Green Chemistry

PAPER

Dual-porous metal organic framework for the room temperature CO_2 fixation via cyclic carbonate synthesis

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A novel approach of employing dual-porous metal organic framework (MOF) in CO_2 fixation at room temperature was demonstrated using a micro-mesoporous MOF, UMCM-1-NH_2, in the synthesis of various five membered cyclic carbonates under solventless conditions. Mesopores allow easy guest diffusion and molecular accessibility, while micropores are predominantly helpful in regulating the catalytic interactions in active centres; thus outperforming the properties of pure microporous or pure mesoporous MOFs in cycloaddition. Structural features, acid-base characteristics and physical properties were studied in detail for carrying out a systematic investigation on the cooperative influences of porosity, functionalization and synergism with quaternary ammonium salts in the cycloaddition reaction of CO_2 with propylene oxide, so as to arrive at the underlying mechanism. Catalyst was totally recyclable up to five times without compromising the activity and the extent of heterogeneity was also studied. Effects of various reaction parameters like catalyst-cocatalyst ratio, reaction time and reaction temperature has been investigated.

Introduction

Comprehensive scientific assessments of our current climatic behaviors and its forthcoming days have made it clear that the atmospheric CO_2 concentrations would rise beyond 450 ppm before the mid-21st century as a result of anthropogenic activities. Several conceptual schemes such as integrated carbon capture and storage (CCS) techniques are still under development for mitigating the excessive emission of CO_2 from industrial exhausts.[1a-e] Meanwhile, the abundance of CO_2, and its physicochemical properties *viz*; non-toxicity and non-flammability, have inspired the scientific community to invent technologies that use CO_2 as C_1 feed stock. Considering the toxic nature of the currently practiced C_1 sources such as phosgene and CO, technologies that use CO_2 could be accounted for its advantages like safety in handling, economic viability and environmental friendliness. The cycloaddition of CO_2 with epoxides to produce cyclic carbonates are highly desirable on aspects of efficient resource utilization and 100% atom economicity of the process. Cyclic carbonates, the non-toxic liquids with low odor are excellent in applications such as green and aprotic solvents, electrolytes in lithium-ion batteries, precursors for polymer synthesis including polycarbonates, in pharmaceuticals agriculture etc., and are expected to expand their applicability with the increasing importance of green and sustainable chemistry in coming decades.[2a-g]

However, high operating pressure and temperature are required for cyclic carbonate production, owing to the thermodynamic stability of CO_2, which in turn, limits the exploitation of the process both interms of energy and economy.[2h-j] Therefore, highly efficient catalysts that are feasible interms of energy and reusability are essential for making it a green, sustainable and economic pathway that also offers easy product separation and operation simplification. Numerous homogeneous catalysts like ionic liquids, organic and metal complexes have been reported for cyclic carbonate synthesis.[3a-d] The recognition of some inherent limitations, i.e., non-viability for industrial scale up due to the challenges in separation, purification and recycling, led to a flourishing activity that attempts the development of heterogeneous catalysts like metal oxides, zeolites, titanosilicates and ion-exchanged resins.[4a,b] By docking highly active homogeneous species such as ionic liquids on support materials, even high activities were obtained, and the heterogeneity and reusability issues were addressed. However, several reports including ours in which ionic liquids were immobilized on supports such as silica, polystyrene and biopolymers were still fraught with inefficiencies in catalytic activities under ambient conditions or suffered from leaching of the active phase into the reaction mixture.[5] Fixation under least energy supply is crucial in maintaining a positive balance between CO_2 release from power plants and energy expenditure for its mitigation.

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Electronic Supplementary Information (ESI) available: Arrangement of adjacent 1D hexagonal mesopores in UMCM-1-NH_2, XPS Spectra, Nitrogen adsorption-desorption isotherm, Pore size distribution curve, Instrumentation. See DOI: 10.1039/x0xx00000x

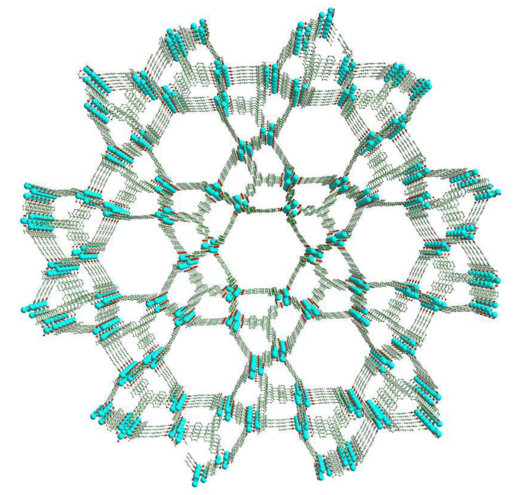


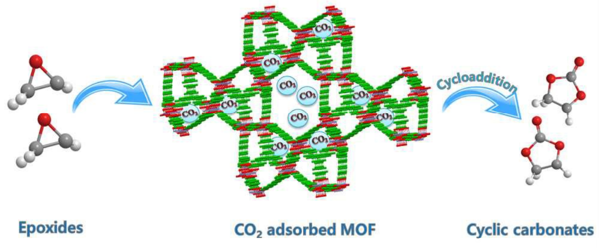
Fig. 1 Perspective view of UMCM-1-NH_2 along c-axis depicting the arrangement of 1D hexagonal mesopores and microporous clusters.

Metal organic frameworks (MOFs), are providing new fields of opportunities as active and selective catalysts for environment relevant applications. Assembly of frameworks through a judicious choice of constituent ligands and transition metals provide MOFs high internal surface area, ordered pore structure, tuneable porosities and functionalities, putting them at the frontier between zeolites, metal-organic catalysts, and enzymes apparently extending their scope over the heterogeneous catalysis regime.[6a-c] In 2009, Han et al.[7a] reported the first MOF-5/n-Bu_4Br binary system as catalyst for the synthesis of cyclic carbonates from CO_2 and epoxides. In a short span of time, a series of carboxylate MOFs and their diverse structural and functional counterparts *viz*., MIXMOFs, IRMOF-3, Cu-BTC, MIL-68, 101 and 125, UIO-66 etc. were reported.[7b-h] Apart from this various zeolitic imidazolate frameworks (ZIF-8, ZIF-68 and ZIF-90),[8a-c] mixed carboxylate-N-donor MOFs (ZnHipBpy, CHB, and CCB), metal complex-containing MOFs (Ni-Salphen and Ni-Saldpen complexes) were also reported efficient in cycloaddition by various groups including ours.[9a-e] Among these reports, most were microporous or non-porous in nature. High surface area and large pore volumes are desirable for many catalytic applications, since narrow pores or anchoring molecular functions may hinder the mass diffusion and transfer of substrates, intermediates or product molecules.

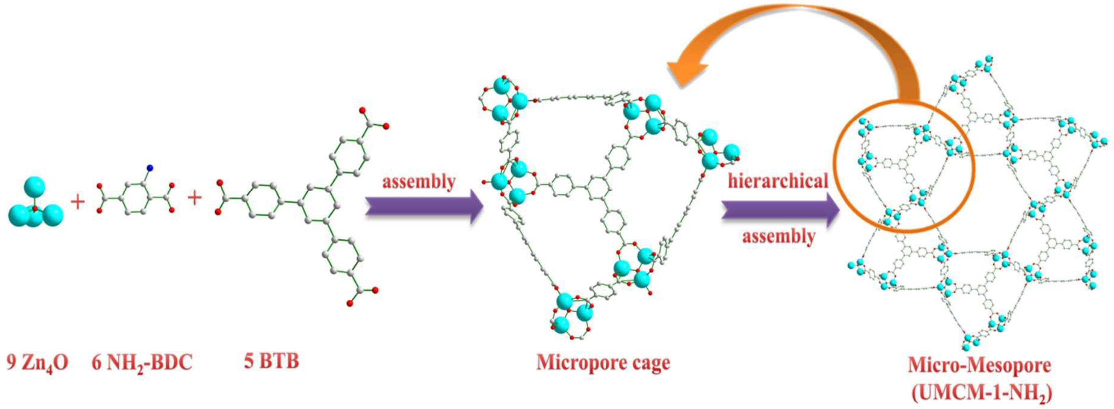
Mesoporous MOFs are regarded as hosts to accommodate large bulkier molecules, allowing their free reaction or transformation without any diffusional limitations.[10a-c] With metal organic frameworks, the class of materials with versatility in pore sizes, catalysis is expected to be more efficiently carried out if pores belong to mesopores. Only a few MOFs of mesopores nature have been reported in CO_2 cycloaddition till date.[11,7f] Combination of meso- and micro-porous nature is expected to provide attractive features which overcome the limitations of pure microporous or purely mesoporous structures and to combine the advantages of each pore size regime (Fig. 1).[12a,b,c] Taking into account the lessons learned from the previous reports, it is clear that the co-existence of metal nodes (Lewis/Bronsted acid sites) and basic functional groups such as amine groups into the organic linkers are effective in cycloaddition, where the metal nodes are used to activate the epoxides while the CO_2 is mostly activated by basic sites.[12d] Herein, we report an amine functionalized micro-mesoporous MOF UMCM-1-NH_2 employing two different linkers with Zn_4O secondary building units (SBUs), and its synergistic enhancement in catalytic activity with a cocatalyst containing strong nucleophilic anion for the room temperature synthesis of cyclic carbonates from epoxide and CO_2 (Scheme 1).[13] While the first type of linker (1,3,5-Tris(4-carboxyphenyl)benzene, BTB) engages in constructing mesoporous architecture, the second linker (2-Aminoterephthalic acid, NH_2-BDC) affords amine functional groups that are beneficial in enhancing the CO_2 binding and subsequent transformation during catalysis.

Results and discussion

Generally, MOF structures get assembled by the bridging of metal or metal oxide clusters by exo-multidentate ligands that grow regularly to 1D, 2D or 3D structures. Though the factors such as the nature of counter anions, solvent, and synthesis conditions are influential in the self-assembly of MOFs, the final topology and pore dimensions is the reflection of the length and orientation of donor atoms of ligands towards metal/metal clusters that adopt the suitable coordination mode. In UMCM-1-NH_2 also, Zn_4O clusters are present as nodes, and the BTB and NH_2-BDC as bridging ligands are existent; but is not limited to the concept of SBUs in MOF chemistry. UMCM-1-NH_2 has its broad arrangement proceeding in a multi-level, hierarchical assembly as follows (Scheme 2). Nine Zn_4O clusters, six NH_2-BDC units and five BTB units form three dimensional microporous cages with the pore dimension 14 x 17 Å. Such microporous cages are arranged further in an edge-sharing fashion that, six such cages give rise to a mesoporous space (dimension 27 x 32 Å).[13,14a] This mesoporous structure extends as 1D channel in the whole framework, as we move along the crystallographic c-axis. Thus,



Scheme 1 Schematic representation of synthesis of cyclic carbonate from epoxides and CO_2.



Scheme 2 Representation of hierarchical assembly in UMCM-1-NH$_2$; where micropores are built from Zn$_4$O clusters and linkers, and subsequent formation of 1D mesopores from the hexagonal arrangements of microporous cages.

the whole structure may be seen as a hexagonally channeled mesoporous material developed from microporous building units (Fig. S1, ESI†). A comparison with mesoporous silica material MCM-41 (hexagonal mesoporous silica) reveal that MCM-41 is built from edge-sharing [SiO$_4$] units (non-porous units), while UMCM-1-NH$_2$ is built from edge-sharing, microporous, [(Zn$_4$O)$_9$(NH$_2$-BDC)$_6$(BTB)$_5$] units. As per crystallographic data, in UMCM-1-NH$_2$, 43% of the volume belongs to mesopores, while the remaining 57% are in microporous range.

Thus UMCM-1-NH$_2$ is not purely microporous or mesoporous, but a hybrid micro-mesoporous material with its catalytic active centres most probably being the metal oxide clusters and amino groups. It is noteworthy that the amino group does not participate directly in cementing the framework, and it rather possesses high order of mobility (along the rotational axis), due to which the single crystal structure of UMCM-1-NH$_2$ has failed to fix the amino groups at a particular orientation. Interestingly, this sort of hybrid micro-mesoporous MOFs have seldom been explored for their potential in the cycloaddition of epoxides and carbon dioxide, where both types of pores have their own significance. Mesopores provide improved accessibility for the reactants with minimal diffusional limitations, so that in a limited time they can diffuse much more and interact with more catalytic sites. Meanwhile, the micropores provide favorable platform for the catalysis to proceed in a particular pathway leading to the desired products by virtue of its reduced retention times. Further, it is interesting that the NH$_2$ groups are dynamic such that they are accessible for substrates that reside in micro pores as well as meso-pores.

UMCM-1-NH$_2$ was conceived by the solvothermal treatment of the metal salt (Zinc nitrate tertrahydrate), tripodal ligand (1,3,5-Tris(4-carboxyphenyl)benzene, BTB) and the amine functional exobidentate ligand (2-Aminoterephthalic acid, NH$_2$-BDC) at 85 °C for 3 days. Needle shaped single crystals were obtained upon solvothermal synthesis.[14b]

In order to verify the phase homogeneity of the bulk solvothermal sample, and its structural integrity, powder X-ray diffraction (PXRD) pattern of the UMCM-1-NH$_2$ catalyst was compared to the single crystal simulated pattern generated from the CIF file of the original report for UMCM-1-NH$_2$. XRD reflections in Fig. 2 (b) match perfectly with the simulated pattern in Fig. 2 (a), confirming that the catalysts correspond to the hexagonal crystal system as reported.[13] Solvothermal synthesis allows precise control over the size, morphology (sphere (3D), rod (2D), or wire (1D)), shape distribution, and crystallinity by employing the solvent supersaturation, and kinetic control.[6b]

Further verification of UMCM-1-NH$_2$, for its chemical integrity was analyzed by using FT-IR (Fig. 3). The broad peak observed at 3426 cm^{-1} corresponds to the N-H stretching vibration. The peak at 1600 cm^{-1} corresponds to the N-H bending vibration of the –NH$_2$ group of UMCM-1-NH$_2$. The absence of peak at 1650 cm^{-1} confirms the removal of DEF

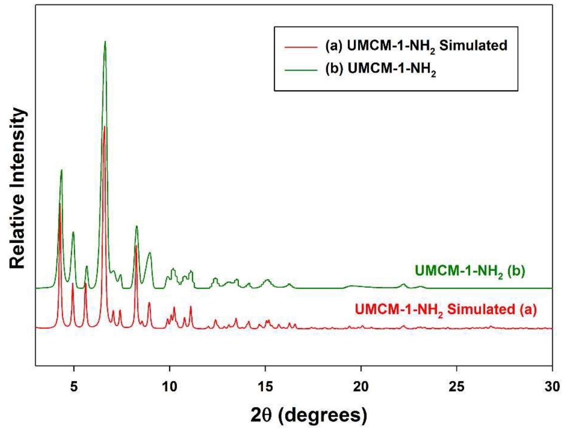


Fig. 2 XRD pattern of UMCM-1-NH$_2$ compared to the simulated single crystal pattern.

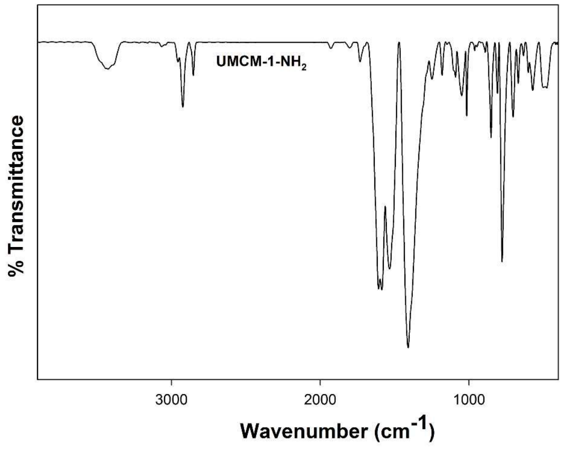


Fig. 3 FT-1R spectra of UMCM-1-NH$_2$

molecules from the framework. The peak at 500 cm^{-1} is related to the stretching vibrations of Zn-O bonds in the framework. The peak around 2853 to 3000 cm^{-1} corresponds to C-H stretching vibrations. Similarities in the FTIR peaks with the previous reports also validate the originality of the chemical environments of this MOF.[14c,d] The presence of active NH$_2$ group in the surface of UMCM-1-NH$_2$ group was analyzed using N1s spectra from the XPS data (Fig. S2, ESI†). The N1s peak for amine group appeared at 400 eV.

Further, the thermal stability and the nature of framework construction, was evaluated by means of thermogravimetric analysis (TGA) (Fig. 4). TGA was conducted after the complete drying of sample in vacuum, so that their degradation curves do not reflect the loss of solvent molecules. The first major loss was observed within 400-420 °C for UMCM-1-NH$_2$ indicating that the catalyst is thermally stable up to approx. 400 °C.[13] N$_2$ adsorption experiments have been carried out at 77 K on the thermally activated UMCM-1-NH$_2$ (Fig. S3, ESI†). The isotherm which has a typical Type IV behavior has been analyzed by the BET method yielding a very high surface area of 4200 m^2/g. The micro- and meso- porous nature of UMCM-1-NH$_2$ that was observed in the crystallographic structure was physically confirmed from the pore size distribution curve (Fig. S4, ESI†). The total pore volume of the UMCM-1-NH$_2$ was approximately estimated as 2.4 cm^3/g.

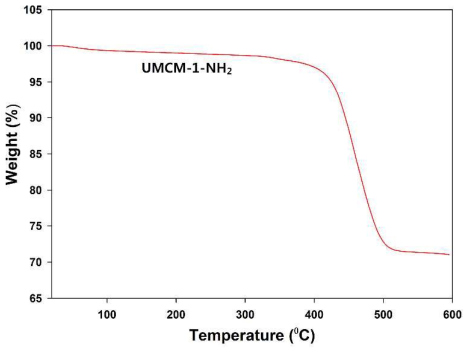


Fig. 4 Thermogravimetric analyses (TGA) of UMCM-1-NH$_2$

From the cumulative insights obtained from various recent reports,[7,8,9] we intend to investigate the catalytic ability of UMCM-1-NH$_2$ at ambient conditions (room temperature) in the presence of TBAB co-catalyst.[15a,b,c,7a] Neither UMCM-1-NH$_2$ nor TBAB separately produced any noticeable PO conversion under an employed reaction condition of RT, 1.2 MPa with 0.64 mol% catalyst in 24 h (Table 1, entries 2 and 3). However, a tremendous rise in PC yield was observed with the combination of UMCM-1-NH$_2$ and TBAB which served as a binary catalyst system, that manifested a promising result of 90% PO conversion with nearly 100% selectivity (propylene carbonate) under the same reaction conditions (Table 1, entry 7). Since the individual catalyst precursors did not displayed any catalytic activity with TBAB (Table 1, entries 4 and 5), the above mentioned catalytic activity of UMCM-1-NH$_2$/TBAB system shall be positively surmised to the crucial role played by the metal organic framework environment such as its porosity in modifying the catalytic route. It has been reported earlier that, iodides are a better nucleophile for eventuating the synergism with Lewis/Bronsted acid catalysts in CO$_2$-epoxide cycloaddition reaction.[16a,b] However, it was observed that, UMCM-1-NH$_2$ rendered lesser PO conversion with iodide containing co-catalysts (TBAI) than its bromide analogue (TBAB) in contrast to the literature reports. This shall be attributed most probably to the easier access offered to the bromide ions (which are of smaller size in comparison to the iodide ion) inside the meso and micro pores of UMCM-1-NH$_2$ which again is a direct evidence that the catalysis occurs to the major part inside the micro/mesopores of UMCM-1-NH$_2$ and not on its external surface. Should the catalysis happened over the surface of the MOF, the UMCM-1-NH$_2$/TBAB must have had lesser catalytic activities than UMCM-1-NH$_2$/TBAI system but the reverse of which was observed. This supplements the rationale that the porous nature of the MOF plays a critical role in devising the catalytic route (Table 1, entry 9). Thus altogether, the reduced activity of iodides compared to the bromide indicates that the diffusion of bulky iodide ions into the pore is hampered, where the reaction predominantly occurs. A similar result was reported by Baiker et al.[7b] in case of MIXMOF. We also noticed that UMCM-1-NH$_2$ can act as a standalone catalyst at high temperatures. A 95% conversion of PO occurred using UMCM-1-NH$_2$ at 120 °C and 1.2 MPa pressure over 24 h without the use of the any cocatalyst or solvent (Table 1, entry 10). However, the PC selectivity was slightly affected by small amounts of dimers as side products. This could be ascribed to the absence of strong nucleophilic anions for epoxide ring opening, which are crucial in the addition of ring opened epoxide to CO$_2$ molecule. In the absence of such nucleophilic species in UMCM-1-NH$_2$, the reverse binding is reported to occur, i.e., the catalyst polarized CO$_2$ attacks the epoxide to cause addition step. Therefore, in the absence of enough polarized CO$_2$ molecules epoxide may

Table 1 Cycloaddition of CO_2 and PO using different catalysts under various reaction conditions.

No	Catalyst(a)	Temperature (°C)	Conversion (%)(b)	Selectivity (%)(b)	Yield (%)(b)
1	None	RT	0	0	0
2	UMCM-1-NH_2	RT	< 3	-	< 3
3	TBAB	RT	< 3	-	< 3
4	$Zn(NO_3)_2$/TBAB	RT	< 5	-	< 5
5	$Zn(NO_3)_2$+ BTB+ NH_2-BDC/TBAB	RT	< 5	-	< 5
6(c)	UMCM-1-NH_2/TBAB	RT	52	> 99	52
7	UMCM-1-NH_2/TBAB	RT	90	> 99	90
8(d)	UMCM-1-NH_2/TBAB	RT	78	> 99	78
9	UMCM-1-NH_2/TBAI	RT	34	> 99	34
10	UMCM-1-NH_2	120	95	95	91

I(a) Reaction conditions: Propylene oxide (PO) = 42.8 mmol (3ml), 1.2 MPa P_{CO2}, 24 h, 600 rpm, Catalyst mol% = 0.64, Semi-batch. (b) Determined by GC. (c) Catalyst mol% = 0.44. (d) Catalyst mol% = 0.88.

prefer to dimerize with another epoxide than undergoing addition with the inert molecule.

Having identified the potential of UMCM-1-NH_2 to materialize the cyclic carbonate synthesis with the assistance of co-catalysts even at room temperature, we deemed it worthwhile to compare the efficiency of UMCM-1-NH_2 to the earlier MOFs reported in CO_2-PO cycloaddition. For the purpose, the catalytic abilities of a series of carboxylate spacer MOFs were compared with that of the UMCM-1-NH_2 in Table 2. Albeit the different sets of reaction conditions employed in the literature, we attempted a comparison of the MOF catalysts at the closest reaction conditions reported. While the microporous zinc dicarboxylate framework, widely known as MOF-5 afforded 56% yield of PC (Table 2, entry 1), the meso-micropore hybrid MOF UMCM-1-NH_2 manifested 78% PC yield (Table 2, entry 2) at room temperature, 0.4 MPa CO_2 pressure, with 2.5 mol% each of catalyst and TBAB co-catalyst in 4 h. IRMOF-3, an amine functionalized microporous carboxylate spacer MOF, produced a moderate yield of 57% (Table 2, entry 3), while at the same time, UMCM-1-NH_2 gave 90% PC yield under the same reaction conditions (RT, 1.2 MPa, 24 h, 0.64 mol% each of catalyst and co-catalyst) (Table 2, entry 10). From entries 4, 5, 6, 7 and 8 (Table 2, Hf-Nu-1000, Cr-MIL-100, Ni-Saldpen MOF),[12a,7f,9e,18a,b] it is evident that the UMCM-1-NH_2 performed the CO_2-PO cycloaddition in the most effective manner. An interesting thing observed from this comparison was that, while the activity (conversion) with the micropore containing MOF/TBAB system (MOF-5, IRMOF-3 etc.) was inferior to the mesopores possessing MOF/TBAB binary system (Cr-MIL-101, UMCM-1-NH_2), better selectivity to the desired product (cyclic carbonates) was manifested by the microporous MOFs than the latter. This shall be considered in connection with the theory that, the shortened diffusion pass length may lead to the reduced retention times of products in the micropore which in turn leads to a lower probability of secondary reactions and hence affording enhanced selectivity to the primary products which in this case is the thermodynamic product, cyclic carbonates.[17] Thus, the higher activity of UMCM-1-NH_2 in comparison to the other MOFs on aspects of both epoxide conversion and selectivity shall be

Table 2 Comparison of the catalytic activities of UMCM-1-NH_2 catalyst with previously reported MOF catalyst at the closest reaction conditions in room temperature

No	Catalyst	Catalyst (mol%)	Co-catalyst (mol%)	Reaction Conditions		Conversion (%).	Yield (%)	Ref.
				Pres. (MPa)	Time (h)			
1	MOF-5	2.5	2.5	0.4	4	-	57	7a
2	UMCM-1-NH_2	2.5	2.5	0.4	4	78	78	+
3	IRMOF-3	0.64	0.64	1.2	24	56	56	-
4	Hf-Nu-1000	4	10	0.1	26	100	100	15c
5	Cr-MIL-101	1.2	0.62	0.8	24	91	82	7f
6	Ni-Saldpen-MOF	0.7	2	2	4	28	-	9e
7	MMCF-2	0.13	7.2	0.1	48	-	95.4	18a
8	MMPF-9	0.13	7.2	0.1	48	-	87.4	18b
9	UMCM-1	0.64	0.64	1.2	24	85	85	+
10	UMCM-1-NH_2	0.64	0.64	1.2	24	90	90	+

Epoxide: Propylene oxide, Temperature: RT, Cocatalyst: Tetrabutylammonium bromide (TBAB), +: This work.

Table 3 NH_3-, and CO_2-TPD profiles of the UMCM-1-NH_2 catalyst

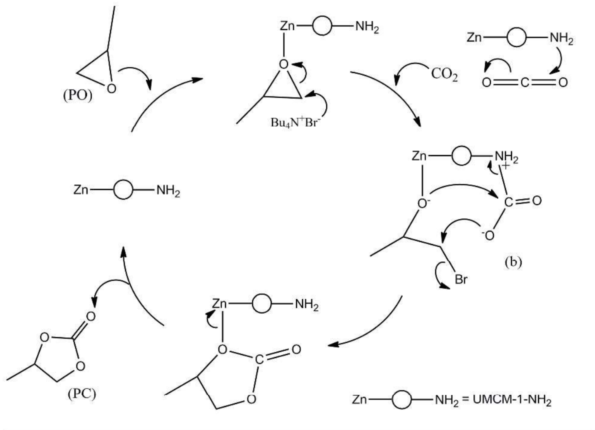
Catalyst	CO_2-TPD (Total mmol/g)	NH_3-TPD (Total mmol/g)
UMCM-1-NH_2	53	7

attributed to the presence of both the micro and meso pores as depicted in Scheme 2. While the mesopore channels of UMCM-1-NH_2 facilitates easier diffusion of reactant molecules, the catalytic interactions might have occurred predominantly in the micropores of UMCM-1-NH_2, as indicated by its high selectivity. Thus, in summary, a hybrid micro-meso MOF serves the synergism with halide nucleophiles better than either a purely micro or meso MOF, which on a broader view indicates that, even with the same Lewis acidic centers, the porosity of the MOF plays critical role in exploiting the synergistic catalysis effects of co-catalysts.

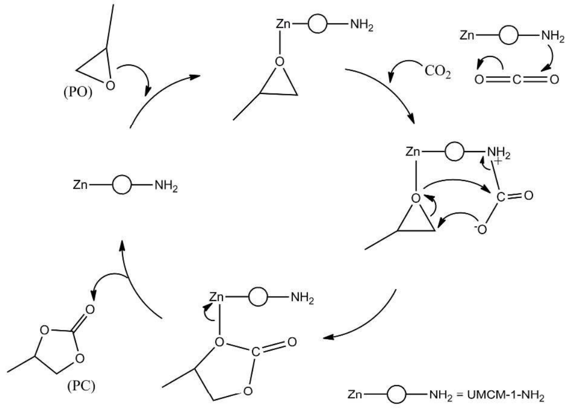
In order to understand, whether the amine groups on UMCM-1-NH_2 plays any significant role in this room temperature synthesis of cyclic carbonates, a UMCM-1/TBAB system was also investigated. As shown in Table 2, entry 9 and 10, the catalytic activity of both systems were not so different, that the UMCM-1-NH_2 excelled over the amine devoid UMCM-1 only slightly. This comparable yield of UMCM-1 with UMCM-1-NH_2 leads to the conclusion that when it comes to a broader aspect, pore size of the catalyst becomes as important as the effect of amine or similar functional group. This suggests that the combined effects of suitable acidity/basicity and thereby micro-mesoporosity play roles on the promotion of the diffusion and the accessibility to the catalytic active sites. It should also be concluded that the Lewis base sites in the metal oxide cluster actively participates when it comes to reaction occurring in both micropores and mesopores.

Since the catalysis for the cycloaddition of carbon dioxide and epoxide is expected to occur in a concerted pathway involving both acid and base sites, a physical evaluation of the potential acid and base sites in the UMCM-1-NH_2 material was conducted using temperature programmed desorption (TPD) *viz*., NH_3- and CO_2- TPD respectively (Table 3). The total adsorbed CO_2 during the course of analysis was estimated as 53 mmol/g, which is also the equivalent number of base sites in the catalyst. It is assumed that the NH_2- functional groups of the ligand and the carboxylate O^- atoms attached to the metal centers in its Zn_4O metal clusters are responsible for CO_2 adsorption. Similarly, in the case of NH_3- TPD, the acid sites counts to 7 mmol/g, which corresponds to the metal centers (Lewis acid sites).

Previous reports for MOF catalyzed cycloaddition of CO_2 and epoxides suggest that in the presence of a strong nucleophilic anion, Lewis/Bronsted acid sites can activate the epoxides for ring opening, and certain groups which can polarize the thermodynamically stable CO_2 molecule to facilitate CO_2 insertion, can effectively catalyze the epoxide-CO_2 cycloaddition.[12d] A plausible mechanism based on these observations for the cycloaddition of PO in presence of UMCM-1-NH_2 co-catalyzed by TBAB is illustrated in Scheme 3. In UMCM-1-NH_2, the O^- atom of PO interacts with Zn Lewis acid site. Subsequently, the Br^- of TBAB attacks the least hindered carbon atom, resulting in epoxide ring opening. Concomitantly, CO_2 is polarized by amine groups of UMCM-1-NH_2. This interaction is facilitated further by the possibilities of



Scheme 3 Proposed mechanism for the cycloaddition of PO and CO_2 catalyzed by UMCM-1-NH_2/TBAB.



Scheme 4 Cycloaddition of PO and CO_2 catalyzed by UMCM-1-NH_2.

Table 4 Effect of UMCM-1-NH_2 : TBAB ratio in the yield of propylene carbonate[(a)]

Entry	UMCM-1-NH_2 (mol%)	TBAB (mol%)	Ratio of UMCM-1-NH_2 /TBAB	Yield (%)
1	0.24	0.64	1:3	45
2	0.44	0.64	2:3	75
3	0.64	0.64	1:1	90
4	0.64	0.44	3:2	78
5	0.64	0.24	3:1	40

[(a)] Reaction conditions: PO = 42.8 mmol, 1.2 MPa P_{CO2}, 24 h, RT.

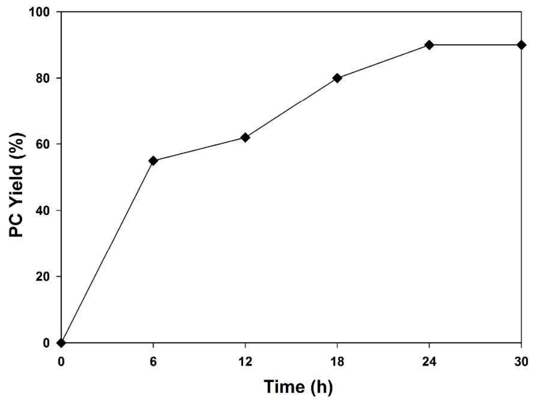


Fig. 5 Effect of reaction time on cycloaddition of propylene oxide and CO_2 using 0.64 mol% UMCM-1-NH_2 at room temperature and 1.2 MPa P_{CO2}.

rotating –NH_2 groups present in the micro pores. Experimental evidence to this disorder is available from the single crystal X-ray diffraction of UMCM-1-NH_2 reported by Cohen et. al.[13] Smaller substrates that diffuse into micropores helps enhanced interaction with reactant molecules. In the succeeding step, the O^- atom of the polarized CO_2 molecule attacks the β-carbon of the ring opened epoxide, forming an intermediate (b) with the elimination of Br^-. Finally, the ring closure takes place to generate PC and the regenerated UMCM-1-NH_2 moves to the next cycle of cycloaddition by coordinating to the next epoxide molecule. In the absence of TBAB, the mechanism proceeds via UMCM-1-NH_2-PO interaction that undergoes a ring-opening by the O^- atom of the polarized CO_2 molecule (polarized by the presence of NH_2 groups) at the β-carbon of the epoxide. Finally the ring closure takes place similar to that of UMCM-1-NH_2/TBAB catalyzed reaction as mentioned above (Scheme 4). The high temperature required for this pathway is justified by the higher energy associated with the polarizing molecule.

Table 5 Recyclability studies of UMCM-1-NH_2.

No	Recycles	Conversion (%)	Selectvity (%)	Yield (%)
1	Fresh	90	> 99	90
2	1st	90	> 99	90
3	2nd	90	> 99	90
4	3rd	90	> 99	90
5	4th	90	> 99	90
6	5th	89	> 99	89

Reaction conditions: 42.8 mmol propylene oxide, 0.64 mol% UMCM-1-NH_2, room temperature, 1.2 MPa P_{CO2}, 24 h

Since a synergism is involved between catalyst/cocatalyst/substrate in this system, the effects of varying catalyst concentrations were studied for different ratios of UMCM-1-NH_2 in the range of 0.24-0.64 mol% (Table 4). A gradual increment in the PC yield was observed from 0.24-0.64 mol% for UMCM-1-NH_2 with a constant cocatalyst concentration of 0.64 mol% (Table 4, entry 1, 2 and 3). The same trend was observed for further studies that use 0.24-0.64 mol% TBAB with 0.64 mol% UMCM-1-NH_2 (Table 4, entry 4 and 5). Thus, 0.64 mol% of UMCM-1-NH_2 and TBAB were identified as the optimal catalyst ratios that give maximum PC yield with > 99% selectivity under room temperature and 24 h (Table 4, entry 3). Also, a time dependent study on the catalytic activity was carried out at RT using 0.64 mol% UMCM-1-NH_2/TBAB (Fig. 5). PC conversion increase gradually with increasing reaction duration in the range of 0 to 24 h. Prolonged reactions beyond 24 h did not give any noticeable increase in the PC yield, indicating that the optimum reaction time was 24 h with 90% PC yield and > 99% PC selectivity.

Since the catalyst concentration and time are important factor in determing TON and TOF of the catalysts, the yield of

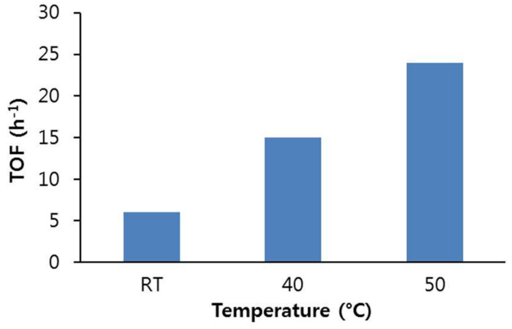


Fig. 6 Turnover frequency (TOF) calculated based on the yield of propylene carbonate at different temperatures, 1.2 MPa P_{CO2} and 0.64 mol% UMCM-1-NH_2.

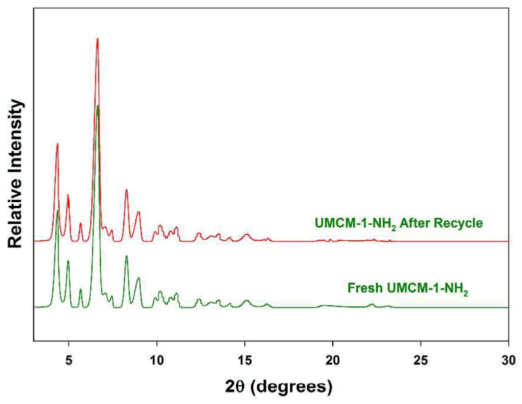


Fig. 7 Powder XRD patterns of the fresh and recycled UMCM-1-NH_2 catalyst

PC at various temperatures in different time intervals were studied. 92% PC yield was achieved in 10 h at 40 °C and 1.2 MPa. Around 89% PC yield was obtained in 6 h itself when the temperature was set to 50 °C. TON and TOF of the UMCM-1-NH_2 was calculated at different temperatures based on the yield per equivalent of metal ions. TON is calculated for the catalyst based on its formula weight available from the crystallographic information file (CIF) from the Cambridge Structural Data base, based on the assumption that the synthesized sample is purely homogeneous crystals. It was found that, when the temperature was increased from RT to 50 °C, the TOF of the UMCM-1-NH_2/TBAB mediated catalysis was raised four fold. Since 50 °C is still low compared to most of previous reports on the synthesis of PC, this multifold increase in TOF is significant (Fig. 6).

Another crucial criterion to be considered in heterogeneous catalysis is the recyclability of the catalyst. An easier catalyst separation is critical for industrial processes to minimize the waste streams and to develop potential catalyst recycling strategies owing to its economic and environmental aspects.[19] We performed catalyst recycling studies for UMCM-1-NH_2 at RT, 1.2 MPa pressure (Table 5). UMCM-1-NH_2 maintained its activity (90%) and > 99% selectivity throughout the first five recycles. The recycled UMCM-1-NH_2 catalyst was analyzed by PXRD analysis (Fig. 7). The catalyst maintained its structure throughout the recycling process, which was determined by the retention of the peaks in comparison with the fresh catalyst. FT-IR analysis was also conducted on the recycled UMCM-1-NH_2 catalyst. The similarities in the peaks with the fresh catalyst confirmed that the chemical integrity is maintained throughout the recycling process (Fig. 8). We also assessed the heterogeneity and stability of UMCM-1-NH_2 in a more accurate way by using inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of the supernatant for metal leaching. The ICP-OES showed that less than 1.5% of the zinc ions had leached into the reaction mixture after five recycle.

A fundamental and much popular method to estimate the presence of any leached species such as metal ions from the catalyst in the reaction media is the hot filtration test.[20] But since the UMCM-1-NH_2/TBAB system will always contain the halide ions, hot filtration test with this system would be meaningless. Hence, the hot filtration test was conducted with UMCM-1-NH_2 alone but at high temperature, since, at 120 °C, UMCM-1-NH_2 alone has furnished 95% PO conversion (Table1, entry 10). The cycloaddition was carried out with 0.64 mol% UMCM-1-NH_2 at 1.2 MPa pressure and 120 °C until a 55% conversion of PO was achieved (at 12 h) (Fig. 9). The contents were filtered, analyzed by gas chromatography and the remaining filtrate was fed back in to the reactor. Sampling was performed every 2 h thereafter. No further substrate conversion in the filtrate occurred after the catalyst removal at the reaction temperature, indicating that there are no homogeneous species catalyzing the reaction in solution.

A series of different epoxides were examined for the chemical fixation of CO_2 to produce corresponding cyclic carbonates in presence of UMCM-1-NH_2 under 1.2 MPa pressure, 24 h and room temperature (Table 6). Comparatively lower conversion was observed for the epoxides using styrene oxide, allyl glycidyl ether and cyclohexene oxide. The lower conversion of epichlorohydrin than PO could be explained on the basis of electron withdrawing effect of CH_2Cl group, which reduces the electron density of epoxide oxygen system (Table 6, entry 1). The poor reactivity of SO is probably due to the bulky nature of epoxide that hinders the reaction with CO_2 that resides inside micropores and low reactivity of its β-carbon center (Table 6, entry 3). Cyclohexene oxide the internal epoxide was the least active one among these, probably because of its high steric hindrance (Table 6, entry 4). Therefore, it should be concluded that the bulkiness of the substrate is highly relevant in micro-mesoporous MOFs since the reacting molecule that reside inside the micropores may not be easily vulnerable to the bulky epoxides, eventhough the epoxide could successfully diffuse into the mesopore. This inturn supplements our rationale that, the catalysis majorly occurs inside the micropores of UMCM-1-NH_2 than the

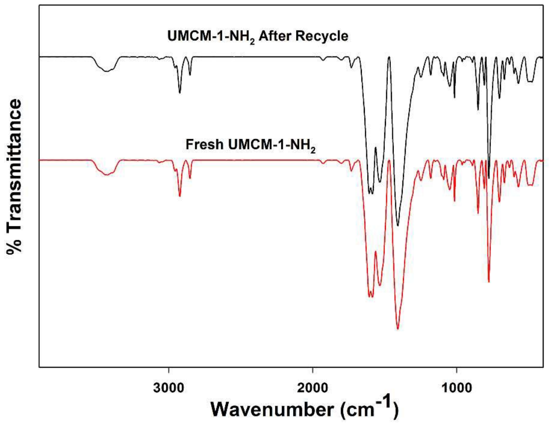


Fig. 8 FTIR spectra of the fresh and recycled UMCM-1-NH_2

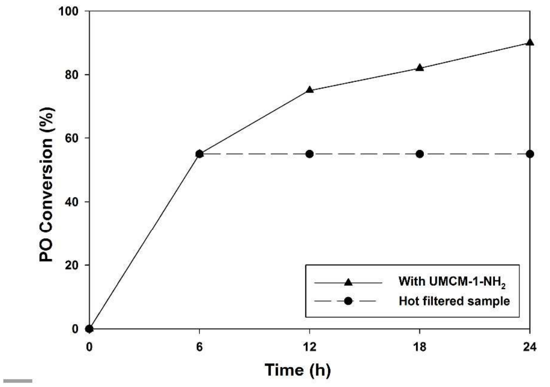
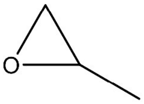
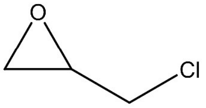
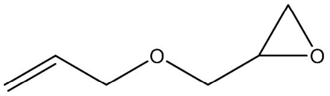
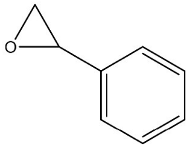
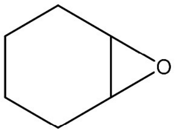


Fig. 9 Hot filtration test. Reaction conditions: 120 °C, 0.64 mol% UMCM-1-NH_2 and 1.2 MPa P_{CO2}. Hot filtration was done at 55% conversion at 6 h.

Table 6 Scope of various epoxides coupled with CO_2 catalyzed by UMCM-1-NH_2/TBAB

Entry	Epoxide	Conversion (%)	Selectivity (%)	Yield (%)
1		90	> 99	90
2		78	> 99	78
3		55	> 99	55
4		53	> 99	53
5		10	> 99	10

Reaction conditions: UMCM-1-NH_2 = 0.64 mol%, TBAB = 0.64 mol%, Epoxide = 42.8 mmol, P_{CO2} = 1.2 MPa, RT, 24 h, Semi-batch.

mesopore channels. Thus, micro-mesoporous hybrid materials are more efficient in the CO_2 cycloaddition with smaller epoxides such as propylene oxide or epichlorohydrin. Still, it is more noteworthy that cyclic carbonates can be obtained at room temperature with high selectivity than many of the reported MOFs.

From the previous results reported so far about CO_2 adsorption in MOFs proves that CO_2 adsorption mainly depends on surface areas and pore volumes.[21a] UMCM-1-NH_2, possessing high surface areas and large pore volume were tested as potential candidate for CO_2 capture applications.[21b] The excellent catalytic performances of propylene oxide are attributed to the combined effects of suitable acidity/basicity and the micro-meso porosity. So a better mass transfer between CO_2 and catalytic centre is expected. Catalysis is expected to occur inside the micropores of UMCM-1-NH_2, because the bulky epoxides are found to be less reactive (Table 6, entry 4 and 5). Mesopores appears mainly as highways, which improves the mass transport of reactants and products to/from active sites located inside the micropores. In general, micro-meso porous materials with high surface area and proper functionalities,[22] confers high catalytic performance towards the synthesis of cyclic carbonates at room temperature with 100% selectivity.

Conclusions

A mixed linker dual-porous amine functionalized 3D MOF, UMCM-1-NH_2, constituting Zn_4O SBUs with two-fold symmetric (NH_2-BDC) and three-fold symmetric (BTB) ligands, were synthesized, characterized and its structural peculiarities were exploited for its catalytic potentials. We proposed a novel approach of synchronizing of micro and mesopores in catalysis, so as to overcome the limitations of microporous materials, *viz*., hindrance to pore accessibility, molecular transport and mass transfer, while harvesting the potentials of micropores in enhancing the catalyst-substrate interactions. This enhancement of catalytic efficiencies was demonstrated in the chemical fixation of CO_2 by its cycloaddition with epoxides to yield cyclic carbonates. UMCM-1-NH_2 showed a TON of 141 at room temperature with high selectivities for propylene carbonate (> 99%) in the cycloaddition of propylene oxide and CO_2 using TBAB as cocatalyst. The catalyst was separable by simple filtration, and heterogeneous nature of the catalyst was investigated using physico-chemical techniques. The catalyst framework did not degrade even after several repetitions of the cycles and promisingly no fall in the conversion rate of the cycloaddition occurred. A plausible mechanism was suggested based on literature and experimental inferences. It was demonstrated that the cautious design and judicious selection of building blocks so as to accommodate apt pores (hybrid micro-mesopores) are as equally important as the role of active sites and functional groups in attaining a viable chemical fixation of CO_2. This hybrid nature of UMCM-1-NH_2, which offers easy accessibility to the substrates along with easily modifiable amine groups provides a handle for post synthetic functionalization in forming a single component standalone catalytic species, which shall remove the needs of any co-catalysts, and thereby serves an inspiration to future catalysis using MOFs.

Experimental section

Synthesis of UMCM-1-NH_2

The synthesis of purely needle-shaped UMCM-1-NH_2 was performed by solvothermal reaction between $Zn(NO_3)_2.4H_2O$ (≥ 98%, Sigma-Aldrich), 2-Aminoterephthalic acid (99%, Sigma-Aldrich) and 1,3,5-Tris(4-carboxyphenyl)benzene (97%, Alfa-Aesar) in N,N-Diethylformamide (99%, Alfa-Aesar) at 85 °C for 72 h. The optimal molar ratio of H_2NH_2BDC and H_3BTB for the pure phase production was found to be within the range of 3:2 to 1:1. Liquid exchange of the encapsulated solvent DEF was carried out by dipping the material in dichloromethane (≥ 99.8%, Sigma-Aldrich) for 2 days, followed by pore evacuation under vacuum. Anal. calcd (%) for the sample $C_{44}H_{25}NO_{13}Zn_4$; C: 50.95; H: 2.43; N: 1.35; O: 20.05; Zn: 25.21. Exp. found. (%); C: 51.53; H: 2.851; N: 1.82; O: 20.19 (Elemental analysis), Zn: 23.2 (ICP-OES).

Cycloaddition of epoxide and CO_2

42.8 mmol propylene oxide and 0.64 mol% of the catalyst were mixed together and put into a 25 mL stainless steel reactor equipped with a magnetic stirrer. The reactor was pressurized with CO_2 to the required pressure at room temperature, and stirred at 600 rpm. The reaction vessel was kept connected to a CO_2 source throughout the reaction via a one-way check valve to maintain the pressure at the desired level. After reaction completion, the reactor was cooled and excess CO_2 was carefully vented off. Toluene (3 mL) was added to the product mixture and filtered. The filtrate was subsequently analyzed by gas chromatography (GC, HP 6890, Agilent Technologies) to determine conversion, selectivity, and yield using toluene as internal standard.

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Graphical Abstract

Dual-porous metal organic framework for the room temperature CO_2 fixation via cyclic carbonate synthesis

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An approach employing dual-porous metal organic framework as catalyst for room temperature CO_2 fixation via cyclic carbonate synthesis with high selectivity towards cyclic carbonates under solvent free conditions were demonstrated. Structural features, acid-base characteristics and physical properties were studied in detail for carrying out a systematic investigation on the cooperative influences of porosity, functionalization and synergism with quaternary ammonium salts in the CO_2 cycloaddition reaction.