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Communication

Zeolitic Tetrazolate–Imidazolate Frameworks with SOD Topology for Room Temperature Fixation of CO_2 to Cyclic Carbonates

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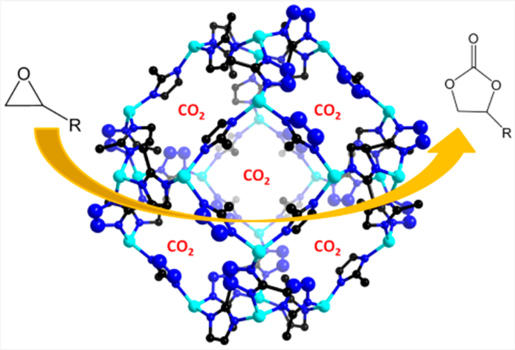
ABSTRACT: Presented here is an SOD-type zeolitic tetrazolate–imidazolate framework (ZTIF-8) based on 5-methyltetrazole (5-Hmtz) and 2-methyimidazole (2-Hmim) ligands. Owing to the uncoordinated N-sites on the framework, ZTIF-8 has shown high chemical fixation of CO_2 to cyclic carbonates at room temperature and ambient pressure.



The greenhouse gas carbon dioxide (CO_2) mainly originates from combustion of fossil fuels and has become one of the greatest environmental problems.[1−3] Chemical insertion of CO_2 into epoxides has become one of the most efficient methods for synthesis of cyclic carbonates. For the synthesis of cyclic carbon, CO_2 acts as a cheap and renewable C1 resource.[4−7] Varied materials such as zeolites,[8−10] ionic liquids,[11,12] and metal–organic frameworks (MOFs)[13−17] have been used as catalysts in the cycloaddition reaction of CO_2 and epoxides into cyclic organic carbonates. Among them, MOFs as heterogeneous catalysts show their advantages in the cycloaddition reaction, such as high porosity, tunable structures, high CO_2 capture, and crystalline solids make them easy to separate and reuse.[18−22]

Zeolitic imidazolate frameworks (ZIFs) are one of the most important subfamilies of metal–organic frameworks (MOFs)[23−31] and have potential applications in gas adsorption and separation,[32−37] catalysis,[38−42] etc. Recent results have shown that ZIF-8 can be employed as an effective catalyst in the cycloaddition of CO_2 and epichlorohydrin to form chloropropene carbonate with a mild yield without cocatalyst (70−100 °C, 7 bar CO_2).[43] It was reported that the activity of ZIF-8 catalyst was based on the surface defects from Lewis acidic Zn^{2+} sites and the basic nitrogen atoms from the imidazolate ligands, and ZIF-8 was unstable at high pressures.[43]

Compared to the limitation of catalytic activity by the uncontrollable surface defects in ZIF-8, this is an effective way to introduce more uncoordinated N atoms in the frameworks to improve the catalytic activity.[18] It has been reported that triazole and tetrazole derivatives can adopt a similar coordination mode to that of imidazole to construct N-rich frameworks.[44,45] In addition, Zhang et al. synthesized the solid solution frameworks by mixing imidazole and triazole ligands.[44] Our group also reported the porous zeolitic tetrazolate–imidazolate frameworks (ZTIFs) by introducing tetrazole ligands into ZIFs.[46−49] In both cases, the uncoordinated N atoms of azole ligands improved the CO_2 uptake and selectivity. Since tetrazole can supply rich N sites, we deduced that ZTIFs may be good catalysts via their basic nitrogen atoms as active sites for fixation of CO_2 to cyclic carbonates.[18] In this work, by employing 5-methyltetrazole (5-Hmtz) and 2-methyimidazole (2-Hmim) ligands, we report a new SOD-type ZTIF-8 (Zn(5-mtz)(2-mim)). Compared to ZIF-8, half of the 2-mim ligands were replaced by 5-mtz to form the framework of ZTIF-8, so ZTIF-8 can be considered N-functionalized ZIF-8. As expected, ZTIF-8 showed higher uptake of CO_2 than that of ZIF-8. More importantly, ZTIF-8 exhibited high catalytic activity on chemical fixation of CO_2 to cyclic carbonates even at room temperature and ambient pressure.

ZTIF-8 was solvothermally synthesized by mixing $ZnAc_2\cdot 2(H_2O)$, 2-methyimidazole (2-Hmim), and 5-methyltetrazole (5-Hmtz) in DMF and ethanol, and heated at 120 °C for 48 h to give colorless crystals (see Supporting Information).

Single crystal X-ray analysis revealed that compound ZTIF-8 crystallizes in the cubic system with space group $I\bar{4}3m$. By the

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^{1}H NMR method, the ratio of 5-mtz to 2-mim is around 1:1 (Figure S1) in ZTIF-8. Each zinc center is tetrahedrally coordinated by two 5-mtz and two 2-mim ligands (Figure 1a), which leads to a 3D framework with zeotype SOD topology (Figure 1c,d). Both ligands are μ_2-linker. The SOD-type ZTIF structure is illustrated by an SOD cage (Figure 1b) which contains 24 Zn atoms and 36 azole ligands (Figure 1b,c). The solvent-accessible volume of ca. 50.3% was found by the PLATON program.[50] These voids were filled by the structurally disordered DMF molecules.

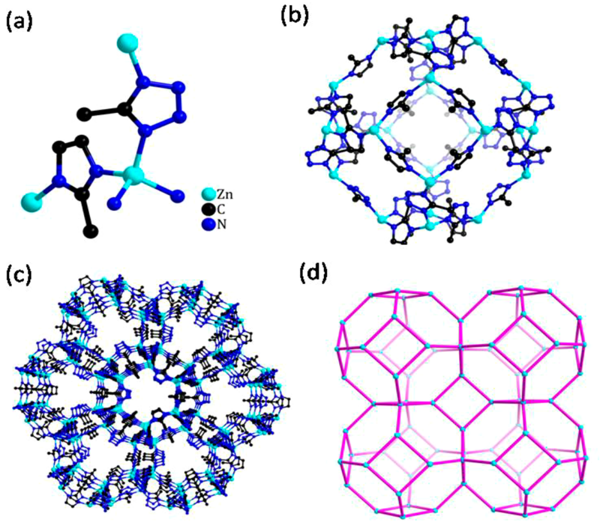


Figure 1. (a) Coordination mode of zinc atoms of ZTIF-8; (b) SOD cage constructed by Zn-tetrazolate-imdazolate; (c) view of the 3D framework of ZTIF-8 along the (111) direction; (d) topology of ZTIF-8.

The chemical stability was examined by suspending samples of ZTIF-8 in common solvents, such as ethanol, methanol, acetone, and DMF (Figure S3). The as-synthesized samples were soaked in the solvents for 7 days at ambient temperature. PXRD patterns collected for each sample showed that the solid samples of ZTIF-8 maintained their full crystallinity. These results proved the good chemical stability of ZTIF-8, which is similar as its isostructural analogue ZTIF-1.[46−49]

Gas adsorption measurements of ZTIF-8 were performed on a Micromeritics ASAP 2020 surface area and pore size analyzer. The samples were activated by solvent exchange with dry ethanol followed by evacuation at 80 °C for 6 h, respectively. The permanent porosity of ZTIF-8 was confirmed by the reversible N_2 sorption measurements at 77 K, which showed type I adsorption isotherm behavior (Figure 2a). The Langmuir and BET surface areas were 1981 m^2/g and 1430 m^2/g for ZTIF-8, respectively. A single data point at relative pressure at 0.98 gives a pore volume of 0.705 for ZTIF-8 by the Horvath−Kawazoe equation.

Furthermore, the single component sorption isotherms for CO_2 were measured at 1 atm and 273 and 288 K, respectively (Figure 2). As shown in Figure 2, the CO_2 uptake at 1 atm was 65.5 cm^3/g (2.92 mmol/g) at 273 K and 46.2 cm^3/g (2.06 mmol/g) at 288 K, which is comparable to triazole based MAF-7 and higher than that of ZIF-8, suggested that N rich surface helps to the adsorption of CO_2.

Encouraged by these results, we further explored its chemical fixation of CO_2 with epoxides to form cyclic carbonates. The experiments were carried out at room temperature and 1 atm pressure in the presence of tetra-*n*-*tert*-butylammonium bromide (TBAB) as the cocatalyst (see Supporting Information). The yields of the cyclic carbonates produced from the coupling reaction of CO_2 with epoxides were determined by the ^{1}H NMR measurements. As shown in Table 1, even at room temperature and under 1 atm CO_2 pressure, ZTIF-8 still demonstrated high catalytic activity for the cycloaddition of epichlorohydrin and CO_2 into chloropropene carbonate with a yield of >99% over 48 h. With ZIF-8 as catalyst under the same condition, a yield of 50% was achieved (Figure S6). The comparison of these results suggested uncoordinated N atoms in ZTIF-8 indeed promoted the coupling reaction of CO_2 with epoxides.[18]

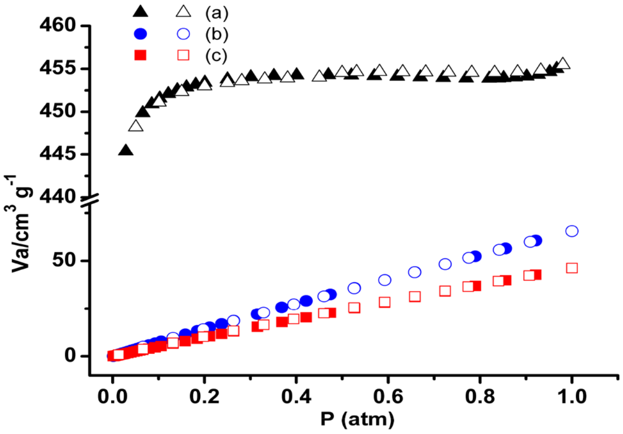
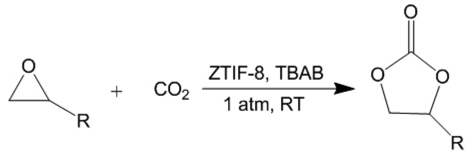


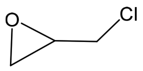
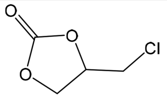
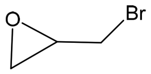
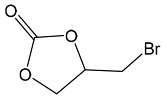
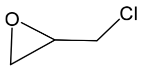
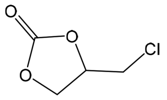
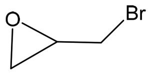
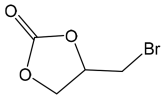
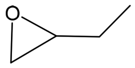
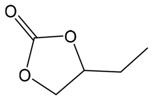
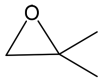
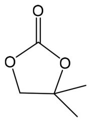
Figure 2. N_2 sorption isotherms of ZTIF-8 at 77 K (a); CO_2 sorption isotherms of ZTIF-8 at 273 K (b) and 288 K (c).

Besides this, the catalytic activity for the cycloaddition of other derivatives and CO_2 was also researched. With ZTIF-8, the yields (Table 1) of 4-ethyl-1,3-dioxolan-2-one and 4,4-dimethyl-1,3-dioxolan-2-one are 86.9% and 83.3%, respectively. The lower yield of 4,4-dimethyl-1,3-dioxolan-2-one may be due to the steric hindrance effect.[15,29] The reusability test of ZTIF-8 (Figures 3, S5 and S7) shows that the yield of chloropropene carbonate decreased from >99% (the first cycle) to 81.5% (the third cycle), and the yield of bromopropene carbonate decreased from 97.2% (the first cycle) to 81.2% (the third cycle). The decrease in yield may be due to the pore blockage of the recycled ZTIF-8 by the carbonaceous products.[43] The PXRD results of the recycled sample also confirmed that its structure showed no obvious change (Figure S10). This suggested that it can be a stable catalyst in room temperature epoxide−CO_2 cycloaddition reaction.

According to some previous reports,[6,51−53] a mechanism is proposed for the cycloaddition of epoxides and CO_2 into cyclic carbonates catalyzed by ZTIF-8. As illustrated in Figure S11, the coupling reaction is initiated by binding of the epoxide with the defective Lewis acidic Zn^{2+} sites forming the Zn−O bond. Subsequently, Br^- from TBAB attacks the coordinated epoxide to produce the ring-opening of the epoxy species. The uncoordinated N atom could easily trap CO_2, which facilitates the coupling of CO_2 and the opened epoxy to form an alkylcarbonate anion. Finally, the corresponding cyclic carbonate forms in the ring closure step with release of Br^-, and the original catalysts can be recycled for the next catalytic reaction.

Table 1. ZIF-8-Catalyzed and ZTIF-8-Catalyzed Coupling of Epoxides with CO_2



Entry	Substrate	Product	Yield (%)
1			50.0[a]
2			53.2 [a]
3			>99[b]
4			97.5[b]
5			86.9[b]
6			83.3[b]

[a] Yields are the first run of ZIF-8 as catalyst. [b] Yields are the first run of ZTIF-8 as catalyst.

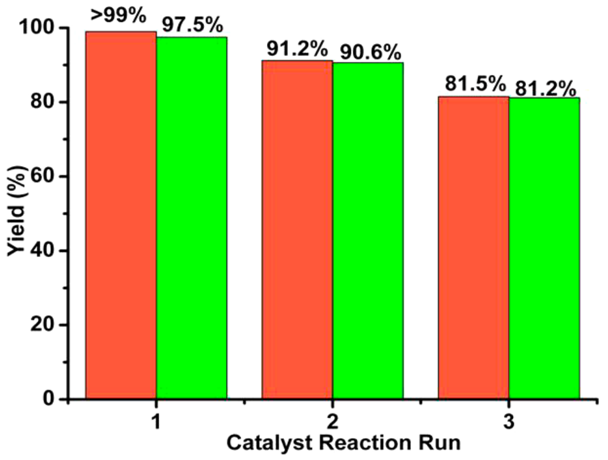


Figure 3. Histogram of recyclibility study (three cycles) for catalytic activities of ZTIF-8 in coupling of epichlorohydrin (orange bars); (b) epibromohydrin (green bars) with CO_2, respectively.

In summary, we report here a new ZTIF-8 with SOD topology by employing 2-methylimidazole and 5-methyltetrazolate ligands. ZTIF-8 exhibited permanent porosity and high catalytic activity for the chemical fixation of CO_2 at room temperature and under 1 atm CO_2 pressure.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.0c00258.

Experimental details, crystallographic studies, additional figures, and general characterization (PDF)

Accession Codes

CCDC 1959201 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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