



Triazole Appended Metal–Organic Framework for CO₂ Fixation as Cyclic Carbonates Under Solvent-Free Ambient Conditions

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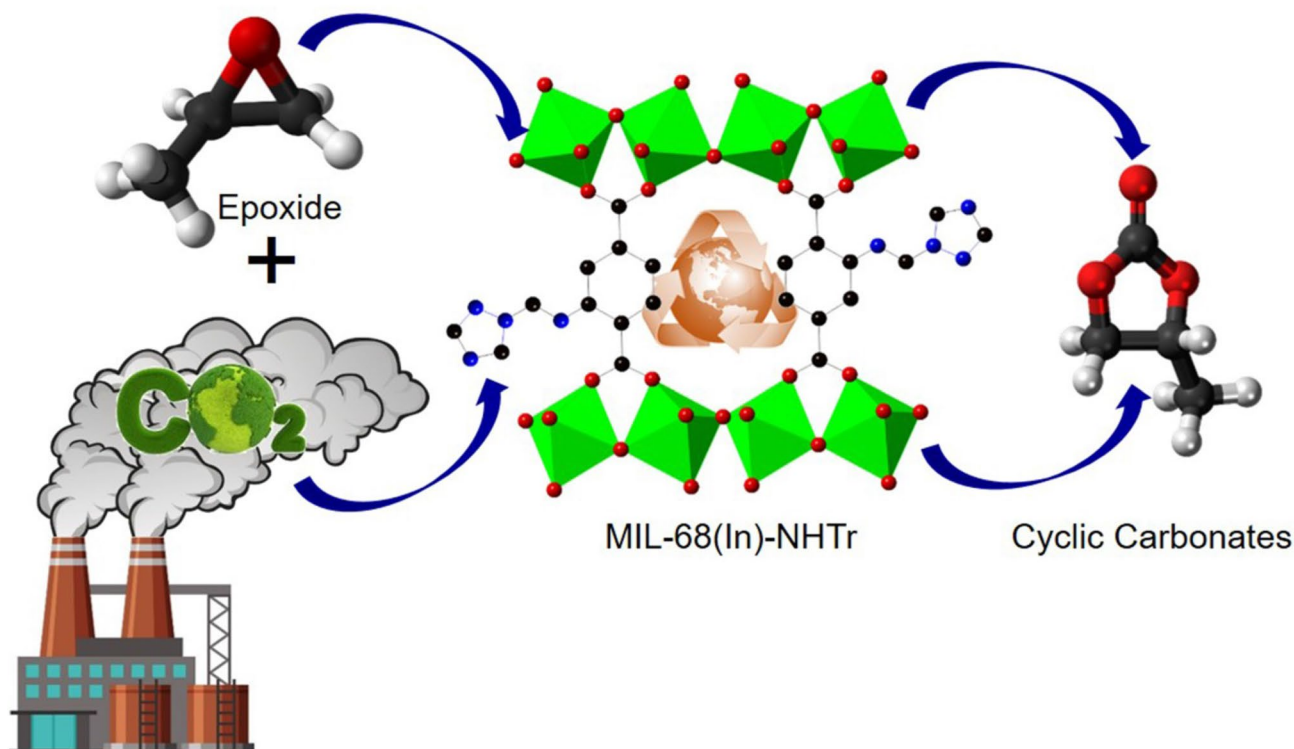
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Abstract

One of the efficient approaches to achieving net-zero greenhouse gas emissions is the 100% atom-economical conversion of the greenhouse gas carbon dioxide (CO₂) to cost-effective, less toxic cyclic carbonates that can act as green solvents and abundant C1 synthon in organic synthesis. In this work, we have synthesized an Indium Metal–Organic Framework (MOF), functionalized with triazole MIL-68(In)-NHTr (Tr = 1-methylene-1,2,4-triazole) as a bifunctional catalyst for the synthesis of cyclic carbonates from epoxides with high yield (96%) and selectivity (100%) under solvent-free ambient reaction conditions (CO₂ pressure 1 bar, temperature 50 °C, and reaction time 6 h). The synergistic acid–base effect of Indium SBU and the triazole of MIL-68(In)-NHTr make this a better catalyst than the conventional MIL-68(In)-NH₂. This new catalyst was non-leachable and was reusable for six consecutive catalytic cycles without appreciable loss in the catalytic efficiency and crystallinity of the MOF framework.

Graphical Abstract



Keywords Atom- economical · Indium Metal–Organic Framework · Greenhouse gas · Bifunctional · Cyclic carbonates

Extended author information available on the last page of the article

1 Introduction

The breakneck increase in anthropogenic carbon dioxide (CO_2) into the atmosphere has ensued in various environmental and societal solicitude such as global warming, glacier retreat, ocean acidification, thawing of frozen soil, and unpredictable weather patterns [1–3]. The dependence on fossil fuels to meet the world's burgeoning energy demands in industries and transportation has resulted in sufficient accretion of CO_2 in the atmosphere. Thus, to allay the level of CO_2 , the main focus was on sustainable CO_2 capture and storage (CCS) and consecutive utilization as a C1 source for the manufacture of fine chemicals [4–9]. All the chemical combustion results in CO_2 , an inexpensive, abundant, and thermodynamically stable gas (bond energy of +805 kJ/mol), as the final product. However, to overcome this inertness of CO_2 , a significant synthetic challenge, several suitable catalysts have been designed for the functionalization of the CO_2 into value-added energy-related products such as *N, N'*-disubstituted urea, dimethyl carbonates, cyclic carbonates, formic acid, methane, methanol, olefin, and other products under environmental-friendly conditions [10–14]. Among these catalytic transformations, the coupling of CO_2 with epoxides, high energy strained heterocyclic substrates, to form cyclic carbonates is considered to be not only a green chemical but also the most atom economical process. These cyclic carbonates are valuable intermediates for manufacturing agricultural, pharmaceuticals, and fine chemicals [15, 16]. They are also used as aprotic, polar, green solvents in organic reactions [17], in lithium-ion batteries as electrolytes [18], in cosmetics, as precursors for the synthesis of polycarbonates, polyurethanes, furazolidone, fuel additives [19], and lubricating grease [20]. Different homogeneous catalysts based on transitional metal complexes, metallic oxides, organic bases, ionic liquids, and organocatalysts have been used in the synthesis of cyclic carbonates. However, recycling and separation of catalysts from the product is the primary obstruction in the industrialization of this process [21, 22]. Thus, heterogeneous catalysts based on Metal–Organic Frameworks (MOFs) [23], porous carbon [24], mesoporous silica [25], metal oxides [26], zeolites [27], and polymers [28, 29] with simple separation methods and excellent recyclable performances, became promising catalysts for cycloaddition reactions.

MOFs are structurally tunable extended crystalline porous materials prudently designed by the coordination-driven integration between different types of functionalized linkers and metal ions or clusters. Diversifying these two structural components bestows MOF with resilience in the design of channel type and sizes, and functionalization

of the surface, pores, and open metal sites [30]. These render MOFs as excellent porous functional materials for application in catalysis [31], sensors [32], CO_2 capture and utilization [33], and biological applications [34]. MOF-catalyzed CO_2 -epoxide cycloaddition was first reported in 2009 [35], since then, the number of MOFs reported has increased rapidly, with the majority zinc-based [36]. Indium-based MOF, due to its unique electronic configuration [37], forms different secondary building units (SBU) such as $[\text{In}(\text{O}_2)_4]$ [38], $[\text{In}(\text{OH})]_\infty$ [39], and $[\text{In}_3\text{O}_4(\text{O}_2)_6]$ [40]. The strong affinity of the dicarboxylate linkers towards In^{3+} makes In-based MOF stable towards the air, water, temperature, and common organic solvents. Their reusability and non-leaching properties make them environmentally favorable catalysts [41]. Moreover, it can easily accept electrons in its readily accessible high-level p-orbitals and act as a strong Lewis acid. MOFs are often functionalized with N-heterocyclic functional groups such as pyridine, imidazole, or triazole to provide Lewis basic sites (LBS) that increase the interaction with CO_2 , thus enhancing CO_2 capture [42–44]. However, functionalization with the N-heterocycles should always take place on the framework of the MOF to avoid undesirable coordination with metal nodes. Thus, in this paper, we have carried the isorecticular synthesis of triazole functionalized MIL-68(In)- NH_2 to form MIL-68(In)-NH-Tr that was employed as bifunctional catalysts containing Lewis acid and basic sites for the capture of carbon dioxide and synergistic conversion to cyclic carbonates (Fig. 1).

2 Result and Discussion

2.1 Characterization of the Linker H_2L

This work involves the functionalization of 2-aminoterephthalic acid with a 1,2,4-triazole moiety to produce the linker H_2L (Fig. 2). Methyl ester of 2-aminoterephthalic acid (compound 1), formaldehyde, and 1,2,4-triazole were coupled together to give compound 2, and subsequent deprotection of 2 by alkaline hydrolysis gave H_2L in good yield (Scheme S1, Section S1.2, SI (Supporting Information)). The structures of 2 and H_2L were corroborated by ^1H NMR, ^{13}C NMR, and elemental analysis data (Figure S1–S4 of Section S1.2, SI). The ^1H NMR spectra of H_2L exhibited a doublet peak at δ 6.38 ppm, which corresponds to the ($-\text{CH}_2-$) protons bridging the 2-aminoterephthalic acid with 1,2,4-triazole. Furthermore, the peaks at δ 8.8 ppm and 8.02 ppm are assigned to the protons of the triazole ring, while the doublet peaks at δ 8.09 ppm, δ 7.21 ppm, and a singlet at δ 7.85 ppm correspond to the benzene ring protons of the terephthalate.

Fig. 1 The schematic representation of MIL-68(In), MIL-68(In)-NH₂, MIL-68(In)-NHTr

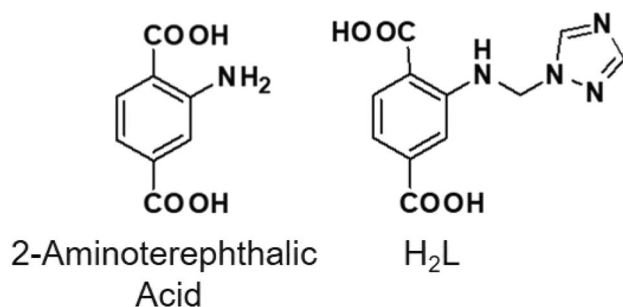
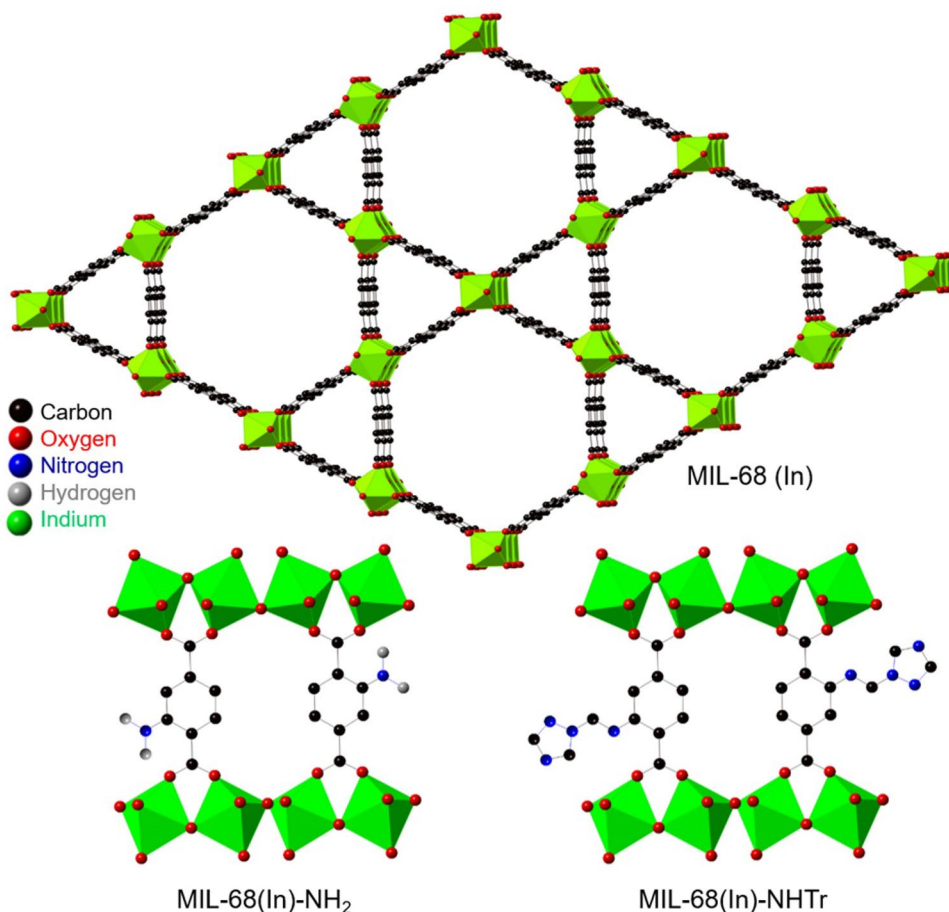


Fig. 2 The linkers used in this work

2.2 Characterization of MIL-68(In)-NH₂ and MIL-68(In)-NHTr

The MIL-68(In)-NH₂ and MIL-68(In)-NHTr were prepared by a slight modification of the literature procedure (Section S1.2, SI) [45]. The PXRD of MIL-68(In)-NH₂ exhibited characteristic peaks at $2\theta = 4.78^\circ$, 8.2° , 9.48° , and 12.52° . These distinctive peaks were also present in the triazole functionalized MIL-68(In)-NHTr (Fig. 3), which demonstrates that appending triazole moiety to the main backbone

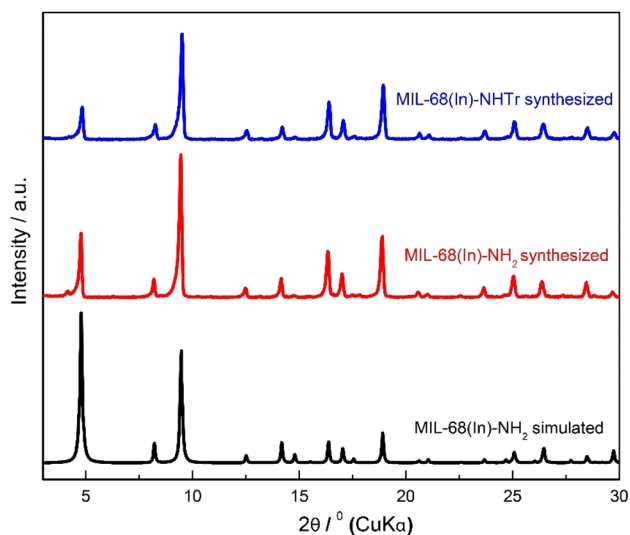


Fig. 3 Powder X-ray diffraction (PXRD) analysis of MIL-68(In)-NHTr (blue), MIL-68(In)-NH₂ (red), and MIL-68(In)-NH₂ simulated (black)

of MIL-68(In)-NH₂ does not disturb its framework connectivity and the crystallinity is intact. The study of the Fourier Transform Infrared spectrum of MIL-68(In)-NHTr and MIL-68(In)-NH₂ (Figure S5, SI) exhibited a broad band centered at 3442 cm⁻¹ and 3426 cm⁻¹ due to the O–H stretching vibrations of the coordinated water molecules and the N–H stretching vibrations respectively. Peaks at 1697 cm⁻¹, 1658 cm⁻¹, and 1559 cm⁻¹, 1560 cm⁻¹ correspond to asymmetric and symmetric stretching of the coordinated carboxylated groups (COO⁻) of MIL-68(In)-NHTr and MIL-68(In)-NH₂. The sharp peaks at 1390 cm⁻¹ and 1342 cm⁻¹ are assigned to the C–N stretching vibrations of the benzene ring in MIL-68(In)-NHTr and MIL-68(In)-NH₂, respectively. Other sharp peaks at 1384 cm⁻¹ in both MOFs represent the C=C stretching vibration of the benzene ring. Peaks at 746 cm⁻¹ and 769 cm⁻¹ are due to the stretching vibration of the C–H bond of the benzene ring of the framework in MIL-68(In)-NHTr and MIL-68(In)-NH₂, respectively. In MIL-68(In)-NHTr, the additional peaks from the appended triazole ring are the C=N stretching peak at 1613 cm⁻¹, C–N stretching peak at 1505 cm⁻¹, and 1295 cm⁻¹, and N–N stretching peak at 1156 cm⁻¹. The FESEM image of the microcrystalline MIL-68(In)-NHTr shows evenly distributed rod-shaped cuboid particles (Figure S6, SI).

The thermal stability of MIL-68(In)-NHTr was determined by the thermogravimetric analysis (TGA) with a heating rate of 5 °C min⁻¹ under air (Fig. 4). There is a preliminary weight loss of 7% within 100 °C due to the removal of water and another mass loss of 14.4% at 200 °C to remove trapped solvent molecules (DMF) from the pores and attached to the framework of the MOF. Finally, there is an abrupt mass loss of 50.9% at 390 °C due to the decomposition of the MIL-68(In)-NHTr framework, with a remaining residue of 27.7% corresponding to In₂O₃. This indicates that

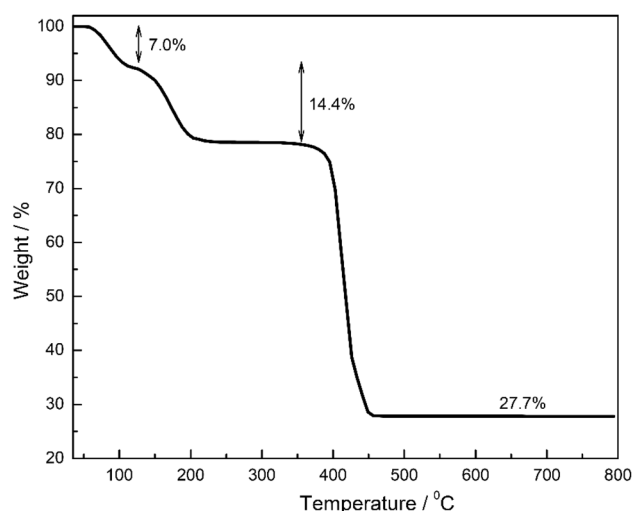


Fig. 4 TGA of MIL-68(In)-NHTr

triazole functionalized MOF has good thermal stability up to 390 °C. Comparative X-ray photoelectric emission spectroscopy (XPS) studies of MIL-68(In)-NHTr and MIL-68(In)-NH₂ were performed in Fig. 5. In both spectra, we found the characteristic peaks of In3d_{3/2} and In3d_{5/2} at 451.0 eV and 443.9 eV, respectively. The spectra of both the MOF characteristic peaks at 284.1 eV and 531.9 eV are assigned to C1s and O1s, respectively. Furthermore, the peak at 398.0 eV is assigned to the N1s, but in the case of MIL-68(In)-NHTr, the peak of N1s is broader and more intense. This also implies the coupling of the triazole moiety with the framework.

The nitrogen physisorption isotherm of both MIL-68(In)-NHTr and MIL-68(In)-NH₂ indicated that it is Type I with a sharp uptake at low relative pressure (P/P_0) of 0 to 0.05, which predicts that both are microporous (Fig. 6). The BET surface area obtained from the isotherms for MIL-68(In)-NH₂ was 750 m²g⁻¹ and for MIL-68(In)-NHTr was 405 m²g⁻¹. This curtail in the surface area of MIL-68(In)-NHTr signifies the successful attachment of the triazole moiety with the MIL-68(In)-NH₂ framework. The CO₂ adsorption isotherm for MIL-68(In)-NHTr was investigated at two different temperatures (273 K and 298 K), with the maximum adsorption of 83.5 cc g⁻¹ at 273 K (Fig. 7). The CO₂ adsorption in the triazole appended MOF was more than MIL-68(In)-NH₂ (52.6 cc g⁻¹ at 273 K) [46] due to the CO₂-phillic nature of the nitrogen-rich triazole moiety. The isosteric heat of adsorption (Q_{st}) was determined using the Clausius–Clapeyron equation and CO₂ adsorption isotherm at 273 K and 298 K (Figure S7, SI). The Q_{st} value of CO₂ for MIL-68(In)-NHTr was determined to be 32.5 kJ mol⁻¹, indicating a strong interaction between CO₂ and MIL-68(In)-NHTr. To interpret the structural features

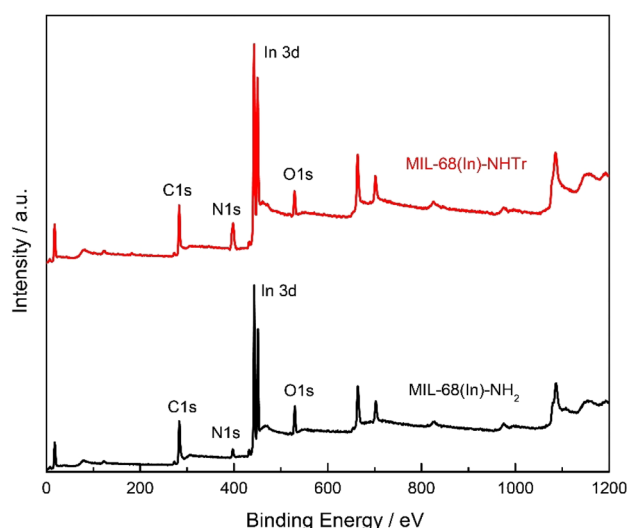


Fig. 5 XPS analysis of MIL-68(In)-NHTr (red) and MIL-68(In)-NH₂ (black)

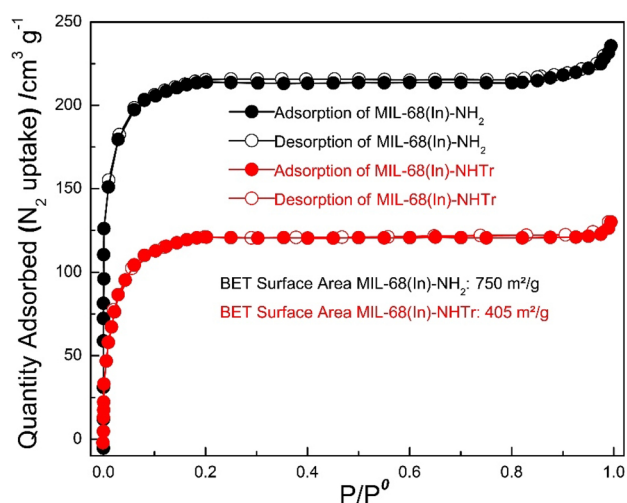


Fig. 6 N₂ Adsorption isotherm of MIL-68(In)-NHTr and MIL-68(In)-NH₂

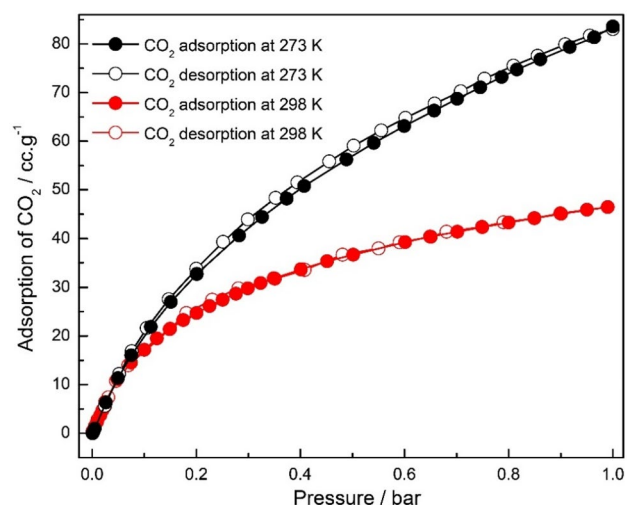


Fig. 7 CO₂ Adsorption isotherm of MIL-68(In)-NHTr

of MIL-68(In)-NHTr and its basic characteristics compared to MIL-68(In)-NH₂, we also carried CO₂-

TPD (Figure S8, SI). The basicity in these kinds of MOFs is of two types, weak (323–450 K) and medium to strong (450–773 K) [43]. CO₂-TPD of the MIL-68(In)-NHTr showed a TPD peak around 554 K which corresponds to the medium Lewis basic sites due to the presence of triazole. In contrast, MIL-68(In)-NH₂ showed meager weak and medium basicity around 400 to 550 K. The NH₃-TPD (Figure S9, SI) of both MIL-68(In)-NHTr and MIL-68(In)-NH₂ showed one desorbed peak at 200 °C that corresponds to the Lewis acidic sites originating from the coordinatively unsaturated sites (CUS) of the Indium clusters. The NH₃-TPD of both MIL-68(In)-NHTr and MIL-68(In)-NH₂

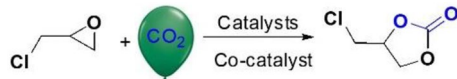
were analogous due to the identical nature of the Indium clusters as the Lewis acidic sites.

2.3 Catalysis

This Lewis acidic Indium-based MOF, MIL-68(In)-NHTr was designed with triazole to have a Lewis basic site. It was employed as a single-site acid–base catalyst for the synthesis of cyclic carbonates from the CO₂ fixation cycloaddition reaction of epoxides with CO₂. The evaluation studies for the catalytic activities of MIL-68(In)-NHTr and optimization of the reaction conditions were done using Epichlorohydrin (EC) as the model substrate, under the pressure of 1 bar, and tetrabutylammonium salts as the co-catalysts in a green solvent-free.

Reaction conditions: Epichlorohydrin-10 mol, catalysts-2.0 mol%, co-catalyst-1.0 mol%, Pressure -1 bar, temperature- 50 °C, reaction time- 6 h. ^aSelectivity was based on ¹H NMR spectra of the crude reaction mixtures. condition. In the absence of the catalyst and co-catalyst, there was no product formation, and in presence of only catalysts, the yield was only 28%, even after heating at 50 °C for 6 h (Entry 1 and 2, Table 1). MIL-68(In)-NH₂, and 1,2,4-triazole independently in the presence of co-catalysts (tetrabutylammonium bromide, TBABr), reaction temperature 50 °C for 6 h yields 21%, and 13% products respectively (Entry 3, and 4, Table 1). Only MIL-68(In)-NHTr in presence of TBABr, reaction temperature of 50 °C for 6 h, and pressure of 1 bar produce 96% yield (Entry 5, Table 1). In the case of MIL-68(In)-NHTr, along with the Lewis acidic In(III) SBU, the covalently linked nitrogen-rich triazole provides Lewis basic sites. The synergistic acid–base effect of MIL-68(In)-NHTr

Table 1 Catalytic activity optimization

				
Entry	Catalysts	Co-catalysts	Yield (%)	Selectivity (%) ^a
1	–	–	0	–
2	MIL-68(In)-NHTr	–	28	100
3	MIL-68(In)-NH ₂	TBABr	21	100
4	1,2,4-Triazole	TBABr	13	100
5	MIL-68(In)-NHTr	TBABr	96	100
6	MIL-68(In)-NHTr	TBAI	45	96
7	MIL-68(In)-NHTr	TBACl	22	98
8	–	TBABr	10	100

Reaction conditions: Epichlorohydrin-10 mmole, catalysts- 2.0 mol%, co-catalyst-1.0 mol%, Pressure -1 bar, temperature- 50 °C, reaction time- 6 hours. ^aSelectivity was based on ¹H NMR spectra of the crude reaction mixtures

escalates the productivity of the cycloaddition reaction in comparison to the unfunctionalized MIL-68(In)-NH₂. We also used tetrabutylammonium iodide (TBAI) and tetrabutylammonium chloride (TBACl), to optimize the co-catalyst, but the yields of the product deteriorated (Entry 6 and 7, Table 1). Though iodide ions (TBAI) are a strong leaving group and have high nucleophilicity compared to the bromide ion (TBABr), the size of the iodide ion is larger than the bromide ion, which makes it less accessible to the catalytic sites than the bromide ion. Moreover, bromide ions are a stronger leaving group and more nucleophilic than the chloride ion (TBACl). Thus, TBABr was found to be a more suitable co-catalyst than the TBAI or TBACl.

Furthermore, we also optimized the reaction parameters for the cycloaddition of epoxides to form EC carbonate at an ambient CO₂ pressure of 1 bar. Figure 8 demonstrates the optimization of the catalyst and co-catalyst loading (Fig. 8a, b), temperature (Fig. 8c), and reaction time (Fig. 8d) for maximum productivity. Thus, these reactions provide us with the optimum reaction parameters of catalysts loading of 2.0 mol%, co-catalysts loading of 1.0 mol%, reaction

temperature of 50 °C, and reaction time of 6 h, which leads to the maximum yield of EC to its respective cyclic carbonate.

To demonstrate the versatility of MIL-68(In)-NHTr, its catalytic behavior in the formation of cyclic carbonates from different aliphatic and aromatic epoxides was investigated. Interpretation of Table 2 exhibits that MIL-68(In)-NHTr can competently convert all the aliphatic epoxides to the corresponding cyclic carbonates at a reaction temperature of 50 °C, the reaction time of 6 h, with 2.0 mol% of the catalyst, and 1.0 mol% of the co-catalysts, and 1 bar pressure (yield 94–96%) (Entry 1, 2, 3, 5 and 6, Table 2). However, in the case of bulky epoxides such as styrene epoxides and phenyl glycidyl ether (Entry 7 and 8, Table 2) the yield is relatively low due to the small pore size from functionalization that hinders the substrate from entering the catalyst's active site within the MOF. Similarly, due to the steric hindrance of the bulky disubstituted cyclohexene oxide, the corresponding cyclic carbonates yield is also reduced. In all the cycloaddition reactions with different epoxides, the cyclic carbonates yield and selectivity were confirmed by ¹H NMR and ¹³C

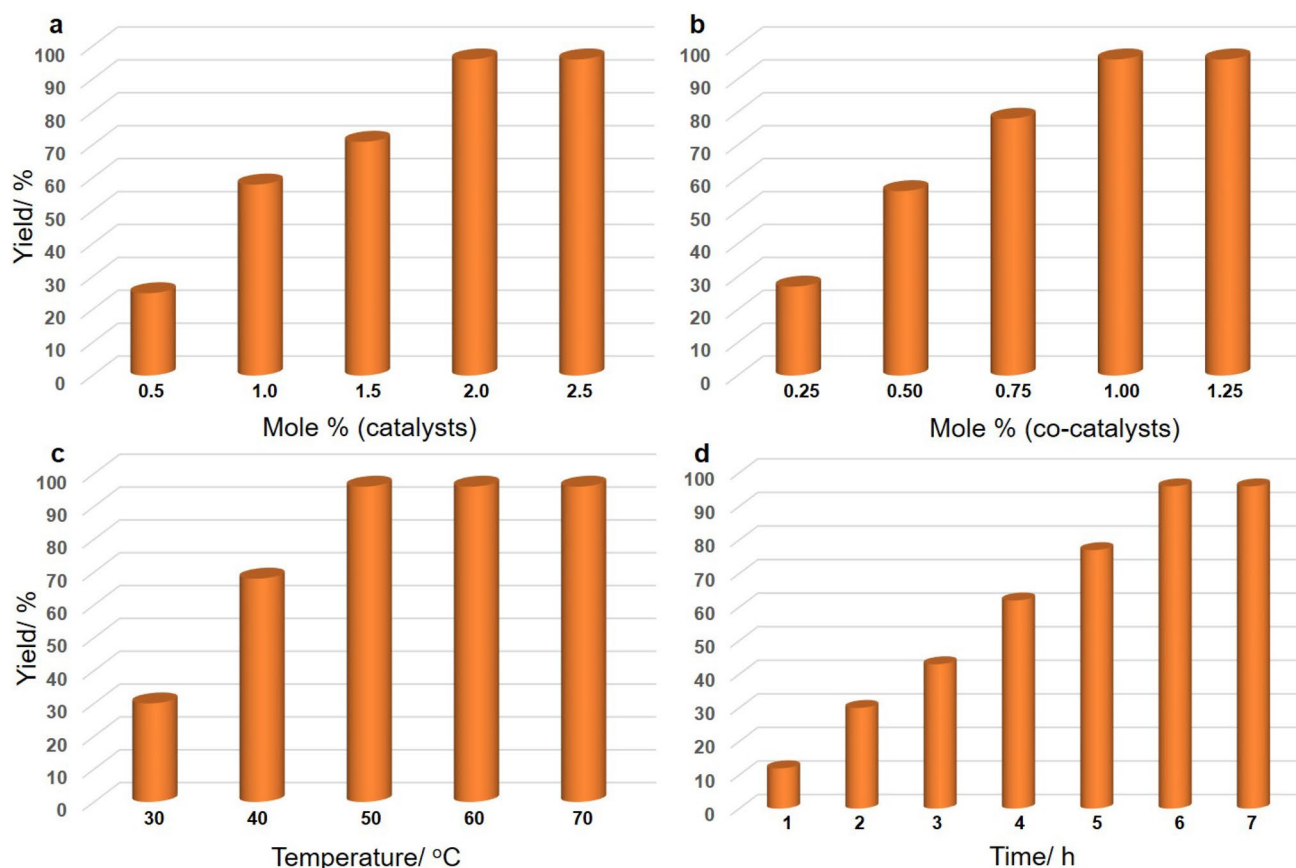
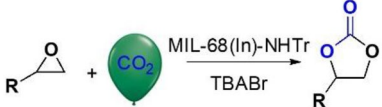

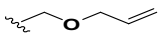

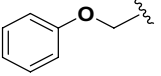
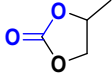
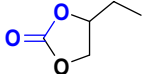
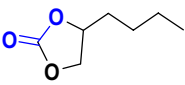
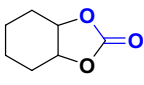
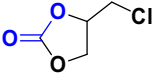
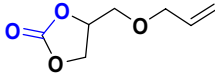
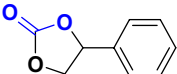
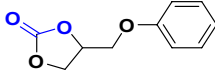


Fig. 8 Effect of reaction parameters for MIL-68(In)-NHTr on the cycloaddition of EC and CO₂: (a) catalyst amount (50 °C, 6 h, 1.0 mol% co-catalyst, 1.0 bar P_{CO_2}), (b) co-catalyst amount (2.0 mol% catalyst, 50 °C, 6 h, 1.0 bar P_{CO_2}), (c) reaction temperature

(2.0 mol% catalyst, 1.0 mol% co-catalyst, 6 h, 1.0 bar P_{CO_2}), and (d) reaction time (2.0 mol% catalyst, 1.0 mol% co-catalyst, 50 °C, 1.0 bar P_{CO_2})

Table 2 Synthesis of cyclic carbonates from various epoxides

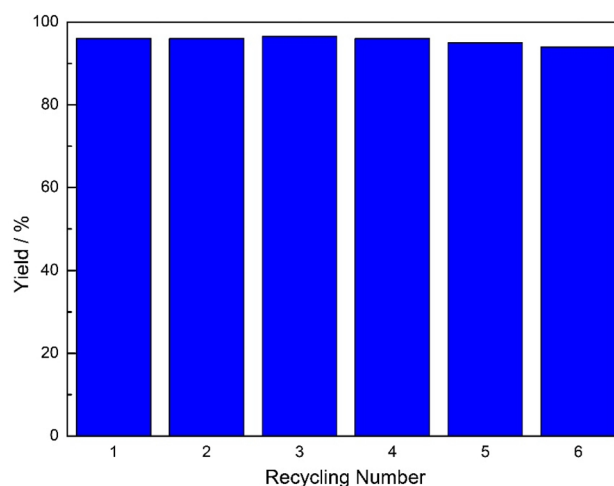
			
Entry	R	Products	Yield ^a (%)
1	–CH ₃		94
2	–CH ₂ CH ₃		96
3	–CH ₂ CH ₂ CH ₂ CH ₃		95
4			66
5	–CH ₂ Cl		96
6			95
7			80
8			74

^aReaction conditions: Substrate-10 mol, catalysts- 2.0 mol%, co-catalyst-1.0 mol%, reaction time- 6 h, temperature-50 °C, pressure-1 bar. The yield was determined from the ¹HNMR

NMR of the isolated products (Supporting Information, Section S3, and S4, Figure S10–S25). The potential of the catalyst MIL-68(In)-NHTr to catalyze epoxide-cycloaddition reaction was compared with the recently reported catalytic systems (Table S1, section S5, SI). After analyzing the data it was confirmed that efficient MOF-based catalysts such as MIL-68(In)-NHTr for CO₂ cycloaddition conversion under ambient conditions with high yields are limited in the literature.

In addition, the recyclability of MIL-68(In)-NHTr was investigated for the cycloaddition of EC with CO₂ to form cyclic carbonates. It was found that MIL-68(In)-NHTr displayed good conversion of epoxides to cyclic carbonates up to six cycles (Fig. 9) without any damage to the crystallinity and framework integrity of the catalyst (Figure S26, SI). The leaching test of MIL-68(In)-NHTr by the hot filtration method also confirmed that the catalyst is not leaching into the product (Figure S27, SI).

From the mechanistic viewpoint, we find that this bifunctional MIL-68(In)-NHTr contains highly dense Lewis acidic


Fig. 9 Recycle tests with MIL-68(In)-NHTr for the reaction of CO₂ with EC to form cyclic carbonates

In(III) sites in the SBU and CO₂-philic nitrogen-rich basic sites of the triazole that promotes the polarization of the epoxides and the CO₂ respectively. These Lewis acidic Indium SBU coordinate with the oxygen atom of the epoxides (EC) producing the adduct I, which then undergoes a nucleophilic reaction with the bromide ion of the TBABr, causing the opening of the three-membered epoxide ring II. Further, the CO₂ being polarized by the triazole moiety go through a nucleophilic attack by the negatively charged oxygen of the opened epoxy ring resulting in the formation of an alkyl carbonate anion III. Following this, the ring closure step takes place with the formation of the corresponding cyclic carbonate. Finally, the cyclic carbonates detach themselves from the catalyst (Indium SBU) for consecutive cycles (Fig. 10) [36].

3 Conclusion

In the denouement, we have prepared an Indium-based bifunctional MOF catalyst, MIL-68(In)-NHTr by coupling a triazole to the main framework of the MIL-68(In)-NH₂. It acts as a single-site acid–base catalyst for CO₂ fixation through cycloaddition reaction of epoxides with CO₂ to form cyclic carbonates with high yield and selectivity. The synergistic acid–base effect of the Lewis acidic Indium SBU and the Lewis basic triazole of MIL-68(In)-NHTr helps in the transformation of different aliphatic and aromatic epoxides to cyclic carbonates with good yields under solvent-free ambient reaction conditions (CO₂ pressure 1 bar, temperature 50 °C and time 6 h). The catalyst was non-leachable and can be recycled for 6 consecutive cycles without substantial change in the catalytic activity.

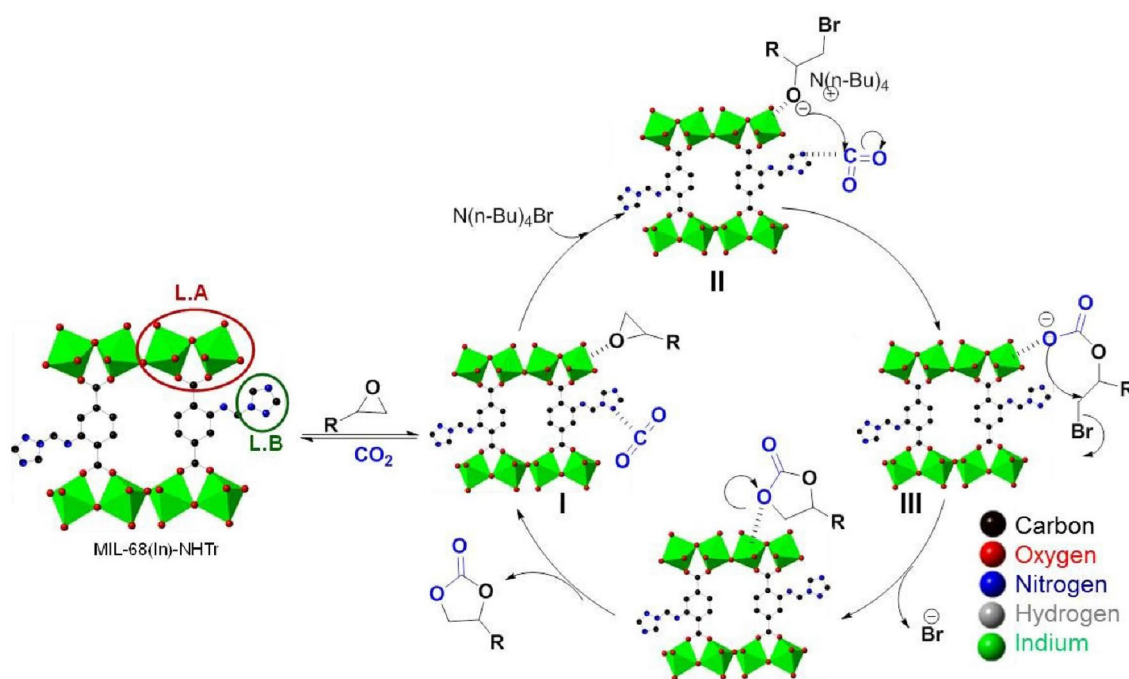


Fig. 10 The plausible mechanism for cyclic carbonate formation catalyzed by MIL-68(In)-NHTr (L.A-Lewis acidic sites, L.B-Lewis basic sites)

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10562-022-04213-x>.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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