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Catalytic activity of metal organic framework $Cu_3(BTC)_2$ in the cycloaddition of CO_2 to epichlorohydrin reaction

Eugenia E. Macias[a], Paul Ratnasamy[a], Moises A. Carreon[b,*]

[a] Conn Center for Renewable Energy Research, University of Louisville, Louisville, KY, 40292 United States
[b] Department of Chemical Engineering, University of Louisville, Louisville, KY, 40292 United States

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ABSTRACT

We demonstrate the novel, catalytic activity of metal organic framework of $Cu_3(BTC)_2$ catalysts in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin. The catalysts display moderate epoxide conversions, and moderate selectivities to chloropropene carbonate at 100 °C. No solvents or co-catalysts were required. It is suggested that Lewis acid copper (II) sites in the $Cu_3(BTC)_2$ framework promoted the adsorption of carbon dioxide on the solid surface and its further conversion to the carbonate.

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1. Introduction

The utilization of CO_2 as a renewable raw material for the production of useful chemicals is an area of great interest. In particular, the conversion of CO_2 into cyclic carbonates, which are useful chemical intermediates employed for the production of plastics and organic solvents, represents an attractive route for the efficient use of carbon dioxide. The catalytic conversion of CO_2 to cyclic carbonates and polycarbonates over conventional solid catalysts, including zeolites and mesoporous oxides has been described by Ratnasamy et al. [1–11]. Recently, we have reported the catalytic activity of zeolitic imidazolate framework-8, ZIF-8, catalysts in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin [12].

Solid catalysts for CO_2 conversion require high CO_2 adsorption capacity and Lewis acid sites to catalyze the reaction of CO_2 with epoxides (like epichlorohydrin, and styrene oxide) to give cyclic carbonates and other precursors of carbonates [6–8,10]. The metal organic framework, $Cu_3(BTC)_2$ (BTC = benzene-1,3,5-tricarboxylate) [13–15], is an appealing material to employ as catalyst for the CO_2 conversion to cyclic carbonates due to the presence of Lewis acid coordination sites (Cu) in its framework and due to its high CO_2 adsorption capacity. $Cu_3(BTC)_2$ is a porous metal organic framework which forms a face-centered cubic crystalline structure which is composed of dimeric cupric tetracarboxylate units, which give an intersecting 3D-channel system with micropore diameter of 0.7–0.8 nm [14].

Some examples on the potential of $Cu_3(BTC)_2$ as heterogeneous catalyst have been reported [15–21]. $Cu_3(BTC)_2$ is an active catalyst for the liquid phase cyanosilylation of benzaldehyde [15], isomerization of terpene derivatives [16], CO oxidation [17], synthesis of quinolines [18], p-xylene acylation [19], cyclopropanation of alkanes [20], and aldol condensation [21]. Herein, we report, the catalytic performance of the metal organic framework $Cu_3(BTC)_2$ catalysts in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin. The catalysts displayed moderate epoxide conversions, and moderate selectivities to chloropropene carbonate at 100 °C. To our best knowledge, the catalytic activity of $Cu_3(BTC)_2$ in the Lewis acid catalyzed cycloaddition reactions has not been reported, so far.

2. Experimental

2.1. Catalyst preparation

$Cu_3(BTC)_2$ was prepared by a modified method reported by Schlichte et al. [15]. In a typical synthesis, 3.5 g of copper (II) nitrate hemi(pentahydrate) were dissolved in 48 ml of deionized water. To this solution, 1.68 g of 1,3,5-benzenetricarboxylic acid, 98% dissolved in 48 ml of ethanol were added. The resultant solution was loaded in a 250 ml stainless steel high pressure Parr reactor, Model 4576A. The synthesis was carried out under stirring at 120 °C for 8 h. The solid particles were separated from the solution by centrifugation at 3000 rpm and washed with ethanol. The

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* Corresponding author.
E-mail address: macarr15@louisville.edu (M.A. Carreon).

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centrifugation-washing step was repeated 3 times. The resultant $Cu_3(BTC)_2$ crystals were dried overnight at 100 °C. All chemicals were bought from Alfa-Aesar.

2.2. Characterization

The morphology of $Cu_3(BTC)_2$ was inspected with a FE-SEM (FEI Nova 600) with an acceleration voltage of 6 kV. Powder XRD patterns were collected using a Bruker D8-Discover diffractometer at 40 kV, 40 mA with Cu Kα radiation. The surface area and adsorption–desorption isotherm measurements were carried out with a Micromeritics Tristar 3000 porosimeter at 77 K using liquid nitrogen as coolant. The samples were degassed at 150 °C for 3 h before the measurements. The relative surface acidity of the catalysts was measured by the adsorption of dipropyl amine. In a typical experiment, 1 g of catalyst was evacuated overnight at 220 °C and equilibrated with a 1 wt% solution of dipropylamine in toluene at 25 °C for 3 h. The fraction of the dipropyl amine adsorbed at equilibrium was determined by gas chromatography of the supernatant solution.

2.3. Catalytic studies

The catalytic activity of $Cu_3(BTC)_2$ was evaluated in the cycloaddition of CO_2 to epichlorohydrin to form chloropropene carbonate. In a typical reaction, 18 mmol of epichlorohydrin and 100 mg of $Cu_3(BTC)_2$ were placed in a 250 ml stainless steel high pressure Parr reactor, Model 4576A. The reactor was pressurized with CO_2 at 7 bar, and the reaction was carried out at 70–100 °C for 4 h. After the reaction, the reactor was cooled to room temperature, the unreacted CO_2 was vented out, the catalyst was separated by centrifugation, and the products were analyzed by GC–MS in a HP 5890 Gas Chromatograph equipped with 5970 Mass Selective Detector, 30 m × 0.32 mm HP-5 column coated with 5% phenyl poly siloxane stationary phase. The temperature ramp rate during the GC analysis was as follows: 70–220 °C at 15 °C/min.

3. Results and discussion

The XRD pattern of the as-synthesized $Cu_3(BTC)_2$ catalyst, shown in Fig. 1a, corresponds to the typical known structure of $Cu_3(BTC)_2$ [15,16]. Small changes in the relative intensities of the XRD peaks are due to variations in the degrees of hydration [15]. In particular, the similar I_{200}/I_{220} ratio as well as the absence of the (3 1 1) reflection in our sample suggests a hydrated state [15]. The morphological features of $Cu_3(BTC)_2$ crystals were investigated by SEM (Fig. 2), which shows well-defined octahedral crystals of ~1–1.5 μm. This octahedral-like morphology is typical for $Cu_3(BTC)_2$ [14,16,22]. The BET surface area of the $Cu_3(BTC)_2$ crystals was 995 m^2/g, in agreement with previous reports [13,14]. As shown in Fig. 3, N_2 adsorption–desorption isotherms indicate the porous nature of the $Cu_3(BTC)_2$ crystals. The pore size distribution (not shown) confirms the microporous nature of the crystals.

The cycloaddition of CO_2 to epichlorohydrin yielded chloropropene carbonate, diols and dimers of epichlorohydrin. Controlled experiments under our reaction conditions confirmed that the reaction did not proceed to a significant extent in the absence of the $Cu_3(BTC)_2$ catalyst. Different from other metal organic frameworks in which most of the coordination sites are blocked by the organic ligand, in $Cu_3(BTC)_2$ the Lewis acid coordination sites (copper sites) are accessible for potential catalytic conversions [15]. Table 1 shows the catalytic performance of $Cu_3(BTC)_2$ as a function of temperature in the cycloaddition of CO_2 to epichlorohydrin reaction.

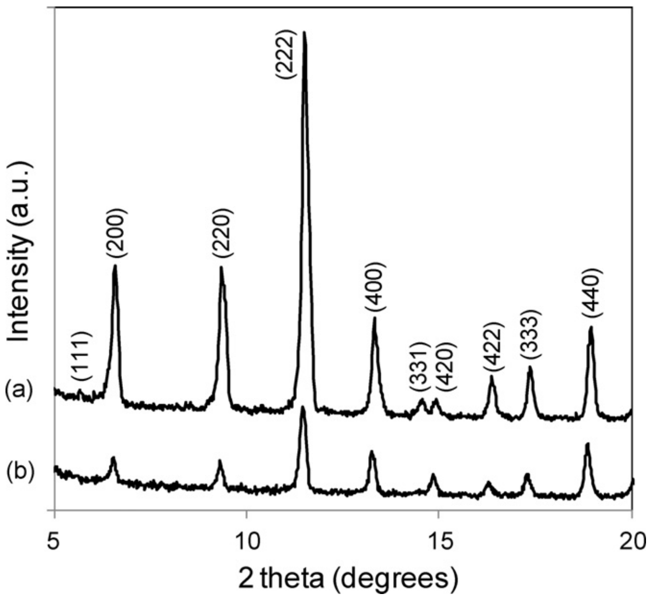

Fig. 1. X-ray diffraction patterns of the (a) as-synthesized and (b) recycled $Cu_3(BTC)_2$ crystals.

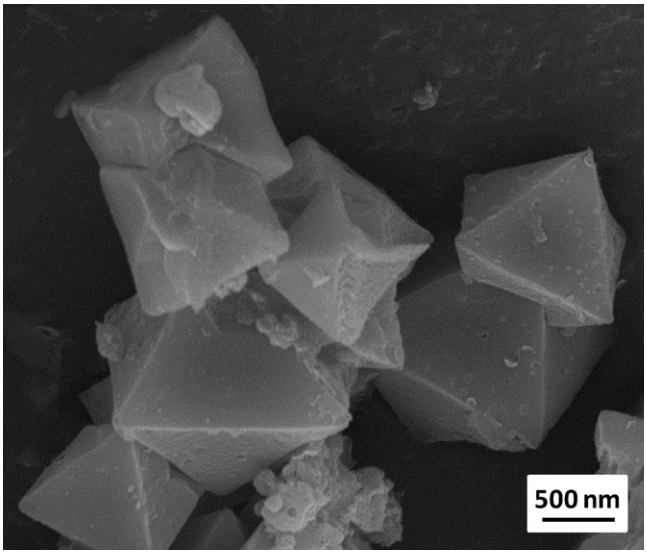

Fig. 2. Representative SEM of $Cu_3(BTC)_2$ crystals employed as catalysts in the cycloaddition of CO_2 to epichlorohydrin.

$Cu_3(BTC)_2$ was catalytically selective to chloropropene carbonate only at 100 °C (Table 1). Only diols of the epoxide and dimers of epichlorohydrin were observed below 100 °C. Over zeolites and mesoporous solid acid catalysts, this reaction usually occurs at temperatures at or above 100 °C [1–11]. The chloropropene carbonate yield at 100 °C was ~33%. Lewis acid sites are known to catalyze the reaction of carbon dioxide with epoxides to give propylene carbonates and other precursors of polycarbonates [6,8]. In the case of $Cu_3(BTC)_2$, it is likely that the Lewis acid copper (II) sites play an important role in catalyzing the cycloaddition of CO_2 to

Table 1
Catalytic performance of $Cu_3(BTC)_2$ in the cycloaddition of CO_2 to epichlorohydrin.

Reaction temperature (°C)	Epichlorohydrin conversion (%)	Selectivity (%)		
		Chloropropene carbonate	Diol	Dimer
70	35.0	0.0	68.2	31.8
80	24.6	0.0	100	0.0
100	63.8	51.8	33.9	14.3

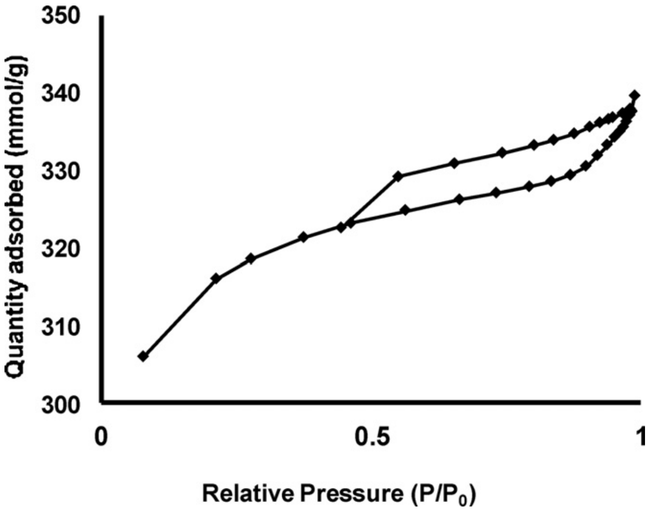

Fig. 3. Nitrogen adsorption-desorption isotherms of $Cu_3(BTC)_2$ crystals.

epichlorohydrin. In addition, the partial positive charges on the unsaturated copper metal sites of $Cu_3(BTC)_2$ promote the binding and activation of the polar carbon-oxygen bonds of carbon dioxide, resulting in high CO_2 adsorption capacities. Unsaturated cooper metal sites have been identified by theoretical and experimental investigations as CO_2 adsorption sites [23]. CO_2 adsorption capacities for $Cu_3(BTC)_2$ range from 8.0 to 12.7 mol/kg at room temperature and 15 bar [14,24,25]. The copper acid sites, probably, promote the adsorption of carbon dioxide on the solid surface and its further conversion to the carbonate. The significant formation of the diols over $Cu_3(BTC)_2$ even at low temperature is probably related to the presence of a hydrophilic interior (with 12 water molecules per pore) in the catalyst wherein the Cu^{2+} ions (in the binuclear Cu_2 cluster) are connected through a weak bond and the residual axial coordination site is filled by a weakly bound water molecule. The weakly bound water molecules pointing towards the center of the pore are, probably, active in the hydration of the epoxide to the diols.

We have compared the activity of $Cu_3(BTC)_2$ vs zeolites beta, TS-1, and HY, mesoporous silica SBA-15 and ZIF-8 at 100 °C and 7 bar for 4 h (Fig. 4). Zeolites beta ($SiO_2/Al_2O_3 = 28$), TS-1 and HY were provided by Sud-Chemie Inc. SBA-15 was prepared according to reported literature [26]. ZIF-8 was prepared as described in our previous report [12]. Of all these catalysts, zeolite beta shows the highest yield to chloropropene carbonate at ~82%. The relatively high catalytic activity of zeolite beta is interesting. The $Cu_3(BTC)_2$, ZIF-8, HY and SBA-15 catalysts formed significant amounts of carbonaceous deposits during this reaction (see results of recycle experiments below). The absence of such carbonaceous deposits over the beta zeolite during the reaction can, perhaps, account for the greater yield of the chloropropene carbonate over this catalyst. The lower yield of the chloroprene carbonate over TS-1 is due to the absence of strong acid sites on its surface. The lower formation of carbonaceous deposits over beta zeolite and its greater stability in hydrocarbon reactions as compared to other large pore zeolites, like HY, HX and mordenite is well known.

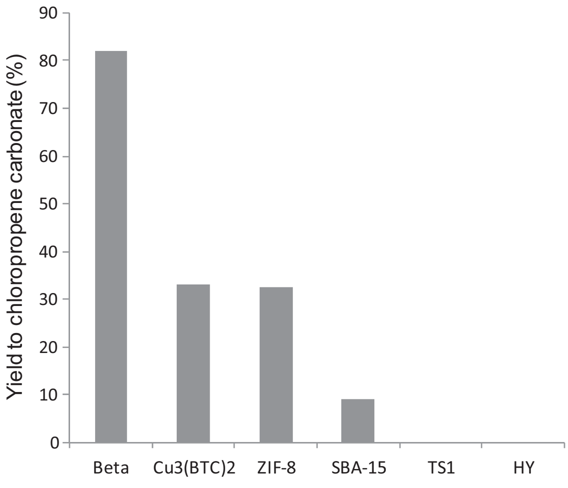

Fig. 4. Catalytic performance of $Cu_3(BTC)_2$ as compared to representative zeolites, mesoporous SBA-15, and ZIF-8 in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin. Reaction conditions: 100 °C and 7 bar for 4 h.

Table 2
Selected physicochemical properties of the catalysts.

Catalyst	Physicochemical properties		
	Surface area (m^2/g)	Pore volume (cc/g)	Relative acidity[a]
Beta	451	0.44	1.6
$Cu_3(BTC)_2$	995	0.53	1.5
ZIF-8	1173	0.52	1.2
SBA-15	390	0.42	0.8
TS1	394	0.28	1.7
HY	585	0.33	1.5

[a] Moles of dipropylamine adsorbed/g of dry catalyst ($\times 10^{-8}$).

The catalytic performance of $Cu_3(BTC)_2$ is better than zeolites TS1, HY and SBA-15 and comparable to that of ZIF-8. For zeolites TS-1, and HY, the only observed product was diol. The yield to diol was 18%, and 32% for TS-1 zeolite, and HY zeolite, respectively. Although a clear correlation between surface area, pore volume or relative acidity as a function of catalytic activity is not observed (Table 2), in general, catalysts with larger pore volumes (Beta, $Cu_3(BTC)_2$ and ZIF-8) led to higher yields to chloropropene carbonate.

We have also investigated the catalytic performance of the $Cu_3(BTC)_2$ catalyst after use in a first run and subsequent recycling. In the recycle experiments, the catalyst, after use in the cycloaddition reaction, was washed with ethanol and acetone, centrifuged and air dried before reuse. The catalytic activity of the recycled $Cu_3(BTC)_2$ catalyst was evaluated at 100 °C. The yield to chloropropene carbonate decreased from ~33% (fresh) to ~23% (recycled). The XRD of the recycled $Cu_3(BTC)_2$ catalyst (Fig. 1b) suggests that the $Cu_3(BTC)_2$ structure is preserved. However, the absence of the (1 1 1) and (3 3 1) planes of the recycled catalyst as well as the presence of less intense XRD reflections as compared to the as-synthesized catalyst may indicate that although the $Cu_3(BTC)_2$ crystals maintained long-range crystallinity, its framework may have a greater degree of local structural disorder. Therefore the reduced activity of recycled catalyst can be attributed, in part, to this local structural disorder and to active site/pore blocking by residual carbonaceous deposits formed during the reaction. Similar phenomena have been observed for SBA-15 [6] and ZIF-8 [12] catalysts also for this particular reaction.

In summary, we have demonstrated the novel catalytic activity of metal organic framework $Cu_3(BTC)_2$ catalysts in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin. $Cu_3(BTC)_2$ displayed moderate epoxide conversions, and moderate selectivities to chloropropene carbonate at 100 °C. Lewis acid copper (II) sites in the $Cu_3(BTC)_2$ framework promote the adsorption of carbon dioxide on the solid surface and its further conversion to the carbonate. The activity of recycled $Cu_3(BTC)_2$ catalyst decreased, in part due to active site pore blocking by residual carbonaceous deposits.

Acknowledgments

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