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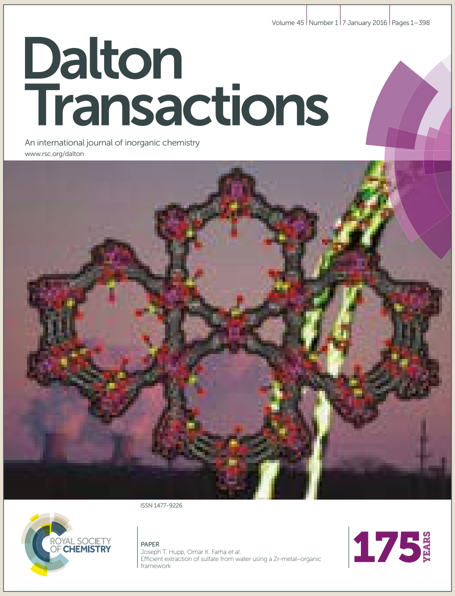

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ARTICLE

Amine Functionalized Zn(II) MOF as an Efficient Multifunctional Catalyst for CO_2 Utilization and Sulfoxidation Reaction

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Parth Patel,[a,c] Bhavesh Parmar,[b,d] Rukhsana I. Kureshy,[a,d] Noor-ul H. Khan*[a,c,d] and Eringathodi Suresh*[b,d]

Zinc (II) based 3D mixed ligand metal organic framework (MOF) was synthesized by versatile routes including green mechanochemical synthesis. MOF $\{[Zn(ATA)(L).H_2O]\}_n$ (**ZnMOF-1-NH$_2$**) has been characterized by various physico-chemical techniques including SCXRD and composed of bipyridyl-based Schiff base, (E)-N'-(pyridin-4-ylmethylene)isonicotinohydrazide (L) and 2-aminoterephthalic acid (H_2ATA) ligands as linkers. The MOF material has been explored as a multifunctional heterogeneous catalyst for the cycloaddition reaction of alkyl and aryl epoxides with CO_2 and sulfoxidation reactions of aryl sulfides. The influence of various reaction parameters were examined and optimized the performance of the catalytic reactions. Solvent free catalytic reaction offered good catalytic conversion in the case of cyclic carbonates and for sulfoxide good conversion and selectivity is achieved in presence of DCM as a solvent medium at ambient reaction conditions. Chemical and thermal stability of the catalyst was good and the catalyst was active up to four catalytic cycles without significant loss of activity. Based on the catalytic activity and structural evidence plausible mechanism for both catalytic reaction is also proposed.

Introduction

The quests for green technologies that utilize the emission of CO_2 from industries and power plants as well as sulfoxidation of organic compounds to value added chemical intermediate by appropriate catalytic reaction is a prime area of research to contain the greenhouse effect and human healthcare respectively.[1-3] Recent years have witnessed the advent of adaptable catalysts that promote the transformation of CO_2 to cyclic carbonates which has relevance in green and sustainable environment and oxidation of organic sulfides to value added drug intermediate in pharmaceutical industry.[4-9] For justifying the adverse effect of the greenhouse gas, utilization of CO_2 as a chemical feedstock to produce valuable chemicals is an alternative sustainable approach. Significant efforts are therefore currently being devoted for the development of appropriate materials that are able to selectively capture the CO_2 and facilitate catalytic conversion through chemical fixation into useful products.[10-14] The coupling reaction of CO_2 with epoxides to provide cyclic carbonates in presence of different catalysts is considered as one of the best strategies for CO_2 conversion due to its excellent reactivity and high atom efficiency. Cyclic carbonates are well known with significant and extensive applications as aprotic polar solvents, precursors for affording polycarbonates, and chemical intermediates in organic synthesis.[15-26] Many homogeneous catalysts have been developed for cycloaddition reaction with CO_2 and epoxides as well as for sulfoxidation reactions with good activity and efficiency.[27-39] Complex separation, purification, and recycling problems in homogenous catalysis severely limit their application in industry. This demands the need for a robust, recyclable multifunctional heterogenous catalyst with good chemical and thermal stability that can works efficiently under mild reaction conditions.[40] Materials with following features such as high surface area/ porosity and good adsorption capacity, adequate Lewis/Brønsted acidic or basic sites, high chemical and thermal stability upon exposure to the reaction conditions including substrates favors efficient heterogenous catalytic reactions. Several types of heterogeneous catalysts based on porous materials such as zeolites, silica-supported salts, microporous organic polymers (MOPs) have been explored for the synthesis of cyclic carbonates and sulfoxidation reactions.[41-48]

As a new kind of crystalline porous material, Metal organic frameworks (MOFs) are constructed from multidentate organic building blocks linking metal or metal clusters which

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[a] Inorganic Materials and Catalysis Division, CSIR-Central Salt and Marine Chemicals Research Institute, G. B. Marg, Bhavnagar-364 002, Gujarat, India.
[b] Analytical and Environmental Science Division and Centralized Instrument Facility, CSIR-Central Salt and Marine Chemicals Research Institute, G. B. Marg, Bhavnagar-364 002, Gujarat, India.
[c] Charotar University of Science & Technology, Changa- 388 421, Anand, Gujarat, India.
[d] Academy of Scientific and Innovative Research (AcSIR), CSIR-Central Salt and Marine Chemicals Research Institute, G. B. Marg, Bhavnagar-364 002, Gujarat, India.
E-mail: nhkhan@csmcri.res.in; esuresh@csmcri.res.in; sureshe123@rediffmail.com

† Footnotes relating to the title and/or authors should appear here.

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display periodic architectures and inherent porosity with wide range of application. The captivating uniqueness of MOFs is the tunability and tailoring of the structure through a delicate design of molecular building units in the form of organic linkers and the coordination geometry around the metal nodes. MOFs have emerged as porous frameworks for various applications attributable to their robust/ high thermal stability, large surface area and tunable composition for the adsorption and separation of gas molecules including greenhouse gas CO_2.[49-54] Recently, MOFs have also been revealed as efficient catalysts for heterogeneous catalysis reactions.[55-60] Nevertheless, the field of MOFs as heterogeneous catalysts for CO_2 conversion and sulfoxidation reaction in particular has remained largely untapped. Park *et al.* and Ma *et al.* has done some pioneering work in the area of MOF catalyzed CO_2 fixation reactions at ambient reaction condition to yield value added intermediates.[61-72] It is worth mentioning here reports by Ma *et al.* and Jiang's group for CO_2 cycloaddition under mild condition (at room temperature and under 1 bar CO_2 pressure) by MOF with *nbo* topology and Al based MOF USTC-253-TFA respectively.[73-74] On the other hand, one of the most important catalytic reactions is the oxidation of sulfides to sulfoxides and sulfones, which has potential usage in the chemical industry, biology, and medical chemistry.[75-79] There are many reports of the H_2O_2-based oxidation of sulfides by homogeneous organo-catalysts and heterogeneous polyoxometalates.[80-84] Heterogeneous oxidative desulfurization of sulfides by MOF catalyst is scantly reported in the literature and most of these reactions involves polyoxometalates (POMs) encapsulated metal organic framework (MOF). Albeit, enantioselective sulfoxidation has been studied using chiral MOFs as catalyst.[85-92] In these contexts, the development of an efficient oxidation of various kinds of sulfides with high yield and selectivity to sulfoxide is still in demand.

MOF with functional moieties in the ligand such as amino/amide group aligned on the pore wall can act as active sites which can increase the affinity to the substrate/ CO_2 in the catalytic reaction by supramolecular interactions. Presence of active Lewis acidic sites of the metal ions uniformly distributed in the MOF can also activate the catalytic efficiency.[93-96] The robust nature of MOF and their chemical and thermal stability imparts excellent recyclability of these materials. From the above background and perspective, we envisioned that the rationally designed MOF materials could serve as a good candidate for heterogeneous catalysts for the chemical conversion of CO_2 to cyclic carbonates and sulfoxidation reaction. Herein, we report a mixed ligand three dimensional MOF $\{[Zn(ATA)(L)].H_2O\}_n$ (**ZnMOF-1-NH₂**) synthesized by versatile synthetic routes, viz., diffusion of precursor solutions, conventional reflux, and green mechanochemical (grinding) reactions from bipyridyl-based Schiff base, (E)-N'-(pyridin-4-ylmethylene)isonicotinohydrazide (L) and amino functionalized 2-aminoterephthalic acid (H_2ATA) as linkers and its catalytic performance. Uniformly distributed Zn(II) Lewis acidic sites and amino/ amide functional groups of the ligand moiety on the pore walls attributes **ZnMOF-1-NH₂** an efficient heterogeneous catalyst for the chemical fixation of CO_2 to cyclic carbonates and sulfoxidation of organic sulfides under mild reaction conditions. Interestingly, **ZnMOF-1-NH₂** catalyst could be synthesized in good yield, crystallinity and phase purity by green mechano-chemical method.

Results and discussion

Characterization and Structural Features of ZnMOF-1-NH2

Physical characterization of **ZnMOF-1-NH₂** synthesized by adaptable routes to elucidate the bulk phase purity and detailed structural analysis by SCXRD has been reported by us elsewhere.[97] Conventional synthetic approach of MOF is based on reflux and solvothermal methods which often lead to the issues of solvent molecules remaining in the network as well as low yield. Mechano-chemistry (milling or grinding) offers an alternative green approach for the preparation of MOFs using the metal salts and the ligand precursors in appropriate stoichiometry.[98-99] In addition, mechanochemical (milling or grinding) reactions supports advantages such as low energy requirement, less time consumption, minimal solubility issues and environment friendly for synthesis MOF materials with good yield and phase purity. Our synthetic strategy of the bulk catalytic material (**ZnMOF-1-NH₂**) cover adaptable approaches which includes conventional reflux and the green mechanochemical method. Particulars of the MOF synthesis by different route and their characterization by Powder X-ray diffraction (PXRD), FTIR and TGA is provided in the supporting data.

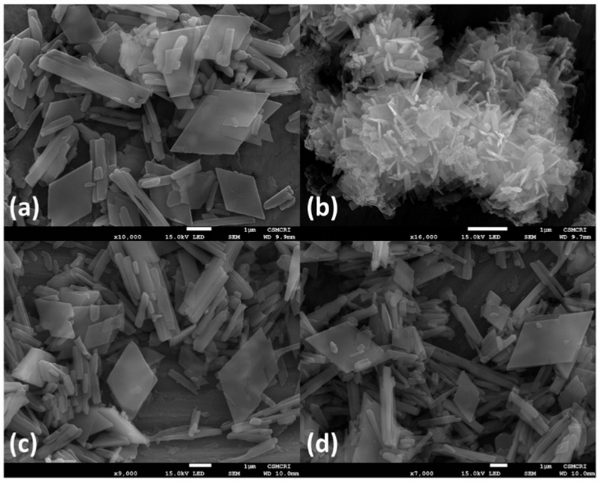

Figure 1. FE-SEM images for **ZnMOF-1-NH₂** (a) conventionally synthesized, (b) mechanochemically synthesized, (c) recovered after 4th catalytic cycle of cycloaddition, and (d) recovered after 4th catalytic cycle of sulfoxidation reaction.

The phase purity/ bulk homogeneity, chemical /thermal stability of the pristine catalyst as synthesized and recovered after 4 catalytic cycles have been characterized PXRD, FTIR, FE-SEM and TGA analysis. Simulated PXRD data of the CIF file from CCDC data matches well with the experimental PXRD pattern of the MOFs synthesized by different routes, suggesting bulk phase purity of the catalysts (Figure S1). As

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depicted in Figure S2, FTIR data of both pristine and recovered catalyst revealed good agreement establishing the structural and chemical stability of **ZnMOF-1-NH$_2$** after the catalytic reaction and the TGA profile indicate the thermal stability up to ~ 280-310 ^{o}C. (Figure S3). FE-SEM images depicted in Figure 1 clearly revealed well defined morphology for the crystalline material for the pristine MOF as well as the compound recovered after 4 catalytic cycles retaining the textural features of the catalyst.

Gas sorption analysis of activated **ZnMOF-1-NH$_2$** in vacuum at 120 °C reveals selectively towards CO_2 over N_2 (Figure S4). Due to their structural flexibility, 2D Zn(II) MOFs belonging to the same family having different substituents in the dicarboxylic acid and the same N-donor Schiff base ligand has been reported to show very interesting sorption properties and disclosed selective adsorption of CO_2 over N_2. Pores size, polarity or kinetic issue can influence the sorption property of the nets for the preference of CO_2 over N_2 adsorption. The polar amide functional group of the acyl hydrazone Schiff base ligand /-NH_2 from the ATA ligand of the framework can interact with high quadrupole moment of CO_2.[100-101] The adsorption analysis reveals that activated **ZnMOF-1-NH$_2$** adsorb CO_2 having smaller kinetic diameter (3.30 Å) over larger N_2 (3.64 Å) and no significant uptake of N_2 is observed. As depicted in (Figure S4), CO_2 adsorption curve with hysteresis in the present case can be attributed to the guest-induced framework response. BET surface area and Langmuir surface area for **ZnMOF-1-NH$_2$** are 1.1554 m²/g and 0.4612 ± 0.1069 m²/g respectively.

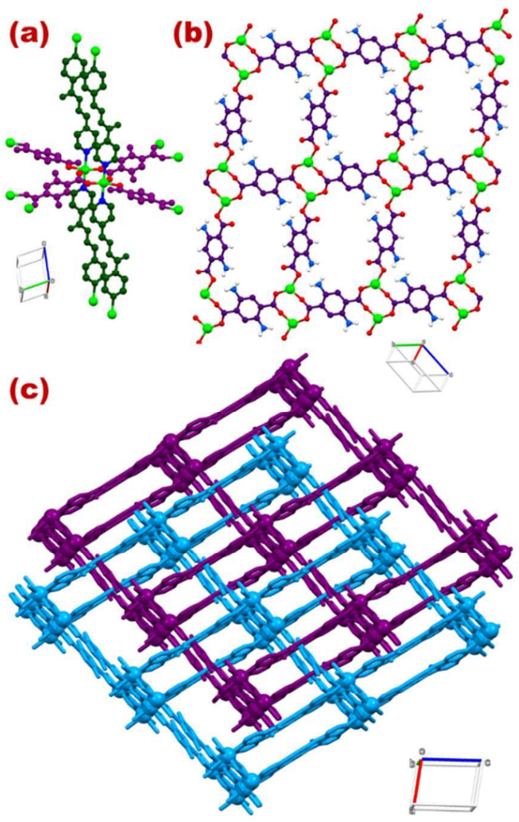

Figure 2. (a) Coordination environment around Zn metal centre in **ZnMOF-1-NH$_2$**, (b) 2D $[Zn_2(ATA)_2]_n$ *sql* sheets of **ZnMOF-1-NH$_2$** showing amino decorated dicarboxylate moiety coordinated with Zn(II) metal centre and (c) Packing along *b*-axis showing 2-fold interpenetrated 3D network in **ZnMOF-1-NH$_2$**

3D framework with interpenetration can self-orient themselves upon supramolecular interaction between the polar CO_2 groups with arylhydrazones moiety of the Schiff base ligand /NH_2 group of the dicarboxylate decorating the framework pores favoring better affinity for CO_2 over N_2 and the hysteresis observed in the adsorption profile. The measured CO_2 uptakes at 273 K is 1.4181 mmol of CO_2 per gram of MOF at 0.99 Relative Pressure (P/Po) which can favors the cycloaddition reaction in the present investigation. The acidity (amount and strength) of the catalyst was determined by NH_3-TPD measurement (Figure S29). The NH_3-TPD experiment shows that NH_3 is desorbed in the temperature range of 50–400 ^{o}C with major peaks at 315 ^{o}C (desorbed amount of NH_3 27.081 mmol/g). Crystal structure analysis revealed that **ZnMOF-1-NH$_2$** crystalized in triclinic system with $P\overline{1}$ space group and comprehend a 3D framework in which Zn(II) metal nodes are linked via dicarboxylate and N-donor Schiff base ligand (Figure 2a). As depicted in Figure 2b, dimeric clusters of $[Zn_2(COO)_2]$ secondary building units are linked by the carboxylate oxygens of symmetrically disposed ATA ligands creating a two dimensional $[Zn_2(ATA)_2]_n$ *sql* sheets. Double-pillaring of $[Zn_2(ATA)_2]_n$ *sql* net by the terminal nitrogen atoms of the bipyridyl-based N-donor Schiff base ligand ensuing a three dimensional network with *pcu* topology for **ZnMOF-1-**

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NH_2 (Figure 2c). The effective void of the 3D framework is reduced due to the two-fold interpenetration of the 3D nets via N-H···O hydrogen bonding between the amide hydrogen of L and carboxylate oxygen of ATA and probably the lattice water molecules are occupied in the void by supramolecular interactions. Penta coordination with coordinatively unsaturated Zn(II) metal center can act as an active catalytic site and the amide/amine functional groups of the ligand moiety may also favours the catalytic performance of the MOF material by efficient supramolecular interaction with the substrates (Figure 2a).

Cycloaddition of CO_2 with Epoxides

The cycloaddition of CO_2 with styrene oxide (SO) was selected as a model reaction to optimize the reaction conditions. Our preliminary catalytic experiments on the cycloaddition of carbon dioxide and epoxides by **ZnMOF-1-NH_2** were focused mainly to establish the reaction parameters in presence of a co-catalyst tert-butyl ammonium bromide (TBAB), tert-butyl ammonium Iodide (TBAI) and potassium Iodide (KI) using styrene oxide (SO) as a model substrate under solvent free condition. The reactions were performed at 0.8/1.0 MPa CO_2 pressure, temperature 60/80 °C with the reaction mixture covering SO (20 mmol), catalyst (0.21 mmol) and the respective co-catalyst (0.5 mmol) in a 50-mL stainless-steel autoclave with a magnetic stirrer at 600 rpm. Details of the reaction conditions and parameters are given in Table 1 and controlled experiments with complete absence of catalyst/co-catalyst and in presence of only TBAB, SO conversion was negligible (Table 1, entry 1 and 2), while catalytic reaction with pristine MOF yielded 38% styrene carbonate (SC) within 8 h reaction time (Table 1, entry 3). Keeping CO_2 pressure 0.8 MPa, variation of time and temperature was also monitored for **ZnMOF-1-NH_2**/TBAB system and a maximum of 95% SO conversion is achieved at 80 °C with 8 h reaction time (Table 1, entry 4-7). When the pressure is increased up to 1.0 MPa retaining other reaction conditions (Table 1, entry 10) revealed slight reduction in product yield. Notably, the conversion of SO is comparatively lower when TBAB was replaced by TABI or KI as the co-catalyst (Table 1, entry 9 and 10). Under the same reaction condition using 2.5 mol% of respective co-catalyst the product yield is in the order TBAB > KI > TBAI with % yield of product (SO to SC) is 88%, 85% and 81% respectively (Table 1, entry 7, 9 and 10).

Table 1. Cycloaddition of styrene oxide and CO_2 for styrene carbonate.*

Entry	Catalyst/ Co-catalyst	P_{CO2} (MPa)	Temp. (°C)	Time (h)	SO Conversion (%)	SC Selectivity (%)
1	None	0.8	80	8	11	99
2	TBAB	0.8	80	8	14	99
3	ZnMOF-1-NH_2	0.8	80	8	38	99
4	ZnMOF-1-NH_2/ TBAB	0.8	60	4	72	98
5	ZnMOF-1-NH_2/ TBAB	0.8	60	6	78	98
6	ZnMOF-1-NH_2/ TBAB	0.8	80	6	88	97
7	ZnMOF-1-NH_2/ TBAB	0.8	80	8	95	96
8	ZnMOF-1-NH_2/ TBAB	1.0	80	8	93	97
9	ZnMOF-1-NH_2/ TBAI	0.8	80	8	86	97
10	ZnMOF-1-NH_2/KI	0.8	80	8	90	98
11	ZnMOF-1-NH_2G/ TBAB	0.8	80	8	94	96

*Table Footnote Reaction conditions: SO = 20 mmol (2.28 mL at 25 °C), 600 rpm. Catalyst mol%: **ZnMOF-1-NH_2** = 1.0 mol% (0.21 mmol, 0.1 g); tetrabutyl ammonium bromide (TBAB) = 2.5 mol% (0.5 mmol, 0.161 g).

Higher activity was observed with the bromide compared to iodine salts in contrast to literature reports in which iodide was found to be the best promoters (in accordance to the increasing nucleophilicity). This may be due to bigger size of the iodide hindered the diffusion in the reaction process.[102-103] Thus, we can deduce that the co-catalyst TBAB has an important role in the catalytic reaction which may be attributed to the presence of labile leaving group Br^-. Representative reaction for mechanochemically prepared **ZnMOF-1-NH_2** for the cycloaddition reaction of CO_2 with SO has been conducted which showed no significant deviation in the product yield (Table 1, entry 11).

To explore the optimal reaction conditions, a series of reactions were designed upon incremental variation in CO_2 pressure, temperature, reaction time duration and catalyst amounts to obtain the best possible combination. The effect of variation of incremental addition of CO_2 on **ZnMOF-1-NH_2**-catalyzed SO-CO_2 cycloaddition is depicted in Figure 3. The conversion of SO steadily increased up to 32% upon 0.4 MPa pressure and faster styrene carbonate formation is observed in the pressure range 0.4-0.8 MPa with a maximum of 95% and no further significant conversion above 0.8 MPa CO_2 pressure. The improved SO conversion can be attributed to the

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enhancement in the solubility of CO_2 in the liquid phase in presence of the heterogeneous catalyst with pressure which is in agreement with the previous report by Han et al.[104]

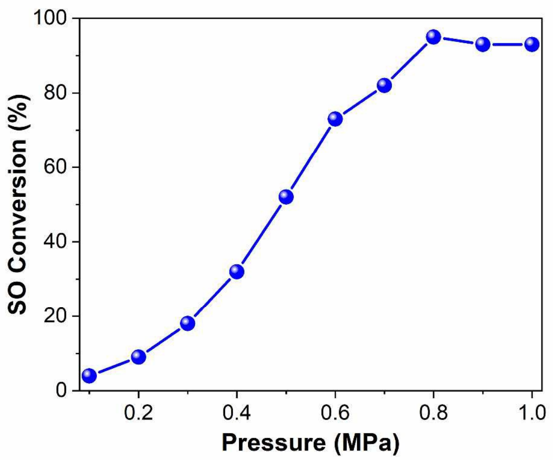

Figure 3. Effect of pressure (MPa) on styrene carbonate formation. (Reaction conditions: SO = 20 mmol (2.28 mL at 25 °C), Catalyst mol%: **ZnMOF-1-NH$_2$** = 1.0 mol% (0.21 mmol, 0.1 g); tetrabutyl ammonium bromide (TBAB) = 2.5 mol% (0.5 mmol, 0.161 g), 80 °C, 8 h, 600 rpm)

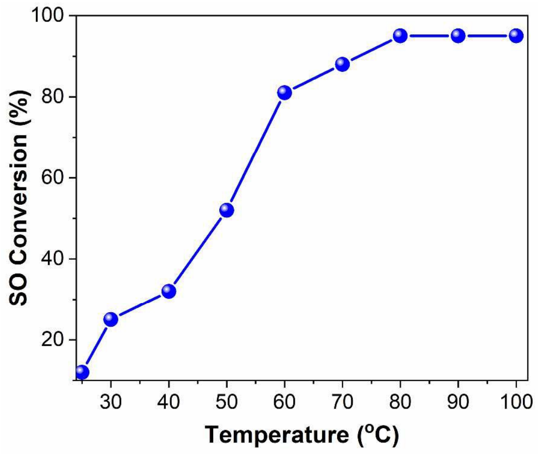

Figure 4. Effect of temperature (°C) on styrene carbonate formation. (Reaction conditions: SO = 20 mmol (2.28 mL at 25 °C), Catalyst mol%: **ZnMOF-1-NH$_2$** = 1.0 mol% (0.21 mmol, 0.1 g); tetrabutyl ammonium bromide (TBAB) = 2.5 mol% (0.5 mmol, 0.161 g), P_{CO2} = 0.8 MPa, 8 h, 600 rpm)

Effect of temperature upon conversion of styrene carbonate is provided in Figure 4. The efficiency of substrate conversion is improved with temperature keeping other parameters constant; increasing temperatures from 25 to 80 °C, conversion of SO increases from 25% to the final 95% employing 8 h of catalytic reaction. As shown in Figure 5, conversion of styrene oxide increases with increasing reaction time and finally a total conversion of 95% is achieved with in 8 h reaction time and no further improvement is observed upon additional increment in reaction time. Effect of catalyst loading is also optimised which is shown in Figure 6. Keeping all other parameters set, upon incremental addition of the catalyst revealed that maximum conversion of 95-96% is achieved at 1-1.2 mol% of catalyst loading. 1 mol% catalyst is retained as optimised loading in further catalytic experiments.

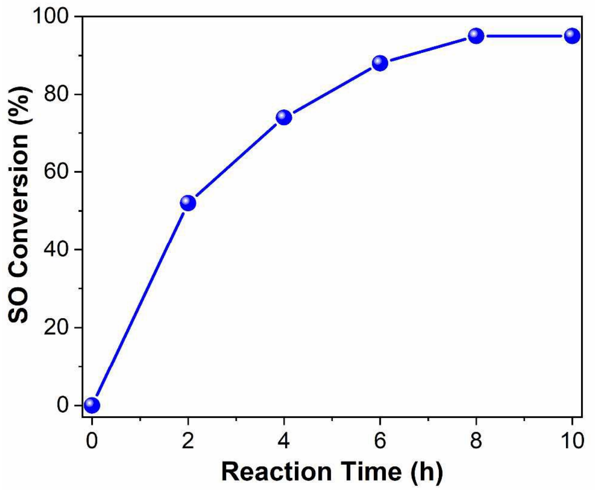

Figure 5. Effect of reaction time (h) on styrene carbonate formation. (Reaction conditions: SO = 20 mmol (2.28 mL at 25 °C), tetrabutyl ammonium bromide (TBAB) = 2.5 mol% (0.5 mmol, 0.161 g), P_{CO2} = 0.8 MPa, 80 °C, 8 h, 600 rpm)

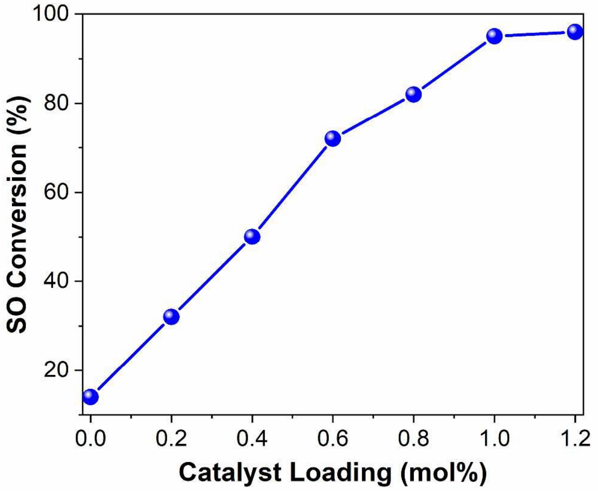

Figure 6. Effect of catalyst loading (mol%) on styrene carbonate formation. (Reaction conditions: SO = 20 mmol (2.28 mL at 25 °C), tetrabutyl ammonium bromide (TBAB) = 2.5 mol% (0.5 mmol, 0.161 g), P_{CO2} = 0.8 MPa, 80 °C, 8 h, 600 rpm.

The scope and generality of the mentioned series of experiments clearly authenticate for setting up optimized parameters for catalyst/co-catalyst, temperature and pressure as **ZnMOF-1-NH$_2$**/TBAB, 8 h, 0.8 MPa respectively in cycloaddition reactions for different aromatic and aliphatic substrates to yield the respective cyclic carbonate. Thus, coupling reactions of CO_2 with different epoxides catalyzed by **ZnMOF-1-NH$_2$**/TBAB were investigated, and the results are summarized in Table 2. The catalytic system could convert all epoxides studied to the corresponding cyclic carbonates effectively under the optimized reaction conditions with good yield and selectivity (Table 2, entry 1 to 6) except in the case of cyclohexene oxide (Table 2, entry 7). In the case of

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functionalized aliphatic propylene oxide, increase in substituents/chain length has a decreasing effect in product yield (Table 2, entry 2, 3, and 5).

Table 2. Substrate Screening Using **ZnMOF-1-NH$_2$** Catalyst in the cycloaddition of epoxide with CO$_2$.*

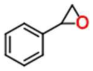
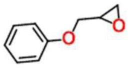
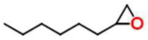
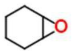
Entry	Epoxide	Conversion (%)	Yield (%)
1		93	88
2		96	93
3		91	89
4		92	89
5		88	84
6		73	72
7		18	18

*Table FootnoteReaction conditions: Epoxide = 20 mmol, Catalyst mol%: **ZnMOF-1-NH$_2$** = 1.0 mol% (0.21 mmol, 0.1 g); tetrabutyl ammonium bromide (TBAB) = 2.5 mol% (0.5 mmol, 0.161 g), P_{CO2} = 0.8 MPa, 8 h, and 80 °C, 600 rpm.

For aromatic epoxide, bulky substitution such as Br on the aromatic ring showed radical decrease in the corresponding cyclic carbonate product, may be due to the steric factor retarding the approach of the substrate towards Lewis acidic metal nodes (Table 2, entry 1, 4 and 6). Compared to terminal epoxide, internal epoxide 1,2-epoxycyclohexane does not undergo any significant cycloaddition reaction (18% product yield) can be attributed to sterically hindered cyclohexene moiety (Table 2 entry 6).[105] In all the catalytic reactions, the product analysis is performed by both GC and NMR spectroscopy (Figure S6-S17).

Based on the previous reports[61,65,106-107] and on the basis of crystal structure of **ZnMOF-1-NH$_2$** probable mechanism of the catalytic reaction is projected and illustrated in Figure 7**.** The proposed coupling reaction mechanism is initiated by the attack of the oxygen atom from the epoxide with the vacant coordinatively unsaturated Zn(II) Lewis acid site of **ZnMOF-1-NH$_2$** which could activate the epoxy ring. In the second step Br$^-$ generated from the TBAB attack the less hindered carbon atom of the coordinated epoxides followed by the ring-opening step. Subsequently, CO$_2$ interacted with the oxygen anion of the opened epoxy ring forming alkyl carbonate anion which is converted into the corresponding cyclic carbonate through the ring closure. The good catalytic performance of **ZnMOF-1-NH$_2$** is believed to be synergistic effect of the catalytic system in presence of TBAB. Presence of Lewis basic site such as amine functionality in the ligand moiety can also assist the activation of CO$_2$ by the MOF favoring the catalytic performance.

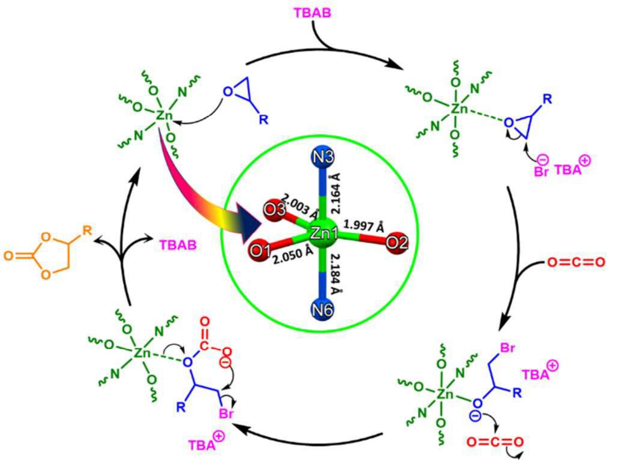


Figure 7. Proposed catalytic mechanism for the cycloaddition of CO$_2$ to epoxide using **ZnMOF-1-NH$_2$** as catalyst and TBAB as co-catalyst.

Catalytic Oxidation of Sulfides to Sulfoxide

Bearing in mind the importance of sulfoxides as efficient synthetic auxiliaries and as valuable pharmaceuticals precursors, we explored the catalytic oxidation of aromatic sulfides using **ZnMOF-1-NH$_2$** possessing good thermal and chemical stability as a heterogeneous catalyst. The oxidation of thioanisole (0.5 mmol) was selected as a model reaction to evaluate the catalytic performance of **ZnMOF-1-NH$_2$** in presence of tert-butyl hydroperoxide (TBHP, 1.0 mmol) as an oxidant and dichloromethane (DCM, 4.0 mL) as solvent in a 10-mL glass tube at 200 rpm to optimise the reaction condition (Table 3). The influence of oxidants (H$_2$O$_2$/TBHP/UHP) was firstly studied for oxidation of thioanisol in optimization experiments. Of the three oxidants, TBHP proved to be the best one, which gave the product with satisfactory conversion when 1 mmol was used. Subsequently oxidation reactions were performed at 25 °C with varying reaction time as 1, 2 and 3 h and the corresponding sulfide conversion was 77, 91 and 99% with selectivity 78, 88 and 95% respectively (Table 3, entry 5-7). Indeed, TBHP and H$_2$O$_2$ alone produced 23% and trace amount of product at 3 h and 12 h reaction time, but catalyst/ H$_2$O$_2$ combination at 25 and 40 °C offered 22 and 50% sulfide conversion upon 12 h of reaction time (Table 3, entry 1-4). **ZnMOF-1-NH$_2$**/UHP combination at 25 °C also furnished poor yield with 25% conversion of sulfide in 3 h reaction time (Table 3, entry 10).

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Table 3. Oxidation of thioanisole into methyl phenyl sulfoxide*

Entry	Catalyst/ Oxidant	Temp. (^{o}C)	Time (h)	Sulfide Conversion (%)	Sulfoxide Selectivity (%)
1	H_2O_2	25	12	Trace	-
2	ZnMOF-1-NH_2/ H_2O_2	25	12	22	4
3	ZnMOF-1-NH_2/ H_2O_2	40	12	52	38
4	TBHP	25	3	23	72
5	ZnMOF-1-NH_2/ TBHP	25	1	77	78
6	ZnMOF-1-NH_2/ TBHP	25	2	91	88
7	ZnMOF-1-NH_2/ TBHP	25	3	99	95
8	ZnMOF-1-NH_2/ TBHP	40	1	99	93
9	ZnMOF-1-NH_2/ TBHP	40	2	99	86
10	ZnMOF-1-NH_2/ UHP	25	3	28	90

*Table Footnote Reaction conditions: Thioanisole = 0.5 mmol (0.06 mL at 25 ^{o}C), Catalyst mol%: **ZnMOF-1-NH_2** = 2.1 mol% (0.021 mmol, 0.010 g); H_2O_2/tert-Butyl hydroperoxide (TBHP)/ UHP = 1.0 mmol, DCM = 4.0 mL, 200 rpm.

Reaction variable such as temperature and time was modulated in **ZnMOF-1-NH_2**/TBHP and the sulfide conversion at 40 ^{o}C with 1 and 2 h interval time displayed 99% conversion; however, the selectivity was 93 and 86% respectively (Table 3, entry 8 and 9). The lower selectivity in the entry 8 and 9 may be due to the further oxidation of sulfoxide to sulfone under the protracted settings.

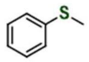
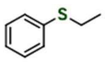
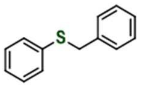
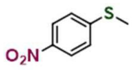
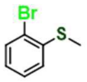
Table 4. Oxidation of thioanisole into methyl phenyl sulfoxide in different solvent.*

Entry	Solvent	Conversion (%)	Selectivity (%)
1	DCM	99	95
2	DMSO	99	81
3	Ethanol	83	95
4	Ethyl Acetate	72	94
5	Diethyl Ether	55	98
6	H_2O	42	92

*Reaction conditions: Thioanisole = 0.5 mmol (0.06 mL at 25 ^{o}C), Catalyst mol%: **ZnMOF-1-NH_2** = 2.1 mol% (0.021 mmol, 0.010 g); tert-Butyl hydroperoxide (TBHP) = 1.0 mmol, Solvent = 4.0 mL, 200 rpm.

The solvent effect on thioanisol conversion in catalytic reactions were also investigated in a variety of solvents including water and displayed in Table 4. With DCM as solvent medium the product yield and selectivity was maximum (99% conversion and 95% selectivity) and DCM is chosen as the ideal solvent for further catalytic reactions (Table 4, entry 1). Tracing the above experiments, the reaction conditions are optimized at 25 ^{o}C with **ZnMOF-1-NH_2**/TBHP as catalyst/oxidant combination in DCM with cocentration of the precursors as mentioned in the Table 3., for further sulfoxidation reaction of different aromatic substrates (Table 5). As revealed in Table 5, maximum product yield and selectivity under the optimized reaction condition was obtained in the case of thioanisole and upon increase in chain length/ substitution on the phenyl ring in subrates showed decrese in product yield. In the case of ortho bromo thioanisole extended reaction time from 3 h to 6 h produced the desired sulfoxide product with lower conversion and selectivity (Table 5, Entry 5). This may be attributed to the slow diffusion and steric hindrance sustained upon substitution by the bulky substrates hampers the easy accessibility towards the catalytically active metal sites.

Table 5. Substrate Screening Using **ZnMOF-1-NH_2** Catalyst in the Oxidation of Sulfides into Sulfoxide.*

Entry	Sulfide	Time (h)	Conversion (%)	Yield (%)
1		3	99	95
2		3	95	92
3		3	89	83
4		3	90	88
5		6	73	71

*Reaction conditions: Sulfide = 0.5 mmol, Catalyst mol%: **ZnMOF-1-NH_2** = 2.1 mol% (0.021 mmol, 0.010 g); tert-Butyl hydroperoxide (TBHP) = 1.0 mmol, DCM = 4.0 mL, 200 rpm. 25 ^{o}C, 3 hr.

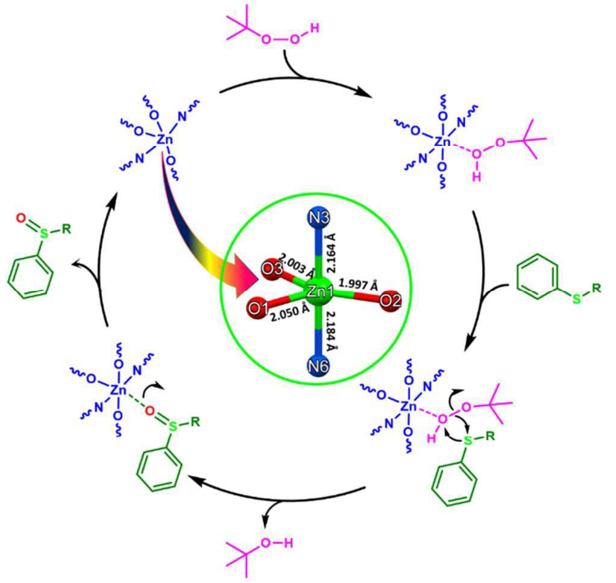


Figure 8. Proposed catalytic mechanism for the sulfoxidation reaction using **ZnMOF-1-NH_2** and TBHP as oxidant.

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In summary, it is reasonable to conclude that the activity and selective oxidation of various sulfides retained using **ZnMOF-1-NH$_2$** as an efficient heterogenous catalyst and with increase in size of the substrates the conversion and selectivity decrease slightly owing to the larger steric hindrance. In all the catalytic reactions, the product analysis is performed by both GC and NMR spectroscopy (Figure S18-S27). The sulfoxide formation is further established unambiguously by crystalizing the product obtained in reaction (Table 5, entry 3) and solving the crystal structure of phenyl methyl benzyl sulfoxide (Figure S28). Plausible mechanism for sulfoxide formation is shown in Figure 8. Penta coordinated Zn(II) dimeric cluster possessing a vacant coordination site is accessible for coordination with the oxygen atom of the TBHP in the formation of an oxygenated intermediate. The oxygenated intermediate undergoes a nucleophilic attack on the sulfide ensuing concerted oxygen transfer resulted in the formation of sulfoxide.[91]

Chemical Stability and Catalytic recyclability of ZnMOF-1-NH$_2$

In the catalytic process, the chemical stability and recyclability of catalyst is highly important for industrial application. The catalytic performance remains high in both catalytic reactions using **ZnMOF-1-NH$_2$** as a catalyst and the recovered catalyst is reused till four consecutive cycles without much loss of efficiency (figure 9a).

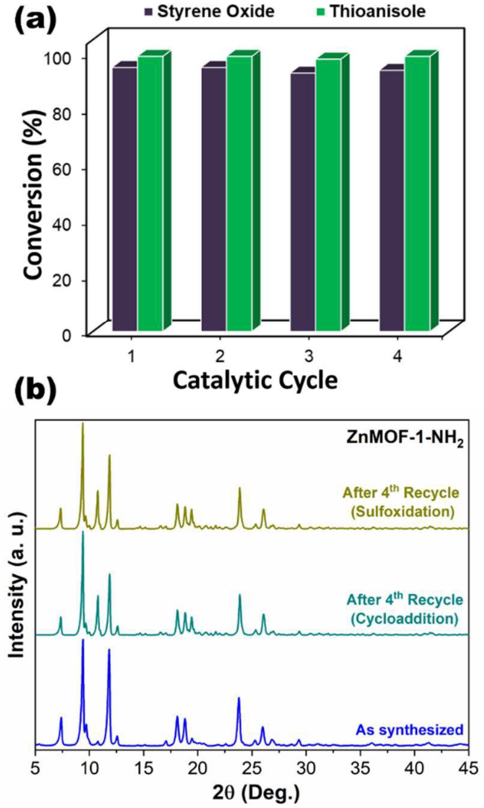

Figure 9. (a) Recycling of catalyst **ZnMOF-1-NH$_2$** up to 4 recycles for cycloaddition and sulfoxidation reactions and (b) Comparison of PXRD data of **ZnMOF-1-NH$_2$** as synthesized with recovered after 4 catalytic recycle of cycloaddition and sulfoxidation reactions.

The catalyst is recovered after 4 cycles by centrifugation and filtration followed by through washing is subjected to different physico-chemical analysis such as FTIR, PXRD and SEM to establish the chemical stability. As shown in Figure 9b, the PXRD patterns before and after the catalytic reaction are identical and matches well with the simulated from of SCXRD data and the FTIR spectrum of the material after the catalytic perfomance retains the characteristic peaks of the compound, indicating that the structural components are stable (Figure S2). To support further, the FE-SEM images of the compound also retained the well-defined crystalline morphology and texture of the material before and after the catalytic reactions (Figure 1). To estimate any leaching out of the metal from the **ZnMOF-1-NH$_2$** catalysts during the reaction, solid catalyst was separated from both the reaction mixture after 50% reaction time. The reaction was further continued without catalyst in presence of only filtrate. No further increase in the product yield for both reactions clearly confirms the catalytically active sites resides on the catalyst and no leaching of the metal has been taken place (Figure S5). Therefore, the above evidence clearly support that **ZnMOF-1-NH$_2$** is a robust and excellent multifunctional heterogeneous catalyst for CO$_2$ fixation as well as sulfoxidation reactions which can be synthesized by green mechanochemical method having good recyclability. The good catalytic activity of **ZnMOF-1-NH$_2$** for the catalytic reactions can be mainly credited to synergic effect of well oriented high density of active metal sites/ amino and amide functional moieties of the ligand exposed for interactions with the substrates.

Conclusions

Judicious choice of catalytically active metal nodes and ligands incorporating appropriate functional groups as linkers has great influence in developing efficient and benign catalysis systems. In summary, we have synthesized and characterized amine functionalized three-dimensional metal organic framework involving Zn(II) metal nodes and aromatic dicarboxylate/ N-donor Schiff base ligand as linkers by different routes. The synthesized **ZnMOF-1-NH$_2$** possessing unsaturated coordination sites and functional groups in the ligand moiety has been exploited as a multifunctional heterogeneous catalyst for the CO$_2$-epoxide coupling reaction and oxidative desulfurization of sulfides with high conversion and selectivity. Excellent chemical stability, easy separation and recyclability with no obvious decrease in catalytic activity approve this material as a potential heterogenous catalyst.

Conflicts of interest

There are no conflicts to declare.

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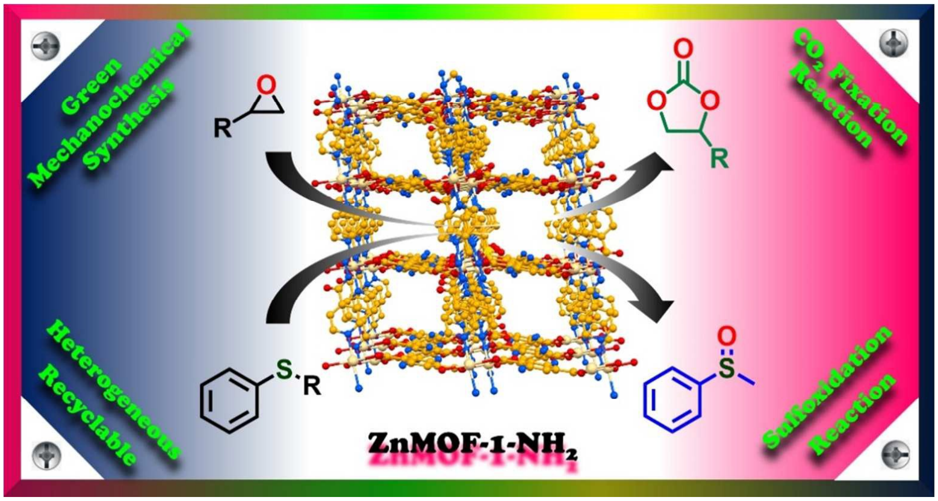
Graphical Abstract



Zn(II) based 3D MOF used as a heterogenous multifunctional catalyst for cycloaddition of CO_2 with epoxides and sulfoxidation reaction.