

Cycloaddition of carbon dioxide with propylene oxide using zeolitic imidazolate framework ZIF-23 as a catalyst

Hyeongseok Ryu*, Roshith Roshan*, Moon-Il Kim**, Dong-Woo Kim**,
Manickam Selvaraj***, and Dae-Won Park*,†

*School of Chemical and Biomolecular Engineering, Pusan National University, Busan 46241, Korea

**Korea Research Institute of Chemical Technology, Ulsan 44412, Korea

***Nanotechnology and Catalysis Research Center, University of Malaya, Kuala Lumpur 50603, Malaysia

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Abstract—Zeolitic imidazolate framework ZIF-23 was prepared and used as catalyst for the solventless synthesis of cyclic carbonate from CO₂ and propylene oxide with or without TBAB co-catalyst. ZIF-23 catalysts were prepared by a solvothermal or microwave method and they were characterized by various physicochemical techniques such as XRD, FT-IR, BET, TGA, and FE-SEM. The effects of reaction parameters such as temperature, reaction time, CO₂ pressure, and co-catalyst on the reactivity of catalyst were investigated. ZIF-23 was recyclable up to four times without any considerable loss of its initial activity. Reaction mechanism containing the role of ZIF-23 with TBAB co-catalyst was also proposed.

Keywords: Zeolitic Imidazolate Framework, ZIF-23, Cycloaddition, Propylene Oxide, CO₂

INTRODUCTION

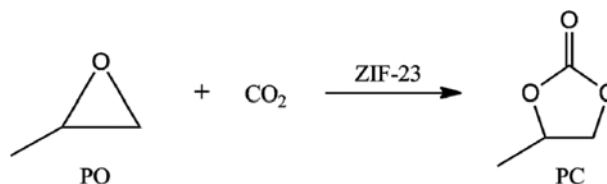
The catalytic conversion of CO₂ to cyclic carbonates has attracted increasing interest in research aimed at resource utilization and mitigation of global warming due to greenhouse effects. The reaction of CO₂ with epoxides is considered as an atom efficient synthesis for the cyclic carbonates [1]. However, the high thermodynamic stability of CO₂ necessitates the need for a catalyst to materialize the CO₂-epoxide cycloaddition. Various catalysts such as metal halides [2-4], organic bases [5,6], metal oxides [7-9], metal complexes [10-12], ionic liquids (ILs) [13-17], and homogeneous metal salen-based catalysts [18-20] have been developed. However, since heterogeneous catalysts have the inherent advantage of easier separation and work-up process, the research in CO₂-epoxide cycloaddition has been much devoted to the development of highly efficient heterogeneous catalysts. Ionic liquids grafted to various heterogeneous solid supports like silica [21-25], synthetic polymer resin [26,27] and biopolymers [28-32] have been extensively reported as catalysts for the formation of cyclic carbonates.

Recently, the material research world has reported a class of advanced nano/micro porous materials termed zeolitic imidazolate frameworks (ZIFs), which have some very peculiar similarities with the actual zeolites [33-35]. Zeolitic imidazolate frameworks primarily are constituted of an imidazole linker coordinated with a tetrahedral metal atom, basically Zn or Co. Since these ZIFs sim-

ultaneously bear the characteristics of both metal organic frameworks (MOFs) and zeolites, they generally display properties that combine the advantages of both zeolites and MOFs, such as ultrahigh surface areas, high crystallinities, abundant functionalities and relatively appreciable thermal stabilities. Therefore, ZIFs have mediated a handful of organic transformations such as the Knoevenagel reaction [36,37], Friedel-Crafts acylation [38], monoglyceride synthesis [39], oxidation [40,41], and epoxidation [42]. Our group and others have recently used ZIFs having high surface area and porosity for the epoxide-CO₂ cycloaddition reactions [43-51].

ZIFs were found to serve standalone catalysis, i.e., they exhibited catalytic activity by themselves without the assistance of any co-catalysts or specific organic solvents [45,48,51-53]. Not only does this render greener credentials to this way of CO₂ fixation, but provides an elite way of exploiting the co-operative catalysis of the highly active Lewis acidic metal centres with the basic imidazole functionalities.

ZIF-23 was first reported by Hayashi et al. in 2007 [33] and it has a diamond topology. However, to the best of our knowledge, there is no report on the catalytic conversion of CO₂ by using ZIF-23 as a catalyst. We report here the catalytic prospective of ZIF-23 for the cycloaddition of propylene oxide (PO) and CO₂ (Scheme 1).



Scheme 1. Synthesis of PC from PO and CO₂ with ZIF-23 catalyst.

†To whom correspondence should be addressed.

E-mail: dwpark@pusan.ac.kr

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EXPERIMENTAL

1. Preparation of Catalyst

4-Azabenzimidazole (azb) (99%), the metal salts (>99%), and all the epoxides and DMF were bought from Sigma-Aldrich, Korea. CO_2 (99%) was purchased from MS Corp, Korea, and anhydrous organic solvents were purchased from TCI Chemicals, Korea. ZIF-23 was synthesized by solvothermal method according to the procedure reported by Hayashi et al. [33]. A solid mixture of zinc nitrate tetrahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (52 mg, 0.2 mmol) and 4-azabenzimidazole (119 mg, 1.0 mmol) was dissolved in 1 mL DMF in a 4 mL vial. The vial was tightly capped and heated at 100 °C in an isothermal oven for one day to yield pale yellow prism crystals. After cooling of the vial to room temperature, the crystals were rinsed three times with DMF (5 mL) and dried in air for 30 min. ZIF-23 was also prepared by the microwave method. A solid mixture of zinc nitrate tetrahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.26 g, 1 mmol) and 4-azabenzimidazole (0.6 g, 5.0 mmol) was dissolved in 15 mL DMF in a 30 mL flask. The solution was placed in a microwave reactor and irradiated at 100 W of power for 3 min. The cooling and washing procedure was the same as that of the solvothermal method.

2. Characterization of Catalyst

The synthesized ZIF-23 was characterized according to the previous reports [33]. Fourier transform infrared (FT-IR) spectra were obtained on an AVATAR 370 Thermo Nicolet spectrophotometer with a resolution of 4/cm. Thermogravimetric analysis (TGA) was with an AutoTGA 2950 apparatus with a heating rate of 10 °C/min from 40 °C to 600 °C in nitrogen under a flow of 100 mL/min. X-ray diffractions (XRD) were recorded as powders in a Rigaku Ultima IV diffractometer using the $\text{Cu K}\alpha$ radiation (40 kV, 40 mA) with step size $\Delta 2\theta = 0.02^\circ$, time per step = 4 s. The surface morphology was observed using S-4200 field emission scanning electron microscope

(FE-SEM, Hitachi-3500N). The metal content of the catalysts was obtained from ICP-OES analysis using ULTIMA2 CHR (1.5 kW, 40.68 MHz, 130-800 mm) with mono chromat HDD and a poly chromat PMT detector.

3. CO_2 -epoxide Cycloaddition Reaction

All the reactions were in a 25 mL stainless-steel batch reactor with a magnetic stirrer at 600 rpm. In a typical batch reaction process, a predetermined amount of the catalyst was charged into the reactor containing the epoxide. The reactor was pressurized with CO_2 to the preset pressure at room temperature. The reactor was then heated to the desired temperature, and the reaction was started by stirring at 600 rpm. In a semi-batch operation, a back-pressure regulator was installed to maintain reactor pressure constant. Therefore, CO_2 was supplied automatically as soon as it was consumed by the reaction. The reaction was carried out under various temperatures and pressures of carbon dioxide with different reaction times. After the completion of the reaction, the reactor was cooled to room temperature (zero degree in case of propylene oxide) and the products were identified by a gas chromatograph (Agilent

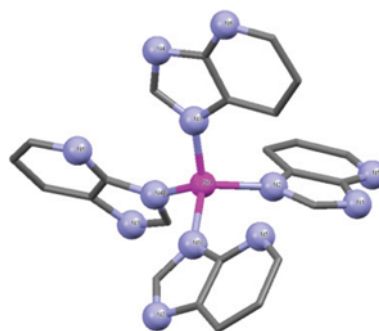


Fig. 1. Basic asymmetric unit of ZIF-23 (hydrogens are omitted for clarity).

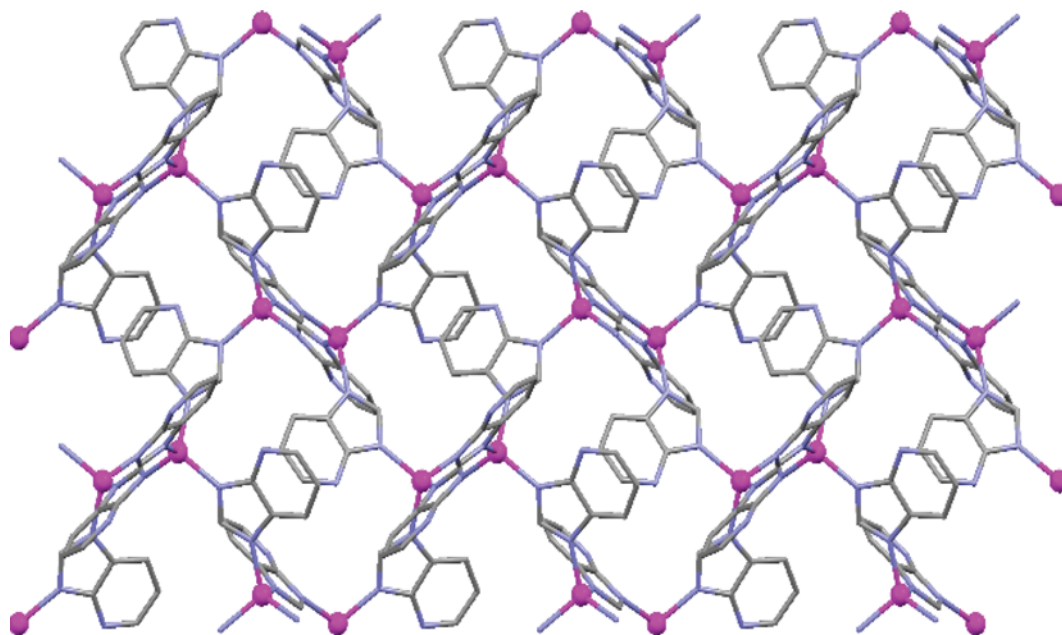


Fig. 2. Packing diagram of ZIF-23 viewed along b-axis [33].

HP 6890 A) equipped with a capillary column (HP-5, 30 m*0.25 μm) using a flame ionized detector. The product yield was determined by using toluene as internal standard.

RESULTS AND DISCUSSION

1. Characterization of Catalysts

ZIF-23 was obtained in crystalline form suitable for single crystal X-ray diffraction studies. The repeating unit is shown in Fig. 1. The structure consists of Zn(II) ions linked by single 4-azabenzimidazole bridges, giving a 3-D extended array (Fig. 2). The X-ray powder diffractograms of ZIF-23 prepared by the solvothermal method and microwave method are compared with that calculated from the single crystal data (Fig. 3). The prepared ZIF-23 samples by the two methods confirm the crystalline ZIF-23 structure.

ZIF-23 samples were further analyzed for FT-IR, as shown in Fig. 4. The C-N stretching vibration of the aromatic imidazole rings

was observed at $1,590\text{ cm}^{-1}$, and Zn-N vibration was observed at 421 cm^{-1} .

The 3-D diamond-like structure seems to confer thermal stability on ZIF-23, as shown by thermal gravimetric analysis (TGA) in

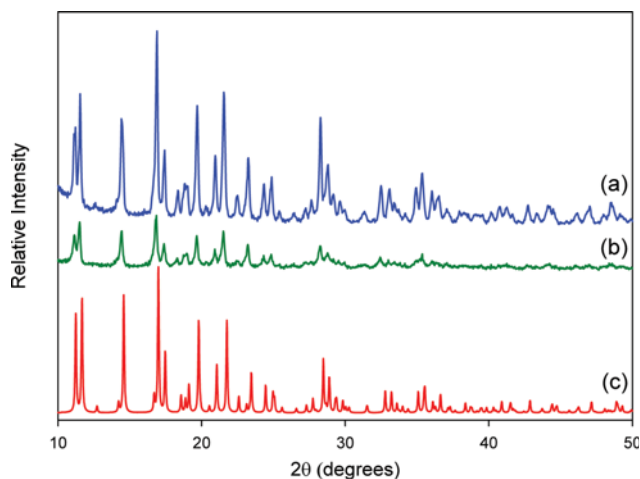


Fig. 3. XRD analysis of (a) ZIF-23 (solvothermal) (b) ZIF-23 (microwave) (c) ZIF-23 (single crystal simulated).

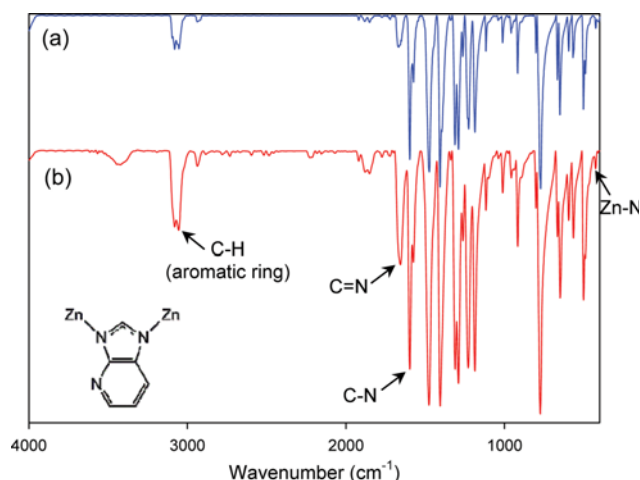


Fig. 4. FT-IR analysis of (a) ZIF-23 (solvothermal) (b) ZIF-23 (microwave).

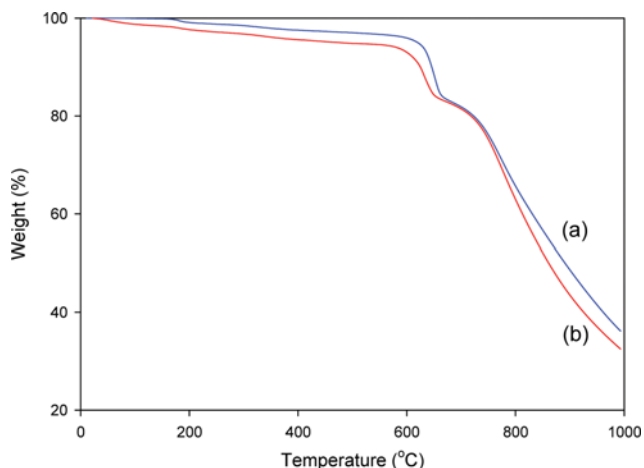
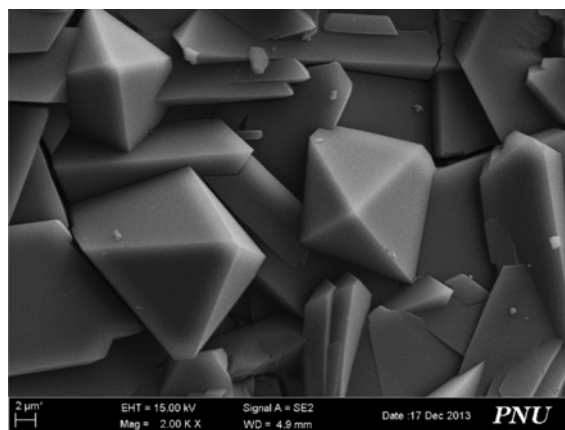
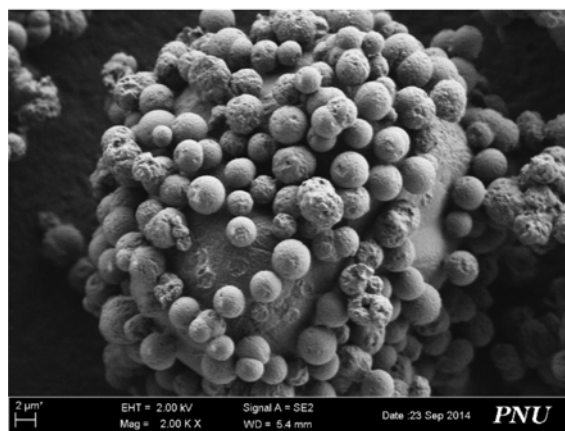


Fig. 5. TGA analysis of (a) ZIF-23 (solvothermal) and (b) ZIF-23 (microwave).



(a) ZIF-23 (Solvothermal)



(b) ZIF-23 (Microwave)

Fig. 6. FE-SEM images of ZIF-23.

Table 1. Reactivity test results with ZIF-23

Catalyst (mmol)	Co-catalyst (mmol)	Temperature (°C)	Pressure (MPa)	Time (h)	Conversion (%)	Yield (%)
-	-	60	1.2	6	0	0
ZIF-23 (0.8)	-	60	1.2	6	2.6	2.3
ZIF-23 (0.8)	-	140	3.0	24	71.2	70.3
ZIF-23 (0.1)	-	140	3.0	24	30.6	30.2
-	TBAB (0.8)	60	1.2	6	18.5	17.9
ZIF-23 (0.8)	TBAB (0.8)	60	1.2	6	50.0	49.1

Reaction conditions: PO=3 mL (42.87 mmol). Batch operation

Fig. 5. ZIF-23 samples were stable to about 600 °C. Decomposition with continuous weight loss occurred from this, and a total weight loss of about 65% of the initial mass was observed. Therefore, ZIF-23 was highly thermally stable, especially in the range of its catalytic reaction carried out at 60–120 °C.

The physical appearance of ZIF-23 was analyzed upon using FE-SEM microscopy. The crystalline nature of the octahedral form ZIF-23 was revealed for the solvothermally prepared ZIF-23. However, a spherical form was observed for ZIF-23 prepared by the microwave method. As evident from Fig. 6, the width of each ZIF-23 crystal falls into between 2–20 µm.

2. Reactivity Test of ZIF-23

Propylene oxide (PO) was used as the model substrate to evaluate the catalytic activity of ZIF-23. Since ZIF-23 prepared by the microwave method showed very similar reactivity to that prepared by the solvothermal method, the following reactivity test studies were performed with the ZIF-23 prepared by the solvothermal method.

Table 1 shows the conversion of PO and yield of propylene carbonate (PC). No reaction occurred at 60 °C, 1.2 MPa, in 6 h without a catalyst. Even ZIF-23 alone showed only very low PO conversion at the same reaction condition. However, at 140 °C and after 24 h, ZIF-23 alone exhibited 71.2% of PO conversion with over 98% of PC selectivity. When a co-catalyst tetrabutylammonium bromide (TBAB) was used together with ZIF-23, a big increase of PO conversion (50.0%) was obtained compared to the conversion by the co-catalyst TBAB alone (18.5%) at 60 °C in 6 h. Therefore, a

synergistic effect of ZIF-23 and TBAB was observed; their co-operative role will be discussed for the mechanism.

The effect of different reaction conditions on PO conversion and PC selectivity was investigated for ZIF-23. Table 2 shows the effect of temperature on the reactivity of ZIF-23. The conversion of PO increased from 3.4 to 63.3% upon increasing with the temperature from 20 °C to 140 °C. The selectivity of cyclic carbonate was maintained over 97% at the temperature range lower than 120 °C, but decreased to 95% when the temperature was increased to 140 °C. Similar trend in the decrease in selectivity was also reported in other literature, where the authors have mentioned the formation of diols and dimers as side products of cyclic carbonate [51]. In a semi-batch operation where CO₂ is continuously supplied to maintain the reactor pressure constant at 1.2 MPa, the conversion increased to 84.3% at 120 °C, much higher than that in the batch operation (61.9%). This might be due to the high concentration of CO₂ in the semi-batch operation. In the batch operation at 120 °C, the reactor pressure decreased from 1.2 MPa to 0.5 MPa after 6 h by the consumption of CO₂ during the reaction.

Since the chemical fixation of CO₂ is a 'so-called' green reaction and the ultimate intention in this field of research is aimed at energy conservation, we continued our ZIF-23 based catalysis studies at low temperature of operation such as 60 °C. Table 3 exhibits the dependence of the reactivity on the reaction time between 2 and 20 h. Even though the PO conversion increased from 18.2% to 57.5% with increasing reaction time from 2 to 15 h, it was maintained nearly constant at 20 h.

The effects of the applied CO₂ pressure on the formation of cyclic carbonate are shown in Table 4. The PO conversion was found

Table 2. Effect of temperature on the reactivity of ZIF-23

Temperature (°C)	PO Conversion (%)	PC Selectivity (%)
20	3.4	99
40	20.3	99
60	50.0	99
80	55.6	99
100	58.8	98
120	61.9	97
140	63.3	95
120 ^a	84.3	97

Reaction conditions: ZIF-23 (0.8 mmol), TBAB (0.8 mmol), PO=3 mL (42.87 mmol), initial CO₂ pressure=1.2 MPa, reaction time=6 h, batch operation

^aSemi-batch operation where CO₂ is continuously supplied to maintain the reactor pressure constant

Table 3. Effect of reaction time on the reactivity of ZIF-23

Reaction time (h)	PO conversion (%)	PC selectivity (%)
2	18.2	99
4	37.3	99
6	50.0	99
8	53.3	99
10	55.8	99
15	57.5	97
20	57.9	96

Reaction conditions: ZIF-23 (0.8 mmol), TBAB (0.8 mmol), PO=3 mL (42.87 mmol), Initial CO₂ pressure=1.2 MPa, temperature=60 °C, batch operation

Table 4. Effect of CO₂ pressure on the reactivity of ZIF-23

Pressure (MPa)	PO conversion (%)	PC selectivity (%)
0.6	19.8	99
0.9	43.4	99
1.2	50.0	99
1.5	52.8	99
1.8	53.3	99
1.2 ^a	74.5	98

Reaction conditions: ZIF-23 (0.8 mmol), TBAB (0.8 mmol), PO=3 mL (42.87 mmol), temperature=60 °C, reaction time=6 h, batch operation

^aSemi-batch operation where CO₂ is continuously supplied to maintain the reactor pressure constant

to have significant dependence on the pressure of CO₂. The conversion increased from 19.8 to 53.3% when the pressure was increased from 0.6 to 1.8 MPa, ensuring that more and more fruitful interactions between the active site of the catalyst and CO₂ were made possible by additional amounts of CO₂. The selectivity remained high for all the experiments. In the semi-batch operation at 60 °C and 1.2 MPa, the conversion was increased to 74.5% since higher amount of CO₂ was continuously supplied to maintain the reactor pressure constant.

The influence of the different quaternary ammonium co-catalysts was studied with TBAC(Cl), TBAB(Br), and TBAI(I), as shown in Table 5. The order of nucleophilicity of halide anion was Cl⁻ < Br⁻ < I⁻; however, the PO conversion increased as TBAC < TBAI < TBAB. Lower PO conversion for more nucleophilic TBAI compared to TBAB seems due to its steric hindrance for the approach of PO or CO₂ to the ZIF-23 catalyst.

Next, we investigated the activity of ZIF-23 for other epoxides, and performed cycloadditions in the presence of 1.87 mol% of ZIF-23 at a reaction temperature of 120 °C, CO₂ pressure of 1.2 MPa and reaction time of 12 h under semi-batch operation. As shown in Table 6, the catalytic system was found to be effective for a variety of terminal epoxides. The styrene oxide showed lower substrate activity among the terminal epoxides, probably because of the low reactivity of the β -carbon atom of styrene oxide [54]. Cyclohexene oxide showed the lowest activity, which might be due to the high steric hindrance caused by the cyclohexene ring [55].

Table 7 illustrates the reusability performance of ZIF-23 catalyst in PO-CO₂ cycloaddition. After the reaction, the catalyst was separated by mere centrifugation using dichloromethane and dried at

Table 5. Effect of other co-catalysts on the reactivity

Co-catalyst	Conversion (%)	Selectivity (%)
TBAB	50.0	99
TBAC	22.8	99
TBAI	40.6	99

Reaction conditions: ZIF-23 (0.8 mmol), TBAX (0.8 mmol), PO=3 mL (42.87 mmol), initial CO₂ pressure=1.2 MPa, temperature=60 °C, batch operation

Table 6. Synthesis of cyclic carbonates from other epoxides

Reactant	Conversion (%)	Selectivity (%)
Propylene oxide	91.3	99
Styrene oxide	84.9	98
Allylglycidyl ether	90.2	98
Epichlorohydrin	92.2	99
Cyclohexene oxide	34.0	97
Epoxy hexane	89.7	97

Reaction conditions: ZIF-23 (0.8 mmol), TBAB (0.8 mmol), epoxide=42.87 mmol, temperature=120 °C, reaction time=12 h, pressure=1.2 MPa, semi-batch operation

80 °C for a few hours. The appearance of the recycled catalyst was exactly similar to that of the fresh ZIF-23. Even on the third reuse, ZIF-23 catalyst showed only a slight decrease in PO conversion without any compromise in the selectivity to PC. The XRD and FT-IR analyses of the third reused ZIF-23 showed the same results as the fresh one. The recyclability of ZIF-23 was also confirmed by ICP-AES analysis of the third reused catalyst, which showed less than 1.2 wt% of Zn leaching in the liquid phase after the reaction.

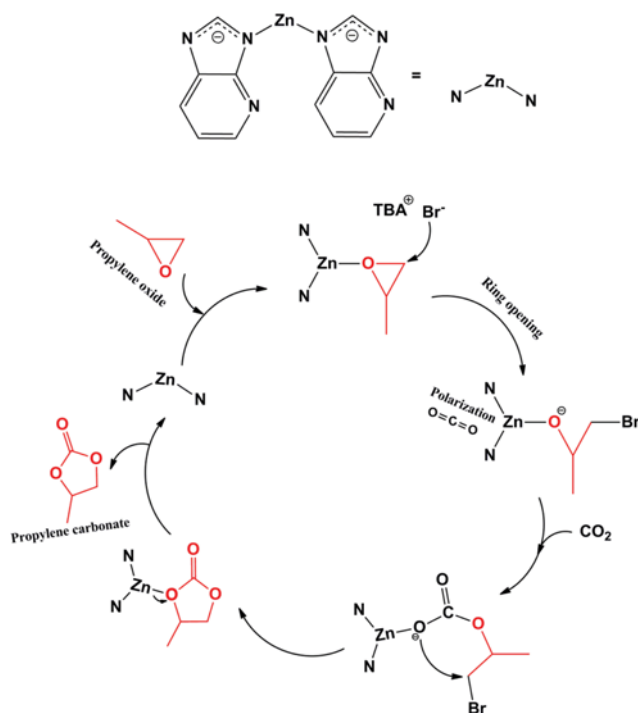
3. Reaction Mechanism

Previous reports for MOF-catalyzed cycloaddition of CO₂ and epoxides suggest that in the presence of a strong nucleophilic anion, Lewis/ Brønsted acid sites can activate the epoxides for ring opening, and certain groups, which can polarize the thermodynamically stable CO₂ molecule to facilitate CO₂ insertion, can effectively catalyze the cycloaddition of epoxide and CO₂ [56]. Based on these observations and our previous studies by DFT [57-59], a plausible mechanism for the cycloaddition of PO in presence of ZIF-23 co-catalyzed by TBAB is illustrated in Scheme 2. In ZIF-23, the O⁻ atom of PO interacts with Zn Lewis acid site. Subsequently, the Br⁻ of TBAB attacks the least hindered carbon atoms, resulting in epoxide ring opening. The succeeding step is the insertion of CO₂ between the Zn metal and alkoxide group, forming an intermediate with the elimination of Br⁻. Finally, the ring closure takes place to generate PC, and the regenerated ZIF-23 moves to the next cycle of cycloaddition by coordinating to the next epoxide molecule. Different from scheme 2, ZIF-23 alone showed 71.2% of PO conversion at 140 °C, 3.0 MPa and 24 h (Table 1) since a concerted ring-opening and insertion of CO₂ can occur with ZIF-23. The transition state relates to the simultaneous stretching/breaking of C-O bond of PO, and the bending of the CO₂ molecule, leading to the

Table 7. Reusability test

Run	Conversion (%)	Selectivity (%)
1	91.3	99
2	89.4	97
3	88.7	97
4	87.6	98

Reaction conditions: ZIF-23 (0.8 mmol), TBAB (0.8 mmol), PO=42.87 mmol, temperature=120 °C, reaction time=12 h, pressure=1.2 MPa, semi-batch operation



Scheme 2. Reaction mechanisms containing the role of ZIF-23 with TBAB.

formation of two new C-O bonds [60].

CONCLUSIONS

A zeolitic imidazole framework, ZIF-23 was prepared by a solvothermal and microwave method. ZIF-23 was found to render appreciable catalytic results towards the synthesis of five membered cyclic carbonates in a solventless medium. A plausible reaction mechanism was proposed with the co-catalyst TBAB. The synergistic effects for the ZIF-23/TBAB system come from the Lewis acidity of Zn atom, polarizability of N atom, and nucleophilicity of TBAB. ZIF-23 exhibited promising reusability, which displayed the good chemical and thermal stability possessed by the framework under the conditions employed for the cycloaddition reaction.

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