Facile Green Synthesis of New Copper-Based Metal–Organic Frameworks: Experimental and Theoretical Study of the CO₂ Fixation Reaction

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Abstract

Two new entangled Cu(II)-based metal–organic frameworks (MOFs) have been synthesized, namely $[\text{Cu}(\text{BDC})(\text{BPDB})_{0.5}]_n$ (PNU-25) and $[\text{Cu}(\text{NH}_2\text{-BDC})(\text{BPDB})_{0.5}]_n$ (PNU-25-NH₂), using a H₂O-MeOH solvent mixture. Both the PNU-25 and PNU-25-NH₂ MOF materials were characterized by various analytical techniques and their catalytic potential of CO₂ fixation into cyclic carbonates at an atmospheric pressure, a low reaction temperature, and in the neat conditions were demonstrated. The amine-functionalized PNU-25-NH₂ exhibited a significant high conversion of epichlorohydrin (ECH) at the 1 bar of CO₂ pressure, at 55 °C, and a moderate catalyst amount (1 mol%), with over 99% selectivity toward the corresponding cyclic carbonate of ECH. The superior catalytic activity of PNU-25-NH₂ may be attributed to its high amount of acidic-basic sites and large BET surface area in comparison with the PNU-25. The PNU-25-NH₂ catalyst could be reused up to four cycles without compromising its structural integrity and the ECH conversion. The reaction mechanism of CO₂ and ECH cycloaddition reaction mediated by the PNU-25-NH₂ was investigated in detail based on the experimental inferences and periodic calculations of density functional theory (DFT). The energy barrier of the rate-determining step of the PNU-25-NH₂/TBAB-catalyzed reaction was significantly lower than those of the rate-determining steps of un-catalyzed and TBAB-catalyzed reactions.

Keywords: Copper based MOF, CO₂ conversion, ambient pressure, cyclic carbonate

Introduction

The anthropogenic emission of carbon dioxide (CO_2), which is the cause of global climate change, has significantly impacted the concept of green and sustainable chemistry. Because CO_2 is an attractive, abundant, low-cost, non-toxic, and sustainable chemical feedstock, the utilization of CO_2 is of great interest in terms of atom economy.¹⁻⁵ As an inexpensive C1 feedstock for many fine chemicals, the utilization of CO_2 has gained considerable interest over the last decade.⁶⁻¹² Additionally, the selective coupling between CO_2 and epoxides to produce cyclic carbonates has also attracted significant attention in this area because of its wide applications (Scheme 1).¹³⁻²⁵ However, the use of catalysts and co-catalysts under low temperature and pressure conditions is challenging for the cycloaddition reactions. One solution is to design catalytic systems that can easily attract and activate CO_2 , which will allow them to be used at low reaction temperatures and ambient pressures.

Scheme 1 Represented schematic diagram of synthesis of PNU catalysts and their application for the cycloaddition reaction of CO_2 and epoxide.

Metal–organic frameworks (MOFs), comprising metal ions coordinated to organic linker units to form one-, two-, or three-dimensional (3D) frameworks, have an exceptionally large surface area and high porosity and offer ease of functionalization.^{26–31} Because of their adjustable pore size, topology, surface area, and aperture size and their ability to incorporate various functional groups into the framework, MOFs have been used as promising functional porous materials for diverse applications.^{32–36} Recently, MOFs have inspired extensive research in the field of gas storage and separation, and have been shown to be exceptionally efficient in CO₂ capture and chemical fixation through heterogeneous catalysis.³⁴ The epoxide-CO₂ transformation reactions catalyzed by heterogeneous MOFs under mild reaction conditions enable easier separation and reusability. Song *et.al.* documented a first report on the synthesis of cyclic carbonates from CO₂ and epoxides using an MOF-5/n-Bu₄NBr binary catalyst system.³⁷ Thereafter, a series of carboxylate^{38–41} MOFs or N-donor^{42–44} MOFs and their functionalized^{45–47} catalysts were reported by many research groups. MOFs designed using dual linker units and functionalized groups are expected to provide attractive features in the coupling reactions of CO₂, particularly N-donor linkers and basic groups, such as NH₂. These basic moieties can activate the CO₂ molecules easily by a nucleophilic attack. However, the preparation of novel MOF catalysts rich in basic sites (both N-donor linkers and basic groups) remains challenging and has not yet been explored in detail in the field of cyclic carbonate synthesis.

Herein, we report the preparation of a novel class of triple interpenetrated Cu(II)-based dual ligand MOFs, [Cu(BDC)(BPDB)_{0.5}]_n (PNU-25) and [Cu(NH₂-BDC)(BPDB)_{0.5}]_n (PNU-25-NH₂), composed of an N-donor Schiff base ligand, 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (BPDB), along with 1,4-benzene dicarboxylic acid (BDC) (for PNU-25) and 2-aminoterephthalic

acid (NH₂-BDC) (for PNU-25-NH₂) using a H₂O-MeOH solvent mixture, and their structural analysis using single-crystal X-ray diffraction (SXRD).

Results and Discussion

Structural description of PNU-25

Single-crystal X-ray diffraction (SXRD) analysis has been given a valuable structural information about block shaped green colored Cu(II)-MOF, PNU-25. Single-crystal analysis reveals that PNU-25 adopted monoclinic space group P2₁/n and contains a repeated unit formula of [Cu(BDC)(BPDB)_{0.5}]_n. The extended unit cell possesses an interpenetrated 3D coordination network with the asymmetric unit comprises each one Cu(II) metal ion, BDC ligand, and half a BPDB ligand, as illustrated in Figure 1. Symmetrically disposed BDC ligands are involved in the formation of dimeric Cu(II) clusters, [Cu₂(CO₂)₄], with a paddlewheel motif in which the Cu-Cu bond distance is 2.6740(15) Å. The coordination geometry around each Cu1 in the bimetallic cluster is octahedral, where the square base is established by the four BDC units with their four carboxylate oxygen atoms (O1, O2, O3, and O4), while the fifth position at axial one is occupied by the pyridyl nitrogen atom (N1) of the BPDB ligand. Moreover, another axial site is full-filled by the Cu-Cu bond. The symmetrically disposed BDC ligands are involved in the Cu₂(CO₂)₄ paddlewheel secondary building unit (SBU) that comprises four BDC ligands linked through their carboxylate oxygen in the syn-syn mode generating two-dimensional (2D) square grid-type *sql* sheets with the general formula [Cu₂(BDC)₄]_n along the *ab*-plane. Furthermore, the 2D [Cu₂(BDC)₄]_n sheets are pillared axially through the terminal nitrogen of the BPDB ligand from either end, creating a 3D framework (Figure 1(a) and (b)). The Cu(II) metal centers are separated by 10.80 Å and 15.62 Å between BDC and BPDB in the 2D and 1D motifs of [Cu₂(BDC)₄]_n and

[Cu₂(BPDB)_{0.5}]_n, respectively. As listed in Table S1 and Table S2, there are different bond lengths observed for Cu-O which are ranges from 1.964(4) Å to 1.975(4) Å and the bond length of Cu-N is found to be 2.186(5) Å. The PNU-25 structure contains 3D channels with rectangular windows of dimensions 15.21×10.80, which undergo interpenetration *via* various supramolecular interactions forming an overall triple interpenetrated network, as depicted in Figure 1(d–f). As illustrated in Figure 1(g–i), the overall network topology of PNU-25 is a 6-connected uninodal-type 3D interpenetrated *pcu* network with the point symbol {4¹².6³}.⁴⁹

Figure 1. (a) Coordination environment around Cu(II) centers in the paddlewheel secondary building unit of PNU-25 composed by BDC and BPDB ligands, (b) *sql* [Cu₂(BDC)₄]_n sheets, (c) pillaring of *sql* sheet [Cu₂(BDC)₄]_n by BPDB ligands resulting in *pcu* network, (d-e) overall *pcu*

network of PNU-25, (f) viewing bilateral networks along a -axis with triangle pores and (g-i) pcu network topology and 3D interpenetrated networks of PNU-25.

Figure 2. (a) PXRD patterns of both PNU-25 and PNU-25-NH₂ catalysts in comparison to the simulated pattern and (b) FT-IR spectra of PNU-25 and PNU-25-NH₂.

Characterization of PNU-25 and PNU-25-NH₂

To determine the phase purity and crystalline nature of the synthesized PNU-25 and PNU-25-NH₂ samples, we performed powder X-ray diffraction (PXRD) analysis. The bulk phase purity was confirmed by the comparing experimental PXRD patterns of bulk PNU-25 and PNU-25-NH₂ with the simulated profile of PNU-25 single crystal (Figure 2(a)). Furthermore, the structural unit of the amine-functionalized PNU-25-NH₂ was similar to that of its parent, PNU-25. The FT-IR spectra of the as synthesized PNU-25 and PNU-25-NH₂ confirm their successful formation from the metal precursor and linker units (Figure 2(b)). The Characteristic broad peaks of O-H stretching vibrations of surface adsorbed water molecules in the PNU catalyst observed in the range of 3400–3450 cm⁻¹. The broad peaks in the range of 3400–3450 cm⁻¹ correspond to the O-H stretching vibrations of lattice water molecule in the PNU catalyst. Meanwhile, the band

at 3250 cm^{-1} is assigned to the N-H stretching vibrations of the amine functionality in the PNU-25-NH₂ catalyst, which may overlap with the O-H peak. The carboxylic (C=O) symmetric and asymmetric stretching vibration peaks appear at approximately 1655 and 1500 cm^{-1} , which correspond to the BDC ligand. The stretching frequencies of C-N and C=N functional groups correspond to the BPDB ligand assigned to 1385 and 1580 cm^{-1} , respectively. The Cu-N and Cu-O vibration peaks appear at 460 and 657 cm^{-1} , respectively.

Figure 3. FE-SEM images of (a) PNU-25 and (b) PNU-25-NH₂ catalysts, (c) SEM-EDX elemental mapping of PNU-25-NH₂.

Figure 4. (a) XPS survey spectra of PNU-25-NH₂, b) Cu 2p spectra of PNU-25-NH₂, (c) and (d) XPS deconvolution spectra of the C 1s and N 1s, respectively.

The field emission scanning electron microscope (FE-SEM) images of the PNU catalysts show block-shaped particles of different sizes (Figure 3(a) and (b)). Furthermore, elemental mapping analysis was performed by scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX) to determine the elemental distribution in PNU-25-NH₂ (Figure 3(c) and S1). Elemental mapping confirmed the presence and homogeneous distribution of C, O, N, and Cu in the PNU-25-NH₂ catalyst. The chemical state of both as synthesized PNU catalyst studied by the X-ray photoelectron spectroscopy (XPS) survey spectra which exhibited a peak at a binding energy of approximately 934.82 eV, which implies the presence of Cu metal atom

(Figure 4(a) and S2). As can be seen in Figure 4(b), the Cu 2p_{3/2} (934.9 eV) and Cu 2p_{1/2} (954.7 eV) peaks are well separated in the Cu 2p spectra of the PNU-25-NH₂ catalyst. The presence of a strong shake-up satellite peak around 943 eV in the Cu 2p spectra indicates the presence of Cu(II) species.⁵⁰ The three peaks centered at 284.4, 285.2, and 288.4 eV derived from the deconvolution C 1s spectrum are assigned to the binding energies of C=C, C–N and C=O, respectively correspond to NH₂-BDC and BPDB linkers (Figure 4(c)). The two deconvoluted characteristic peaks of N 1s spectra positioned at 399.1, 400.2 eV are corroborated to N–H of pendant amine functional group of NH₂-BDC and C=N of azine functional unit of BPDB ligand, respectively (Figure 4(d)).

The thermal behaviors of the activated PNU catalysts were analyzed by thermogravimetric analysis (TGA). The weight loss at approximately 260 °C (Figure 5(a)) shows good thermal stabilities of the PNU catalysts which indicates also suitable heterogeneous catalysts for the cycloaddition reaction in the present study. The NH₃ and CO₂ temperature programmed desorption (TPD) analyses carried out to calculate the acid-base strengths of as synthesized catalysts, PNU-25 and PNU-25-NH₂. The acidic and basic sites were divided into weak (50-200 °C), medium (200-400 °C) and strong (400-600 °C) regions. As depicted in Figure 5(b), the only medium acidic sites of PNU-25 and PNU-25-NH₂ are observed at 300-400 °C (45.2 mmol g⁻¹) and 200-400 °C (53.2 mmol g⁻¹), respectively which are attributed to the Cu(II) centers in both catalysts. Meanwhile, the desorption amount of CO₂ disclosed the basic sites of PNU-25 and PNU-25-NH₂, from the CO₂-TPD analyses: the peaks at 300-380 °C (13.57 mmol g⁻¹) indicate the medium basic sites of PNU-25, whereas the peaks at 200-400 °C (18.79 mmol g⁻¹) indicate the medium basic sites of PNU-25-NH₂. The excess amount of basic sites in the PNU-25-NH₂ catalyst is responsible for supramolecular interaction between CO₂ and the –NH₂

functional groups of the NH_2 -BDC ligand. Additionally, binding affinity of both the catalysts toward CO_2 enhanced to the greater extent by the free lone pairs on the oxygen atoms of the carboxylate groups.

Figure 5. (a) TGA profiles, (b) CO_2 and NH_3 -TPD, (c) adsorption-desorption isotherms of N_2 gas and (d) CO_2 adsorption-desorption analysis of the both PNU-25 and PNU-25- NH_2 catalysts at 298 K.

The textural properties of PNU MOFs were studied by the N_2 gas adsorption-desorption experiments at 77 K (Figure 5(c)). Type III adsorption-desorption isotherm with a slight hysteresis confirms that both catalysts are nonporous materials with low external surface areas. When both activated samples of PNU-25 and PNU-25- NH_2 catalysts were subjected to the N_2 gas

adsorption, they exhibited low BET external surface areas, $6.3 \text{ m}^2 \text{ g}^{-1}$ and $28.8 \text{ m}^2 \text{ g}^{-1}$, respectively. The low external surface areas of the PNU catalysts were due to their triple interpenetrated 3D structures. And it has been suggested that a slight hysteresis in N_2 isotherm of PNU-25- NH_2 may be due to the inter particle voids of triple interpenetrated MOF's aggregated particles. The PNU-25- NH_2 catalyst exhibited a high CO_2 adsorption capacity of $20.83 \text{ cm}^3 \text{ g}^{-1}$, in spite of having low BET surface area at an absolute pressure of 850 mmHg, as determined by the CO_2 sorption isotherms measured at 298 K (Figure 5(d)). Due to the amine functionality in PNU-25- NH_2 , the higher CO_2 adsorption capacity of PNU-25- NH_2 observed in comparison with PNU-25 is because of the increasing of attraction between CO_2 and MOF.

Catalytic Activity: Reaction of Epoxides with CO_2

The catalytic abilities of PNU catalysts were performed with epichlorohydrin (ECH) as the primary epoxide system in the coupling reaction with CO_2 for 18 h at 55°C and 1 bar CO_2 pressure under solvent-free conditions. The cycloaddition reaction yielded 33% ECH carbonate with the use of nucleophilic co-catalysts, tetrabutylammonium bromide (TBAB) alone (Table 1, entry 2). The metal precursor ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and the ligands (BPDB, BDC and $\text{NH}_2\text{-BDC}$) showed low epichlorohydrin conversion (Table 1, entries 3–6). PNU-25 and PNU-25- NH_2 showed quite low conversion of ECH (Table 1, entries 7 and 8). The use of nucleophilic co-catalysts (tetraalkylammonium halides, NR_4X ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)) has been reported beneficial for the synthesis of cyclic carbonates through the synergistic effect with the Lewis acidic center of the catalysts. The PNU-25/TBAB system significantly increased the ECH conversion (70%) with excellent selectivity towards ECH carbonate (Table 1, entry 9). In contrast, the PNU-25- NH_2 /TBAB catalyst system exhibited a considerably better ECH conversion of 92% (Table 1, entry 10). The higher catalytic activity of PNU-25- NH_2 /TBAB is because of the synergistic role

of copper Lewis acidic sites, amine functionality, and nucleophilic anion of TBAB. The calculated turnover number (TON) of PNU-25 (160) and PNU-25-NH₂ (180) revealed their higher catalytic activity in comparison with previously reported MOFs.

Table 1. Catalyst tests for cycloaddition reactions of epichlorohydrin and CO₂.^[a]

Entry	Catalyst	Conversion ^[b] (%)	Selectivity ^[b] (%)
1	None	-	-
2	TBAB	33	>99
3	Cu(NO ₃) ₂ ·3H ₂ O	22	>99
4	BPDB	18	>99
5	BDC	12	>99
6	NH ₂ -BDC	21	>99
7	PNU-25	35	>99
8	PNU-25-NH ₂	46	>99
9	PNU-25/TBAB	70	>99
10	PNU-25-NH₂/TBAB	92	>99

Reaction Conditions: [a] ECH = 15 mmol, catalyst = 1 mol%, TBAB = 0.5 mol%, pressure = 1 bar CO₂, temperature = 55 °C, time = 18 h. [b] conversion and selectivity were determined by GC.

The best catalytic efficiency in terms of ECH conversion and yield of cyclic carbonates was obtained by optimizing the reaction parameters (1 mol% catalyst used at 55 °C and CO₂ pressure of 1 bar for 18 h for 15 mmol of epoxides). Following the catalytic reactions of PNU-25-NH₂ with ECH, the versatility of the catalyst was examined for various aliphatic (propylene oxide, allyl glycidyl ether and 1,2-epoxybutane) and cyclic (styrene oxide and cyclohexene oxide) epoxides. PNU-25-NH₂/TBAB exhibited better catalytic efficiency for the conversion of aliphatic epoxides under the optimized reaction conditions (55 °C, 1 bar CO₂, and 18 h; Scheme 2). As shown in Scheme 2, propylene oxide, allyl glycidyl ether, and 1,2-epoxybutane exhibited

maximum conversions of 93, 81, and 62%, respectively. The smaller size of these substrates facilitates their conversion to the corresponding cyclic carbonates owing to their better access to the active sites. Meanwhile, the bulky terminal epoxide styrene oxide converted into styrene carbonate in a moderate yield (35%) with >99% selectivity. The internal epoxide, cyclohexene oxide, showed very low conversion (12%) owing to the sterically hindered cyclohexene ring.^{51–53}

Scheme 2. Coupling reaction with various epoxides catalyzed by PNU-25-NH₂. Reaction conditions: epoxide = 15 mmol, catalyst = 1 mol%, TBAB = 0.5 mol%, pressure = 1 bar CO₂, temperature = 55 °C, time = 18 h.

To verify the heterogeneous character of the PNU-25-NH₂ catalyst, reusability studies were performed with ECH under the optimized reaction conditions of 18 h, 55 °C, and 1 bar CO₂ pressure. All the reactions were conducted using 1 mol% of reused PNU-25-NH₂ catalyst (separated by simple centrifugation, washed with methanol, and activated) and 0.5 mol% of TBAB. The reusability experiments demonstrated no remarkable change in ECH conversion in the first three cycles; however, the conversion considerably decreased in the next two cycles (Figure 6(a)). The reused PNU-25-NH₂ catalyst was characterized by PXRD analysis, FT-IR

spectroscopy, TGA, and FE-SEM. The catalyst maintained its structural and chemical integrity throughout the reusability process. As shown in Figure 6(b) and (c), the main peaks of the reused PNU-25-NH₂ in the PXRD and FT-IR spectra remain unchanged, and the thermal stability of the reused PNU-25-NH₂ is similar to that of fresh PNU-25-NH₂ (Figure 6(d)). Moreover, the FE-SEM images of the reused PNU-25-NH₂ catalyst show no noticeable change in its block-shaped morphology (Figure 7(a)), and the FE-SEM elemental mapping images confirm the presence and homogeneous distribution of C, O, N, and Cu in the reused PNU-25-NH₂ catalysts (Figure 7(b-f)). These results prove that the new heterogeneous PNU-25-NH₂ catalytic system has high potential of its heterogeneous catalytic application in the production of cyclic carbonates.

Figure 6. (a) Reusability study of PNU-25-NH₂ (Reaction condition: 55 °C, CO₂ pressure of 1 bar for 18 h), (b) PXRD spectra, (c) FT-IR spectra, and (d) TGA curve of the reused PNU-25-NH₂ catalyst.

Figure 7. (a) FE-SEM images of reused PNU-25-NH₂ and (b-f) SEM-EDX elemental mapping of reused PNU-25-NH₂.

Computational Study: Reaction Mechanism

The details of the computational method^{54–57} and the un-catalyzed and TBAB-catalyzed DFT calculations are presented in the supplementary information (Figure S3 and S4). For the PNU-25-NH₂/TBAB-catalyzed computational calculation, we simplified the PNU-25-NH₂ structure with 59 atoms (Figure S5) and selected Br[−] ion for the bulky TBAB. The total relative energies of the catalyst, co-catalyst, and reactants were set as 0 kcal/mol. Figure 8 depicts the relative free energy diagram and the mechanistic pathways of the PNU-25-NH₂-catalyzed reactions. As per the DFT calculation, −9.16 kcal/mol of energy was required for the interaction of the oxygen atom of ECH (O_(ECH)) with the Cu atom to form Int-1 (the distance between Cu and O_(ECH) is 2.26 Å). A sudden drop in relative energy (−39.05 kcal/mol) was observed when the Br[−] ion approached the beta carbon of ECH (βC), resulted in the formation of initial complex

(IC). The interaction between the Cu atom and $O_{(ECH)}$ became stronger (2.22 Å) when the Br^- ion approached the βC located at a distance of 3.53 Å. In the ECH ring-opening step (TS-1), i.e., rate-determining step (RDS) of the reaction,⁵³ the breaking of the $\beta C_{(ECH)}-O_{(ECH)}$ bond and the generation of the $\beta C_{(ECH)}-Br$ bond occurred simultaneously at a relative imaginary frequency of $559.6i\text{ cm}^{-1}$. In TS-1, having a relative energy of -33.05 kcal/mol , the distance of the $\beta C_{(ECH)}-Br$ bond was 2.55 Å and the interaction of Cu with $O_{(ECH)}$ became stronger (2.08 Å). Herein, the activation energy required for the ECH ring opening step was 15.16 kcal/mol , which is significantly lower than those of the rate determining steps of the TBAB-catalyzed and uncatalyzed cycloaddition reactions (see supporting information).

Figure 8. Energy profile diagram of PNU-25-NH₂/TBAB catalyzed coupling reaction between ECH and CO₂. The hydrogen atoms of intermediates and transition states are omitted for clarity. All the distances are in Å.

In the following step, CO₂ insertion occurred at a relative free energy of −43.73 kcal/mol, which transformed TS-1 into an intermediate, Int-2. Another intermediate (Int-3) was formed when CO₂ interacted with the O_(ECH) atom. As depicted in Figure 8, the formation of C_(CO2)-O_(ECH) bond (bond length of 1.69 Å) resulted in the formation of a new TS (TS-2) with a total energy of −50.57 kcal/mol. TS-2 underwent intramolecular ring-closure step by the attack of the negatively-charged O_(CO2) atom on the βC_(ECH), which led to the generation of new Int state (Int-4) with a relative energy of −53.62 kcal/mol. Int-4 transformed into Int-5 with a relative energy of −64.54 kcal/mol, where the formation of a new Cu-O_(CO2) bond and the scission of the C_(ECH)-Br bond occurred simultaneously. In Int-5, the Cu-O_(CO2) bond distance was 2.25 Å, and the C_(ECH)-Br bond weakened (bond distance increased from 2.04 Å to 3.31 Å). In the last step, ECH carbonate (product (FC)) was formed with the elimination of the Br[−] ion, and the relative free energy of the FC state was −13.09 kcal/mol. Herein, the computational results match well with the experimental study for the PNU-25-NH₂/TBAB and demonstrated the high efficiency of the binary catalyst system in comparison with the un-catalyzed and TBAB-catalyzed epoxide-CO₂ reactions.

Proposed Reaction Mechanism

On the basis of computational calculations, experimental data, and previous studies,^{58,59} a possible reaction mechanism for the coupling reaction catalyzed by PNU-25-NH₂ is demonstrated in Scheme 3. The coordinatively unsaturated Lewis acidic sites of the paddlewheel SBU, i.e., Cu²⁺ centers activate the epoxide for ring-opening. Subsequently, the Br[−] ions initiates the attack towards the least-hindered carbon atom, resulting in the ring-opening of the epoxide. The amine functional groups in PNU-25-NH₂ can polarize the CO₂ molecule and thereby facilitating CO₂ insertion. The attack of O[−] of the epoxide onto the carbon atom of CO₂, leads to

the formation of the carbonate complex (intermediate). Finally, ring-closure step occurs to generate cyclic carbonates and the regenerated PNU-25-NH₂ moves to the next catalytic cycle.

Scheme 3. Plausible reaction mechanism for the epoxide-CO₂ coupling reaction catalyzed by PNU-25-NH₂/TBAB.

The catalytic efficiency of PNU-25-NH₂ in the cycloaddition reactions was compared with previously reported copper based MOF catalysts (Table 2). The performance PNU-25-NH₂ was comparable or even higher than the previously reported Cu based MOFs.

Table 2 Comparison study of PNU-25-NH₂ with the previously reported copper based MOFs.

No	Catalysts	Epoxide	T (°C)	P _{CO₂} (MPa)	t (h)	Yield (%)	Ref.
1	[(Cu ₂ BPDSDC.4DMF).2DMF] _n	ECH	80	2.5	5	98	[60]
2	Cu-DABCO	ECH	100	0.8	12	13	[61]
3	CHB	ECH	120	1.2	6	72	[40]
4	Cu-BTC	ECH	60	1.2	8	78	[18]
5	UiO-66/Cu-BTC	ECH	60	1.2	8	91	[18]
6	PNU-25-NH ₂	ECH	55	0.1	18	92	This work

Conclusion

We successfully synthesized two new Cu(II)-based MOFs, namely PNU-25 and PNU-25-NH₂, using a H₂O-MeOH solvent mixture, and characterized them by SXRD and various analytical techniques. The heterogeneous PNU catalysts efficiently catalyzed the synthesis of cyclic carbonates by the coupling of epoxide and CO₂ under ambient pressure and lower reaction temperature. The PNU catalysts demonstrated remarkably good thermal stability for the cycloaddition reaction. The coordinatively unsaturated Cu(II) units and the basic N atoms resulted in a large number of acidic-basic sites, facilitating the conversion of epoxides. The amine-functionalized PNU catalyst exhibited the maximum ECH conversion of 92% at a low reaction temperature and 0.1 MPa CO₂ pressure. PNU-25-NH₂ was easily separable from the reaction medium, and could be reused multiple times without any noticeable loss in the ECH conversion. Furthermore, the mechanism of the PNU-25-NH₂-mediated cycloaddition reaction

was investigated by DFT calculations. The energy barrier of the RDS of the PNU-25-NH₂/TBAB-catalyzed reaction was significantly lower than those of the RDSs of the uncatalyzed and TBAB-catalyzed reactions.

Supporting Information

Experimental section, crystallographic information tables of PNU-25, elemental composition, XPS spectra, simplified the PNU-25-NH₂ catalyst structure for computational calculation and NMR spectra of the cyclic carbonates.

Accession Codes

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Synopsis

Two new mixed linker 3D interpenetrated Cu(II)-based metal–organic frameworks (MOFs), namely PNU-25 and PNU-25-NH₂ has been synthesized and used as potential heterogeneous catalysts for the cycloaddition reaction of CO₂ and epoxides.

254x190mm (96 x 96 DPI)