



Catalytic Conversion of Carbon Dioxide by Metal-Organic Frameworks: an Effective Approach for CO₂ Utilization

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ABSTRACT

Due to the increase in carbon dioxide emission, there is a need for achieving efficient ways to reduce CO₂ harmful effects. There are several strategies to mitigate atmospheric CO₂ concentration. The catalytic cycloaddition of carbon dioxide with epoxides to provide cyclic carbonates employing metal-organic frameworks is a promising method for this purpose. Herein the application of two porous porphyrinic MOFs (Co-PMOF and Cu-PMOF) as catalysts in CO₂ conversion was investigated. These MOFs demonstrated good crystallinity and porosity, providing them with two promising platforms to study CO₂ conversion reactions. These heterogeneous porphyrin-based MOFs are catalytically efficient towards the chemical conversion of CO₂ under moderate conditions because these MOF matrices contain a high density of active Lewis acidic and basic sites for activating CO₂ and epoxide compounds. These MOFs exhibited high catalytic efficiency for the chemical fixation of CO₂ at ambient temperature and solvent-free conditions. The reactions formed the proportionate cyclic carbonates in good yields. These products are valuable compounds in a variety of chemical fields.

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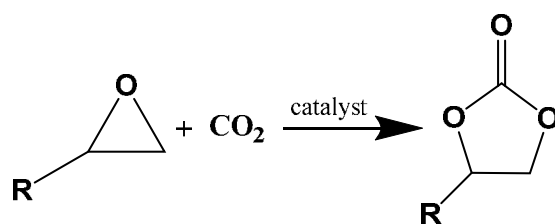
INTRODUCTION

Increased emission of greenhouse gases (GHG) results in global climate change, and carbon dioxide is considered the main greenhouse gas. Fossil fuel consumption releases a significant amount of CO₂ into the atmosphere. Though, there are many promising methods to solve this environmental problem and minimize atmospheric carbon dioxide (Gulati et al., 2023). Utilizing and converting CO₂ into valuable chemicals like methanol (Liu et al., 2013; Wu et al., 2023), formic acid (Fu et al., 2012; X. He et al., 2023), dimethyl carbonate (Honda et al., 2013), cyclic carbonate (Deng et al., 2023; Jeong, Kathalikkattil, Babu, Chung, & Park, 2018; Liang et al., 2017), and carbon monoxide (Ye et al., 2018) is a desirable approach for mitigating the harmful effect of atmospheric concentration of CO₂. So far, considerable efforts have been made to find practical technologies to convert CO₂ into valuable chemical compounds. Among various approaches for the conversion of carbon dioxide, chemical fixation of carbon dioxide via cycloaddition of CO₂ with epoxides is an effective strategy to utilize CO₂ which would positively convert CO₂ into organic products, specifically cyclic carbonates (Scheme 1). Cyclic carbonates are useful intermediates that are utilized as electrolytes in lithium-ion batteries,

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aprotic polar solvents, and raw materials for polymer synthesis (polycarbonates) (Pescarmona, 2021). Thus, finding appropriate catalyst systems for the cycloaddition of carbon dioxide to epoxides has gained much interest. Metal-organic frameworks are one of the most fascinating and potent porous materials comprising inorganic building units (metal ions or metal-oxo units) formed by strong chemical bonds via organic ligands. MOFs have essential features such as 3D tunable porous frameworks, adjustable pore shape, high specific surface area, large pore size, and diverse environments of the cages (by functionalization of the pores). Because of these characteristics, MOFs have potential applications in catalysis (Lee et al., 2009), gas separation (Kang, Fan, & Sun, 2017), gas storage (Sculley, Yuan, & Zhou, 2011), drug delivery (Horcajada et al., 2010; Sun et al., 2011), and biomedical sensing (C. He, Lu, & Lin, 2014). The MOFs act as a suitable platform for CO₂ capture because the open frameworks allow MOFs to hold guest molecules in their cages properly. So far, extensive efforts have been made to develop efficient heterogeneous catalyst systems for converting CO₂ into valuable chemicals. Accordingly, MOFs have attracted widespread attention as heterogeneous catalyst platforms for the cycloaddition of epoxides and carbon dioxide. Constructing MOFs via introducing N-rich aromatic compounds like porphyrin rings as linkers leads to porphyrin-based MOFs with exciting properties. The porphyrin-based MOFs possess some significant characteristics, including the light absorbing and energy transferring, the long lifetime of the excited state, and proper redox performance. These features make porphyrinic MOFs appropriate catalyst systems. The incorporation of porphyrin or metalloporphyrin within MOFs enhances the Lewis acid sites and improves the catalytic efficiency.

Mechanistically, coupling epoxides with CO₂ requires a catalyst containing a Lewis acid and base sites. The Lewis acid is responsible for activating epoxide and the Lewis base site within a catalyst performs CO₂ activation as well as ring-opening of the epoxide. The co-existence of Lewis acid metal sites and Lewis base sites (organic linkers) introduces MOFs as a new family of heterogeneous porous catalysts for carbon dioxide cycloaddition reactions. Therefore, the development of porphyrin-based MOFs, which provide both Lewis acid sites (metal centers) and Lewis base sites (porphyrin linkers), is a significant achievement that can easily facilitate the CO₂ cycloaddition reaction and enhance the catalytic performance. A hafnium-based MOF (Hf-NU-1000) was synthesized using Hf₆ clusters by Omar K. Farha and coworkers (Beyzavi et al., 2014). The Hf-NU-1000 is an appropriate catalyst system for the cycloaddition of epoxides to CO₂. This Hf-based MOF has strong M–O bonds, which can act as a potent Brønsted acid. Also, a Zn-based anionic MOF has been synthesized and successfully played the role of a new catalyst for coupling epoxides and carbon dioxide under ambient conditions. The MOF catalyzes cycloaddition reactions dually. First, Lewis acid sites in the MOF matrix may link to the epoxide. Afterward, since the framework has an anionic nature, MOF interacts with the ammonium ion and increases the availability of the Br⁻ ion. Thus ring opening happens more quickly (Kumar et al., 2016). To provide heterogeneous catalysts based on porphyrinic MOFs, a bifunctional porphyrin catalyst incorporating metal tetraphenyl porphyrin (M(TPP)) has been developed in 2012. This MOF showed high efficiency in the production of cyclic carbonate from carbon dioxide and epoxide (Ema, Miyazaki, Koyama, Yano, & Sakai, 2012). The metal ion (Mg^{II}) available in MOF cooperatively activates epoxides and effectively drives the reaction. The application of porphyrin-based MOFs has also been reported for some metallated PCN-222 (Co, Ni, Cu, and Zn) (Carrasco, Sanz-Marco, & Martín-Matute, 2019). These MOFs efficiently catalyze the cycloaddition of epoxides and aziridines with CO₂ under mild conditions, moreover, they can be recycled for up to 4 runs. Jin Yang's group has investigated the synthesis of a porous rtl MOF using a new porphyrin-based octacarboxylic acid ligand and its catalytic activity for chemical fixation of CO₂ with epoxides (Jiang, Yang, Liu, Song, & Ma, 2016). The MOF has high Mn^{II} density in its framework and plays a significant Lewis acid heterogeneous catalytic role. This flexible MOF is stable, active, and easily recyclable. Zhang et al., in 2022, reported



Scheme 1. Catalytic cycloaddition of CO₂ with epoxides.

the construction of a two-dimensional porphyrin-based MOF (FeTPyP) which exhibited catalytic activity for visible-light-assisted cycloaddition of CO₂ with epoxides with a yield of styrene carbonate as high as 106.13 mmol/(g h) (Zhang et al., 2022). To facilitate the ring-opening of propylene oxide, Liu et al. introduced the Lewis acid Bi atom into the porphyrin ring of PCN-224, and therefore the cycloaddition reaction of CO₂ to epoxides was carried out at room temperature under light irradiation (Zhai et al., 2021). In another research work, an Mg-centered porphyrin-based MOF has been constructed which facilitated the ligand-to-metal charge transfer and showed good CO₂ capture capacity and sunlight-promoted sustainable fixation ability of CO₂ (Das, Manna, Pathak, & Nagaraja, 2022).

In this work, we have investigated the employment of MOFs as catalysts in the conversion of carbon dioxide to value-added chemicals. Indeed, the role of the porphyrin-based MOFs, including Co-PMOF and Cu-PMOF, as catalysts for CO₂ fixation with epoxides was studied. These MOFs contain Lewis acid sites for epoxide activation. Also, they have Lewis base sites (porphyrin linkers), which can exhibit high catalytic performance for cycloaddition reactions. We have previously reported the synthesis of two new porphyrinic MOFs, including Co-PMOF and Cu-PMOF. These MOFs were formed by incorporating metalloporphyrins (Co-TCPP, Cu-TCPP) as organic linkers linked to cobalt and copper SBUs (Tayebi et al., 2022). These MOFs could convert CO₂ to the corresponding cyclic carbonate with good yield.

MATERIALS AND METHODS

All the reagents in the present work were obtained from Sigma-Aldrich. All solvents were commercial reagent grade purchased from Sigma-Aldrich and used as received. The CO₂ gas of 99% purity was used for the cycloaddition reactions. The catalytic products were characterized and determined by a Perkin Elmer Clarus 500 Gas Chromatograph Mass Spectrometer.

Two new porphyrin-based MOFs, Co-PMOF and Cu-PMOF, were prepared at room temperature by a solvothermal method, as previously reported (Tayebi et al., 2022). Prior to the synthesis of MOFs, the TCPP ligand was prepared according to the procedure reported earlier (Rabbani, Bathaee, Rahimi, & Maleki, 2016; Rabbani, Heidari-Golafzani, & Rahimi, 2016). Porphyrin-based Co-PMOF was prepared based on the previous report, using cobalt (II) nitrate hexahydrate and Tetrakis(4-carboxyphenyl)-porphyrin as ligand. The Co(NO₃)₂·6H₂O and TCPP were dissolved in a mixed solvent of DMA (dimethylacetamide), MeOH, and H₂O. Then the mixture was allowed to be heated in a closed vessel in an oven. Finally, a dark solid (Co-PMOF) was obtained.

Synthesis of Cu-PMOF was conducted by dissolving the copper (II) nitrate trihydrate and TCPP in a mixed solvent of N,N-dimethylformamide, and formic acid. The mixture was heated in an oven. Then the as-synthesized sample was purified via washing with DMF and dried at room temperature to yield dark red crystals. The prepared catalysts were activated at 100°C for 4 h under a vacuum before use.

Afterward, in a typical procedure, 1 mmol of epoxide and 10 mg of catalyst (Co-PMOF or Cu-PMOF) were charged in a closed apparatus. Then tetrabutylammonium bromide (32.2

mg, 0.1 mmol) was added to the vessel. The vessel was sealed with a Teflon-lined cap and was purged several times with CO_2 . Then the container was pressurized with CO_2 up to 1 atm. and agitated at room temperature. After 24 hours, the reaction mixture was evaluated by GC/MS to calculate the conversion of epoxide (Figure 1).

RESULTS AND DISCUSSION

The Co-PMOF and Cu-PMOF crystals were prepared through a solvothermal procedure according to the method previously stated (Tayebi et al., 2022). For the construction of Co-PMOF, cobalt (II) nitrate links to TCPP ligand Cu-PMOF, whereas, for preparation of copper (II) nitrate reacts with TCPP ligand in a mixed solvent of formic acid and DMF. The TCPP ligand has four carboxylate functional groups, which are readily available to connect to metal SBUs. Moreover, the TCPP can be metalized by metal ions (Co^{2+} and Cu^{2+}), providing metalloporphyrin linkers. MOFs are predicted to possess characteristics identical to their parent compounds, and their features can be matched to the reference materials. Figure 2 represents the schematic synthesis path for Co-PMOF and Cu-PMOF.

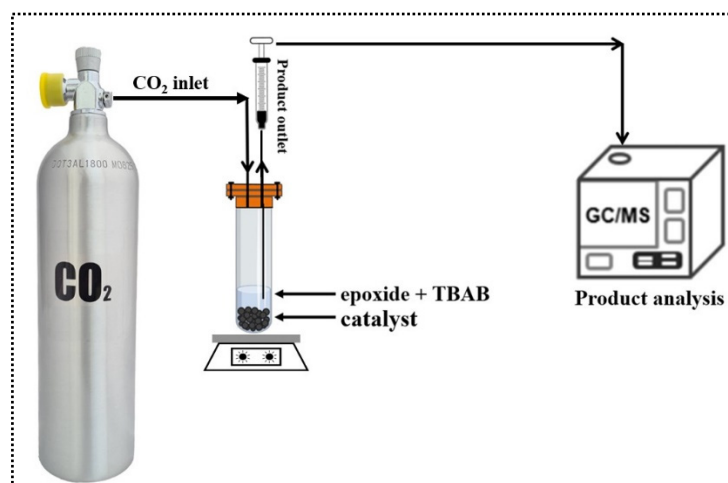


Fig. 1. The experimental apparatus for catalytic CO_2 fixation.

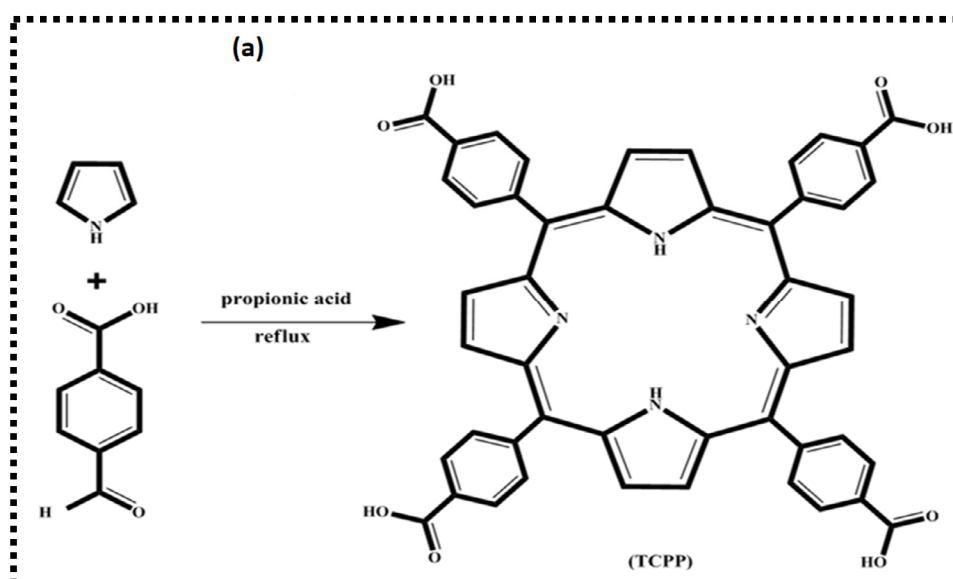


Fig. 2. The synthesis path of (a) TCPP, (b) Co-PMOF, and (c) Cu-PMOF.

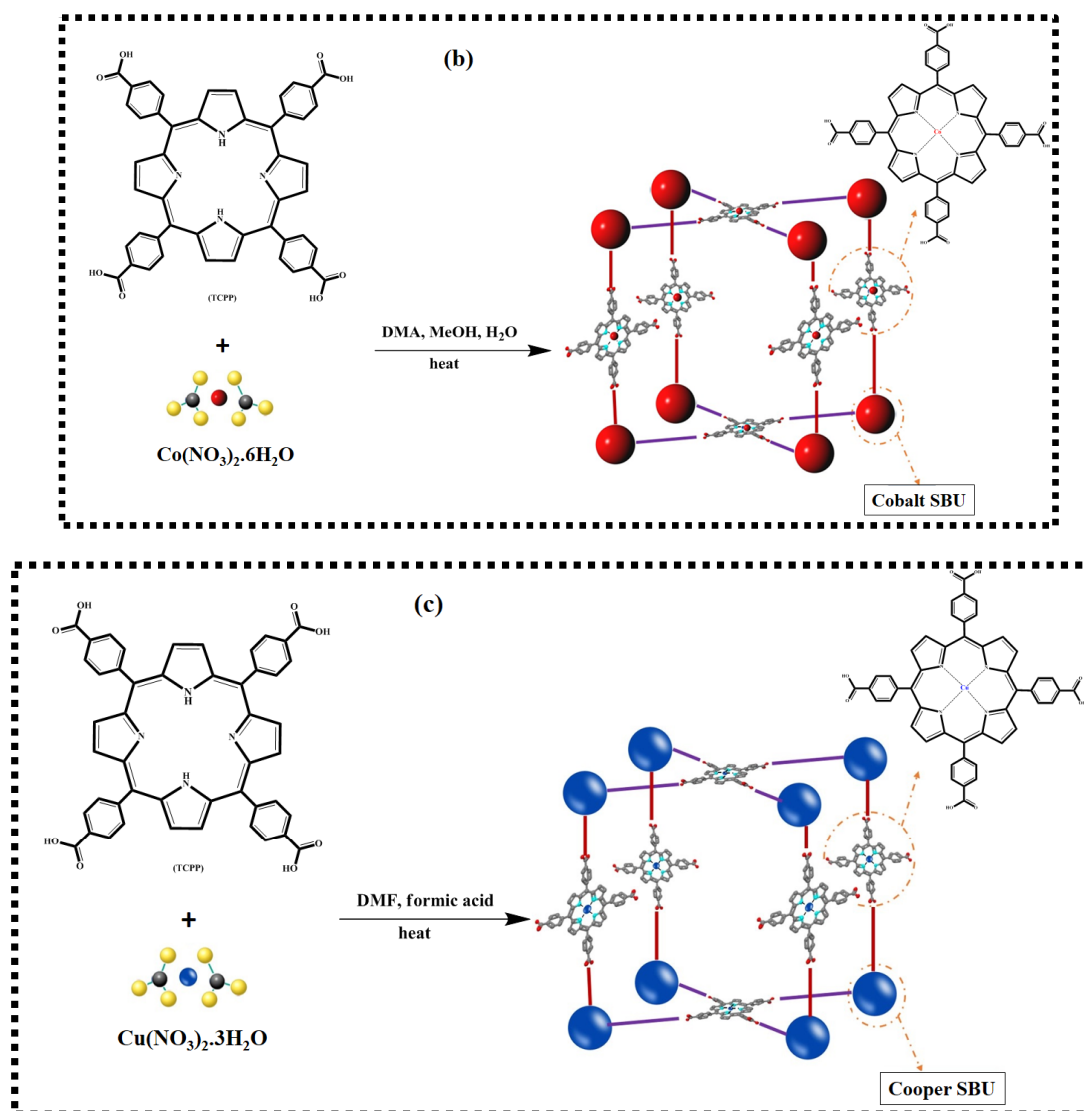


Fig. 2. The synthesis path of (a) TCPP, (b) Co-PMOF, and (c) Cu-PMOF.

As already indicated (Tayebi et al., 2022), the FTIR spectra were helpful in the structure analysis of TCPP, Co-PMOF, and Cu-PMOF. Their FTIR spectra displayed the characteristic and typical peaks for TCPP, Co-PMOF, and Cu-PMOF, which confirmed the presence of desired functional groups (such as $=\text{C}-\text{N}$, $\text{C}=\text{N}$, $\text{N}-\text{H}$, OH , $\text{OC}-\text{O}-\text{Co}$, and $\text{OC}-\text{O}-\text{Cu}$ bonds) in the structure of these compounds. Besides, by comparing the peaks of Co-PMOF and Cu-PMOF with TCPP, it was observed that the peaks related to the $\text{N}-\text{H}$ bonds of the pyrrole rings have shifted, and their intensities have decreased, due to the presence of $\text{Co}-\text{N}$ and $\text{Cu}-\text{N}$ bonds.

XRD analyses revealed that the crystal structures of Co-PMOF and Cu-PMOF were successfully achieved, consistent with the literature. The phase purity and crystal structure of Co-PMOF was ascertained by high similarities between the XRD pattern of synthesized Co-PMOF and MMPF-2 as the parent compound (Wang et al., 2012). All the substantial peaks in the XRD pattern of MMPF-2 can be observed in the XRD pattern of Co-PMOF, proving the formation of the pure phase of Co-PMOF. Likewise, Cu-PMOF was prepared through a synthesis method like MMPF-9 as its parent compound (Gao et al. 2014). There is a good agreement between the XRD pattern of the new MOF (Cu-PMOF) and the reference compound

pattern (MMPF-9). This agreement indicates that Cu-PMOF was successfully constructed since all the significant peaks, which are presented in the XRD pattern of MMPF-9, can be seen in the XRD pattern of Cu-PMOF (Tayebi et al., 2022).

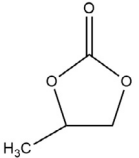
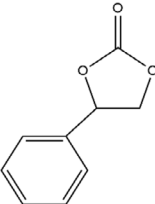
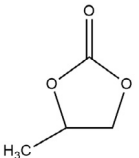
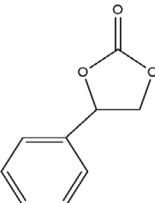
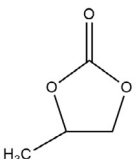
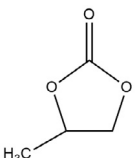
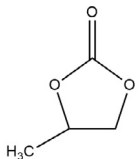
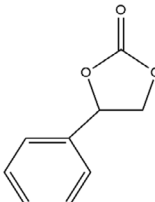
Co-PMOF and Cu-PMOF were then characterized using the Brunauer–Emmett–Teller (BET) analysis at 77 °K under 1 atm. Detailed methods of characterization of the MOFs have already been described in our previous study (Tayebi et al., 2022). The BET surface area of the synthesized Co-PMOF was obtained at 974.06 m²/g, while Cu-PMOF was highly porous with a BET surface area of 932.64 m²/g. The total pore volume of Cu-PMOF is 0.6173 cm³/g however the total pore volume of Co-PMOF is slightly higher than that of Cu-PMOF (0.7853 cm³/g). The large total surface area of Co-PMOF and Cu-PMOF helps to adsorb high amounts of CO₂ in the MOF cavities. Therefore, these MOFs can be applied in the role of highly potent catalysts for the fixation of CO₂ by epoxides.

Among different pathways to convert CO₂, the cycloaddition of CO₂ with epoxide has been widely investigated because of the extensive applications of cyclic carbonates (Scheme 1). Therefore, in this study, CO₂ conversion into cyclic carbonates catalyzed by Co-PMOF and Cu-PMOF were explored at room temperature. The results of these experiments have been presented in Table 1. Coupling of propylene oxide and CO₂ into corresponding cyclic carbonate gives a yield of 53% within 24 h, in the presence of Cu-PMOF, at room temperature (Table 1, entry 1), while the use of Co-PMOF as catalyst leads to a 30% yield under the same reaction conditions (entry 3). As well, the same reaction proceeds by applying epoxystyrene with Cu-PMOF as a catalyst; the reaction gave the corresponding cyclic carbonate with a yield of 35% at 25 °C and 1 atm. pressure (entry 2), Co-PMOF as a catalyst was also used to synthesize the 1,3-dioxolan-2-one,4-phenyl yielding in 28% (entry 4). To investigate catalyst efficiency, a few blank reactions were run without catalysts and tetrabutylammonium bromide (TBAB) (entry 5,6). No desired cyclic carbonates were generated in a measurable yield which indicated that Co-PMOF and Cu-PMOF display helpful catalytic performance for the cycloaddition of epoxides using carbon dioxide. To evaluate the activity of catalysts, the results of two other MOFs, including PCN-224(Co) and Yb-DDPY, as catalysts for the cycloaddition reaction of CO₂ to epoxides have been illustrated in Table 1. Reactions were performed under similar conditions, except for the reaction time, which is 48 hours for PCN-224(Co) and Yb-DDPY (Feng et al., 2013; Wei, Zhang, Liu, Han, & Yuan, 2017).

According to the literature (Kumar et al., 2016; North, Pasquale, & Young, 2010; Yang et al., 2012; Yu, Liu, Ma, Niu, & Cheng, 2016) and current catalytic results, we proposed a reasonable reaction mechanism for the cycloaddition of epoxides and carbon dioxide catalyzed by Co-PMOF and Cu-PMOF, as represented in Figure 3. Due to the superb porous structure of MOFs, carbon dioxide simply enters the pores and channels and approaches the active sites of MOFs (metal clusters and metalloporphyrin linkers). In other words, metal nodes and porphyrin/metalloporphyrin linkers provide Lewis acid and mild Lewis base sites, respectively. Therefore, incorporating metalloporphyrin linkers within Co-PMOF and Cu-PMOF may improve the catalytic efficiency during the CO₂ fixation process (Chen, Zhang, Chen, Chen, & Yu, 2015).

The epoxide coordinates with the active site of MOF, particularly the Lewis acidic cobalt or copper sites of Co-PMOF and Cu-PMOF. Indeed, the oxygen atom of the epoxide links to the Lewis acidic sites. The less sterically hindered carbon atom of the epoxide is then attacked by the Br⁻ ion from ⁿBu₄NBr to open the epoxy ring and generate a haloalkoxide intermediate. The oxygen atom of haloalkoxide further reacts with CO₂ to produce a new intermediate, an alkyl carbonate anion, followed by the ring-closing and releasing of the Br⁻ anion. In other words, forming the corresponding cyclic carbonate and regenerating the catalyst (MOF) and co-catalyst (ⁿBu₄NBr) occurs at this step.

Table 1. The results of the cycloaddition reaction of CO₂ to epoxides by Co-PMOF and Cu-PMOF and comparison of some reported MOFs.

Entry	Catalyst	epoxide	Cyclic carbonate	CO ₂ pressure (atm.)	T (°C)	Time (h)	Yield (%)	Ref.
1 ^a	Cu-PMOF	Propylene oxide		1	R.T.	24	53	This work
2	Cu-PMOF	Epoxy styrene		1	R.T.	24	35	This work
3	Co-PMOF	Propylene oxide		1	R.T.	24	30	This work
4	Co-PMOF	Epoxy styrene		1	R.T.	24	28	This work
5 ^b	No catalyst	Propylene oxide		1	R.T.	24	<3	This work
6 ^c	No TABA	Propylene oxide		1	R.T.	24	<1	This work
7 ^d	PCN-224(Co)	Propylene oxide		1	R.T.	48	42	(Feng et al., 2013)
8 ^e	Yb-DDPY	Epoxy styrene		1	R.T.	48	28	(Wei et al., 2017)

^a Reaction conditions: epoxide (1 mmol), 10 mg catalyst, n-Bu₄NBr (32.2 mg, 0.1 mmol), at room temperature for 24 hours; ^b Without catalyst; ^c in the absence of TABA; ^{d, e} Comparison of previously reported catalysts.

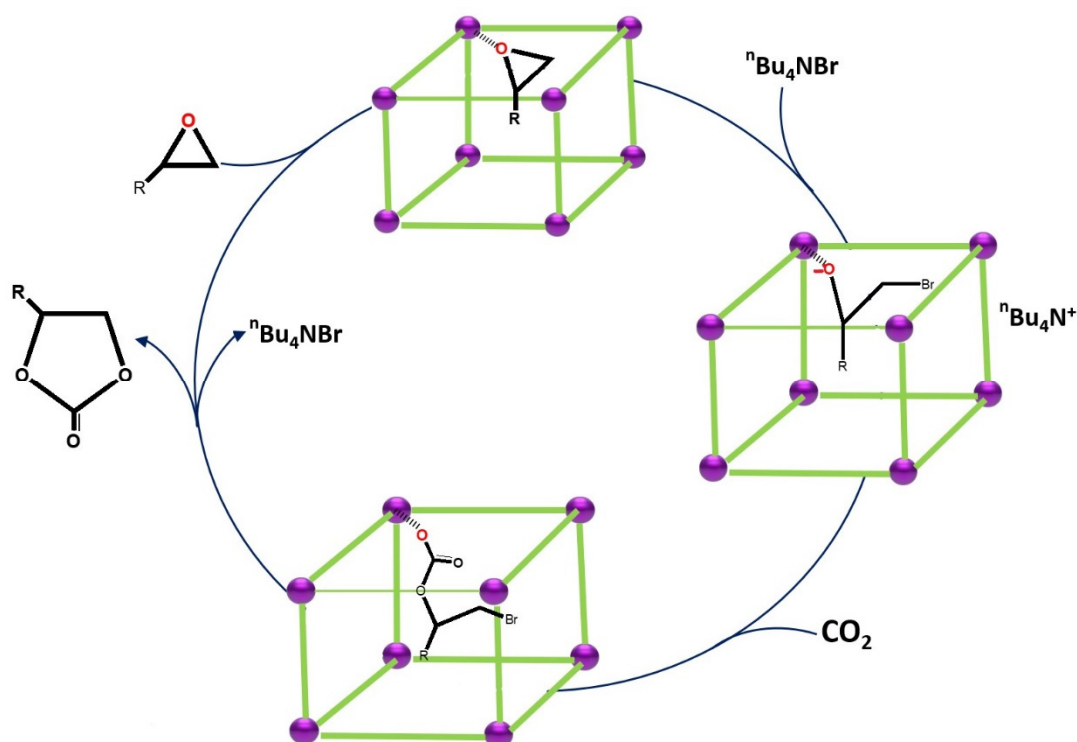


Fig. 3. The proposed reaction mechanism of the cycloaddition of CO₂ to epoxides catalyzed by Co-PMOF and Cu-PMOF.

CONCLUSION

In this study, to overcome the challenges related to environmental pollutants, specifically carbon dioxide, CO₂ conversion technologies were studied. The investigation was performed through CO₂ coupling reactions with epoxides using heterogeneous catalysis methodologies. Since there are both Lewis acid sites (metal centers) and Lewis base sites (porphyrin bonds) in the structures of Co-PMOF and Cu-PMOF, it provided us insight into utilizing these MOFs as effective catalysts for carbon dioxide cycloaddition reaction with epoxide. Furthermore, a high surface area of 974.06 and 932.64 m²/g for Co-PMOF and Cu-PMOF, respectively, proved that these MOFs could be appropriate heterogeneous catalysts to capture and convert CO₂. We employed the MOFs in the role of potent catalysts for the chemical fixation of carbon dioxide. The cycloaddition reactions of CO₂ with epoxides were carried out under ambient temperature, under 1 atm. pressure with good yields for 24 hours in the presence of Co-PMOF and Cu-PMOF.

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The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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