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A room temperature synthesizable zeolitic imidazolium framework catalyst for the solvent-free synthesis of cyclic carbonates

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ABSTRACT

A zinc-based zeolitic imidazolium framework ZIF-71 was synthesized at room temperature and its structural and physical properties were exploited for the CO_2-epoxide cycloaddition reactions. ZIF-71 is found to catalyze the synthesis of cyclic carbonates under both high (120 °C, co-catalyst free) and low temperature (room temperature, with co-catalyst) conditions with > 99% selectivity. The reaction conditions, turnover frequency (TOF), selectivity, reusability and non-leaching properties of ZIF-71 was compared with that of the earlier reported Zn based ZIFs in this area of CO_2 transformation and the results showed that the ZIF-71 reporting here stays along or a step ahead of the previously reported ZIFs. More than 99% selectivity to the final five-membered products was achieved by using ZIF-71 throughout the reactions; thereby the essential criterion of 100% atom economy is well maintained. With its permanent porosity and low leaching, the ZIF-71 catalyst is reusable for more than five times. Finally, a reaction mechanism for the catalytic activity of ZIF-71 was also proposed based on the previous density functional theory (DFT) studies.

1. Introduction

A plethora of methodologies have been developed over the past few years that utilize CO_2 as a chemical feedstock to produce high-value added products owing to its abundance, renewability, non-toxicity, non-flammability, and abundance nature [1–5]. However, only a small percentage of the total amount of CO_2 is presently being consumed in chemical synthesis, which is mainly ascribed to its thermodynamic stability and chemical inertness. Catalysis plays a pivotal role in transformation reactions by using CO_2 as an alternative and sustainable C_1 source rather than treating as a waste [6,7]. The coupling reaction of CO_2 with epoxides offers a promising mode of cyclic carbonate synthesis, which is highly desirable on the grounds of efficient resource utilization and 100% atom economicity of the process (Scheme 1) [8–11]. Cyclic carbonates are non-toxic and low odor organic compounds with a wide range of industrial applications [12–16]. Detailed studies by using an extensive number of homogeneous and heterogeneous catalysts have shown that the bi-functional catalyst with either a Lewis acid/base or Lewis acid with a nucleophile can efficiently catalyze the CO_2-epoxide cycloaddition reaction [17–23].

Zeolitic imidazolate frameworks (ZIFs) are a subclass of microporous metal organic frameworks (MOFs) constituted of tetrahedrally coordinated metal atoms (Zinc or Cobalt being the major) where the M-Im-M angle is found to be resembles that of the Si-O-Si bonds of zeolites. ZIFs are poised with such a great potential to catalyze the transformations of choice on a large scale, owing to its desirable properties such as, 1) high surface area and easy synthesizability, 2) high thermal stabilities, 3) in expensiveness in synthesis, 4) less environmental impacts, and 5) modifiable porosity, acidic-basic strength, metal exchange, etc [24–34]. Most recently ZIFs have been widely accepted as new generation materials for post-capture transformation of CO_2 through the cycloaddition reaction using epoxides to produce cyclic carbonates [35–39].

The earlier reported ZIFs for CO_2-epoxide cycloaddition reaction, viz., ZIF-8, ZIF-68, ZIF-95, ZIF-23, ZIF-90 and F-ZIF-90 are basically built from tetrahedral zinc and imidazole units as ligand [40–45]. ZIF-8 is a crystalline microporous material which has the same topology as like that of the some aluminosilicate zeolites. The T-O-T (T = Si, Al, P) bridges in zeolites are substituted by M-Im-M (M = Zn or Co, Im = Imidazole ligand) bridges in ZIFs [46]. The framework of the ZIF-8 consists of large pores of diameter 11.6 Å, which are accessible through small apertures of 3.4 Å [47]. ZIF-68 has **gme** topology and it consists of one 2-nitroimidazole and one benzimidazole ligands per Zn in an asymmetric unit, displaying large pores with diameter of 10.3 Å [48]. ZIF-95 has **poz** topology exhibiting large pores with diameter of 24 Å and accessible through apertures of 3.7 Å [49]. ZIF-23 has **dia**

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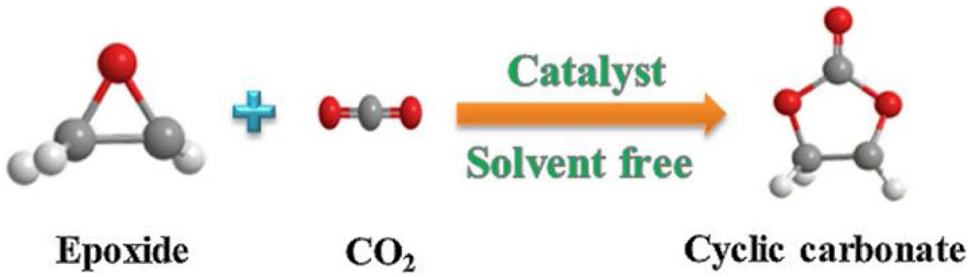

Scheme 1. Solvent free synthesis of cyclic carbonates from CO_2 and epoxides.

topology consisting of zinc as metal coordinated by 4-azabenzimidazole linkers, and it has pores with diameter of 4.2 Å [50]. The asymmetric unit of ZIF-90 consists of tetrahedral zinc and imidazolate-2-carboxaldehyde units. The carbonyl groups present in the ZIF-90 has a favorable chemical potential to interact with substrates. The free aldehyde groups present in the framework of ZIF-90 allowed its covalent functionalization to yield F-ZIF-90 [51]. Eventhough, the earlier reported Zn-based ZIFs have been achieved moderate yields at relatively mild reaction conditions, the selectivity towards the final cyclic carbonate was found to substantially decreased at higher temperature and longer reaction times. The CO_2 fixation reactions via cyclic carbonate synthesis adorn the tag of being green due to its 100% atom economic nature, therefore it is necessary to bring forth high selectivity to the final desired product both at higher and lower reaction temperatures. Here in this work, we report the catalytic potential of a Zn-based ZIF-71 as a room temperature synthesizable heterogeneous catalyst for CO_2 fixation reactions, and its reaction conditions, selectivity, reusability and non-leaching properties were compared with that of the earlier reported ZIFs in this area of CO_2 transformation.

2. Experimental section

2.1. Synthesis of ZIF-71

ZIF-71 was synthesized in room temperature from inexpensive precursors using low boiling ethanol as solvent [52]. 73.4 mg zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$, 97%, Alfa Aesar) and 21.9 mg 4,5-dichloroimidizole ($C_3H_2Cl_2N_2$, 98%, Alfa Aesar) were dissolved separately in total 30 mL of ethanol. After dissolving separately, zinc acetate was added to 4,5-dichloroimidizole and stirred for 24 h at room temperature. After finishing the time, the final filtrate was centrifuged and washed with ethanol and air dried at 70 °C for one day to remove the remaining the solvents. Elemental analysis calculated (%) for $C_6H_2Cl_4N_4Zn$: C 21.37, H 0.60, Cl 42.04, N 16.61, Zn 19.38; found: C 21.36, H 0.80, Cl 42.10, N 16.44, Zn 19.30.

2.2. Cycloaddition of epoxides and CO_2

The CO_2-oxirane coupling reactions were carried out in a steel autoclave reactor of 25 mL volume equipped with a magnetic stirrer. The calculated amounts of catalyst, co-catalyst and epoxide were charged into the reactor. The coupling reactions were performed for different time intervals using different temperatures and pressures of CO_2. After finishing the pre-desired reaction time, the reactor was allowed to cool down naturally to room temperature (0 °C in case of PO). Toluene/dichloromethane was used as an internal standard cum solvent. The final filtrate was centrifuged to remove the catalyst completely and the supernatant was tested using a gas chromatograph (GC, Agilent HP 6890 A), equipped with a capillary column (HP-5, 30 m × 0.25 mm, flame ionization detector) to determine the conversion, selectivity and yield of the desired cyclic carbonate.

3. Results and discussions

3.1. Crystal structure of ZIF-71

Generally in ZIF materials, the Zn^{2+} and Co^{2+} metal atom ions are linked with the N-atoms of deprotonated imidazolate derivatives to form neutral frameworks. ZIF-71 was first reported by Yaghi and it has RHO topology which consists of Zn as metal center and 4,5-dichloroimidazole as the ligand [53]. The coordination environment of the framework consists of zinc metal center surrounded by four 4,5-dichloroimidazole linkers with aperture size of 4.2 Å and pore cavity of 16.5 Å. The coordination environments built by 4,5-dichloroimidazole ligands around Zn^{2+} centers and their packing are displayed in Fig. 1. The average Zn-N distance in ZIF-71 was measured to be ranging from 1.9 to 2.0 Å. The C-C distance was measured to be around 1.7 Å and the C-N distance was found to be around 1.3 Å.

3.2. Characterization results of ZIF-71

The crystallinity of ZIF-71 was probed by PXRD analysis (Fig. 2). The position and intensity of peaks obtained for the as-synthesized ZIF-71 was compared with that of the simulated single crystal XRD pattern obtained from the crystallographic information file (CIF) of ZIF-71. Detailed information about the presence of functional groups in the framework was obtained from the FT-IR spectra of ZIF-71 (Fig. S1, ESI†). The textural features of ZIF-71 were analyzed by FE-SEM analysis and its image shows the presence of uniformly formed rhombic dodecahedron shaped crystals with similar morphology (Fig. 3). The thermal stability, nature of the framework and robustness of ZIF-71 catalyst was analyzed by using thermogravimetric analyses (Fig. 4). No severe degradation was observed between room temperature and 400 °C. A major weight loss of 56 wt% was observed after 400 °C, which indicates that the ZIF-71 is thermally stable up to approx. 400 °C.

3.3. Catalytic activity of ZIF-71 compared with that of the earlier reported ZIFs

Cycloaddition reactions using ZIF-71 catalyst was performed under various reaction conditions by employing different epoxides to make a direct comparison with its Zn containing analogues (ZIF-8, ZIF-68, ZIF-95, ZIF-90 and F-ZIF-90) reported previously (Table 1). ZIF-8 was the first reported catalyst among these which catalyzes the CO_2-epichlorohydrin (CO_2-ECH) cycloaddition reaction [40]. Non-Functionalized ZIF-8 obtained an ECH conversion of 84% with only 52% selectivity to the desired product at 80 °C, 0.7 MPa and 4 h time (ECH = 18 mmol, 0.13 mmol Zn, 1.97 mol%) (Table 1, entry 1). Under the same reaction conditions of ZIF-8, ZIF-71 achieved an ECH conversion of only 50% by using a catalyst concentration of 1.2 mol% (Table 1, entry 2). A less catalytic activity was obtained with ZIF-71 catalyst when compared with that of ZIF-8. But it is important to note that ZIF-71 maintained > 99% selectivity to the desired chloropropene carbonate product. The functionalized ZIF-8 achieved an ECH conversion of 100% at 100 °C, the selectivity to chloropropene carbonate was