

## Metal organic frameworks as catalysts in the conversion of CO<sub>2</sub> to cyclic carbonates

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The effective utilization of CO<sub>2</sub> as a renewable raw material for the production of useful chemicals is an area of enormous interest. In particular, the catalytic conversion of CO<sub>2</sub> 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 development of superior performance catalysts requires novel materials with fundamentally different structural, compositional, adsorption and transport properties than those of conventional zeolite, metal oxides or metal phases. In this respect, metal organic frameworks have emerged as a novel type of crystalline porous materials which combine highly desirable properties, such as uniform micropores, high surface areas, flexible chemistries and exceptionally high thermal and chemical stability, making them ideal candidates for catalytic applications. Herein, we discuss the catalytic activity of two prototypical metal organic frameworks, namely ZIF-8 and Cu<sub>3</sub>(BTC)<sub>2</sub> in the synthesis of chloropropene carbonate from CO<sub>2</sub> and epichlorohydrin.

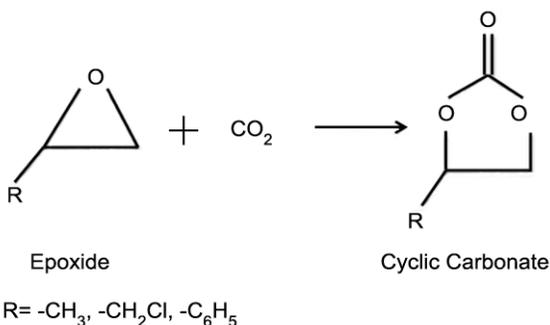
**Keywords:** Metal organic frameworks, Heterogenous catalysts, Cycloaddition reactions, Cyclic carbonates, Carbon dioxide conversion

Cyclic carbonates are useful intermediates for electrolytes in lithium ion batteries, green solvents and polycarbonates.<sup>1,2</sup> Currently, cyclic carbonate precursors are manufactured employing the highly toxic phosgene.<sup>2</sup> An alternative and green approach for the synthesis of cyclic carbonates is the insertion reaction of CO<sub>2</sub> into an epoxide (Scheme 1). This route represents a very useful approach to effectively use CO<sub>2</sub> for the conversion of chemicals. The commercial production of cyclic carbonates employs non-expensive catalysts like homogeneous quaternary ammonium salts.<sup>3,4</sup> However, the reaction in these commercial processes is typically carried out at

elevated temperatures in the 180–200 °C range and high pressures, in the 50–80 bar range. Therefore, there is a need and motivation to develop more efficient heterogeneous catalysts for the conversion of CO<sub>2</sub> into cyclic carbonates.

Aluminum and zinc metal complexes, dialkyltin methoxide and organoantimony halides can catalyze this cycloaddition reaction.<sup>5,6</sup> However, these materials are toxic, water and air-sensitive, causing handling problems and requiring high temperature/pressure for high conversion and selectivity. Non-toxic catalysts including phthalocyanines,<sup>7</sup> porphyrines,<sup>8-10</sup> and Schiff bases<sup>11,12</sup> catalyze this reaction with moderate to high carbonate yields, but require the presence of a co-catalyst. Mg/Al oxide-based is another catalyst which has demonstrated ability to catalyze the cycloaddition reaction.<sup>13</sup> However, high loading of catalyst and long reaction times were needed to observe reasonable carbonate yields.

The catalytic conversion of CO<sub>2</sub> to cyclic carbonates and polycarbonates over conventional zeolites, zeolite-based complexes and mesoporous oxides has been demonstrated.<sup>14-24</sup> In particular, for mesoporous Ti-SBA,<sup>18</sup> zeolite beta<sup>19</sup> and mesoporous SBA-15 silica,<sup>20</sup> high carbonate yields have been



Catalytic conversion of CO<sub>2</sub> into a cyclic carbonate

**Scheme 1**

reported. In addition, the reaction over these catalysts can proceed at relative low temperatures and does not require the presence of any co-catalyst or solvent.

The development of superior performance catalysts requires novel materials with structural, compositional, adsorption and transport properties fundamentally different from those of conventional zeolites, metal oxides or metal phases. In this respect, metal organic frameworks (MOFs) have emerged as novel crystalline microporous materials with highly desirable properties, such as uniform micropores, high surface areas and open porous framework structures with large accessible pore volumes making them potentially interesting candidates for catalytic applications. Herein, the structural features of MOFs, as well as their relevant features that make them appealing for the catalytic conversion of CO<sub>2</sub> to cyclic carbonates are briefly described.

### Metal Organic Frameworks for the Catalytic Conversion of CO<sub>2</sub>

Metal organic frameworks are crystalline materials consisting of metal ions coordinated to organic linker to form one-, two-, or three-dimensional structures that can be porous if the guest molecules (solvent or unreacted organic linkers) are eliminated. The following discussion will focus on two prototypical types of MOFs: ZIF-8, and Cu<sub>3</sub>(BTC)<sub>2</sub>. These two MOF compositions are in particular appealing materials to be employed as catalysts for CO<sub>2</sub> conversion to carbonates due to their high chemical stability, exceptional uptake capacities for CO<sub>2</sub>, open porous framework structure with large accessible pore volumes, and, the presence of Lewis acid sites in its framework. It is known that high CO<sub>2</sub> adsorption capacities and the presence of Lewis acid sites favor the catalytic conversion of CO<sub>2</sub> to cyclic carbonates.<sup>18,20</sup> Scheme 2 shows the hypothetical

adsorption sites and reaction sites in ZIF-8 and Cu<sub>3</sub>(BTC)<sub>2</sub> in the conversion of CO<sub>2</sub> into cyclic carbonates.

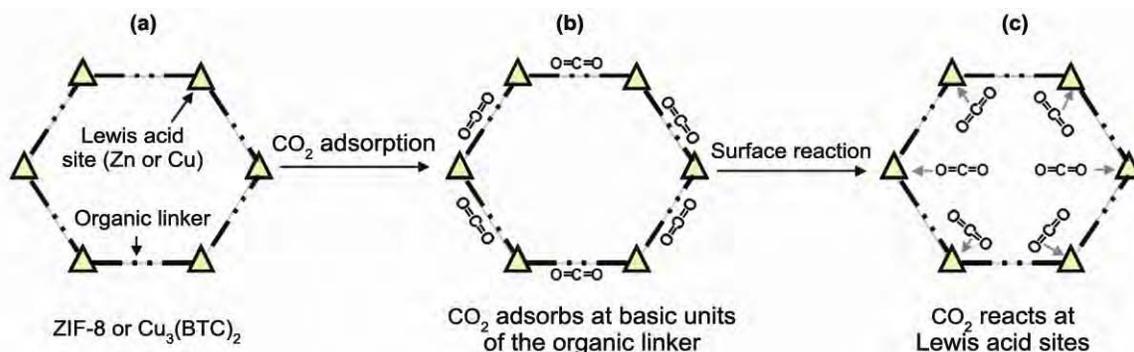
### Structural Features of ZIF-8 and Cu<sub>3</sub>(BTC)<sub>2</sub>

Zeolite imidazolate frameworks (ZIFs) are a subclass of metal organic frameworks. In ZIFs, metal atoms such as Zn and Co are linked through N atoms by ditopic imidazolate (Im<sup>-</sup>) or functionalized Im<sup>-</sup> links to form neutral frameworks and to provide tunable nanosized pores formed by four, six, eight, and twelve membered ring ZnN<sub>4</sub> and CoN<sub>4</sub> tetrahedral clusters. The framework of ZIF compounds closely resembles the framework of zeolites, i.e., the T-O-T bridges (T = Si, Al, P) in zeolites are replaced by M-Im-M bridges (M = Zn, Co); coincidentally, the bond angles in both structures are 145° (Refs 25-30). In particular, ZIF-8 is one of the most studied prototypical ZIF compounds due to its potential functional applications in gas storage, catalysis and gas separations<sup>31-33</sup>. ZIF-8 has large pores of 1.16 nm (which are accessible through small apertures of 0.34 nm) and cubic space group (I-43m) with unit cell dimensions of 1.632 nm (Refs 31-33).

The metal organic framework Cu<sub>3</sub>(BTC)<sub>2</sub> (BTC=benzene-1,3,5-tricarboxylate) is a porous metal organic framework which forms a face-centered cubic crystalline structure which is composed of dimeric cupric tetracarboxylate units, giving an intersecting tri-dimensional channel system with micropore diameter of 0.7–0.8 nm (Refs 34-36). Its larger pores, as compared to ZIFs, make this particular MOF attractive for catalytic applications in which “bulky molecules” are involved.

### Catalytic performance of ZIF-8 in the conversion of CO<sub>2</sub> and epichlorohydrin to chloropropene carbonate

Recently, our group reported the catalytic performance of ZIF-8 and amino-functionalized ZIF-8



Scheme 2

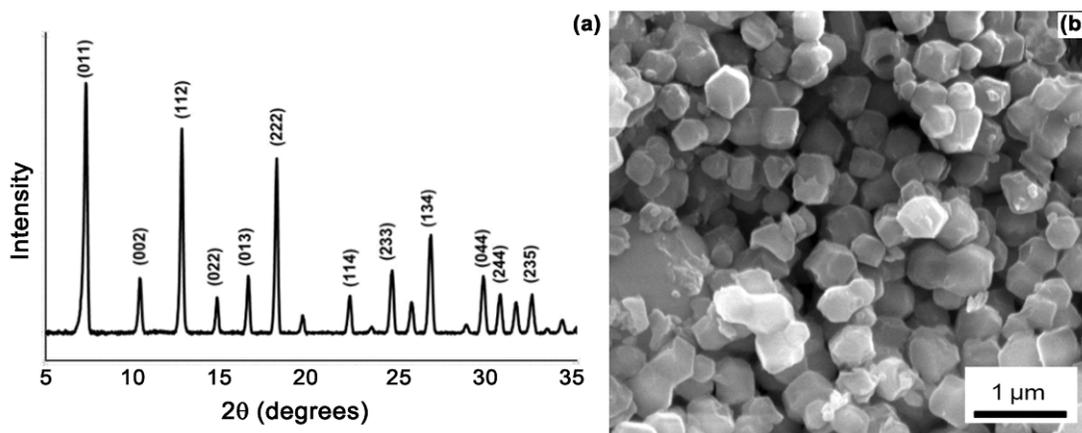


Fig. 1—(a) XRD, and, (b) SEM of ZIF-8 crystals employed as catalysts in the synthesis of chloropropene carbonate from CO<sub>2</sub> and epichlorohydrin. [Reproduced from Ref. 37 with permission from the American Chemical Society, Washington, USA].

in the synthesis of chloropropene carbonate from CO<sub>2</sub> and epichlorohydrin.<sup>37</sup> Herein the most relevant results of this study are summarized. ZIF-8 was prepared at room temperature from methanolic solutions of zinc nitrate hexahydrate and 2-methylimidazole.<sup>37,38</sup> Figure 1 shows the XRD pattern and a representative SEM image of the synthesized ZIF-8. The XRD pattern of the as-synthesized ZIF-8 catalyst (Fig. 1a) corresponds to the sodalite structure, which is the typical, known structure of ZIF-8.<sup>32</sup> Scanning electron microscopy (SEM) shows the presence of 0.4-0.5 μm crystals displaying a relatively narrow size distribution and hexagonal morphology. The CHN microanalysis revealed that the carbon, hydrogen and nitrogen contents in the synthesized ZIF-8 framework are C: 42.0 %, H: 4.3 % and N: 24.4 wt% (theoretical values for ZIF-8: C: 42.2 %, H: 4.4 % and N: 24.6 wt%).<sup>33</sup>

The catalytic activity of ZIF-8 in the cycloaddition of CO<sub>2</sub> to epichlorohydrin to form chloropropene carbonate was evaluated. In a typical cycloaddition reaction, 18 mmol of epichlorohydrin and 100 mg of ZIF-8 were placed in a 250 mL stainless steel high pressure Parr reactor (model 4576A). The reactor was pressurized with CO<sub>2</sub> at 7 bar, and the reaction was carried out at different temperatures for 4 h. The observed products were chloropropene carbonate and diols and dimers of epichlorohydrin. Controlled experiments under our reaction conditions showed that the reaction did not proceed to a significant extent in the absence of the ZIF-8 catalyst. The catalytic performance of ZIF-8 as a function of temperature is shown in Fig. 2. Remarkably, ZIF-8 was catalytically active even at reaction temperatures as low as 70 °C. The highest chloropropene carbonate yield was

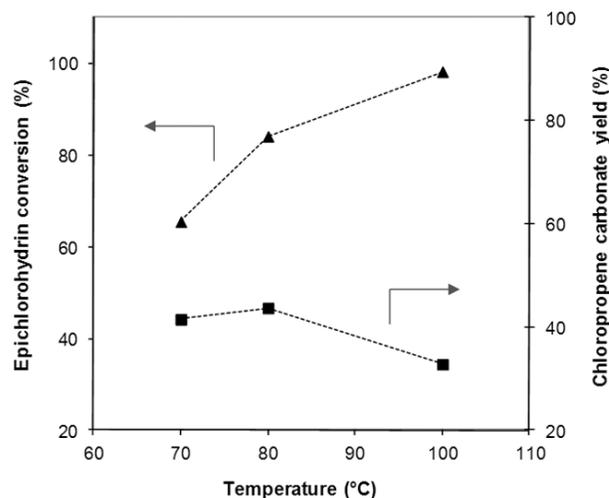


Fig. 2—Catalytic performance of ZIF-8 as a function of temperature in the synthesis of chloropropene carbonate from CO<sub>2</sub> and epichlorohydrin. Conversion and yield are given in wt%. [Reproduced from Ref. 37 with permission from the American Chemical Society, Washington, USA].

observed at 80 °C. Over zeolite-based and mesoporous solid acid catalysts, this reaction usually occurs at temperatures above 100 °C.<sup>14-24</sup> It is well known that Lewis acid sites can catalyze the reaction of CO<sub>2</sub> with epoxides to give cyclic carbonates.<sup>18,20</sup>

Zn<sub>II</sub> sites (strong Lewis acid sites) have been identified as one of the species that coexist on the surface of ZIF-8 framework.<sup>39</sup> Therefore, it is likely that these Lewis acid sites play an important role in catalyzing the cycloaddition of CO<sub>2</sub> to epichlorohydrin. In addition, the presence of the basic nitrogen atoms of the imidazole ligand in the ZIF-8 framework promotes the binding and activation of the polar carbon-oxygen bonds of CO<sub>2</sub>. The presence of Zn<sub>II</sub> acid sites and the nitrogen basic moieties from

the imidazole linker in ZIF-8 facilitated the adsorption of the CO<sub>2</sub> on the solid surface and its conversion to the carbonate.

Amino based organic cations have high affinity for CO<sub>2</sub>. Therefore, the functionalization of ZIF-8 with amino groups should promote CO<sub>2</sub> adsorption and, in principle, should improve catalytic performance. Therefore the surface of ZIF-8 was functionalized with ethylenediamine. The successful grafting of this amine was confirmed by FTIR, and CHN analysis.<sup>37</sup>

Figure 3 shows the FTIR spectra of ZIF-8 and functionalized ZIF-8. Two stretching vibrations typical of ethylene diamine molecule, i.e.,  $\nu(\text{NH})$  at 3400 cm<sup>-1</sup> and  $\nu(\text{CH})$  at 3025 cm<sup>-1</sup> are evident for the ZIF-8 functionalized sample (Fig. 3b), indicating grafting of ethylene diamine in the ZIF-8 framework. The shift in the  $\nu(\text{CH})$  to higher energies as compared to that in the neat ethylene diamine spectrum may indicate that ethylene diamine coordinates to a Lewis acid center. Independent research groups have reported a similar behavior for ethylene diamine functionalized metal-organic-frameworks.<sup>40,41</sup> For comparison the FTIR of the non-functionalized sample is shown in Fig. 3.

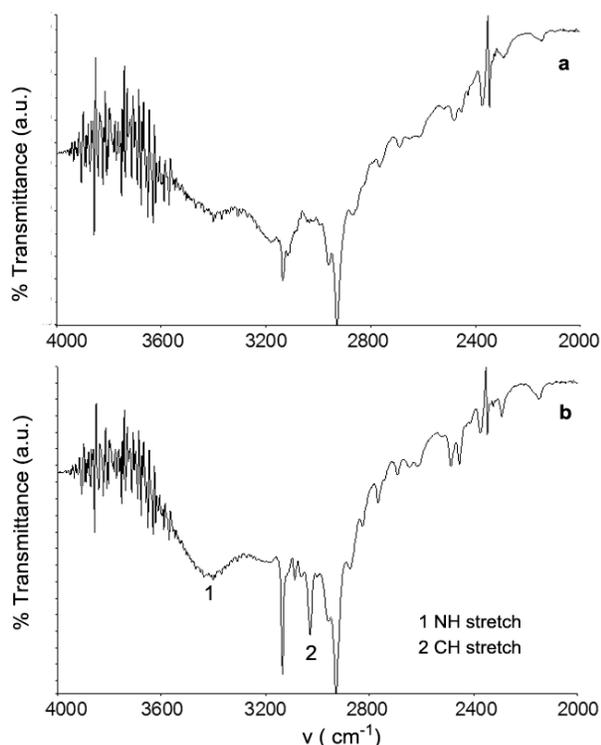


Fig. 3—FTIR spectra of (a) non-functionalized, and, (b) ethylene diamine-functionalized ZIF-8. [Reproduced from Ref. 37 with permission from the American Chemical Society, Washington, USA].

As shown in Fig. 4, for reaction temperatures in the 70–100 °C range, both the conversion and yield to chloropropene carbonate were enhanced for the ethylene diamine functionalized ZIF-8 as compared to the non-functionalized ZIF-8.

In order to understand better the superior catalytic performance of the functionalized samples, CO<sub>2</sub> adsorption isotherms (Fig. 5) were collected for the non-functionalized and the ethylenediamine functionalized ZIF-8. Higher CO<sub>2</sub> uptakes were observed for the functionalized phase. Therefore, it was suggested that the improved catalytic performance of the ethylene diamine-functionalized ZIF-8 as compared to the non-functionalized ZIF-8 may be due, at least partly, to the higher CO<sub>2</sub> adsorption capacity of the former, since it is well known that active catalysts for the insertion of CO<sub>2</sub> into epoxides are those exhibiting high CO<sub>2</sub> adsorption capacities<sup>37</sup>. Table 1 summarizes the catalytic performance of ZIF-8 and ethylene diamine functionalized ZIF-8 in the cycloaddition of CO<sub>2</sub> to epichlorohydrin reaction.

In contrast to known catalysts, the ZIF-8 catalysts displayed high epoxide conversions and moderate to high selectivities to chloropropene carbonate at reaction temperatures as low as 70 °C. In addition, no co-catalysts or solvents were required for the reaction to proceed. One of the limitations of ZIF-8 for this particular reaction is their limited stability

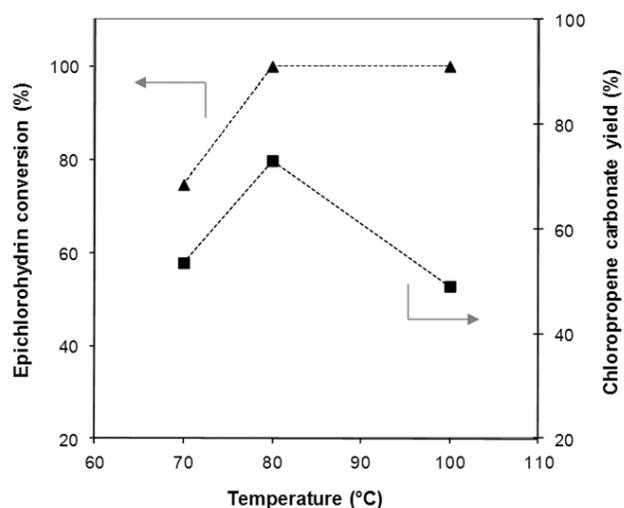


Fig. 4—Catalytic performance of ethylene diamine functionalized ZIF-8 as a function of temperature in the synthesis of chloropropene carbonate from CO<sub>2</sub> and epichlorohydrin. Conversion and yield are given in wt%. [Reproduced from Ref. 37 with permission from the American Chemical Society, Washington, USA].

for recycling. We suggested that the synergistic effect of the presence of CO<sub>2</sub> at high pressures (and temperatures) and the poisoning/blocking of the active sites by carbonaceous matter in the pores are the probable reasons for the observed catalytic deactivation and crystalline instability of ZIF-8.<sup>37</sup> Recently, we have found that in the presence of non-chlorine based epoxides (for example styrene oxide) ZIF-8 shows excellent stability. Therefore, this suggests that chlorine plays an important role in deactivating ZIF-8.

#### Catalytic performance of Cu<sub>3</sub>(BTC)<sub>2</sub> in the conversion of CO<sub>2</sub> and epichlorohydrin to chloropropene carbonate

Cu<sub>3</sub>(BTC)<sub>2</sub> was prepared by a modified method reported by Schlichte *et al.*<sup>36</sup> The detailed synthesis protocol is described in our recent work.<sup>42</sup> The XRD pattern of the synthesized Cu<sub>3</sub>(BTC)<sub>2</sub> catalyst, shown

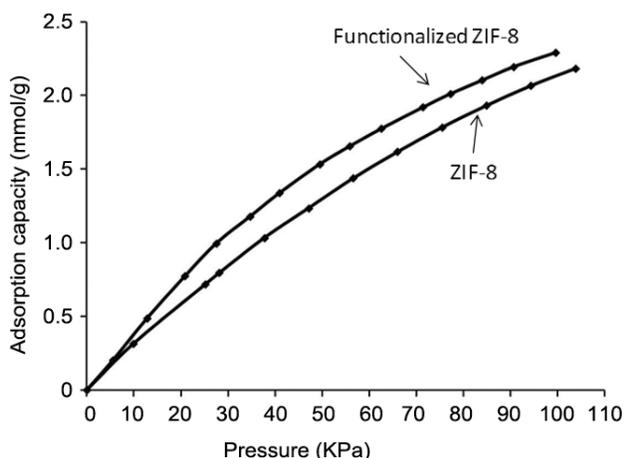


Fig. 5—CO<sub>2</sub> adsorption isotherms of non-functionalized and ethylene diamine functionalized ZIF-8. Adsorption isotherms were measured at room temperature. [Reproduced from Ref. 37 (Supporting Information) with permission from the American Chemical Society, Washington, USA].

in Fig. 6a, corresponds to the typical known structure of Cu<sub>3</sub>(BTC)<sub>2</sub>.<sup>36,43</sup> Small changes in the relative intensities of the XRD peaks are due to variations in the degrees of hydration.<sup>36</sup> In particular, the similar  $I_{200}/I_{220}$  ratio as well as the absence of the (311) reflection in our sample suggests a hydrated state.<sup>36</sup> The morphological features of Cu<sub>3</sub>(BTC)<sub>2</sub> crystals were investigated by SEM, which show well-defined octahedral crystals of ~1-1.5 μm (Fig. 6b). This octahedral morphology<sup>35,43,44</sup> is typical for Cu<sub>3</sub>(BTC)<sub>2</sub>. The BET surface area of the Cu<sub>3</sub>(BTC)<sub>2</sub> crystals was 995 m<sup>2</sup>/g, in agreement with previous reports.<sup>34,35</sup>

The cycloaddition reaction of CO<sub>2</sub> to epichlorohydrin yielded chloropropene carbonate and diols and dimers of epichlorohydrin. Controlled experiments under prevailing reaction conditions confirmed that the reaction did not proceed to a significant extent in the absence of the Cu<sub>3</sub>(BTC)<sub>2</sub> catalyst. Different from other metal organic frameworks in which most of the coordination sites are blocked by the organic ligand, in Cu<sub>3</sub>(BTC)<sub>2</sub> the copper Lewis acid coordination sites are accessible for potential catalytic conversions.<sup>36</sup>

Table 2 shows the catalytic performance of Cu<sub>3</sub>(BTC)<sub>2</sub> as a function of temperature in the cycloaddition of CO<sub>2</sub> to epichlorohydrin reaction. Cu<sub>3</sub>(BTC)<sub>2</sub> was catalytically selective to chloropropene carbonate only at 100 °C (Table 2). Interestingly, diols of the epoxide and dimers of epichlorohydrin were observed below 100 °C. As mentioned previously, over zeolites and mesoporous solid acid catalysts, this reaction usually occurs at temperatures at or above 100 °C. The chloropropene carbonate yield at 100 °C over Cu<sub>3</sub>(BTC)<sub>2</sub> was ~33 %. It is likely that the Lewis acid copper(II) sites play an important role in catalyzing the cycloaddition of CO<sub>2</sub> to epichlorohydrin. In addition, the partial positive

Table 1—Catalytic performance of ZIF-8 and ethylene diamine functionalized ZIF-8 (ZIF-8-f) in the cycloaddition of CO<sub>2</sub> to epichlorohydrin reaction<sup>†</sup>

Catalyst (Temp., °C)	Epichlorohydrin conv. (wt%)	Selectivity (wt%)		
		Chloropropene carbonate <sup>a</sup>	Diol	Dimer
ZIF-8 (70)	65.5	63.4 (41.5)	36.6	0.0
ZIF-8 (80)	84.1	52.0 (43.7)	23.7	24.3
ZIF-8 (100)	98.2	33.4 (32.8)	29.8	36.8
ZIF-8-f (70)	74.6	71.8 (53.6)	28.2	0.0
ZIF-8-f (80)	100	73.1 (73.1)	26.9	0.0
ZIF-8-f (100)	100	49.1 (49.1)	50.9	0.0

<sup>a</sup>Numbers in parentheses indicate yield.

<sup>†</sup>Taken from Ref. 37 with permission from the American Chemical Society, Washington, USA.

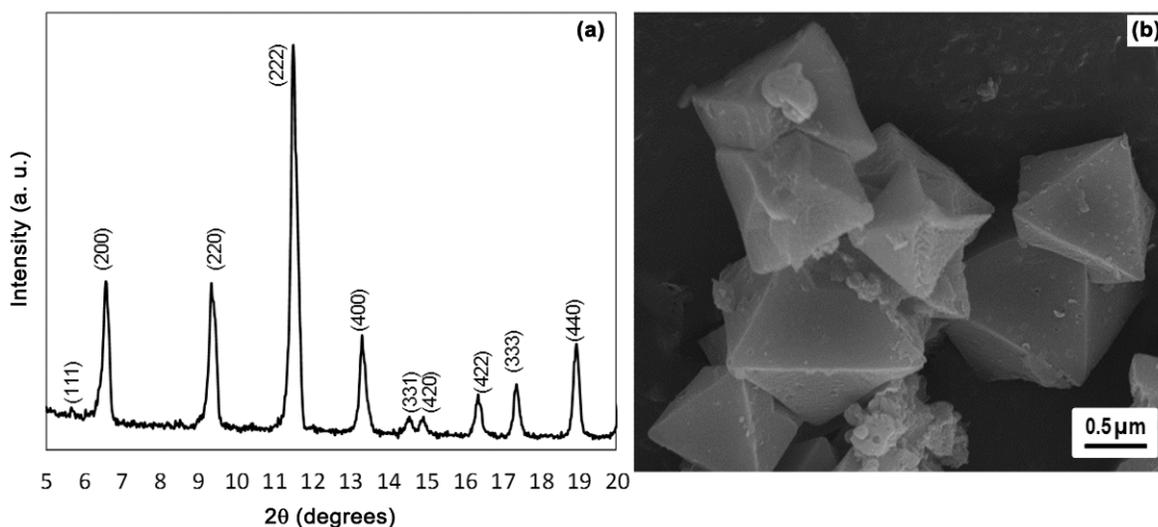


Fig. 6—(a) XRD, and, (b) representative SEM of  $\text{Cu}_3(\text{BTC})_2$  crystals employed as catalysts in the cycloaddition of  $\text{CO}_2$  to epichlorohydrin. [Reproduced from Ref. 42 with permission from Elsevier, Amsterdam, The Netherlands].

Table 2—Catalytic performance of  $\text{Cu}_3(\text{BTC})_2$  crystals in the cycloaddition of  $\text{CO}_2$  to epichlorohydrin<sup>†</sup>

Temp. (°C)	Epichlorohydrin conv. (wt%)	Selectivity (wt%)		
		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

<sup>†</sup>Reproduced from Ref. 42 with permission from Elsevier, Amsterdam, The Netherlands.

charges on the unsaturated copper metal sites of  $\text{Cu}_3(\text{BTC})_2$  promote the binding and activation of the polar carbon-oxygen bonds of carbon dioxide, resulting in high  $\text{CO}_2$  adsorption capacities. Unsaturated copper metal sites have been identified by theoretical and experimental investigations as  $\text{CO}_2$  adsorption sites.<sup>45</sup>  $\text{CO}_2$  adsorption capacities for  $\text{Cu}_3(\text{BTC})_2$  range from 8.0–12.7 mmol/g at room temperature and 15 bar.<sup>35,46,47</sup> The copper acid sites, probably, promote the adsorption of carbon dioxide on the solid surface and its further conversion to the carbonate. The formation of the diols over  $\text{Cu}_3(\text{BTC})_2$  even at low temperature is probably related to the presence of a hydrophilic interior in the catalyst wherein the  $\text{Cu}^{2+}$  ions are connected through a weak bond and the residual axial coordination site is filled by a weakly bound water molecule. Therefore, the weakly bound water molecules pointing towards the center of the pore are likely active sites in the hydration of the epoxide to the diols. In addition, the activated epoxide (unreacted) can undergo side reactions to form dimer of epichlorohydrin.

The catalytic activity of  $\text{Cu}_3(\text{BTC})_2$  versus zeolites beta ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$ ), TS-1, and HY, mesoporous

silica SBA-15 and ZIF-8 at 100 °C and 7 bar for 4 h was compared and is shown in Fig. 7. Zeolite beta displayed the highest yield to chloropropene carbonate at ~82 wt%. The  $\text{Cu}_3(\text{BTC})_2$ , ZIF-8, HY and SBA-15 catalysts formed significant amounts of carbonaceous deposits during this reaction. 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 chloropropene 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 are well known. The catalytic performance of  $\text{Cu}_3(\text{BTC})_2$  is better than that of 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 wt% for TS-1 zeolite and HY zeolite, respectively. In general, catalysts with larger pore volumes (beta,  $\text{Cu}_3(\text{BTC})_2$  and ZIF-8) led to higher yields of chloropropene carbonate, as compared to catalysts with smaller pore

volume (TS1, HY, SBA-15).<sup>42</sup> These three catalysts display moderate to high CO<sub>2</sub> adsorption capacities. At ~1 bar and room temperature, the CO<sub>2</sub> adsorption capacities for Cu<sub>3</sub>(BTC)<sub>2</sub>, zeolite beta, and ZIF-8 are 4.5 mmol/g (Ref. 35), ~2.5 mmol/g (Ref. 48) and ~2.2 mmol/g (Fig. 5). Although, Cu<sub>3</sub>(BTC)<sub>2</sub> crystals displayed moderate epoxide conversions, and moderate selectivities to chloropropene carbonate at 100 °C, this MOF composition showed limited recyclability. It is suggested that the activity of recycled Cu<sub>3</sub>(BTC)<sub>2</sub> catalyst decreased, in part due to active site pore blocking by residual carbonaceous deposits. The limited recyclability of ZIF-8 and Cu<sub>3</sub>(BTC)<sub>2</sub> can be improved by employing organic solvents during synthesis. It has been demonstrated that one of the main roles of organic solvents is to continuously remove carbonaceous deposits from the catalyst surface and keep it clean.<sup>18</sup> Currently our group is studying the effect of different solvents, including toluene, methanol, ethanol, dichloromethane, and acetonitrile.

### Bio-metal Organic Frameworks

Bio-metal organic frameworks (Bio-MOFs)<sup>49-59</sup>, a subclass of MOFs, combine highly desirable properties, such as uniform micropores, high surface areas, and exceptional thermal and chemical stability, making them ideal candidates for catalytic applications. Bio-MOFs are permanently porous materials in which rigid biomolecules, such as nucleobases, saccharides, peptides, and amino acids

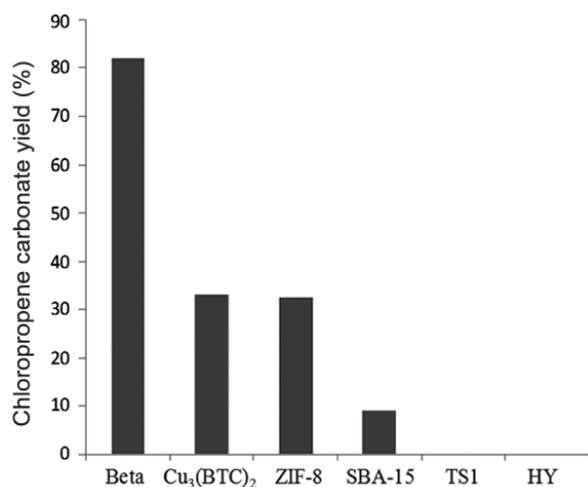


Fig. 7—Catalytic performance of Cu<sub>3</sub>(BTC)<sub>2</sub> as compared to other solid catalysts (including the metal organic framework ZIF-8) in the synthesis of chloropropene carbonate from CO<sub>2</sub> and epichlorohydrin. (Reaction cond.: 100 °C and 7 bar for 4 h. Yield is given in wt%). [Reproduced from Ref. 42 with permission from the Elsevier, Amsterdam, The Netherlands].

have been used as building blocks to form a metal organic framework. Other biomolecules that have been employed to synthesize Bio-MOFs have been recently reviewed.<sup>59</sup> Apart from the advantageous above mentioned properties, Bio-MOFs are in particular appealing materials to be employed as catalysts for CO<sub>2</sub> conversion to carbonates due to the presence of Lewis acid sites in their frameworks (in most cases, exposed metal sites), remarkably high CO<sub>2</sub> adsorption capacity due to the presence of basic linkers, and, high chemical stability, which in principle would translate into robust catalysts which could be recycled without losing catalytic activity. Recently, some examples of the catalytic potential of Bio-MOFs have been reported. For example, amino acid based Bio-MOFs (Ni<sub>2</sub>(L-asp)-(4,4-bipyridine)·2H<sub>2</sub>O) displayed enantioselective sorption capabilities of small chiral diols<sup>57</sup> as well as catalytic activity in the methanolysis of *cis*-2,3 epoxybutane.<sup>60</sup> Bio-MOF (Zn<sub>2</sub>(bdc)(L-lac) DMF; bdc = 1,4 benzenedicarboxylic acid; L-lac = lactic acid) has shown high enantioselective adsorption capability to sulfoxides.<sup>61</sup> Therefore, BioMOFs may be very appealing catalytic phases for the conversion of CO<sub>2</sub> into carbonates.

Figure 8 shows a representative SEM of Bio-MOF-1 crystals recently prepared in our laboratory. Bio-MOF-1, (Zn<sub>8</sub>(ad)<sub>4</sub>(BPDC)<sub>6</sub>O·2Me<sub>2</sub>NH<sub>2</sub>), is a three-dimensional porous metal organic framework with infinite zinc-adeninate columnar secondary building units (SBUs) which are interconnected via biphenyldicarboxylate linkers.<sup>50,52,53</sup> As shown in Fig. 8, well defined rectangular-like shapes with lengths in the ~0.5-4.5 μm range, and widths in the ~0.05-0.15 μm range were observed. The apparent BET surface area ( $P/P_0 = 0.01-0.3$ ) of the Bio-MOF-1 crystals was ~800 m<sup>2</sup>/g. This particular type of

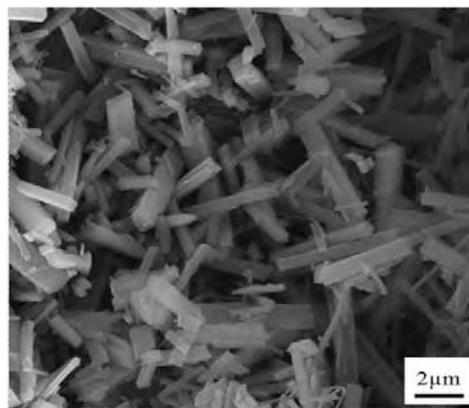


Fig. 8—SEM image of Bio-MOF-1 crystals. [Reproduced from Ref. 62 with permission from the Royal Society of Chemistry, London, UK].

Bio-MOF displayed preferential CO<sub>2</sub> adsorption that was attributed to the presence of adeninate amino basic sites present in its framework. Due to its high CO<sub>2</sub> adsorption capacity, this MOF (in membrane form) was employed to separate CO<sub>2</sub>/CH<sub>4</sub> mixtures.<sup>62</sup> In principle, this type of MOF may be very appealing as catalyst for the synthesis of carbonates from CO<sub>2</sub>.

### Concluding Remarks

Metal organic frameworks possessing highly desirable and tunable structural, textural, morphological and compositional properties are particularly attractive materials to be used as catalytic phases in the conversion of CO<sub>2</sub> and epoxides into cyclic carbonates. It is anticipated that these novel catalytic porous systems would lead to an improved fundamental understanding of the relationships between molecular structure and catalytic properties of a broad range of relevant catalytic reactions involving the conversion of CO<sub>2</sub> into chemicals.

Herein two examples of metal organic frameworks having the ability of catalyzing the cycloaddition reaction of an epoxide and CO<sub>2</sub> to form cyclic carbonates have been discussed. ZIF-8 and Cu<sub>3</sub>(BTC)<sub>2</sub> represent the first examples of any MOF displaying catalytic ability for the conversion of CO<sub>2</sub> into chemicals. As revealed in our studies<sup>37,42</sup>, in the reaction between CO<sub>2</sub> and epichlorohydrin to form cyclic carbonates, surface features of the solid catalyst such as acidity (the presence of Lewis acid sites), and adsorption selectivity (on the MOF linker) play an important role on the overall catalytic performance. However, much research is needed to rationally explore other MOF compositions that could show even superior catalytic performance in the synthesis of cyclic carbonates via the cycloaddition reaction. A subclass of MOFs, bio-metal organic frameworks combine highly desirable properties, such as uniform micropores, high surface areas, and exceptional thermal and chemical stability, making them ideal candidates for catalytic applications.

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