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Zeolitic Imidazole Framework-8 Catalysts in the Conversion of CO_2 to Chloropropene Carbonate

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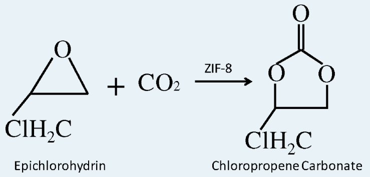
S Supporting Information

ABSTRACT: The catalytic activity of zeolitic imidazole framework-8 (ZIF-8) and amine-functionalized ZIF-8 catalysts in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin is demonstrated. In contrast to hitherto known catalysts, ZIF-8 catalysts displayed high epoxide conversions and moderate to high selectivities to chloropropene carbonate at reaction temperatures as low as 70 °C. No cocatalysts or solvents were required during the reaction. The incorporation of ethylenediamine in ZIF-8 enhanced its catalytic performance as a result of the higher CO_2 adsorption capacity of the amine-functionalized samples. The ZIF-8 catalysts, however, lost their distinctive crystalline structure and superior catalytic performance when attempts were made to recycle them after use.



KEYWORDS: *metal organic frameworks, ZIF-8, cycloaddition, cyclic carbonates, CO_2 conversion*

There is an increasing trend to consider carbon dioxide as a raw material resource and a business opportunity rather than a waste with a cost of disposal. Increasing amounts of low-cost and relatively pure CO_2 will be soon available from plants for carbon sequestration and storage. Carbon dioxide represents potentially a feedstock of nearly zero or even negative cost for conversion to fuels and useful chemicals. The catalytic conversion of CO_2 to cyclic carbonates and polycarbonates over conventional solid catalysts, including zeolites and mesoporous oxides, is well-known.[1−11] However, the development of superior performance catalysts requires new materials with fundamentally different structural, compositional, adsorption and transport properties than those of conventional zeolites, metal oxides or metal phases. In this respect, zeolitic imidazolate frameworks (ZIFs),[12−17] 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 adsorption and catalytic applications.

In particular, ZIF-8, having large pores of 11.6 Å that are accessible through small apertures of 3.4 Å and cubic space group (I-43*m*) with unit cell dimensions of 16.32 Å[18−20] is an appealing material to employ as catalyst for CO_2 conversion to cyclic carbonates because of (a) the presence of Lewis acid sites in its framework and (b) its preferential and high CO_2 adsorption capacity. Lewis acid sites are known to catalyze the reaction of CO_2 with epoxides to give propylene carbonates and other precursors of polycarbonates.[5−7] Another key parameter to consider is the high CO_2 adsorption capacity of these novel phases due to the presence of basic sites associated with the imidazole units. It is highly desirable that catalysts for the conversion of CO_2 to cyclic carbonates also exhibit high CO_2 uptakes. The polar nature of the walls in ZIF-8 favors the binding and preferential adsorption of the polar carbon−oxygen bonds of CO_2.

Only a few examples of the potential of ZIFs as catalysts have been recently published.[21−23] ZIF-8 catalyzes the trans-esterification of vegetable oil[21] and is an active catalyst for the Knoevenagel reaction.[22] ZIF-9 has been used as a catalyst in the oxidation of aromatic oxygenates.[23] Herein, we report the catalytic performance of ZIF-8 and amino-functionalized ZIF-8 in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin. In contrast to hitherto known catalysts, the ZIF-8 catalysts, especially those surface-modified with amines, display high epoxide conversions and moderate to high selectivities to the cyclic carbonate at temperatures even as low as 70 °C.

ZIF-8 was prepared at room temperature from methanolic solutions of zinc nitrate hexahydrate and 2-methylimidazole. In a typical synthesis, 0.3 g of zinc nitrate hexahydrate, ($Zn(NO_3)_2{\cdot}6H_2O$, Fluka, ≥99%) was dissolved in 11 g of methanol (Acros Organics, 99+%). A solution consisting of 0.66 g of 2-methylimidazole ($C_4H_6N_2$, Aldrich, 99%) and 11 g of methanol was added to the Zn-containing solution, and the mixture was vigorously stirred for 24 h to form a homogeneous mixture. The resultant solid particles were separated from the gel by centrifugation at 3000 rpm and washed with methanol. The washing was repeated three times. The resultant ZIF-8 crystals were dried overnight at 100 °C. The functionalized ZIF-8 was prepared as follows: 2 g of dry ZIF-8 was suspended in 30 mL of anhydrous toluene (extra dry, water < 30 ppm, Acros). To this suspension, 0.75 mmol of ethylene diamine ($C_2H_8N_2$, Sigma Aldrich) was added, and the mixture was

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refluxed for 20 h. Ethylene diamine has been used earlier to functionalize metal organic frameworks.[24,25]

The morphology of the ZIF-8 crystals was determined with a FE-SEM (FEI Nova 600) with an acceleration voltage of 6 kV. Powder X-ray diffraction patterns were collected using a Bruker D8-Discover diffractometer at 40 kV, 40 mA with Cu Kα radiation. TEM images were taken on a Technai F20 FEI TEM using a field emission gun, operating with an accelerating voltage of 200 keV. 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, and the samples were degassed at 150 °C for 3 h before the measurements. Fourier transform infrared spectroscopy (BX FTIR, Perkin-Elmer) was used to determine the lattice vibrations in the ZIF-8 framework. The quantitative analysis of elemental carbon, hydrogen, and nitrogen were carried out at Midwest Microlab. LLC, Indianapolis, IN.

The catalytic activity of ZIF-8 was evaluated in the cycloaddition of CO_2 to epichlorohydrin to form chloropropene carbonate. 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_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 (HP 5890 gas chromatograph equipped with 5970 mass selective detector, 30 m × 0.32 mm HP-5 column coated with 5% phenyl polysiloxane stationary phase). The temperature ramp rate during the gas chromatographic analysis was 70−220 °C at 15 °C/min.

The XRD pattern of the as-synthesized ZIF-8 catalyst, shown in Figure 1a, corresponds to a sodalite structure, which is the typical, known structure of ZIF-8.[19] The morphological features of ZIF-8 crystals were investigated by transmission electron microscopy, which shows sharp, hexagonally faceted ZIF-8 crystals of ~500 nm (Figure 1b). Scanning electron microscopy (SEM) also confirmed the presence of 400−500 nm crystals displaying a relatively narrow size distribution and hexagonal morphology (Figure S1 of the Supporting Information).[26] The CHN analysis revealed that the carbon, hydrogen, and nitrogen contents in the ZIF-8 framework are C, 42.0%; H, 4.3%; and N, 24.4% (theoretical values for ZIF-8: C, 42.2%; H, 4.4%; and N, 24.6%).[20] The BET surface area of the ZIF-8 nanocrystals was 1173 m^2/g. Type I N_2 adsorption−desorption isotherms (Figure S1) indicating the microporous nature of the ZIF-8 crystals[26] were observed.

The cycloaddition of CO_2 to epichlorohydrin yielded chloropropene carbonate as the main product. Diols and dimers of epichlorohydrin were the other products. Controlled experiments under our reaction conditions confirmed that the reaction did not proceed to a significant extent in the absence of the ZIF-8 catalyst. Figure 2 shows the catalytic performance of ZIF-8 as a function of temperature. ZIF-8 was catalytically active, even at reaction temperatures as low as 70 °C. Over zeolite-based and mesoporous solid acid catalysts, this reaction usually occurs at temperatures above 100 °C.[1−11] The conversion of epichlorohydrin increased as the temperature was increased, reaching a maximum of ~100% at 100 °C, while the selectivity to chloropropene carbonate decreased. The highest chloropropene carbonate *yield* was observed at 80 °C.

It is known that Lewis acid sites catalyze the reaction of CO_2 with epoxides to give propylene carbonates and other precursors of polycarbonates.[5,7] Recently, Chizallet et al. identified Zn_{II} (strong Lewis acid sites) as one of the species that coexist on the surface of ZIF-8 crystals.[21] It is likely that these Lewis acid sites (associated with Zn ions) play an important role in catalyzing the cycloaddition of CO_2 to epichlorohydrin. In addition, the polar nature of ZIF-8 (i.e., the presence of the basic nitrogen atoms of the imidazole ligand)[12] favors the binding and activation of the polar carbon−oxygen bonds of CO_2. The presence of *both* the Zn_{II} acid sites and the

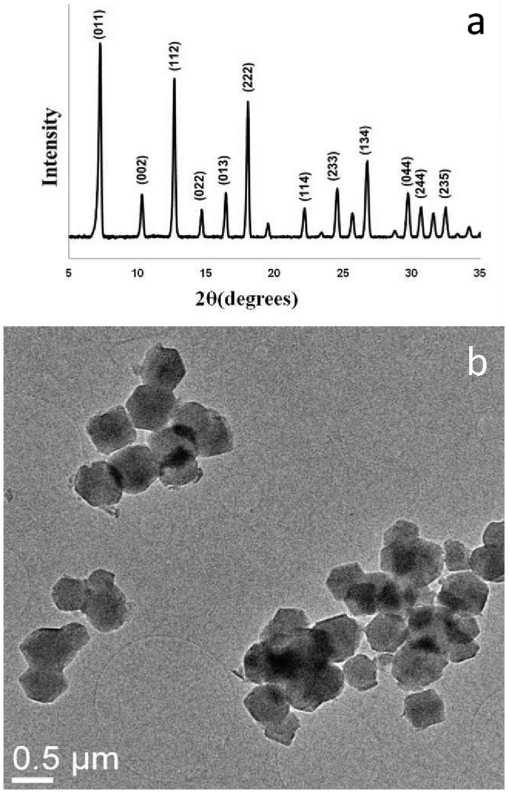

Figure 1. (a) XRD and (b) TEM of ZIF-8 solids employed as catalysts in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin.

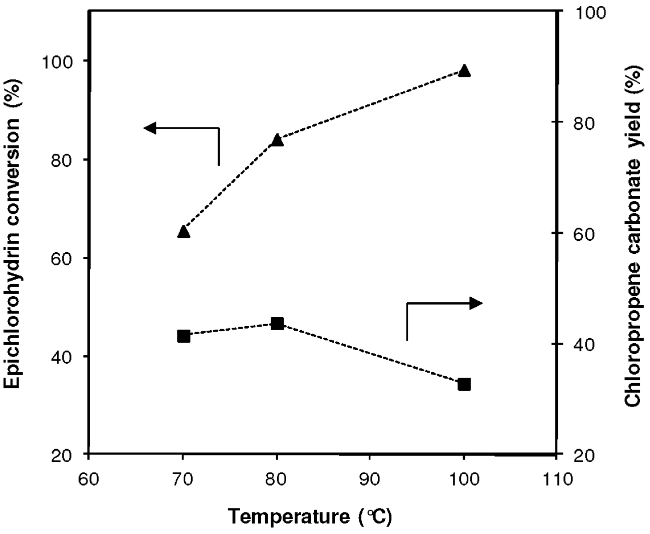

Figure 2. Catalytic performance of ZIF-8 as a function of temperature in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin.

N basic moieties (in adjacent locations) from the imidazole linker in ZIF-8 probably facilitates the adsorption of the CO_2 on the solid surface and its further conversion to the carbonate. As mentioned earlier, the high adsorption capacity of CO_2 is well-known. Table 1 summarizes the catalytic performance of ZIF-8 in the cycloaddition of CO_2 to epichlorohydrin reaction.

Table 1. Catalytic Performance of ZIF-8 and Functionalized ZIF-8 in the Cycloaddition of CO_2 to Epichlorohydrin Reaction

catalyst/ temperature (°C)	epichlorohydrin conversion (%)	[c]selectivity (%)		
		chloropropene carbonate	diol	dimer
[a]ZIF-8 (70)	65.5	63.4 [41.5]	36.6	0.0
[a]ZIF-8 (80)	84.1	52.0 [43.7]	23.7	24.3
[a]ZIF-8 (100)	98.2	33.4 [32.8]	29.8	36.8
[b]ZIF-8-f (70)	74.6	71.8 [53.6]	28.2	0.0
[b]ZIF-8-f (80)	100	73.1 [73.1]	26.9	0.0
[b]ZIF-8-f (100)	100	49.1 [49.1]	50.9	0.0

[a]Pure ZIF-8. [b]Functionalized ZIF-8. [c]Numbers in square brackets indicate respective yields.

In another set of controlled experiments, the activity for zinc nitrate hexahydrate, ethylene diamine, and 2-methylmidazole for carbonate formation in the absence of added ZIF-8 catalysts, was evaluated at 80 °C and 7 bar for 4 h. Zinc nitrate hexahydrate, 2-methylmidazole. and ethylene diamine displayed yields to diol corresponding to only 20%, 100%, and 19%, respectively.

Organic cations containing amino group functionalities have high affinity for $CO_{2.}$ Therefore, the incorporation of amino groups in the surface of ZIF-8 should promote CO_2 adsorption and, in principle, should improve catalytic performance. Recently, our group has demonstrated the successful surface functionalization of zeolite SAPO-34 with ethylenediamine.[27] The XRD pattern of the ethylene diamine-functionalized ZIF-8 (Figure S2 of the Supporting Information) shows that the crystalline structure of ZIF-8 was preserved even after the amine functionalization.[26] The surface area of the functionalized ZIF-8 slightly decreased to 1096 m^2/g (1173 m^2/g for the nonfunctionalized ZIF-8). The grafting of ethylene diamine in the ZIF-8 framework was confirmed by FTIR (Figure S3) which shows ν(NH) and ν(CH) stretching vibrations corresponding to ethylene diamine.[26] The CHN analysis for the ZIF-8-functionalized sample corresponded to C, 47.5%; H, 4.8%; and N, 25.2%. As shown in Figure 3, for reaction temperatures in the 70−100 °C range, both the conversion and yield to chloropropene carbonate were enhanced on functionalization of the ZIF-8 surface with ethylene diamine.

CO_2 adsorption isotherms (Figure S4)[26] were collected for the nonfunctionalized and the amine-functionalized ZIF-8. Higher CO_2 uptakes were observed for the functionalized phase. Therefore, the improved catalytic performance of the amine-functionalized ZIF-8 as compared with the nonfunctionalized ZIF-8 may be due, at least in part, to the higher CO_2 adsorption capacity of the former, since it is well-known that active catalysts for the insertion of CO_2 into epoxides are those exhibiting high CO_2 uptakes.[9] Table 1 summarizes the catalytic performance of ZIF-8 and amine-functionalized ZIF-8 in the cycloaddition of CO_2 to epichlorohydrin reaction. The yield of the carbonate was maximum at 80 °C.

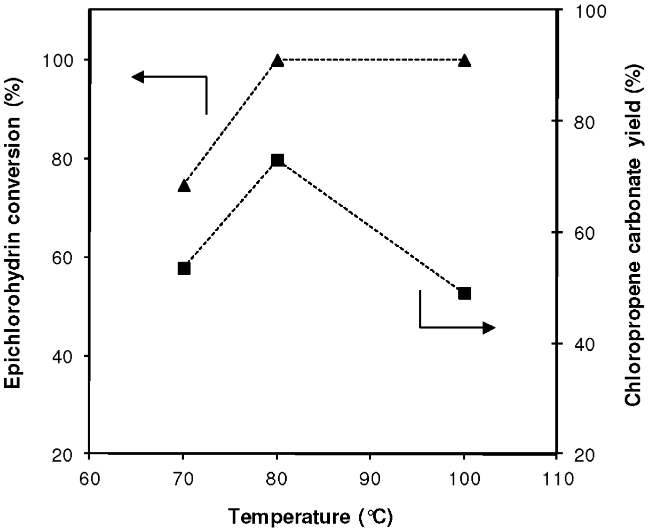

Figure 3. Catalytic performance of functionalized ZIF-8 as a function of temperature in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin.

Zeolite beta is an efficient catalyst for the synthesis of cyclic carbonates.[6] The catalytic performance of zeolite beta (BET surface area 343 m^2/g) in the cycloaddition of CO_2 to epichlorohydrin reaction was compared with that of ZIF-8. At 70 °C, no chloropropene carbonate was formed over zeolite beta. Only the diol was observed. At 80 °C, the yield of chloropropene carbonate was 61.1%, and finally, at 100 °C, the yield of chloropropene carbonate increased to 82.2%. At 70 °C, ZIF-8 (both the nonfunctionalized and amine-functionalized forms) exhibited better catalytic performance than zeolite beta. At 80 °C, functionalized ZIF-8 displayed the best catalytic performance. Zeolite beta performed better at 100 °C. Other catalysts that have been employed for this reaction are zeolite TS-1, HY, and SBA-15. We evaluated the activity of these catalysts at 80 °C and 7 bar for 4 h. The only observed product for zeolite TS-1 and HY was diol. The yield to diol was 17% and 23% for TS-1 zeolite and HY zeolite, respectively. For SBA-15, the yield to chloropropene carbonate was only 37%.

Recyclability is an important and essential feature of any catalyst to be considered for use in industrial applications. We have investigated the influence of catalyst recycle on the catalytic properties of ZIF-8 in the cycloaddition reaction. In the recycle experiments, the catalyst after use in the cycloaddition reaction was washed with acetone, centrifuged, and air-dried before reuse. The catalytic activity of the recycled catalysts (both nonfunctionalized and amine-functionalized) was evaluated at a reaction temperature of 80 °C. The yield of chloropropene carbonate decreased from 43.7% (fresh) to 22.7% (recycled) for the nonfunctionalized ZIF-8 and from 73.1% (fresh) to 30.6% (recycled) for the amine-functionalized ZIF-8. The XRD and FTIR of the recycled ZIF-8 catalysts (both pure and functionalized) after the reaction at 80 °C are shown in the Supporting Information (Figure S5 and S6) and suggest that the ZIF-8 structure is preserved after the first cycle. However, the apparent BET surface area decreased from 1173 to 772 m^2/g for the nonfunctionalized ZIF-8 and from 1096 to 915 m^2/g for the functionalized ZIF-8. This may suggest pore blockage of the recycled ZIF-8 by carbonaceous material formed during the reaction and may explain in part the lower activity of the recycled catalysts. In fact, for other solid catalysts, such as SBA-15, the loss in activity of recycled catalysts has been attributed to active site pore blocking by residual carbonaceous deposits.[5] The recycled catalysts (after the second cycle) lost their structural features after reaction, as confirmed by XRD. The latter revealed the presence of an amorphous phase, indicating that the ZIF-8 framework collapsed during the recycle experiments.

To investigate the loss of crystallinity of the ZIF-8 framework in greater detail, we carried out the following experiments: (1) We measured the changes in the pH of the reaction mixture during the reaction. The pH remained unchanged (7−7.2) during the reaction, thus ruling out enhanced acidity of the reaction mixture (from HCl formed from epichlorohydrin) as the cause of the crystalline collapse. We found that at acidic pH, the ZIF-8 framework was unstable. In fact, pH ~ 5 led to the formation of layered $Zn(OH)_2$. At acidic conditions, the poor deprotonation of the linker may limit the formation of ZIF-8. (2) The H_2O content of epichlorohydrin was measured to be below 0.2%. Although this may account for the small amount of diols sometimes observed in the products, it is not enough to cause crystalline collapse. ZIF-8 is known to be chemically stable in the presence of water and aromatic hydrocarbons[19] as well as thermally stable up to ~200 °C.[20] (3) ZIF-8 was heated in toluene at 100 °C for 6 h at low pressures. There was no change in the XRD pattern, even after the above experiment was repeated twice. There was no formation of carbonaceous matter. (4) ZIF-8 was heated in epichlorohydrin at 100 °C for 6 h. Diols were observed as products. Conversion was low, and there was no significant formation of carbonaceous matter. Significantly, there was no change in the XRD pattern, even after the above experiment was repeated twice.

These results suggest that the *synergistic* effect of the presence of CO_2 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. It may be noted that the instability of the ZIF-8 at high pressures is already well-known.[28]

In summary, we demonstrate the high catalytic activity of ZIF-8 and amino-functionalized ZIF-8 catalysts in the synthesis of chloropropene carbonate from CO_2 and epichlorohydrin. In contrast to hitherto known catalysts, the ZIF-8 catalysts displayed high epoxide conversions and moderate to high selectivities to chloropropene carbonate at reaction temperatures even as low as 70 °C. No cocatalysts or solvents were required for the reaction to proceed. The incorporation of ethylenediamine in the ZIF-8 framework enhanced its catalytic performance as a result of the higher CO_2 adsorption capacity of the amine-functionalized samples. The ZIF-8 catalysts, however, lost their distinctive crystalline nature and superior catalytic performance when attempts were made to recycle them after use.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

SEM and N_2 adsorption−desorption isotherms of ZIF-8. XRD of functionalized ZIF-8. FTIR and CO_2 adsorption isotherms of nonfunctionalized and functionalized ZIF-8. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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