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ARTICLE

Ionic liquid tethered post functionalized ZIF-90 framework for the cycloaddition of propylene oxide and CO₂

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A novel heterogeneous one-component catalyst was developed by the covalent post functionalization of zeolitic imidazolate framework-90 (ZIF-90) with pyridinium based ionic liquid (IL) to generate IL supported ZIF-90 (IL-ZIF-90). The synthesized catalyst has been characterized using a range of analytical, spectroscopic, and electron microscopy techniques followed by successful employment for the solventless cycloaddition of epoxides and CO₂ to yield cyclic carbonates under mild reaction conditions. The effects of reaction parameters like catalyst amount, reaction time, reaction temperature, and CO₂ pressure has been investigated. A reaction mechanism for the IL-ZIF-90 catalyzed PO–CO₂ cycloaddition has been proposed on the basis of density functional theory (DFT) calculations. The catalyst system was separable by centrifugation and reused for four consecutive times successfully. In general, it can be suggested that IL supported porous metal organic frameworks (MOFs) may introduce a new class of highly porous catalyst species showing excellent CO₂ transforming capability.

Introduction

CO₂, its steadily increasing atmospheric concentration and the resulting ramifications on the earth's climate is the primary concern for the scientific community.¹ Several strategies are under assessment for CO₂ reduction and the most effective modes could be carbon capture and storage (CCS) techniques like gaseous storage (geological formations), liquid storage (in oceans), solid storage (metal oxides react with CO₂ and get stable carbonates), cryogenic distillation, membranes, gas hydrates, chemical looping, absorption (alkanol amines, ionic liquids (ILs)) and adsorption (zeolites, metal organic frameworks (MOFs)). Nevertheless it possesses various disadvantages like energy loss, corrosion, slow adsorption kinetics, low CO₂ selectivity, separation difficulties, membrane impurities, ocean acidification etc.² Alternative stratagem to mitigate the CO₂ amounts could be transmuting the captured CO₂ to valuable products, due to the possibility of using CO₂ as a safe and inexpensive C1 component to yield expedient organic compounds. However, the activation of CO₂ is an unnerving task because of its high thermodynamic stability. In order to

overcome its inertness, several catalysts have been developed over the years that are proficient of transforming CO₂ into suitable chemicals. Amongst the many reactions linking CO₂, synthesis of cyclic carbonates from epoxides under catalytic conditions has drawn much devotion because of its 100% atom economy.³ Numerous catalysts have been developed for their production by the coupling of CO₂ with epoxides illustrated by alkali metal salts, metal oxides, transition metal complexes, Schiff bases, ion-exchange resins, functional polymers, ILs etc.⁴ ILs have been employed widely as the most efficient catalysts for the cycloaddition of CO₂ and epoxides, but as of their homogenic nature, product separation and catalyst recovery are difficult.⁵ Henceforth, ILs has been successfully grafted to various solid supports like silica materials, polymers and biopolymers etc.⁶

As a new class of crystalline porous materials, metal organic frameworks (MOFs) have attracted tremendous interest, and an enormous amount of MOF structures have been designed and synthesized for various energy and environment relevant applications, such as gas sorption/ storage, separation, chirality, conductivity, non-linear optics, luminescence, sensors magnetism, drug delivery, as well as catalysis. The major characteristics of MOFs are accessible pore volumes, ordered pores, high internal surface area, high adsorption capacity, diverse means of functionalization etc. By a judicious design of linker length and with variations in coordination modes, pores of desirable size shall be achieved in MOFs.⁷ Generally, the ability to encapsulate guests, pore size tunability, and the potentials to functionalize with desired acid-base sites are the key factors which offer MOFs huge potentials in the field of catalysis.⁸ A subclass of MOF where metal (Zn, Cu) is tetrahedrally connected to imidazolate ligands, known as

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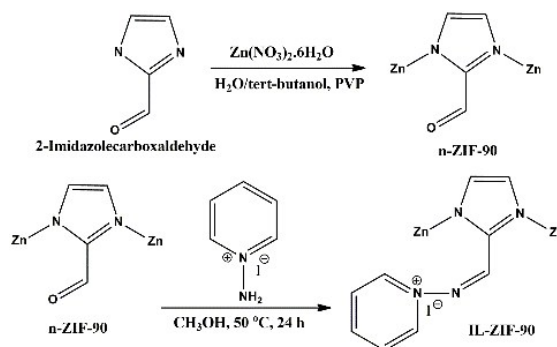
zeolitic imidazolate frameworks (ZIFs), resemble zeolites where Zn^{2+} play the role of silicon and the imidazolate anions form bridges that mimic the role of oxygen in zeolites. ZIFs offer wider porosity, exceptional thermal and chemical stability, exhibit remarkable uptake capacities for CO_2 and can selectively separate CO_2 from industrially relevant gas mixtures.⁹ Recently, few works have been pondering to incorporate ILs to MOFs there by enhance the capability of MOFs for CO_2 capturing.¹⁰ It has seen that amalgamation of functional groups like amino groups into the organic linkers will increase the CO_2 affinity towards MOFs thereby increasing the concentration of CO_2 near by the catalyst sites.¹¹ Combining a solid porous MOF that can meritoriously capture CO_2 with a CO_2 fondness homogeneous species like ILs could introduce not only the advantage of recyclability but also enhance the catalytic activity for the cycloaddition of epoxides and CO_2 . Until now, ILs have been employed as co-catalyst along with MOFs to acquire optimal results for the synthesis of cyclic carbonates from epoxides and CO_2 since catalytic performance was found to be poor for utmost MOFs.¹² Lately, our group has shown the successful employment of ZIF-90, a highly porous ZIF series for the solventless synthesis of cyclic carbonates from epoxides and CO_2 without the presence of co-catalysts.¹³ Even though a few methodologies have been reported for the post functionalization of ZIF-90 by means of amine condensation, an ionic functional group is desirable for catalyzing cycloaddition.^{14a-d} Hence here we perform the synthesis of ZIF-90 (n-ZIF-90) and thereafter execute for the first time the assimilation of IL (aminopyridinium iodide) onto n-ZIF-90 to obtain IL-ZIF-90 (Scheme 1) for the provision of a single component catalyst aimed at the solventless cycloaddition of propylene oxide (PO) and CO_2 (Scheme 2). Moreover, the mechanism prevailing the role of IL-ZIF-90 in activating the PO- CO_2 cycloaddition has been studied through density functional theory (DFT) calculations.

Result & Discussion

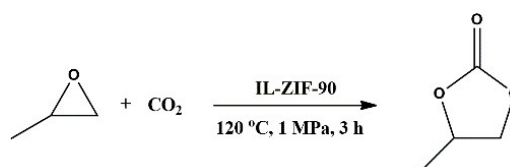
Characterizations

From the XRD peaks of n-ZIF-90 and IL-ZIF-90 shown in Fig. 1, it is clear that all the peaks of synthesized n-ZIF-90 matches with that of simulated ZIF-90, confirming the successful formation of ZIF-90 crystalline structure. It also endorses the maintenance of crystallinity of IL-ZIF-90 even after the covalent post functionalization of n-ZIF-90 with aminopyridinium iodide.^{9c} In addition the intensities of the first peak increased and the rest of the peaks decreased respectively in IL-ZIF-90 indicating the change in electron density inside the micropores of n-ZIF-90 as a result of the introduction of aminopyridinium iodide.^{10b} From our previous report the synthesis of ZIF-90 with DMF as solvent produced non-uniform and micrometric scaled particle size crystals (Fig. S1, supplementary information).¹³ However, here from the SEM images shown in Fig. 2, uniform crystals were obtained. It is due to the presence of PVP during the synthesis of n-ZIF-90 that the particles remain uniform with good

crystallinity and also the employment of $\text{H}_2\text{O}/\text{tert-butanol}$ as solvent reduces the particle size.^{14e} To confirm



Scheme 1. Synthesis of IL-ZIF-90



Scheme 2. Cycloaddition of PO and CO_2 with IL-ZIF-90

the incorporation of aminopyridinium iodide to the n-ZIF-90, nitrogen gas adsorption was carried out. Type I adsorption observed from the Fig. 3 for both n-ZIF-90 and IL-ZIF-90 indicates that the microporous nature was maintained even after the introduction of aminopyridinium iodide.^{9c} The calculated BET surface areas from the adsorption data for n-ZIF-90 and IL-ZIF-90 were 1261 and 153 m^2g^{-1} , respectively as shown in Table 1. The surface area and pore volume of IL-ZIF-90 decreased with the introduction of aminopyridinium iodide, which may indicate the presence of guest materials supported onto the n-ZIF-90.^{10c}

Table 2 demonstrates the composition of n-ZIF-90 and IL-ZIF-90 determined by elemental and ICP-OES analysis. The amount of IL grafted on to the n-ZIF-90 to create IL-ZIF-90 was calculated to be 1.3 mmol I⁻ per g of n-ZIF-90 as revealed from elemental analysis. Fig. S2 of FT-IR validates the molecular interactions of aminopyridinium iodide with n-ZIF-90 to form IL-ZIF-90. A strong band at 1679 cm^{-1} (C=O) represented the aldehyde group in bulk n-ZIF-90. Upon the covalent post-functionalization with aminopyridinium iodide, this peak got subsided into the shoulder of a new peak that appeared at 1610 cm^{-1} . This peak at 1610 cm^{-1} corresponds to C=N bond of imine, thus confirming the partial immobilization with ionic functionality (calculated as ~ 14%).^{9c} The thermal stability of n-ZIF-90 and IL-ZIF-90 was determined by TG analysis (Fig. S3). n-ZIF-90 was found to be stable up to 300 °C whereas in the case of IL-ZIF-90, constant weight loss was observed from 180 to 600 °C most probably from the destruction of the framework.^{14e} An earlier onset of degradation observed from 180 °C confirms the presence of the covalently bound IL on the n-ZIF-90. From CO_2 and NH_3 temperature-programmed-desorption (TPD) (Table S1,

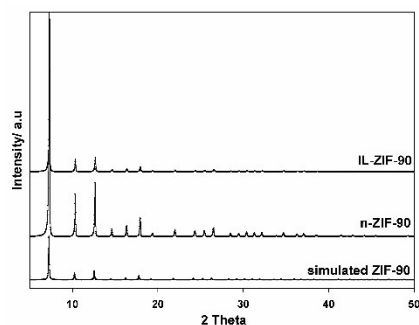
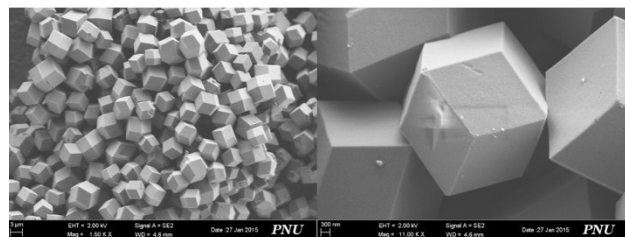
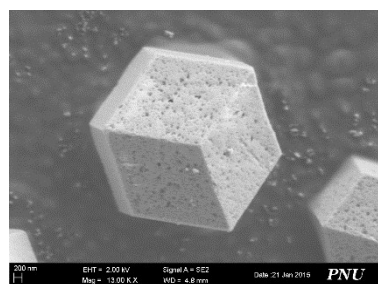


Fig. 1. XRD analysis of n-ZIF-90 and IL-ZIF-90



(a)



(b)

Fig. 2. SEM images (a) n-ZIF-90 and (b) IL-ZIF-90

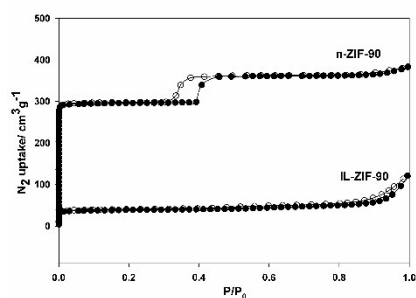


Fig. 3. N₂ isotherms of n-ZIF-90 and IL-ZIF-90

Table 1. Structural properties of n-ZIF-90 and IL-ZIF-90

Entry	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)
n-ZIF-90	1261	0.45
IL-ZIF-90	153	0.05

Table 2. Elemental analysis and ICP-OES of n-ZIF-90 and IL-ZIF-90

supplementary information), the presence of acidic and basic

Sample	C	H	N	O	Zn
n-ZIF-90	38.26	2.84	22.3	14.8	22.32
IL-ZIF-90	33.32	2.77	19.1	9.01	19.28

sites in n-ZIF-90 and IL-ZIF-90 was demonstrated.

Catalytic activity of IL-ZIF-90

For the cycloaddition of epoxides and CO₂ to produce cyclic carbonate, PO was chosen as the model substrate and reaction conditions were assigned to be 120 °C of temperature, CO₂ pressure of 1 MPa and reaction time of 3 h. In the absence of catalyst, no PO conversion could be detected under the reaction condition (entry 1, Table 3) similar outcome was perceived in the case of Zn(NO₃)₂ · 6H₂O when used alone (entry 2). ICA, AmPyl and a combination of both along with Zn(NO₃)₂ · 6H₂O was screened for the cycloaddition as shown from entry 3 to 5 respectively. ICA showed a conversion of 19% and AmPyl showed 44% conversion with 100% selectivity respectively whereas the combined use of all the starting materials for the synthesis of IL-ZIF-90 resulted in slightly higher conversion of 55%. However the usage of n-ZIF-90 (entry 6) synthesized using H₂O as a solvent showed excellent activity of 51% conversion compared the combination of n-ZIF-90 and AmPyl (entry 7). The slightly enhanced activity (65% conversion and 97 % selectivity) prompted us to perform AmPyl grafting onto the n-ZIF-90. The covalent post functionalized IL-ZIF-90 (entry 8) showed utmost conversion of 97% with selectivity of 98% in moderate reaction conditions of 0.49 mol% of catalyst amount, 120 °C of temperature, 1 MPa of CO₂ pressure and reaction time of 3 h. Moreover, a series of reported MOFs was selected to compare the activity of MOFs as a standalone catalyst as shown in Table S2. From the table it is clear that the activity of most MOFs reported till date suffer drastically in the absence of the most active homogeneous counterparts (ILs). This demonstrates the importance of post functionalization in MOFs to extract more activity out of the MOF frameworks.

Reaction parameter study of IL-ZIF-90

After witnessing high catalytic performance for IL-ZIF-90, the effect of reaction parameters (catalyst amount, time, temperature and CO₂ pressure), were investigated over IL-ZIF-90 catalyst. The influence of the amount of the catalyst loaded in the reaction of PO with CO₂ was studied as represented in Fig. 4. The higher activity of the catalyst was observed with increasing the catalyst loading from 0.16 to 0.49 mol% where

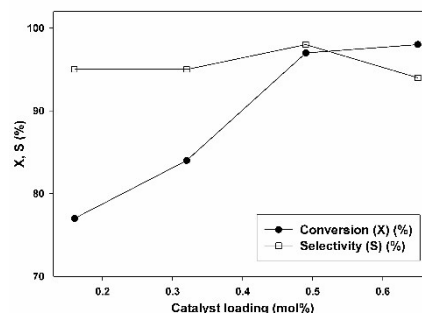
Table 3. Catalyst screening for the cycloaddition of PO with CO₂

Entry	Catalyst	Conversion (%)	Selectivity (%)	Yield (%)
1	-	0	0	0
2	ZnN	0	0	0
3	ICA	19	100	19
4	AmPyl	44	100	44
5	ZnN/ICA/AmPyl	55	96	53
6	n-ZIF-90	51	96	49
7	n-ZIF-90/AmPyl	65	97	63
8	IL-ZIF-90	97	98	95

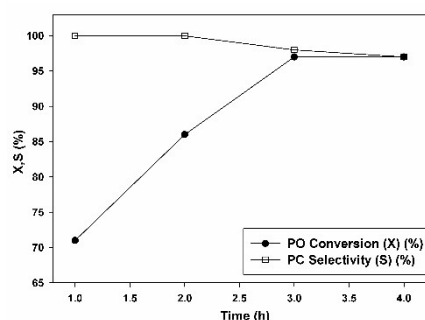
Reaction conditions: PO= 18.1 mmol, PCO₂ = 1 MPa, Temperature = 120 °C, Time = 3 h, Catalyst (n-ZIF-90, IL-ZIF-90) to PO ratio = 0.49 mol% Zn, ZnN, ICA and AmPyl = 0.49 mol % PO.

PO conversion increased from 77 to 97% with a selectivity of 98%. But further increase in catalyst loading to 0.65 mol% didn't alter catalyst activity much but selectivity got decreased. It can be explained by the fact that an excess of catalyst cannot be well dispersed in the reaction mixture and so limits the mass transfer between the active sites and the reactants.^{5a} The dependence of the PO conversion on reaction time at 120 °C and 1 MPa CO₂ is shown in Fig. 5. It illustrates that the yield of PC increased smoothly with the reaction time and nearly all the PO could be converted within 3 h. In all the experiments depicted in Fig. 5, the by-products were minor.

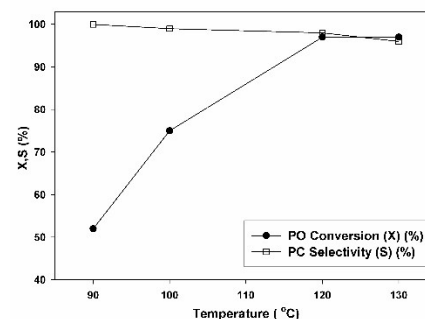
The dependence of the PO conversion and PC selectivity on the reaction temperature is shown in Fig. 6. The results indicate that the activity of the catalyst is strongly dependent on the reaction temperature. In the lower temperature region (90 to 120 °C), the PO conversion increases sharply (52 to 97%) with increasing temperature. A further increase in temperature from 120 to 130 °C had not much effect on the PO conversion. Furthermore, the selectivity to PC is always above 96%. The influence of CO₂ pressure on the conversion of PO was investigated at 120 °C for 3 h with 0.49 mol% of IL-ZIF-90 catalyst (Fig. 7). It could be obviously seen that the reaction pressure showed a great effect on PO conversion. With the rise of CO₂ pressure from 0.6 MPa to 1 MPa, the PO conversion increased rapidly, but CO₂ pressure showed little effect on the PO conversion beyond 1 MPa. According to reports,^{6k,15} it could be explained that PC was in its liquid form under the adopted reaction conditions. The concentration of CO₂ in the liquid phase rose with increasing pressure when the reaction was carried out in the low-pressure region, which promoted the reaction. But a too high CO₂ pressure would decrease PC yield because of the lower concentration of PO in the liquid phase since PO is also a reactant.

**Fig. 4.** Dependence of PO conversion on catalyst loading of IL-ZIF-90

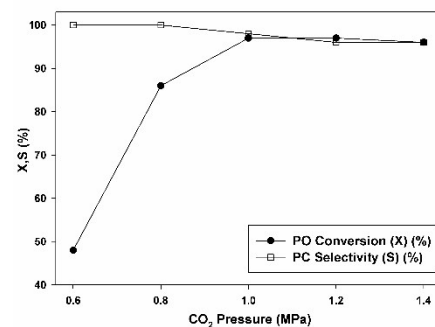
Reaction conditions: PO= 18.1 mmol, PCO₂ = 1 MPa, Temperature = 120 °C, Time = 3 h.

**Fig. 5.** Dependence of PO conversion on reaction time

Reaction conditions: PO= 18.1 mmol, PCO₂ = 1 MPa, Temperature = 120 °C, Catalyst to PO ratio = 0.49 mol% Zn.

**Fig. 6.** Dependence of PO conversion on reaction temperature

Reaction conditions: PO= 18.1 mmol, PCO₂ = 1 MPa, Time = 3 h, Catalyst to PO ratio = 0.49 mol% Zn.

**Fig. 7.** Dependence of PO conversion on CO₂ pressure

Reaction conditions: PO= 18.1 mmol, Temperature = 120 °C, Time = 3 h, Catalyst to PO ratio = 0.49 mol% Zn.

IL-ZIF-90 catalyst activity towards different epoxides

Next, we investigate the activity of IL-ZIF-90 in the other epoxide substrate conversion, and the cycloadditions were performed in the presence of 0.49 mol% of IL-ZIF-90 at a reaction temperature of 120 °C, CO₂ pressure of 1 MPa and reaction time of 3 h. As shown in Table 4, 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.¹⁶ Cyclohexene oxide showed the lowest activity, which might be due to the high steric hindrance caused by the cyclohexene ring.¹⁷

DFT assisted mechanistic exploration

In order to gather intuitive evidence for the mechanism of IL-ZIF-90 catalyzed PO-CO₂ cycloaddition, we conducted theoretical studies using DFT calculations. For simplicity a single repeating unit of IL-ZIF-90 was opted to explain the mechanism. Initially, the total energy of the reactant complex (PO, CO₂ & IL-ZIF-90) were preset to zero and the optimized geometrical arrangement of the reactant complex is shown in Scheme 3. An intermediate (inter1) (-20.4 Kcal mol⁻¹) was originated from the reactant complex. Here, the O atom of PO was at a distance of 2.04 Å from the Zn of IL-ZIF-90. The transition from inter1 to transition state (trans1) resulted in the interaction of Zn atom of IL-ZIF-90 with the O atom of PO (Zn-O = 1.79 Å) thereby resulted in the ring opening at the beta carbon (βC) of the PO. The bond distance between the ring opened βC and O was found to be 1.64 Å. In the following step, trans1 drops to inter2 (-15.28 Kcal mol⁻¹) resulted in slightly more stronger Zn-O_(PO) interaction of 1.77 Å and the ring opened βC_(PO) and O_(PO) bond distance becomes weaker (2.45 Å). Formation of inter3 (-18.6 Kcal mol⁻¹) occurs without transition state when the C atom of CO₂ molecule comes closer with the O atom of PO (2.72 Å). The transition from inter3 to trans2 resulted in more closer of C_(CO2) and O_(PO) (2.64 Å). When inter4 (-17.65 Kcal mol⁻¹) is formed the C_(CO2) makes an interaction with O_(PO) (1.45 Å) whereby the geometry of the CO₂ molecule transformed from linear to bend structure. For the transition from inter4 to trans3, C_(CO2) and O_(PO) bond becomes more stronger (1.32 Å) and Zn atom of IL-ZIF-90 interacts with O_(CO2) (1.85 Å). Then trans3 drops to the most stable intermediate (inter5) (-40.14 Kcal mol⁻¹) where ring closure occurs to obtain the desired PC.

Overall, the rate determining step is the ring opening of the PO by IL-ZIF-90 (inter1 to trans-1 to inter2). The CO₂ is easily inserted chemically (inter4) and then the PC formation has a certain moderate energy barrier. On comparing with DFT results of ZIF-90,¹³ it is seen that the ring opening of the PO has a rather low energy barrier (inter1 to trans1 to inter2). However, the chemical insertion of CO₂ is the rate determining step (inter2 to trans2 to inter3) in this case. The PC formation has also a certain moderate energy barrier.¹⁸ The first difference between the two cases is their rate determining steps. The second difference is the energy state of intermediates. For ZIF-90, inter2 has the

most stable energy state (-39.9 Kcal mol⁻¹) as inter5 for IL-ZIF-90 (-40.14 Kcal mol⁻¹). The higher conversion of IL-ZIF-90 may be attributed to this difference. It is speculated that, the whole reaction proceeds to form inter5 for IL-ZIF-90 and then PC is desorbed from IL-ZIF-90 at final stage. On the contrary, the most stable form is inter2 for ZIF-90, suggesting that inter3 has a good chance of being converted back to inter2 instead of proceeding forwardly.^{11d} In the above calculations, the syn-isomer of imine has been considered. Even though the anti-isomer would be slightly more stable (by about -0.18 kcal/mol), this difference is not expected to reflect significantly in the resulting energetics. Based on the above DFT results and the molecular structure of the IL-ZIF-90 together with the cycloaddition reaction results,^{11,12} a possible mechanism for PC synthesis was proposed in Scheme 4. At first, the zinc (Lewis acidic center) of IL-ZIF-90 interacts with the oxygen atom of epoxide, which activates the epoxide ring. Meanwhile, the halide anion of IL-ZIF-90 makes a nucleophilic attack on the less sterically hindered β-carbon atom of the epoxide, furnishing the opening intermediate. Then, this intermediate further reacts with CO₂ to form the corresponding cyclic carbonate and regenerate the catalyst. This mechanism insists that overall the role of the catalyst involves initial activation of the epoxide and stabilization of the ring-opened and carbonate intermediates formed during the reaction, which is important to reduce the reaction time and the pressure of the reaction.

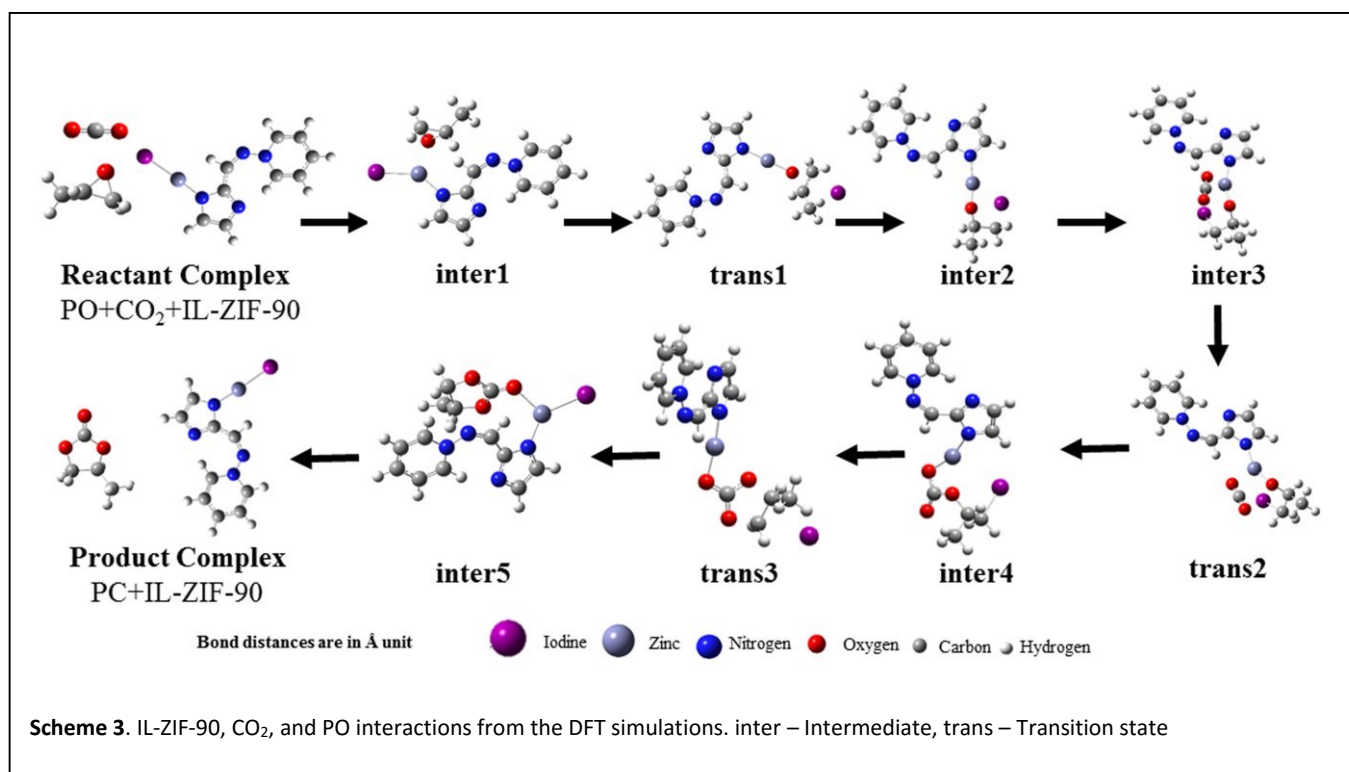
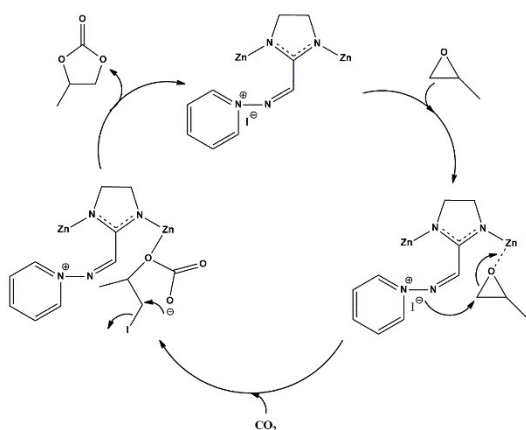
IL-ZIF-90 catalyst recovery

Experiments were also conducted to examine the reusability of the IL-ZIF-90 catalyst using PO as the substrate under the optimal reaction conditions. The results indicate that the IL-ZIF-90 catalyst could be easily separated by centrifugation and reused for four successive runs without any significant loss in its catalytic activity, and the selectivity still remained at 98% (see Fig. 8), reflecting the stability of the catalyst. The comparative XRD analysis of the fresh catalyst and the recovered IL-ZIF-90 after the 4th reuse in the cycloaddition reaction was performed, and the results are shown in Fig. S4. From the XRD analysis the original characteristic peaks of IL-ZIF-90 are repeated corresponding to the stability of the material even after the 4th reuse. In addition ICP-OES analysis of the product mixture revealed only 1.3% leaching of Zn metal after 4 recycle.

Table 4. The reactivity of IL-ZIF-90 for various epoxides

Reactant	Conversion (%)	Selectivity (%)
Propylene oxide (PO)	97	98
Epichlorohydrin (EPH)	94	88
Allyl glycidyl ether (AGE)	94	94
Styrene oxide (SO)	81	98
Cyclohexene oxide (CHO)	9	98

Reaction conditions: Epoxides = 18.1 mmol, PCO₂ = 1 MPa, Temperature = 120 °C, Time = 3 h, Catalyst to epoxide ratio = 0.49 mol% Zn.


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Scheme 4. Plausible mechanism for the IL-ZIF-90 catalyzed cycloaddition of PO and CO₂

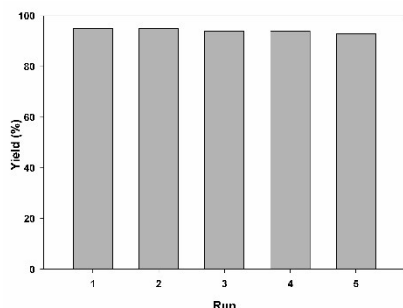


Fig. 8 Recycle test of IL-ZIF-90

Reaction conditions: Epoxides = 18.1 mmol, PCO₂ = 1 MPa, Temperature = 120 °C, Time = 3 h, Catalyst to epoxide ratio = 0.49 mol% Zn.

Conclusions

In summary, a novel synthesis of IL-ZIF-90 by the covalent post-functionalization of n-ZIF-90 via grafting IL (aminopyridinium iodide) have been performed and made use as a catalyst for the solventless cycloaddition reaction of CO₂ with various epoxides to provide cyclic carbonates under mild reaction conditions. A remarkable enhancement of catalytic activity was observed for IL-ZIF-90 compared to n-ZIF-90 when IL was grafted onto the n-ZIF-90 due to the innate “CO₂ capture” capability of n-ZIF-90 plus the presence of IL (most efficient homogeneous catalyst for CO₂ cycloaddition). Among the various epoxides, PO showed the best catalytic activity towards IL-ZIF-90, which afforded PC in good yield (95%) under mild conditions. The influence of IL-ZIF-90 catalyst amount, reaction time, reaction temperature, and CO₂ pressure for the PO-CO₂ cycloaddition has been investigated and the best result was obtained with 0.49 mol% of catalyst at 120 °C under 1 MPa of CO₂ pressure for 3 h. From the DFT calculations, IL-ZIF-90 catalyzed PO-CO₂ cycloaddition has been studied and compared with that of the ZIF-90. Based on this results, a plausible mechanism has been proposed involving Lewis acidic center (Zn) activating epoxide, halide ion making a nucleophilic attack resulting in furnishing ring-open intermediate followed by ring closure step to yield the cyclic carbonate. Furthermore, IL-ZIF-90 could be easily separated by centrifugation and recycled five times without any loss in its catalytic activity. In deduction, many of MOFs has been developed for CO₂ capture purpose and similarly many ILs has been synthesized for CO₂ conversion to useful products, hence a combination of both or in co-operation of both to a single component species could be the next generation materials for CCU technique.

Experimental

To synthesize ZIF-90 (n-ZIF-90) crystals^{14e-f}, solution 1 was prepared by dissolving zinc (II) nitrate hexahydrate (ZnN; 1.488 g; Sigma Aldrich, 98%) in tert-butanol (50 mL; Alfa Aesar, 99%) and solution 2 was prepared by mixing 2-imidazolecarboxaldehyde (ICA; 1.921 g; Alfa Aesar, 97%), polyvinylpyrrolidone (PVP; 2g; Sigma Aldrich) in distilled water. Then solution 1 was added to solution 2 and was heated at 40 °C for few minutes in a 250 mL glass bottle sealed tightly and then cooled to room temperature. The resultant pale grey yellow crystalline material (n-ZIF-90) was separated from the solution by decantation. The crystals were washed with methanol and then dried at 85 °C for 24 h.

To synthesize IL-ZIF-90 crystals^{9c} (Scheme 1), 1.5 g of dried n-ZIF-90 crystals and 1-aminopyridinium iodide (AmPyl; 3.9 g; Alfa Aesar, 97%) was suspended in methanol (100 mL; Sigma Aldrich, 99.8%) and refluxed for 24 hours at 50 °C. The reaction mixture was filtered and the solid was washed 2-3 times with fresh methanol. The solid was further exchanged with fresh methanol (200 mL) for 24 h at 50 °C. The solid was dried for 24 h at 85 °C.

The catalysts were characterized by X-ray diffraction (XRD), field emission electron microscopy (FE-SEM), Brunauer-Emmett-Teller (BET) surface area, Fourier transform infra-red spectroscopy (FT-IR), elemental analysis (EA), inductively coupled plasma optical emission spectroscopy (ICP-OES), thermogravimetric analysis (TGA), and temperature programmed desorption (TPD). XRD patterns were recorded as powders in a Rigaku Ultima IV diffractometer using the CuK α radiation (40 kV, 40 mA). Step size $\Delta 2\theta = 0.02$ °C, time per step = 4s. The surface of the n-ZIF-90 and IL-ZIF-90 crystals was observed with an S-4200 FE-SEM (Hitachi). The textural properties of the n-ZIF-90 and IL-ZIF-90 crystals were analyzed by recording an N₂ adsorption isotherm at 77 K with a BET apparatus (Microneritics ASAP 2020). The specific surface area was determined using the BET model equation. FTIR spectra were obtained with an Avatar 370 Thermo Nicolet spectrophotometer at a resolution of 4 cm⁻¹. EA of the catalysts were carried out using a Vario EL III analyzer. The metal contents of the catalysts were obtained from ICP-OES analysis using ULTIMA2 CHR (1.5 kW, 40.68 MHz, 130–800 mm) with mono chromato HDD and a poly chromato PMT detector. TGA was conducted using n-ZIF-90 (8.085 mg) and IL-ZIF-90 (2.412 mg) with an AutoTGA 2950 apparatus under a nitrogen flow of 100 mL min⁻¹ while heating from room temperature to 600 °C at a rate of 10 °C min⁻¹. CO₂ and NH₃ TPD profiles were acquired with a chemisorption analyzer (BEL-CAT) as follows. Prior to measurements, 0.1 g of the sample was activated in He (30 mL min⁻¹) at 280 °C for 1 h. The sample was subsequently exposed to the pulses of CO₂ (10%) or NH₃ (10%) in He at 40 °C for 1 h. The sample was then flushed with He (30 mL min⁻¹) for 1 h. TPD measurements were carried out by raising the temperature from 40 to 280 °C at a heating rate of 5 °C min⁻¹.

Synthesis of the propylene carbonate (PC) from PO and CO₂ using IL-ZIF-90 crystals (Scheme 2) was performed in a 25 mL stainless-steel autoclave equipped with a magnetic stirrer. For each typical semi-batch operation, where the consumed CO₂ during the reaction was continuously supplied to maintain the initial reactor pressure constant, PO (18.1 mmol) and IL-ZIF-90 crystals were introduced to the reactor without solvent. The reactor was then purged several times with CO₂ and pressurized with CO₂ to a preset pressure of 0.8–1.6 MPa at room temperature. Next, the reactor was heated to the desired temperature, and the reaction was initiated by stirring the reaction mixture at 600 rpm. After the reaction time had elapsed, stirring was turned off, the mixture was cooled to 0 °C and the CO₂ was vented off carefully. The products were identified with a gas chromatograph (Agilent HP 6890 A) equipped with a capillary column (HP-5, 30 m x 0.25 μ m) using a flame ionization detector. The product yield was determined using an internal standard method with biphenyl (0.05 g) as the standard.

DFT calculations were performed using Gaussian 09 set package with the B3LYP correlation functional. The basis sets employed were the 6-311++G(d,p) for non-iodine atoms, and the LANL2DZ dp for iodine.

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Graphical Abstract

Ionic liquid tethered post functionalized ZIF-90 framework for the cycloaddition of propylene oxide and CO₂

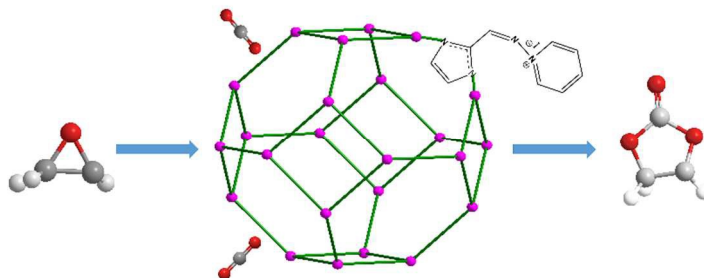
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Covalent post functionalization of ZIF-90: Synthesis of nano sized ZIF-90 (n-ZIF-90) using water as solvent and the assimilation of ionic liquid (aminopyridinium iodide) onto n-ZIF-90 to obtain IL-ZIF-90 for the provision of a single component catalyst aimed at the solventless cycloaddition of propylene oxide and CO₂