Over the past decade and a half, metal organic frameworks (MOFs), a novel class of inorganic-organic hybrid materials as tailored functional materials that simultaneously possess the advantages of both organic and inorganic materials have emerged at an exponential pace, thereby breaking the records of many conventionally employed functional materials [24–29]. Because they are tunable platforms for functional interfaces, and also by virtue of being porosity-tunable, MOFs can be used in task-specific applications including the capture and conversion of CO₂. Transition-metal-based MOFs with diverse metal-linker connectivities have been reported as efficient catalysts for the synthesis of cyclic carbonates from epoxides and CO₂ [30–52]. Mostly transition-metal-based MOFs have been used in cycloaddition catalysis because of their proven proficiency as CO₂-capture materials, whereas a few other MOFs had foreseen the utility of metal sites with co-catalytic ionic species/immobilized ionic groups. In this work, three MOFs *M*(HBTC)(4,4'-bipy)·3DMF (*M* = Ni, Co, or Zn) that contain two differently shaped channels were synthesized using a pillaring approach [53,54]. The structural peculiarities (porous structure with nonlinearity of the channels) and physical properties (acid-base characteristics) of these three MOFs were efficiently used for the transformation of CO₂ to cyclic carbonates through a solventless CO₂-epoxide cycloaddition reaction under mild conditions (Scheme 1).

2. Experimental

2.1. Materials

To synthesize *M*(HBTC)(4,4'-bipy)·3DMF (*M* = Ni, Co, Zn), both HBTC (also known as trimesic acid) and 4,4'-bipy were purchased from Sigma-Aldrich, Korea. Ni(NO₃)₂·6H₂O (≥ 98.5%), Co(NO₃)₂·6H₂O (> 98%), and Zn(NO₃)₂·6H₂O (98%) were also obtained from Sigma-Aldrich. *N,N*-dimethylformamide (DMF, 99%) was used as a solvent to form the MOF and was purchased from TCI Chemicals. Propylene oxide (PO) and all other epoxides used in this study were purchased from Sigma-Aldrich. The CO₂ gas (99.9%) used for the cycloaddition reaction was used without any additional purification.

2.2. Synthesis of MOFs

2.2.1. Solvothermal synthesis of Ni(HBTC)(4,4'-bipy)·3DMF

Scheme 1. Representation of the synthesis of cyclic carbonate from epoxides and CO₂.

A solvothermal method was employed for the synthesis of Ni(HBTC)(4,4'-bipy)·3DMF MOF. A mixture of HBTC (0.211 g, 1.0 mmol), Ni(NO₃)₂·6H₂O (0.292 g, 1.0 mmol), and 4,4'-bipy (0.192 g, 1.0 mmol) was dissolved in 40 mL DMF. The synthesis was performed in a 100-mL Teflon-lined autoclave at 120 °C for 4 h. After the autoclave was cooled to room temperature, green-colored crystals were collected and washed several times with DMF, and then air-dried at 55 °C for 24 h.

2.2.2. Solvothermal synthesis of Co(HBTC)(4,4'-bipy)·3DMF

A solvothermal method was employed for the synthesis of Co(HBTC)(4,4'-bipy)·3DMF MOF. A mixture of HBTC (0.422 g, 2.0 mmol), Co(NO₃)₂·6H₂O (0.582 g, 2.0 mmol), and 4,4'-bipy (0.384 g, 2.0 mmol) was dissolved in 100 mL DMF. The synthesis was performed in a 100 mL Teflon-lined autoclave reactor at 80 °C for 72 h. After the autoclave was cooled to room temperature, red-colored crystals were collected and washed several times with DMF, and then air-dried at 55 °C for 24 h.

2.2.3. Solvothermal synthesis of Zn(HBTC)(4,4'-bipy)·3DMF

A solvothermal method was employed for the synthesis of Zn(HBTC)(4,4'-bipy)·3DMF MOF. A mixture of HBTC (0.525 g, 2.5 mmol), Zn(NO₃)₂·6H₂O (0.743 g, 2.5 mmol), and 4,4'-bipy (0.395 g, 2.5 mmol) was dissolved in 100 mL DMF. The synthesis was performed in a 100 mL Teflon-lined autoclave reactor at 130 °C for 72 h. After the autoclave was cooled to room temperature, colorless crystals were collected and washed several times with DMF, and then air-dried at 55 °C for 24 h.

2.2.4. Microwave synthesis of Zn(HBTC)(4,4'-bipy)·3DMF

HBTC (0.21 g, 1.0 mmol), 4,4'-bipy (0.16 g, 1.0 mmol), and Zn(NO₃)₂·6H₂O (0.30 g, 1.0 mmol) were dissolved separately in a mixture of DMF and sonicated for 10 min. The three solutions were then mixed together and microwaved at 200 W for 7 min. The microwaved solution was allowed to cool to room temperature. The filtrate was separated, and the obtained crystals were washed a few times with DMF and dried under vacuum.

2.3. Cycloaddition of CO₂ with epoxides

The CO₂-epoxide cycloaddition reactions were performed in a 25-mL steel autoclave reactor. Precalculated amounts of the catalysts, co-catalysts, and epoxides were placed in the reactor, which was connected to a CO₂ cylinder with a two-neck valve head. In a typical semi-batch operation, CO₂ was fed continuously throughout the duration of the cycloaddition reaction using a back-pressure regulator to maintain a constant pressure. After the completion of the reaction, the reactor was allowed to cool externally using an ice bath. The final filtrate was centrifuged to collect the catalyst, and the solution was analyzed using a gas chromatograph (GC; Agilent HP 6890 A, toluene/dichloromethane as internal standard with a capillary column (HP-5, 30 m × 0.25 mm), detector: FID) to estimate the conversion of epoxide and the selectivity of cyclic carbonate.

3. Results and discussion

The $M(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ framework consisted of M^{2+} ($M = \text{Ni}, \text{Co}$ and Zn) active centers and two different types of connecting linkers [53,54]. The first bridging linker in HBTC had a -2 charge, whereas the second $4,4'\text{-bipy}$ linker was neutral. The M^{2+} ions were bridged by the HBTC^{2-} ions to form two-dimensional (2D) sheets. The 2D sheets were further linked by $4,4'\text{-bipy}$ pillars, which resulted in the formation of a highly porous three-dimensional (3D) framework. Two types of channels were present in the framework of $M(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$. One was a normal rectangle-type channel ($7 \text{ \AA} \times 6 \text{ \AA}$), and the other was a nonlinear honeycomb channel ($5 \text{ \AA} \times 8 \text{ \AA}$). The coordination environment around the metal centers generated by the two different types of linkers and the pillar-layered structure of $\text{Ni}(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ is displayed in Fig. 1. The average Ni-O carboxylic bond distance was measured to be $\sim 2.044 \text{ \AA}$, whereas that of Ni-N ($4,4'\text{-bipy}$) was measured to be $\sim 2.091 \text{ \AA}$.

Initially, the crystalline nature of all three MOFs was confirmed by powder XRD analysis. As shown in Fig. 2, the PXRD peaks of $\text{Ni}(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ were consistent with the simulated peaks generated from the crystallographic information in the literature, thereby confirming the formation of $\text{Ni}(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$. Likewise, the PXRD patterns of Zn and Co MOFs were also compared with the simulated patterns of Ni. The similarity of the peaks observed for Zn and Co with those of the Ni MOF confirmed the structural similarity of all three MOFs.

The similarities in structural integrity and chemical composition of the $M(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ MOFs were confirmed by FT-IR (Fig. S1). The two peaks observed at approximately 1600 and 1470 cm^{-1} corresponded to the C=C bonds. The presence of a peak at approximately 3100 cm^{-1} was attributed to the C-H bond in the aromatic structure. Moreover, all three catalysts exhibited two bands in the ranges $1580\text{--}1630$ and $1345\text{--}1420 \text{ cm}^{-1}$, which corresponded to the asymmetric and symmetric C-O stretching vibrations of the COO^- group, respectively. The presence of the M-N bond (approximately 500 cm^{-1}) and the M-O bond (approximately 400 cm^{-1}) confirmed the proper coordination of the metal M (Ni, Co, Zn) with the HBTC and $4,4'\text{-bipy}$ ligands.

The thermal stability of all three MOFs was analyzed using thermogravimetric analysis (TGA) (Fig. 3). The 30% weight loss observed for all three MOFs up to $230 \text{ }^\circ\text{C}$ was attributed to the removal of the guest DMF molecules, which was used as a solvent during synthesis. The structure of $\text{Ni}(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ was maintained up to about $270 \text{ }^\circ\text{C}$

Fig. 1. (a) Coordination environment created around Ni metal center; (b) pillar layered structure of $M(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$.

Fig. 2. PXRD patterns of $M(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ ($M = \text{Ni}, \text{Co}, \text{Zn}$) compared to the simulated single crystal pattern.

with a slight weight loss; the structure started to collapse beyond that temperature. Therefore, the $\text{Ni}(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ MOF could sustain its structure up to approximately $270 \text{ }^\circ\text{C}$. The $\text{Co}(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ and $\text{Zn}(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ MOFs showed similar TGA curves as $\text{Ni}(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$.

The similarities in the textural features of all three catalysts were confirmed by SEM analysis (Fig. 4). The $\text{Ni}(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$, $\text{Co}(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$, and $\text{Zn}(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ MOFs had honeycomb structures, which corresponded with previous reports. X-ray photoelectron spectroscopy (XPS) analysis was performed for all three catalysts (Figs. S2–S4). The presence of Ni $2p_{3/2}$ and Co $2p_{3/2}$ peaks at binding energies of 857 and 782 eV , respectively, confirmed the presence of the two metals in the catalyst. The two peaks at approximately 1045 and 1022 eV corresponded to Zn $2p_{1/2}$ and Zn $2p_{3/2}$, respectively. Elemental analysis (EA) and inductively coupled plasma optical emission spectrometry (ICP-OES) analysis were performed for the three catalysts to

Fig. 3. TGA curves of $M(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$.

Fig. 4. SEM images of Ni(HBTC)(4,4'-bipy)·3DMF (a), Co(HBTC)(4,4'-bipy)·3DMF (b), and Zn(HBTC)(4,4'-bipy)·3DMF (c).

study the composition of the metals and atoms. The values obtained for the three MOFs are displayed in Table 1.

To test the catalytic potential of the M(HBTC)(4,4'-bipy)·3DMF MOF system, the cycloaddition of PO with CO₂ was performed for the production of propylene carbonate (PC). The initial reactions were performed at 80 °C and 1.2 MPa CO₂ pressure for 6 h with the aid of tetrabutylammonium bromide (TBAB) as a co-catalyst (Table 2). First, control test reactions were performed without the catalyst. No conversion to the carbonate was observed under any conditions, which proved that the catalyst was essential for the reaction to take place (Table 2, entry 1). The metal precursors, BTC, and the 4,4'-bipy ligands, as well as their mechanical mixtures showed less than 5% PO conversion. (Table 2, entry 2). A PO conversion 28% was observed in the case of TBAB only (Table 2, entry 3). When the metal salts and TBAB were present, the maximum conversion was still low, < 30% (Table 2, entry 4). However, the combination of metal salts, linkers, and TBAB resulted in a conversion of < 40% (Table 2, entry 5). A combination of M(HBTC)(4,4'-bipy)·3DMF and TBAB as catalyst provided much higher conversion rates and selectivity than that of the individual precursors.

Of the three different MOFs, the Zn(HBTC)(4,4'-bipy)·3DMF catalyst achieved the best conversion rates under the above reaction conditions compared with that of the Ni- and Co-based MOFs. Zn(HBTC)(4,4'-bipy)·3DMF achieved a maximum PO conversion of 95% with > 99% selectivity (Table 2, entry 6). Under the same reaction conditions, the Ni(HBTC)(4,4'-bipy)·3DMF and Co(HBTC)(4,4'-bipy)·3DMF catalysts achieved 60% and 67% PO conversions, respectively. More than 99% selectivity was maintained in both cases (Table 2, entries 7 and 8). Even though a combination of metal and ligand as precursors can catalyze the cycloaddition reaction,

their activities are much lower than that of the M(HBTC)(4,4'-bipy)·3DMF MOF systems.

To investigate the effects of various quaternary ammonium salts, cycloaddition reactions were performed using different TBAX (X = Br⁻, I⁻, Cl⁻) co-catalysts, together with the Zn(HBTC)(4,4'-bipy)·3DMF MOF (Table 2, entries 6, 9, and 10). The use of Br⁻ resulted in the highest conversion followed by the I⁻ and Cl⁻ ions. Theoretically, the catalytic performance of TBAI should provide the highest conversion of epoxides, in compliance with the order of nucleophilicity (I⁻ > Br⁻ > Cl⁻). However, in contrast to previous reports, the low activity observed for TBAI can be explained in terms of its steric factor; despite its high nucleophilicity, the I⁻ ion was too big to access the pores of MOF [55].

To determine the reasons for the higher catalytic activity of M(HBTC)(4,4'-bipy)·3DMF MOF compared with the other MOFs, the acidic and basic properties of the three (Ni, Co, and Zn-based) MOFs were analyzed. CO₂ and NH₃ temperature-programmed desorption (TPD) analysis was performed for all the MOFs (Figs. S5–S10). The total adsorbed CO₂ for Ni(HBTC)(4,4'-bipy)·3DMF, Co(HBTC)(4,4'-bipy)·3DMF, and Zn(HBTC)(4,4'-bipy)·3DMF MOFs were estimated to be 15.3, 20.2, and 33.5 mmol/g, respectively. The carboxylate and nitrogen atoms that were bonded to the metal centers were re-

Table 2

Catalytic tests of M(HBTC)(4,4'-bipy)·3DMF (M = Ni, Co, Zn) catalysts in the cycloaddition of PO and CO₂.

Entry	Catalyst	Conversion * (%)	Selectivity * (%)
1	None	0	—
2	Zn(NO ₃) ₂ ·6H ₂ O, HBTC, 4,4'-bipy	< 5	—
3	TBAB	28	—
4	Zn(NO ₃) ₂ ·6H ₂ O/TBAB	< 30	—
5	Zn(NO ₃) ₂ ·6H ₂ O, HBTC, 4,4'-bipy/TBAB	< 40	—
6	Zn(HBTC)(4,4'-bipy)·3DMF/TBAB	95	> 99
7	Ni(HBTC)(4,4'-bipy)·3DMF/TBAB	60	> 99
8	Co(HBTC)(4,4'-bipy)·3DMF/TBAB	67	> 99
9	Zn(HBTC)(4,4'-bipy)·3DMF/TBAC	64	> 99
10	Zn(HBTC)(4,4'-bipy)·3DMF/TBAI	74	> 99

* Determined by GC using dichloromethane as internal standard. Reaction conditions: PO = 3 mL (42.8 mmol), Catalyst = 0.6 mol%, TBAB = 0.6 mol%, temperature = 80 °C, time = 6 h, CO₂ pressure = 1.2 MPa, semi-batch operation.

Table 1

EA and ICP analyses of M(HBTC)(4,4'-bipy)·3DMF (M = Ni, Co, Zn) catalysts.

Catalyst	C (wt%)	H (wt%)	O (wt%)	N (wt%)	M (wt%)
Ni(HBTC)(4,4'-bipy)·3DMF ^a	52.36	5.18	22.42	10.90	9.14
Ni(HBTC)(4,4'-bipy)·3DMF ^b	47.79	4.94	27.27	9.81	7.81
Co(HBTC)(4,4'-bipy)·3DMF ^b	50.39	4.50	26.45	8.52	8.34
Zn(HBTC)(4,4'-bipy)·3DMF ^b	45.90	4.63	27.34	9.53	10.74

^a Calculated; ^b Experimental.

sponsible for CO₂ adsorption; the adsorption process corresponded to the total number of base sites present in the catalytic system. Similarly, in the case of NH₃-TPD, the amount of acid sites was calculated to be 0.83, 0.96 and 1.75 mmol/g, which were consistent with the order of the Lewis acid nature of the three metals (Ni < Co < Zn). The TPD results were in complete agreement with the catalytic activities of the M(HBTC)(4,4'-bipy)-3DMF MOF series obtained from the experimental results. The higher activity of the Zn(HBTC)(4,4'-bipy)-3DMF MOF compared with that of the Ni- and Co-based MOFs can be explained by the stronger Lewis acid nature of Zn compared with Co and Ni, which are considered to be the sites at which the activation of epoxides occurs for this coupling reaction. The above results were in good agreement with those of the other MOFs that have been reported earlier [56].

To overcome the difficulties of high reaction temperatures and long reaction times that are typically associated with solvothermal synthesis of the Zn(HBTC)(4,4'-bipy)-3DMF MOF, a microwave-assisted synthesis of the MOF was successfully performed in 7 min at 200 W power, which was much faster than the 72 h reaction time at 130 °C required for the conventional synthesis. The PXRD patterns (Fig. S11) and SEM images (Fig. S12) of the two Zn(HBTC)(4,4'-bipy)-3DMF MOFs prepared through the two different methods confirmed that they had the same crystalline structure. The CO₂-adsorption study of the Zn(HBTC)(4,4'-bipy)-3DMF MOF at 25 °C (Fig. S13) confirmed it had a high CO₂ adsorption capacity, which is an essential feature of cyclic carbonate synthesis. The cycloaddition reaction was performed by using the microwave-synthesized Zn(HBTC)(4,4'-bipy)-3DMF MOF under the above mentioned conditions and TBAB as a cocatalyst (Table 3). The catalytic activity (PO conversion 95%, selectivity > 99%) obtained using the microwave-synthesized sample was identical to that obtained using the solvothermally synthesized MOF. Therefore, the use of microwave power provides a more rapid method than the conventional synthesis method for the synthesis of MOF-based catalysts, while retaining the essential catalytic performance.

The effect of various parameters that influence the CO₂-PO cycloaddition reaction was studied using the microwave-synthesized Zn(HBTC)(4,4'-bipy)-3DMF catalyst. The impact of the change in the catalyst or cocatalyst amounts and ratios was studied by changing the amount of Zn(HBTC)(4,4'-bipy)-3DMF and TBAB in the range of 0.2 to 0.6 mol% at 80 °C and 1.2 MPa CO₂ for 6 h (Table 4). A stable in-

Table 3

Catalytic tests of differently prepared Zn(HBTC)(4,4'-bipy)-3DMF catalysts in the cycloaddition of PO and CO₂.

Entry	Catalyst	Conversion (%)	Selectivity (%)
1	Zn(HBTC)(4,4'-bipy)-3DMF(S)/TBAB	95	> 99
2	Zn(HBTC)(4,4'-bipy)-3DMF(M)/TBAB	95	> 99

S: solvothermal method, M: microwave method.

Reaction conditions: PO = 3 mL (42.8 mmol), catalyst = 0.6 mol%, TBAB = 0.6 mol%, temperature = 80 °C, time = 6 h, CO₂ pressure = 1.2 MPa, semi-batch.

Table 4

Effect of Zn(HBTC)(4,4'-bipy)-3DMF/TBAB ratio for the cycloaddition of CO₂ and PO.

Entry	Catalyst (mol%)	TBAB (mol%)	Catalyst/TBAB ratio	Conversion (%)	Selectivity (%)
1	0.2	0.6	1:3	45	> 99
2	0.4	0.6	2:3	80	> 99
3	0.6	0.6	1:1	95	> 99
4	0.6	0.4	3:2	83	> 99
5	0.6	0.2	3:1	42	> 99

Reaction conditions: PO = 3 mL (42.8 mmol), temperature = 80 °C, time = 6 h, CO₂ pressure = 1.2 MPa, semi-batch.

crease in PO conversion was observed as the amount of catalyst and cocatalyst increased from 0.2 to 0.6 mol%, reaching a PO conversion of 95%. The Zn(HBTC)(4,4'-bipy)-3DMF/TBAB ratio was fixed at 1:1 (0.6 mol% each) for the next set of experimental studies.

The dependence of the catalytic activity of the MOFs on the reaction temperature was examined in the range 40–100 °C under the conditions of 1.2 MPa CO₂ pressure, 0.6 mol% each of Zn(HBTC)(4,4'-bipy)-3DMF and TBAB for 6 h. As illustrated in Fig. 5, no significant increase in the PO conversion was observed at 100 °C compared with that at 80 °C, even though approximately 97% of PO was converted. Therefore, 80 °C was chosen as the optimal temperature. To study the rate of PO conversion, the reaction rates were examined in the time range 2–10 h (Fig. 6). A high conversion of PO was observed after 2 h (69% yield), and reached a maximum value of 99% after 10 h. Although the highest conversion was achieved after 10 h, the optimum reaction time was fixed at 6 h. This is because the increase in PO conversion between reaction times of 6 h (95%) and 10 h (98%) was not significant (only 3%).

After the completion of the reaction, the Zn(HBTC)(4,4'-bipy)-3DMF catalyst was used for the next cycle by filtering it from the reaction mixture. The recovered sample was washed three times and dried for the next run. The PO-CO₂ cycloaddition experiments were re-run using the recycled

Fig. 5. Effect of reaction temperature on the reactivity of Zn(HBTC)(4,4'-bipy)-3DMF. Reaction conditions: PO = 3 mL (42.8 mmol), Zn(HBTC)(4,4'-bipy)-3DMF = 165 mg (0.6 mol%), TBAB = 82.9 mg (0.6 mol%), time = 6 h, CO₂ pressure = 1.2 MPa, semi-batch.

Fig. 6. Effect of reaction time on the reactivity of Zn(HBTC)(4,4'-bipy)·3DMF. Reaction conditions: PO = 3 mL (42.8 mmol), Zn(HBTC)(4,4'-bipy)·3DMF = 165 mg (0.6 mol%), TBAB = 82.9 mg (0.6 mol%), temperature = 80 °C, CO₂ pressure = 1.2 MPa, semi-batch.

Zn(HBTC)(4,4'-bipy)·3DMF catalyst under identical (optimal) reaction conditions. The results for five consecutive runs with the recovered Zn(HBTC)(4,4'-bipy)·3DMF MOF showed that there was no considerable loss of catalytic activity, and the PC selectivity remained > 99% (Table 5). This clearly proved the stability of Zn(HBTC)(4,4'-bipy)·3DMF MOF under the conditions used for the cycloaddition reaction. The results of the PXRD and FT-IR analyses of the Zn(HBTC)(4,4'-bipy)·3DMF MOF after five cycles are shown in Figs. 7 and 8 and confirmed that no noticeable structural changes occurred after the reaction.

Based on our earlier computational studies using density-functional theory (DFT), a mechanistic pathway for the M(HBTC)(4,4'-bipy)·3DMF-catalyzed CO₂-epoxide cycloaddition reaction was proposed (Scheme 2) [49,57]. It involved the following steps. (1) The unsaturated Zn, Co, Ni metal centers act as Lewis acid sites that coordinate with the epoxides. (2) The Br⁻ ion from tetrabutylammonium bromide helps to open the epoxide ring. (3) In the next step, the O⁻ ion from the ring-opened epoxide attacks the carbon atom of CO₂, resulting in the formation of a carbonate complex. (4) Finally, ring closure occurs by the attack of the intramolecular carbonate O⁻ on the C-Br carbon, whereby PC is formed. The regenerated

Table 5
Recyclability studies of Zn(HBTC)(4,4'-bipy)·3DMF.

Recycle	Conversion (%)	Selectivity (%)
Fresh	95	> 99
1	94	> 99
2	95	> 99
3	95	> 99
4	94	> 99
5	95	> 99

Reaction conditions: PO = 3 mL (42.8 mmol), catalyst = 0.6 mol%, TBAB = 0.6 mol%, temperature = 80 °C, time = 6 h, CO₂ pressure = 1.2 MPa, semi-batch.

Fig. 7. PXRD patterns of fresh and used Zn(HBTC)(4,4'-bipy)·3DMF(R).

M(HBTC)(4,4'-bipy)·3DMF catalyst moves to the next cycle for cycloaddition by coordinating with the next epoxide.

The conversion of several epoxides was also tested using the Zn(HBTC)(4,4'-bipy)·3DMF/TBAB bifunctional catalyst system (Table 6). Among them, the terminal epoxides such as PO (95%) and epichlorohydrin (90%), allyl glycidyl ether (80%), and the aromatic epoxide styrene oxide (70%) were converted with excellent to moderate reaction rates, wherein the selectivity was always > 99%. However, the internal epoxide, cyclohexene oxide, exhibited very low conversions owing to the steric crowding of the cyclohexene ring. The catalytic activity of Zn(HBTC)(4,4'-bipy)·3DMF was compared with that of other reported MOFs (Table 7). High yields of PC were obtained by using many of the MOFs. Compared with other MOF systems that required higher temperatures and longer reaction times for the synthesis of the catalyst, our Zn(HBTC)(4,4'-bipy)·3DMF MOF was synthesized using a fast microwave-based technique. The microwave-synthesized catalyst showed the same activity as that of the catalyst obtained through a solvothermal synthesis, which proved the efficacy of

Fig. 8. FT-IR patterns of fresh and used Zn(HBTC)(4,4'-bipy)·3DMF(R).

Table 6

Performance of Zn(HBTC)(4,4'-bipy)3DMF for the reaction of various epoxides.

Run	Reactant	Conversion (%)	Selectivity (%)
1	Epichlorohydrin	90	> 99
2	Epoxyhexene	93	> 99
3	Propylene oxide	95	> 99
4	Styrene oxide	70	> 99
5	Cyclohexene oxide	< 5	> 99
6	Allyl glycidyl ether	80	> 99

Reaction conditions: epoxide = 42.8 mmol, catalyst = 0.6 mol%, TBAB = 0.6 mol%, temperature = 80 °C, time = 6 h, CO₂ pressure = 1.2MPa, semi-batch.

our Zn(HBTC)(4,4'-bipy)3DMF/TBAB catalyst system. The Zn(HBTC)(4,4'-bipy)3DMF/TBAB showed comparable and higher PO yields than the previously reported MOFs under mild reaction conditions. The nonlinear honeycomb channels (with appropriate sizes) in Zn(HBTC)(4,4'-bipy)3DMF MOFs were responsible for their high CO₂ adsorption capacity. The open metal centers in the M(HBTC)(4,4'-bipy)3DMF catalysts can easily activate the epoxides and the basic sites present in the framework; this is the reason for the higher catalytic activities observed in the solventless CO₂-epoxide cycloaddition reactions under mild conditions.

4. Conclusions

In this study, three pillar-layered MOFs based on M(HBTC)(4,4'-bipy)3DMF (M = Ni, Co and Zn) were synthesized using a solvothermal method and employed as novel catalysts for solvent-free CO₂-epoxide cycloaddition reactions. Zn(HBTC)(4,4'-bipy)3DMF was synthesized for the first time by using both a solvothermal and a microwave method, and subsequently characterized by various physicochemical methods. The order of the catalytic activity was in agreement with the acidic properties of the respective MOFs, which was confirmed by TPD analysis. Compared with the Ni- and Co-based MOFs, Zn(HBTC)(4,4'-bipy)3DMF achieved the maximum PO conversion with a turnover number of 159 when used in combination with TBAB as a cocatalyst. The microwave-synthesized Zn(HBTC)(4,4'-bipy)3DMF showed the same catalytic activity as that of the catalyst prepared using a conventional solvothermal method, which confirmed that the

use of microwave power provides a faster technique for catalyst synthesis, while retaining the essential catalytic performance. Finally, the scope of various reaction parameters, including recyclability, was studied, and a plausible reaction mechanism was suggested.

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Table 7

Comparison of Zn(HBTC)(4,4'-bipy)3DMF with earlier reported MOFs.

Catalyst	Catalyst synthesis	Catalyst (mol%)	TBAB (mol%)	Temp. (°C)	Time (h)	Yield (%)	Ref.
MOF-5	60 °C/4 h (Oil Bath)	2.5	2.5	60	4	98	[34]
UMCM-1-NH ₂	Solvothermal 85 °C/72 h	0.6	0.6	50	6	89	[41]
Ni-Salpen-MOF	Solvothermal 80 °C/96 h	0.7	2.0	80	4	86	[58]
PCN-224	Solvothermal 120 °C/24 h	–	–	100	4	42	[46]
In ₂ (OH)(btc)(Hbtc) _{0.4} (L) _{0.6}	Solvothermal 160 °C/72 h	–	0.5	80	4	75	[44]
Zn(HBTC)(4,4'-bipy)3DMF	Solvothermal 130 °C/72 h	0.6	0.6	80	6	95	this work
Zn(HBTC)(4,4'-bipy)3DMF	Solvothermal 130 °C/72 h	0.6	0.6	80	10	98	this work
Zn(HBTC)(4,4'-bipy)3DMF	Microwave 200 W/7 min	0.6	0.6	80	6	95	this work

Epoxide: PO.

Graphical Abstract

Chin. J. Catal., 2018, 39: 1311–1319 doi: 10.1016/S1872-2067(17)63005-5

Cycloaddition of CO₂ and propylene oxide by using M(HBTC)(4,4'-bipy)·3DMF (M = Ni, Co, Zn) metal-organic frameworks

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Three pillar-layered metal-organic frameworks (MOFs) based on M(HBTC)(4,4'-bipy)·3DMF (M = Ni, Co, and Zn) were synthesized. Their structure consisted of honeycomb grid layers of M²⁺ ions and BTC units to form a 3D porous framework. The MOFs displayed excellent catalytic activities in the cycloaddition of CO₂ with epoxides.

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采用金属有机骨架材料 $M(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ ($M = \text{Ni}, \text{Co}, \text{Zn}$) 催化 CO_2 与环氧丙烷的环加成反应

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摘要: 采用溶剂热法合成了三种 $M(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ ($M = \text{Ni}, \text{Co}, \text{Zn}$, HBTC = 1,3,5-均苯三甲酸, 4,4'-联吡啶)结构的支柱层金属有机骨架材料(MOFs)。首次采用溶剂热和微波法合成了 $\text{Zn}(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$, 并采用多种物理化学方法对其进行了表征。 $M(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ 中包含有 M^{2+} 离子的蜂窝网格层和BTC单元, BTC单元与4,4'-联吡啶柱进一步交联形成三维多孔骨架材料。在采用烷基铵卤化物作为助催化剂和无溶剂的条件下, 所有MOFs材料均对催化固定 CO_2 与环氧化物环加成制备环状碳酸酯反应表现出非常好的协同催化性能, 其催化活性高低顺序为: $\text{Zn} > \text{Co} > \text{Ni}$, 这可通过酸-碱双功能特性进行解释。采用微波法合成的 $\text{Zn}(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ 材料表现出与常规催化剂相似的物理化学性质和催化性能。考察了不同制备参数的影响和材料的重复使用性能, 并提出了该反应的可能机理。

关键词: $M(\text{HBTC})(4,4'\text{-bipy})\cdot 3\text{DMF}$ ($M = \text{Ni}, \text{Co}, \text{Zn}$); 微波法; 二氧化碳; 环氧化物; 环状碳酸酯

收稿日期: 2017-11-25. 接受日期: 2017-12-25. 出版日期: 2018-08-05.

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基金来源: 韩国电力公司; 韩国国家研究基金会(2016-R1D1A1B-03931325).

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