



Dual-linker metal-organic frameworks as efficient carbon dioxide conversion catalysts

Xianghai Song, Yuanfeng Wu, Donghui Pan, Jiahui Zhang, Siquan Xu, Lijing Gao, Ruiping Wei, Jin Zhang, Guomin Xiao*

School of Chemistry and Chemical Engineering, Southeast University, Nanjing, China

ARTICLE INFO

Keywords:
MOFs
Dual-linker
Carbon dioxide
Cyclic carbonates

ABSTRACT

In the present work, two dual-linker metal-organic frameworks (MOFs) were prepared with metal salts, terephthalic acid and 4, 4'-bipyridine as precursors, and subsequently used for preparing cyclic carbonates from carbon dioxide and epoxides. These two MOFs were characterized by a number of techniques. The two MOFs prepared showed superior catalytic performance under solventless and co-catalyst-free conditions. In this sense, Co(tp)(bpy) achieved epichlorohydrin (ECH) conversions as high as 95.75% and chloropropylene carbonate (CPC) yields of 94.18% under optimal reaction conditions. The high activity of Co(tp)(bpy) was attributed to the co-existence of Lewis acidic and basic active sites on the catalyst derived from incompletely coordinated metal cations and uncoordinated pyridine groups, respectively. In addition, Co(tp)(bpy) maintained this high catalytic performance after five consecutive reaction cycles. A possible reaction mechanism was proposed based on the experimental results.

1. Introduction

The concentration of carbon dioxide (CO₂), an important greenhouse gas, is increasing rapidly in the atmosphere because of the extensive combustion of fossil fuels worldwide. This increase is believed to cause originate global warming, which is associated to global climate changes [1]. This phenomenon may result in a serious threat to society [2]. A number of approaches have been developed to reduce the levels of atmospheric CO₂. These approaches can be roughly divided into three main categories: (1) reduction of the CO₂ produced; (2) permanent storage of CO₂; and (3) usage of CO₂ as a raw material [3]. Despite being an industrial waste gas, CO₂ can be used as an abundant, inexpensive, non-toxic, and renewable C1 precursor [4–7]. Thus, among the three strategies indicated above, the utilization of CO₂ as a feedstock for producing value-added products is a very promising route that has attracted increasing research attention [8–10]. Cyclic carbonates are considered very important CO₂ derivatives owing to their wide applications (e.g., fuel additives, electrolyte solvents for ion batteries, cosmetics, personal care products, and pharmaceutical intermediates, among others) [11–13].

Over the past few decades, a series of homogeneous and heterogeneous catalysts have been developed to carry out the cycloaddition of CO₂ with epoxides to cyclic carbonates [14–24]. Although some of

these catalysts are highly effective and can catalyze the cycloaddition under very mild conditions [25–27], they suffer from high cost, poor reusability, and required the addition of co-catalysts. Thus, further studies on the coupling of CO₂ with epoxides are still needed.

Metal-organic frameworks (MOFs) are a class organic–inorganic hybrid porous materials that have received increasing attention over the past few years owing to their functional and structural diversity [28–30]. The functionalities and structure of MOFs can be easily tuned by varying the organic functional groups and inorganic metal ions. Thus, the porosity (e.g., pore shape and pore volume) and the chemical properties of the MOF materials can be tailored to meet certain requirements [31]. This characteristic makes MOFs ideal candidates for gas separation/purification and heterogeneous catalysis applications [32]. MOFs have been widely used in CO₂ involving applications such as capture, storage, and chemical transformation in the past few years [33–37]. MOFs have also been reported to catalyze the coupling of CO₂ with epoxides (Scheme 1). For instance, Cu₃(BTC)₂ catalyzed the coupling of CO₂, although the conversion of epichlorohydrin (ECH) and the selectivity towards chloropropylene carbonate (CPC) were poor [38]. To improve the catalytic performance of MOFs, quaternary ammonium salts have been usually added as co-catalysts because of their highly synergistic effect with MOFs [39]. For example, the addition of tetra-butyl ammonium bromide (TBAB) provided MOF-5, NH₂-MIL-

* Corresponding author.

E-mail address: xiaogm@seu.edu.cn (G. Xiao).

<https://doi.org/10.1016/j.apcata.2018.08.011>

Received 12 May 2018; Received in revised form 14 August 2018; Accepted 16 August 2018

Available online 23 August 2018

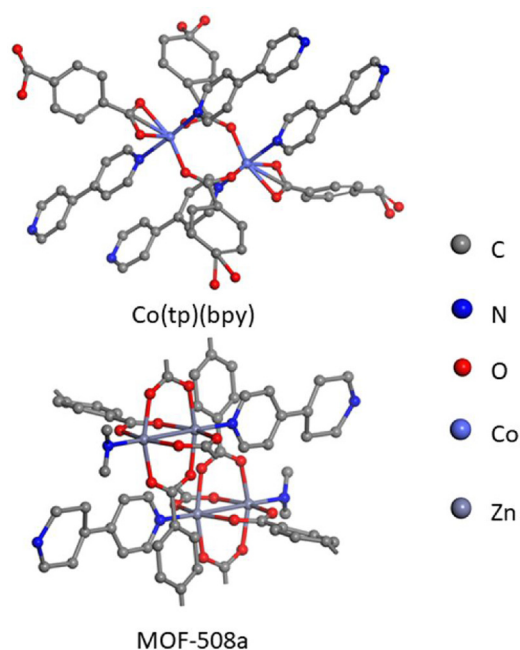
0926-860X/ © 2018 Elsevier B.V. All rights reserved.



Scheme 1. Coupling of epoxides with CO₂ over MOFs.

101(Al), MOF-892, BIT-C with high epoxide conversion and cyclic carbonate selectivities [40–43]. However, recycling of TBAB was hindered during the reaction process owing to the high solubility of the ammonium salt in the reaction solution. To overcome this issue, various active sites have been incorporated into the structure of the MOFs. Jun Kim et al. introduced amino groups in the structure of UIO-66 [44]. The resulting UIO-66-NH₂ material was used as a CO₂ coupling catalyst. Zhou et al. developed an efficient catalyst for preparing CO₂-derived cyclic carbonates by incorporating quaternary ammonium salts into the structure of IRMOF-3 [45]. Despite these advances, these reactions still require the presence of a solvent (e.g., chlorobenzene) or high temperature (e.g., 140 °C). Thus, the solventless preparation of cyclic carbonates under mild conditions and in the absence of co-catalyst remains challenging. High epoxide conversions and moderate cyclic carbonate selectivities were achieved over a ZIF-8 catalyst [46]. This high catalytic performance was ascribed to the co-existence of Lewis acid (from zinc ions) and Lewis basic sites (from the imidazole groups). However, the structure of ZIF-8 collapsed during the recycling process.

During the coupling of CO₂ with epoxides, the unsaturated metal cations on the MOF material can act as Lewis acid sites, activating the epoxides for subsequent ring opening over co-catalysts having Lewis basic sites. In this work, we aimed to synthesize MOF materials: (i) containing both Lewis acid and Lewis basic sites in their structure; (ii) being stable during the reaction process; and (iii) recyclable. With this purpose, Co(tp)(bpy) and Zn(tp)(bpy)_{0.5}(DMF)(H₂O)_{0.5} (MOF-508a) materials with both Lewis acid and Lewis basic sites (Scheme 2) were prepared and used for preparing cyclic carbonates from CO₂. Both catalysts showed high epoxide conversion and cyclic carbonate selectivities. Moreover, Co(tp)(bpy) remained stable during the reaction and retained its structure even after five consecutive cycles.



Scheme 2. Schematic crystal structures of Co(tp)(bpy) and MOF-508a.

2. Experimental section

2.1. Materials

All chemicals used in this work were commercially available and used as received without further purification. CoCl₂·6H₂O (AR), Zn(NO₃)₂·6H₂O (AR), terephthalic acid (99%), cyclohexene oxide (99%) and 4,4'-bipyridine were purchased from Aladdin Industrial Inc. (Shanghai, China). Allyl glycidyl ether (99%), styrene oxide (99%) were obtained from Xilong Chemical Co., Ltd. Epichlorohydrin (ECH) (99.5%), 1,2-epoxypropane (99.5%) and *N,N*-Dimethylformamide were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Carbon dioxide (CO₂ > 99.9%) was obtained from Nanjing Special Gas Factory Co., Ltd.

2.2. Preparation of the catalysts

2.2.1. Preparation of Co(tp)(bpy)

Co(tp)(bpy) was prepared according to a procedure reported elsewhere [47]. Typically, 0.71 g (3 mmol) of CoCl₂·6H₂O, 0.50 g (3 mmol) of terephthalic acid, 0.48 g (3.1 mmol) of 4, 4'-bipyridine, and 0.24 g (6 mmol) of NaOH were dispersed in 180 mL of deionized water. The resulting mixture was stirred at room temperature for 30 min and subsequently transferred to a 250 mL Teflon-lined stainless-steel autoclave. The autoclave was heated to 170 °C and kept at this temperature for 48 h. The reaction system was cooled down to room temperature, and the as-obtained solid was isolated and washed with ethanol. After drying at room temperature, dark brown crystals were obtained (0.80 g, 76%).

2.2.2. Preparation of MOF-508a

MOF-508a was prepared according to a procedure reported elsewhere [48]. Typically, Zn(NO₃)₂·6H₂O (0.71 g, 2.36 mmol), terephthalic acid (0.39 g, 2.36 mmol), and 4, 4'-bipyridine (0.18 g, 1.18 mmol) were placed in a Teflon vessel (250 mL) containing 200 mL of DMF: ethanol mixture (1:1). The mixture was stirred at room temperature until a clear solution was obtained. The resulting solution was subsequently kept at 90 °C for 24 h. The colorless crystals formed were collected by filtration, washed with DMF and hexane, and dried in air (0.86 g, 90%).

A degassing treatment at 120 °C for 12 h under reduced pressure was applied to MOF-508a to remove the guest molecules in the structure, resulting in MOF-508b.

2.3. Catalyst characterization

X-ray diffraction (XRD) data of the MOFs were obtained on an Ultima IV X-ray diffractometer. The scanning was performed in the 20–75° 2θ range with a step function of 0.02 and a scanning rate of 20° min⁻¹.

N₂ adsorption–desorption isotherms were measured by static N₂ physisorption at –196 °C using a Beishide 3H-2000 analyser. Multipoint Brunauer–Emmett–Teller (BET) was utilized to calculate the surface area. The pore size distribution was calculated based on desorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method.

Fourier transform infrared spectrometer (FT-IR) analysis was carried out on a Nicolet 5700 spectrometer. The experiment was performed over the 400–4000 cm⁻¹ wavenumber range with KBr as a reference.

Thermal gravimetric analysis (TGA) was performed on a TG209 F3 instrument. During the experimental process, the sample was heated from 30 to 660 °C with a heating rate of 10 °C/min in N₂ atmosphere.

CO₂/NH₃ temperature programmed desorption (CO₂/NH₃ -TPD) was performed to evaluate the basic and acidic properties of the materials. The sample was first treated at 150 °C for one hour in helium

Download English Version:

<https://daneshyari.com/en/article/8946510>

Download Persian Version:

<https://daneshyari.com/article/8946510>

[Daneshyari.com](https://daneshyari.com)