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Porous Metal Organic Polyhedral Framework Containing Cuboctahedron Cages as SBUs with High Affinity for H₂ and CO₂ Sorptions: A Heterogeneous Catalyst for Chemical Fixation of CO₂

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Abstract: Development of active porous materials that can efficiently adsorb H_2 and CO_2 are in need due to their practical utilities. Here we present the design and synthesis of an interpenetrated Cu(II)-MOF that is thermally stable, highly porous and can act as a heterogeneous catalyst. The Cu(II)-MOF contains highly symmetric polyhedral metal cluster (Cu₂₄) with cuboctahedron geometry as SBU. The double interpenetration of such huge cluster containing nets provides high density of open metal sites due to which it exhibits remarkable H_2 storage capacity (313 cm³g⁻¹ at 1bar and 273K). Further, its propensity towards the CO₂ sorption utilized for the heterogeneous catalysis of chemical conversion of CO₂ into the corresponding cyclic carbonates upon reaction with epoxides with high TON and TOF values.

The phenomenal growth in the area of metal-organic frameworks (MOFs) is emerging over the recent years due to their diverse applications such as gas storage and separation, heterogeneous catalysis, chemical sensing and many more.1-5 The main advantages of MOFs are considered to be their high surface area, well defined pore sizes, exposed metal sites and high thermal stabilities.⁶⁻⁸ The special feature of the MOFs compared to traditional zeolites is that they can be tailor made by introducing organic moieties for targeted absorption of gases. The incorporation of secondary building units (SBUs) such as well-known M₂(carboxylate)₄ paddlewheel moiety was shown to produce variety of MOFs.9,10 Moreover the expansion of the pore size and surface area of MOFs can be strategically achieved by enlarging the ligand or by aggregating several of SBUs in to bigger clusters, supramolecular building blocks (SBBs).11-15 However with the increasing size of the cavities or pores increases probability of interpenetration of the frameworks which reduces the cavity size but increases the stability.16-20

Several porous frameworks containing nitrogen rich functional groups such as pyridine, amine, imidazole, acylamide were shown to have a greater affinity towards the storing of carbon dioxide (CO₂).²¹⁻²⁵ Development of porous materials that can efficiently adsorb and store H_2 , and CO_2 are in demand

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given their practical utility. The problems with the use of carbon based fuel can be sorted out by employing H_2 gas as a dense fuel as it does not produce any kind of carbon emission.²⁶⁻²⁸ It is supposed to be the ideal fuel for the future generation with only water as by-product.

In particular, the CO₂ is one of the primary anthropogenic gas and foremost culprit for global warming and subsequent For the last few decades the CO₂ climate changes. concentration in the atmosphere increased over 380 ppm. and it continues to mount. Due to the toxicity, corrosion and high energy cost of conventional technologies involving amine based wet absorbents for CO₂ capture are becoming less important. Therefore, it became essential for the researchers to develop new solid materials for the efficient and selective capture of CO₂ and its sequestration.²⁹⁻³⁶ Further, the captured CO₂ can be catalytically converted into commercially important value-added chemicals which actually furnish non-toxic and low-cost resource of carbon feedstock.37-47 This approach will help in diminishing the concerned greenhouse gas as well as generation of valuable chemical commodities. Cycloaddition of CO₂ with epoxides to produce a five membered cyclic carbonates is being treated as one of the beneficial strategy for CO₂ fixation. The resulted cyclic carbonates can be used as valuable chemicals in various applications such as intermediates in petroleum products, electrolyte components, pharmaceuticals etc. Due to the difficulties in catalyst separation in homogeneous catalysis for CO_2 fixation, the heterogeneous catalyst has been preferred.

Recently a number of MOFs have been shown to capture CO₂ and catalyse its chemical conversion into the cyclic carbonates.³⁷⁻⁴⁷ However the design and synthesis of more efficient and robust MOFs are very much necessary for the effective fixation of CO2 with high yields and high turnover frequencies. In pursuit of constructing high prolific CO₂ storage which can also efficiently catalyse its fixation reaction; we are immensely fascinated in building of stable porous MOFs with the use of elongated multidentate carboxylic acids as organic ligand containing polar functional groups such as acylamide (H₄DAIA). Herein, we outline a novel interpenetrated 3D-MOF, $\{[Cu_{24}(DAIA)_{12}(H_2O)_{24}](solv.)_x\}_n$ (Cu-MOPF), which has been synthesized using a newly designed tetra carboxylic acid H₄DAIA (scheme 1). Due to the presence of exposed acylamide group as well as open paddlewheel Cu(II) sites, Cu-MOPF found to exhibit high CO2 uptake capacity along with efficient catalytic activity in cycloaddition reaction between CO2 and various types of epoxide. Further Cu-MOPF also displayed remarkable ability for the storage of hydrogen gas.

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Scheme 1. Molecular structure of H₄DAIA.

molecule H₄DAIA was synthesized by the The condensation of diacrylic acid with dimethyl ester of 5-aminoisopthalic acid followed by hydrolysis and was characterized by ¹H and ¹³C NMR (supporting information). Solvothermal reaction by using a sealed tube or by simple refluxing of H₄DAIA with Cu(NO₃)₂ in DMF resulted in light blue coloured octahedral shaped single crystals of Cu-MOPF. Single-crystal X-ray diffraction analysis revealed that Cu-MOPF crystallised in Fmmm space group and the asymmetric unit contains one and half unit of DAIA, six Cu(II) ions and six coordinated water molecules, both with half occupancy. All six Cu(II) ions exhibit square pyramidal geometry as the Cu(II) ions are equatorially coordinated by four carboxylates of four units of DAIA (Cu-O: Supporting Information; Table S2) and the axial positions are occupied by water molecules (Cu-O: Supporting Information; Table S2). The combination of five coordinated two square pyramidal Cu(II) centres leads to the formation a typical inorganic paddlewheel Cu₂(COO)₄ SBUs with the Cu-Cu separation of 2.6470(1), 2.6541(1) and 2.6487(1) Å.

Each bdc unit of DAIA connects to two Cu₂ paddlewheel SBUs, overall twelve such SBUs were bridged by twenty four bdc units of twenty four DAIA to produce a typical metal–organic cuboctahedron containing a cavity (MOC, Cavity A). (Figure 1a) The bent core nature of bdc exhibited the coordination mode at an angle of 120° which produces an edge-directed corner-linked MOC. The 24 bdc units represent the edges while the 12 SBUs represent the corners of cuboctahedron similar to the MOC of BDC and other BDC based MOFs.^{9,10} (Figure 1b) The coordinated water molecules in Cu₂ paddlewheel units are decorated on inner and outer surfaces of MOCs and these can be removed in order to have an activated material for porosity and catalysis studies. There are total of eight triangular and six square windows in each MOC which will allow the gases and small molecules to enter into the interior cavities of the MOCs.

The MOCs are further connected to the vicinal MOCs through the spacers of DAIA such that two more types of cavities are formed: one type of cavity (B) is produced by the linking of two paddlewheel SBUs by four DAIA units and other (C) is produced by the linking of two clusters of four SBUs by the four DAIA units. (Figure 1c & 1d) As a consequence each MOC was found to be connected to the six neighbouring MOCs through twenty four DAIA moieties, such connections resulted in four and two cavities of type B and C, respectively, surrounding each MOC (Supporting Information; Figure S3). Further, a fourth cavity which is very big in size was observed in the middle of eight MOCs of the 3D-framework which are filled through the interpenetration of the networks (Figure 2b).⁴⁸



Figure 1. a) Bridging of twelve Cu₂-paddlewheel SBUs to produce a typical metal–organic cuboctahedron (MOC, cavity A); b) simplified representation of MOC by reducing paddlewheel SBUs as nodes and BDC as edges; c) Linking of MOCs in *XY*-plane by DAIA units; d) Linking of MOCs along *Z*-axis by the DAIA units.

The interpenetrated networks interact via O-H---O and N-H---O hydrogen bonding with water, DMF and amide functionalities. Considering the MOCs as a six connected node, the Cu-MOPF represents a doubly interpenetrated network with PCU topology (33.6 x 33.6 x 32.3 Å³) (Figure 2c). In spite of having an interpenetrated framework, the total accessible free volume in completely desolvated Cu-MOPF was found to be 62% (44223.5 Å³ out of the 71343.0 Å³ unit cell volume) as calculated by PLATON with the calculated density is 0.783 g cm³, revealing the highly porous nature of Cu-MOPF.

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Figure 2. a) Illustration for overall 3D-framework (red: 1,3-BDC unit; green: diacrylamide spacer); b) 2-fold interpenetrated 3D-frameworks; c) PCU network generated by denoting MOCs as six connected nodes and multiple connections by DAIA in the same direction as one connection.

The bulk purity of Cu-MOPF was confirmed by comparing XRPD patterns of the as synthesized bulk material with that of simulated pattern obtained from the crystal structure. Further temperature variable XRPD patterns for Cu-MOPF revealed the thermal stability of the material (Figure 3a). Thermogravimetric analysis (TGA) of Cu-MOPF indicates the solvent loss takes place up to 300 °C and the material is found to be stable beyond

600 °C. The completely activated sample was prepared by exchanging the lattice solvent molecules in Cu-MOPF by acetone followed by the degassing under high vacuum at 110°C for 10 hrs. A typical colour change of the materials was observed from light blue to deep blue due to the generation of open metal sites on removal of the coordinated water molecules (Figure S9).

In order to investigate the permanent porosity of Cu-MOPF, low pressure nitrogen sorption–desorption isotherms were measured for the desolvated and activated phase of Cu-MOPF at 77K and one bar pressure which exhibited type-I behavior along with the reversibility. Cu-MOPF has the capacity to uptake 716 cm³g⁻¹ of N₂ at one bar pressure and the Brunauer– Emmett–Teller (BET) surface area was found to be 2091 m²/g (Figure 3b). All these characteristic of N₂ sorption–desorption isotherms demonstrated the micro porosity nature of Cu-MOPF. Further Cu-MOPF was shown to absorb significant amount of H₂ and CO₂ but not CH₄.

The Cu-MOPF exhibited remarkable H₂ uptake capacity of 313 cm³g⁻¹ (2.8 wt%) at 77 k and one bar pressure without any notable hysteresis of adsorption and desorption curves (Figure 3c). We note here that the H₂ uptake capacity of Cu-MOPF is higher than several recently reported porous materials such as Cu-based MOFs TMOF-1⁴⁰, NOTT-103⁴⁹ and some of the well-known highly porous MOFs such as IRMOF-6 (2476 m²g⁻¹, 1.48 wt%), MOF-177 (4526 m²g⁻¹, 1.25 wt%) and PCN-68 (5109 m²g⁻¹, 1.87 wt%).²⁷ A very few number of MOFs have been reported till date with H₂ uptake capacity of above 2.5 wt% at 77K and one bar (Supporting Information; Table S3). The void spaces in the interpenetrated framework of Cu-MOPF can be optimally used as it contains more number of open metal sites which consequently create the attractive electrostatic interactions between adsorbate and adsorbent.^{50,51}

The presence of acylamide functionality and open metal sites in Cu-MOPF encouraged us to investigate the CO₂ adsorption behavior of Cu-MOPF. The adsorption studies on Cu-MOPF towards CO₂ and CH₄ at ambient conditions indicated the higher affinity of Cu-MOPF towards CO₂ compared to CH₄. At 273 K and one bar pressure, Cu-MOPF can uptake 159 cm³g⁻¹ (31.3 wt%) of CO₂, maintaining the complete reversibility. Whereas a very small amount of CH₄ uptake (21 cm³g⁻¹) was observed by Cu-MOPF at 273 K and one bar pressure (Figure 3d).

The CO2 uptake capacity exhibited by Cu-MOPF is comparable to the recently reported highly porous triazolecontaining Cu-MOFs^{25,41} and higher than many recently reported Cu-based MOFs (eg: JUC-1000, 125; Cu-NTTA, 115.6 cm³g⁻¹; TMOF-1, 47.1 cm³g⁻¹)^{43,39,40} (Table S4, Supporting Information). Further, we note here CO₂ adsorption ability of Cu-MOPF is also comparable with well-known examples such as HKUST-1 (Cu₃(BTC)₂) and PCN-6 (Cu₃(TATB)₂).³³ The preferential uptake of CO2 over CH4 by Cu-MOPF could be due to the presence of polar functionality such as acylamide on the walls of channels and also due to the exposed metal sites which accelerate the attractive interactions with CO₂ due to its quadrupolar moment. Apart from these factors, the linear shape of CO₂ also helps in channels. its passage into the

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Figure 3. a) Temperature variable XRPD patterns for Cu-MOPF; b) Nitrogen adsorption and desorption isotherm of Cu-MOPF at 77 K and one bar; c) Hydrogen uptake isotherm of Cu-MOPF at 77 K and one bar; d) CO₂ and CH₄ adsorption isotherms of Cu-MOPF at 273 K and one bar.

The presence of Lewis acidic open metal sites in the framework as well as high CO_2 adsorption capability of Cu-MOPF prompted us to investigate its catalytic ability in the conversion of epoxides to cyclic carbonates by utilizing CO_2 as a renewable C1 building block. In a typical solvent free conditions, 0.01 mmol of Cu-MOPF as a catalyst along with 2 mol% tetrabutylammonium bromide (TBAB) as a co-catalyst were immersed into the liquid epoxide (25 mmol) and CO_2 purged at 1 atm pressure under reflux conditions (scheme 2). A facile conversion of epoxides to cyclic carbonates was observed for as many as five substrates with high TOF and TON values.

The epoxides considered are un-symmetric in nature and have substitutions such as n-butyl, phenyl, phenyl ether and tbutyl-ether on one side of the ring. The reactions were monitored for 4h, and a good to excellent conversions were achieved (Table 1). The TON and TOF values for Cu-MOPF found to be higher than some of the recently reported similar catalytic conversions by MOFs (Table S5, Supporting Information). From the table 1, it can be seen that the TON as well as TOF values are highest i.e 2500 and 625 h⁻¹ for entry 4. Further, the conversion found to be good (82%) for the substrate containing n-butyl (entry 1) where as for the styrene oxide (entry 2) the conversion found to be moderate (69%). For entries 3 and 4, the conversions found to be excellent (94% & > 99%).



Scheme 2. Formation of cyclic carbonates by the addition of CO₂ to epoxides.

catalytic cycle. The XRPD patterns of Cu-MOPF before and after catalysis remained same revealing its structural integrity.



[a] Reaction conditions: epoxide (25 mmol), catalyst (0.01 mmol per copper paddlewheel unit of Cu-MOPF), TBAB (0.16 g, 2 mol%) under CO₂ (1 bar) atmosphere, 373 K and 4 h. [b] From ¹H NMR (Figure S11-S20, Supporting Information)

These variations can be explained from a tentative mechanism where the epoxide oxygen will bind to the Lewis acidic copper sites and the ring will be activated. Subsequently, the Br⁻ ion, generated from TBAB will attack upon the less hindered carbon atom of the activated epoxide ring to produce the oxygen anion via ring opening. This oxygen anion will attack on the carbon atom of CO₂ to form an alkyl carbonate anion. Finally the ring closure step leads to the desired cyclic carbonates found to reduce with the increasing bulkiness of the side chain of the epoxides due to steric hindrance.

These reactions indicate that Cu-MOPF acts as very promising and perfect heterogeneous catalyst given its stable framework structure which is originated from cuboctahedron building blocks and interpenetration of the networks. The recyclability of Cu-MOPF was studied by reusing the catalyst five times successively for the cycloaddition reaction of CO_2 with glycidyl 2-methylphenyl ether (table 1, entry 4) where the catalytic activity remained almost uniform for those five successive cycles (Figure 4). After each cycle, the Cu-MOPF was recovered through centrifugation, washed with ethyl acetate followed by chloroform and dried in vacuum to use it for next



Figure 4. Recyclability experiment of the catalyst (Cu-MOPF) for chemical conversion of CO_2 .

In conclusion, a newly designed acylamide functionalized tetra carboxylic acid H₄DAIA has been employed for the construction of a thermally stable interpenetrated microporous 3D-MOF. The resultant 3D-MOF exhibited high porosity with the incorporation of exposed metal sites and polar channels which were found to be responsible for the high affinity towards CO₂ sorption. The CO₂ uptake capacity was found to be promising in comparison to the some of the recently reported microporous MOFs. Moreover, the Cu-MOPF also exhibited an excellent ability for H₂ gas sorption at low pressure which is comparable to the MOFs with highest reported values. Further, the superior CO₂ adsorption capacity, the presence of Lewis acidic open metal sites and confinement of the large pores in the framework, make the Cu-MOPF as a perfect heterogeneous catalyst for the chemical reaction of CO2 with various epoxides to form cyclic carbonates. The Cu-MOPF exhibited very high TON and TOF values with excellent recyclability.

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