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Selective CO₂ Adsorption and Lewis Acid Catalytic Activity Towards Naphthimidazole Synthesis by a Zn-MOF

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Abstract: A two-fold interpenetrated, three dimensional Zn-based porous MOF, $\{[Zn(BPBA)CI]\cdot5H_2O\}_n$ (1) [BPBA = 3,5-bis-(4-oxo-4H-pyridin-1-yl)-benzoate], has been synthesized at high temperature under solvothermal conditions by the *in situ* acidic hydrolysis of the tripodal ligand 3,5-bis-(4-oxo-4H-pyridin-1-yl)-benzonitrile (BPBN). The de-solvated MOF exhibited selective CO₂ adsorption at a temperature of 195 K and 1 bar pressure over N₂ and H₂. Interestingly, the four coordinated Zn(II) sites in the MOF exhibited high Lewis acidic heterogeneous catalytic activity for the synthesis of naphthimidazole in excellent yield without pre-activation of the MOF. The Zn(II) sites could directly coordinate to the substrate to catalyze the chemical transformation by an expansion of the coordination number. The π - π supramolecular interactions between the aromatic rings of the framework and the substrate molecule might help in the substrate activation.

Keywords: Metal Organic Framework; Heterogeneous Catalysis; CO₂; Single Crystal; Naphthimidazole

1. Introduction

Metal-organic frameworks (MOFs) are crystalline polymeric materials made up of metal ions and multidentate bridging ligands [1]. These materials have a wide range of applications, especially in gas adsorption [2,3] and heterogeneous catalysis [4], due to their structural diversity, chemical functionality, large surface area, tuneability along with high thermal stability.

Increasing concentrations of CO_2 in the environment from coal fired power plants and burning of fuel in automobiles create serious problems. Thus, there is an urgent need to sequestrate CO_2 and reduce its excessive emissions to the atmosphere [5]. MOFs are excellent candidates for CO_2 capture and storage due to their unique features, such as structural diversity and permanent porosity [6-9]. Presence of functional ligand moieties and open metal sites (OMSs) in the architectures of MOFs not only enhances gas adsorption but also heterogeneous catalytic activities. These free atoms or groups participate in making different types of non-covalent interactions with the guest molecules [10,11]. Alternatively, the open coordination sites along with the confined space of MOF interact with substrates and subsequently activates them to form products.

Generally N-containing heterocyclic compounds have attracted the attention of many researchers because of their utility as pharmaceutical and agrochemical agents due to their biocompatibility [12-17]. Most commonly, these compounds are synthesized by the condensation reaction of ortho-substituted aniline derivatives with carboxylic acids [18,19], nitriles [20] and esters [21], or the oxidative cyclization of substrates with aldehydes [22,23] and alcohols [24,25]. Recently benzimidazoles were synthesized by the reaction of 1,2-arylenediamines with N,N-dimethylformamide (DMF) in highly acidic medium under thermal/microwave conditions [26]. On the other hand, various benzimidazole derivatives have been synthesized by utilizing a variety of *o*-phenylenediamines, N-substituted formamides and a zinc catalyst in the presence of poly(methylhydrosiloxane) [27]. Very recently N-containing heterocycles were obtained by CO_2 promoted cyclization of ortho-substituted aniline derivatives with DMF over a $B(C_6F_5)_3$ catalyst at 120 °C [28]. Due to the requirement of toxic, air-sensitive, costly reagents or highly acidic media, along with the multistep syntheses of the

pre-functionalized precursors, with limited success in terms of yield and selectivity, most of the experimental procedures have disadvantages. Herein, we report for the first time a cheap synthesis of naphthimidazole from 2,3-diaminonaphthalene and DMF at 120 °C with an excellent yield, using **1** as a Lewis acid heterogeneous catalyst.

2. Experimental section

2.1. Materials

Most of the reagent grade chemicals were purchased from Aldrich Chemical Company and used as received without further purification. 4-Hydroxy pyridine was purchased from Avra Chemicals and solvents were purchased from S. D. Fine Chemicals, India. Solvents were dried before use.

2.2. Physical measurements

Infrared spectra were obtained (KBr disk, 400-4000 cm⁻¹) using a Perkin-Elmer model 1320 spectrometer. The ¹H NMR spectrum was recorded using a JEOL-ECX 500 FT (500 MHz and 125 MHz) instrument in CDCl₃ with Me₄Si as the internal standard. Thermograms were recorded on a Mettler Toledo (with a heating rate of 10 °C/min) TGA instrument. Microanalyses for the compounds were obtained using a CE-440 elemental analyser (Exeter Analytical Inc.). Low-pressure gas adsorption measurements were performed on Quantachrome Quadrasorb automatic volumetric instrument.

X-ray structural studies are provided in the Supporting Information.

2.3. Synthesis of 3,5-bis-(4-oxo-4H-pyridin-1-yl)-benzonitrile (BPBN).

4-Hydroxy pyridine (0.68 g, 7.20 mmol), 3,5-difluorobenzonitrile (0.5 g, 3.60 mmol), K_2CO_3 (1.73 g, 12.6 mmol) and DMF (15 ml) were taken in a 50 mL round bottom flask. The mixture was stirred constantly at 80 °C (Scheme 1). After 48 h, heating was stopped and the reaction mixture was allowed to cool down at room temperature. After that, the mixture was poured into ice-cold water to obtain a white solid precipitate. It was filtered and air dried. Yield: 0.96

g, (92%). SI-MS: [M+H], m/z: 290.0934 (100%) (calcd for C₁₇H₁₁N₃O₂, 289.0851) (Fig. S1). Anal. calcd. for C₁₇H₁₁N₃O₂: C, 70.59; H, 3.80; N, 14.53%. Found: C, 70.61; H, 3.82; N, 14.6% IR (cm⁻¹, KBr pellet): 3426 (m), 3044 (m), 2943 (m) 2245 (m), 1651 (s), 1599 (s), 1443 (s), 1349 (s), 1248 (s), 1199 (s), 1090 (m), 892 (m), 843 (s), 690 (m), 557(m), 496 (m) (Fig. S2).



2.4. Synthesis of $\{[Zn(BPBA)Cl] \cdot 5H_2O\}_n$ (1).

A mixture of Zn(NO₃)₂.6H₂O (0.12 g, 0.414 mmol) and BPBN (0.04 g, 0.138 mmol) was taken in EtOH:H₂O (6 mL, 2:1 v/v) with 2 drops of dilute HCl, followed by heating at 180 °C under autogenous pressure in a Teflon-lined steel bomb for 3 days. Slow cooling was done to room temperature. Colourless crystals were obtained and washed with ethanol. Yield ~68%. Anal. calcd. for C₁₇H₂₁ClN₂O₉Zn: C, 40.98; H, 4.25; N, 5.61%. Found: C, 40.88; H, 4.2; N, 5.68% IR (cm⁻¹, KBr pellet): 3543 (m), 3430 (m), 3068 (w), 2924 (w), 1664 (s), 1592 (m), 1527 (s), 1376 (s), 1193 (m), 854 (m), 577 (m) (Fig. S3).

2.5. Procedure for the cyclization of ortho-substituted diaminonaphthalene to naphthimidazole.

In a 50 ml round bottom flask, 2,3-diaminonaphthalene (200 mg), $\{[Zn(BPBA)Cl]\cdot 5H_2O\}_n$ (10 mg) and DMF (10 ml) were taken and equipped with a magnetic stirrer. The suspension was heated at 120 °C for two days. Reaction progress was checked through TLC. After completion of the reaction, the mixture was allowed to cool down, followed by its filtration and the catalyst was washed with DCM. The product was collected from the aqueous layer by extraction with

DCM. The organic layer was collected and evaporated, leaving the solid compound. The product was recrystallized from methanol.

3. Results and discussion

3D porous Zn^{II} -framework 1 was obtained with 2-fold interpenetration through *in situ* acidic hydrolysis of the BPBN ligand under solvothermal conditions at 180 °C.

3.1. Single crystal structure description of 1

Single crystal X-ray diffraction analysis revealed that compound 1 crystallized in the monoclinic space group $C^{2/c}$. The asymmetric unit consisted of one Zn(II) ion, one coordinated chloride ion and one BPBA ligand. The nitrile group of BPBN was hydrolysed to a carboxylate group through HCl hydrolysis. The free C≡N stretching of the ligand BPBN was observed at 2245 cm⁻¹ (Fig. S2), which disappeared in the MOF. Five non-coordinated water molecules were also present in the asymmetric unit. Broad bands at 3441 and 3548 cm⁻¹ revealed the presence of lattice water molecules (Fig. S3). The Zn1 centre adopted a tetrahedral geometry (MO₃Cl), with coordination from two oxygen atoms of pyridine-1-ium-4-olate groups present in the two different BPBA ligands and a third oxygen atom from a carboxylate group of a third BPBA ligand (Fig. 1a). A1D zig-zag chain was formed by metal bonding with the oxygen atom of pyridine-1-ium-4-olate, followed by formation of layered architecture by metal coordination with one of the carboxylate oxygen atoms of the BPBN ligand. Both pyridine-1-ium rings were perpendicular to the central benzene ring, leading to the structure's third dimension. Hexagonal channels were present with diameter of ~10.83 Å (considering the Van der Waals radii), as shown in Fig. 1b, along the b axis. However, mutual interpenetration (Fig. 1c) gave rise to a comparatively small void volume (28.72%), with a reduced diameter of ~6.3 Å of the channel (considering the Van der Waals radii). The interpenetrated framework has been stabilised by π - π non-covalent interactions between the parallel central benzene rings and between the parallel pyridine-1-ium rings of two independent frameworks (Fig. 2). TOPOS software

topological analysis was performed, which revealed that Zn(II) ion has a 3-connected uninodal net with point symbol 10³ and topological type ths/ThSi2; 3/10/t4 (topos&RCSR.ttd) (Fig. 1d). *3.2. Thermal stability*

Thermogravimetric analysis (TGA) of compound 1 (Fig. S4) showed a sharp weight loss of ~10.8%, ascribed to the loss of three lattice water molecules in the temperature range 30-92 °C. After that, a gradual weight loss of the lattice water molecule took place between 92 and 300 °C. Above 365 °C, framework degradation started, signifying its high thermal stability. The observed weight loss was found to be ~14.2% (calculated value ~14.4%), corresponding to the loss of four solvent water molecules. PXRD patterns of the as-synthesized 1 showed similar diffraction peaks compared to the simulated PXRD pattern, revealing phase integrity of the framework (Fig. S5a and b).



Fig. 1. (a) Coordination environment around the metal centre, (b) 3D structure without interpenetration (solvent molecules are omitted for clarity), (c) 3D structure with 2-fold interpenetration and (d) 3-c uninodal net of 1 with the ths/ThSi2 topological type.



Fig. 2. π - π bonding interactions between parallel benzene rings and between pyridine-1-ium rings in the 2-fold interpenetrated framework of 1.

3.3. Gas adsorption studies

Before gas adsorption studies, activation of the sample was done by replacing all the solvent molecules with low boiling DCM (dichloromethane) solvent molecules. To achieve this, the crystals were immersed in DCM for 5 days, during which DCM was refreshed daily. After 5 days the framework was heated at 60 °C under a high vacuum to remove the DCM solvent molecules and to generate the activated or de-solvated compound **1a**. PXRD data have been collected for the activated compound **1a**, which was similar to the as-synthesized PXRD pattern, confirming the phase purity of the de-solvated compound as shown in Figure S5c.

Low pressure gas adsorption isotherms were measured at 77 K for N_2 and H_2 , and CO_2 at 195 and 298 K temperatures. The de-solvated compound showed selective CO_2 gas adsorption at 195 K, with a maximum uptake of 75 cm³ g⁻¹ along with a large hysteresis, as shown in Fig. 3.

The BET surface area was found to be 153.710 m² g⁻¹, as calculated from the CO₂ adsorption isotherm at 195 K. In the 2-fold interpenetration, there are supramolecular π - π interactions between two parallel benzene rings as well as between two parallel pyridine-1-ium rings of the two independent frameworks (Fig. 2), which resist the reversible adsorption of CO₂. Extensive π - π bonding interactions between the aromatic rings having exposed edges and faces stabilize the CO₂ quadrupole (CO₂ quadruple moment 1.34 x 10⁻³⁹ Cm²) through weak electron donation towards CO₂ molecules. On the other hand, dipole-quadrupole interactions take place between the N atoms of the pyridine-1-ium rings and probe molecules [29]. Significant hysteresis was observed at lower temperature (195 K) due to the compact packing of probe molecules in the available voids, but at elevated temperature, the higher kinetic energy of CO₂ hinders uptake and dense packing in the cavities, leading to low gas adsorption with less hysteresis [30]. Due to possessing a zero dipole moment, adsorption of H₂ and N₂ guest molecules did not take place in the polar cavities of **1a** because of the very weak interactions between the non-polar adsorbate gas molecules (N₂ and H₂) and the adsorbent.



Fig. 3. Gas sorption isotherm of 1a at 1 atm pressure: CO_2 at 195 and 298 K temperatures, N_2 and H_2 at 77 K temperature.

Due to the larger void size compared to the kinetic diameters of the probe-adsorptive gas species ($CO_2 = 3.3 \text{ Å}$, $N_2 = 3.64 \text{ Å}$ and $H_2 = 2.8 \text{ Å}$), size selective gas uptake could be ruled out [31]. The effective pore diameter (~6.3 Å) of the framework was relatively larger than the kinetic diameter of any of the probe gases. It confirmed that the selective uptake of CO_2 by **1a** was a combination of Van der Waals interactions and electrostatic interactions.

The literature reveals that modified mesoporous silica structures (with different pore lengths) functionalized with triamine and polyethyleneimine (PEI) show higher as well as faster CO_2 adsorption over a very low range of CO_2 concentrations compared to pure mesoporous silica materials over a wide range of pressures and temperatures, as observed by Sayari and co-workers [32-34]. CO_2 adsorption in Na-A zeolite has been reported by Zukal et. al. at 273–333 K, with desorption at higher temperature due to the formation of surface carbonates with a small portion of CO_2 [35]. Zeolites are very difficult to tune according to requirements.

Exceptionally high uptakes of CO₂ have been shown by functionalized MOFs (Mg-MOF-74), even in the presence of high humidity, by introducing a high density of free amine groups due to the strong affinity of free amine groups towards CO₂, compared with non-functionalized Mg-MOF-74 (CPO-27-Mg) with open metal sites (OMSs) under dry conditions (because in the presence of moisture, water molecules are coordinated with the OMSs) [36-39]. Presence of coordinatively unsaturated sites (CUS) in Cu-BTC MOF helps in CO₂ gas uptake, accurately calculated by a combined DFT-ab initio computational scheme [40]. In the present de-solvated complex **1a**, not only the higher kinetic energy of CO₂ but also a slight contraction in the framework at higher temperature (298 K) leads to gas adsorption of up to 55 cm³g⁻¹ with a small hysteresis. A number of MOFs display selective adsorption of CO₂ by incorporating free -N atoms, along with free carboxylate O atoms [41-43].

3.4. Cyclization of ortho-substituted diaminonaphthalene to naphthimidazole

Naphthimidazole has important pharmaceutical properties and its derivatives have various applications in labelling natural carbohydrates for capillary electrophoresis [44] and in mass spectrometry detection for saccharide labelling with enhanced sensitivity [45]. Due to the presence of the benzimidazole scaffold (N- containing heterocycles) in the structure, naphthimidazoles have vital importance in medicinal chemistry because of various biological activities: antiviral, antibacterial, anticancer, antihistaminic, antitubercular, antihypertensive and anti-inflammatory agents, and also as plant growth regulators [46-51]. This is why the synthesis of naphthimidazole is quite attractive. Various homogeneous catalysts, like strong hydrochloric acid, polyphosphoric acid, boric acid, p-toluene sulfonic acid and some expensive metal complexes, are generally used to catalyse the condensation reactions of aryl-1,2-diamine and *N*,*N*-dimethylformamide (DMF)[26-28]. However, in all these cases the catalyst could not

be recovered and reused. Not only is a fresh catalyst required every time, also its removal needs many steps to purify the compound.

In the present study, for the first time naphthimidazole has been synthesized by employing a Zn-MOF as a heterogeneous catalyst. One most important point is that the MOF catalyst was used as-synthesized and activation was not required. The presence of open Zn(II)-sites made 1 an excellent heterogeneous catalyst for the condensation reaction of 2,3-diaminonaphthalene and DMF to afford naphthimidazole (Scheme 2). This is a very simple and single step reaction towards the synthesis of naphthimidazole. The reaction has been carried out at 120 °C, over 2 days in DMF solvent (10 ml) by utilizing the reactant 2,3-diaminonaphthalene (200 mg). The progress of the reaction was checked through TLC. In the absence of catalyst 1, the reaction did not proceed, even after 24 hrs (entry 1). TLC showed no new spot other than that of the reactant. To check the real effect of the catalyst, the reaction has been carried out in the presence of ZnCl₂. In this case also the reaction did not proceed appreciably (entry 2), but in the presence of catalyst 1 (10 mg, 5 wt%) the reaction was initiated and could be completed within 2 days with an excellent isolated yield (95%) (entry 5 and Fig. S6-S8). In the same way higher temperature (120 °C) was also found to be an essential requirement for this reaction. We tried the reaction at room temperature as well as at 80 °C, resulting in sluggish reactions (entries 3 and 4).

Under the optimum reaction conditions, using 1,2- diaminobenzene as a substrate gave a slightly higher yield (>99%) (entry 7).



Scheme 2. Synthesis of naphthimidazole in the presence of heterogeneous catalyst 1.

Entry	Catalyst	Temperature	Time (h)	% yield ^b
		(°C)		
1	No catalyst	120	24	8
2	ZnCl ₂	120	24	15
3	1	25	24	12
4	1	80	48	31
5	1	120	48	95
6	1 after 4 th run	120	48	85
7°	1	120	48	>99

 Table 1. Synthesis of naphthimidazole from 2,3-diaminonaphthalene and DMF utilizing catalyst 1^a

^aCatalytic reactions have been done at 120 °C temperature and at atmospheric pressure in a 50 ml round bottom flask for two days using 2,3-diaminonaphthalene (200 mg), DMF (10 ml) and catalyst **1** (10 mg, 5 wt%). ^bYields were calculated by isolating the product. ^c1,2-diaminobenzene was used as the substrate.

Recyclability tests have been carried out to prove the heterogeneous nature of catalyst **1**. After complete conversion of the reactant to the product (checked through TLC), the reaction mixture was filtered, followed by washing several times with DCM to collect the catalyst. The solvent was evaporated at room temperature due to its low boiling point, leaving regenerated catalyst which could be used further for successive cycles of the catalysis. The catalyst **1** was reused up to four times with 85% yield for fourth run, as shown in Fig. S9. Powder X-ray diffraction patterns have been collected for the recycled catalyst, with the results displaying that framework was completely intact, without any loss of its integrity. Sharp peaks of the recycled catalyst matched well with the as-synthesized PXRD peak pattern (Fig. S10).

The MOF provided not only a confined space for the catalytic reaction but also a number of interaction sites where DMF molecules covalently interacted with the open Zn(II)-sites. On the other hand, 2,3-diaminonaphthalene was stabilised by π - π interactions. So, the nucleophilic attack of the substrate with DMF was much easier, forming the formylated intermediate. Dimethyl amine was liberated from DMF, followed by intramolecular cyclization and then a dehydration reaction occurred to generate the product and the catalyst **1** was released.

4. Conclusions

In summary, a three dimensional Zn(II)-MOF with 2-fold interpenetration has been synthesized through the *in-situ* acidic hydrolysis of the tripodal ligand 3,5-bis-(4-oxo-4H-pyridin-1-yl)-benzonitrile (BPBN) at high temperature. The activated framework showed selective uptake of CO_2 at low pressure (1 bar) and at 195 K temperature. In this first report, the cyclization of ortho-substituted diaminonaphthalene to naphthimidazole has been carried out in a one pot synthesis using the thermally stable as-synthesized Zn-MOF as a heterogeneous catalyst. This catalyst was reusable in several catalytic cycles, maintaining its structural integrity.

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Appendix A. Supplementary data

CCDC 1873571 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge viahttp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail:deposit@ccdc.cam.ac.uk.

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Selective CO₂ Adsorption and Lewis Acid Catalytic Activity Towards Naphthimidazole Synthesis by a Zn-MOF

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Graphical Abstract



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Graphical Abstract Legend

A three dimensional, as-synthesized Zn-MOF with 2-fold interpenetration exhibits excellent Lewis acidic heterogeneous catalytic activity towards the synthesis of naphthimidazole for the first time. It shows selective CO_2 capture from flue gas.



Selective CO₂ Adsorption and Lewis Acid Catalytic Activity Towards Naphthimidazole Synthesis by a Zn-MOF

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Highlights

1) A 3D, Zn(II) based metal organic framework has been synthesized at high temperature.

2) Four coordinated Zn(II) sites act as high Lewis acidic sites for catalytic activity.

3) π - π supramolecular interactions are present in the MOF, facilitating substrate activation.

4) The as-synthesized Zn(II) MOF converts diaminonaphthalene to the naphthimidazole compound.

5) Naphthimidazole is an important compound in the medical field.

6) The de-solvated MOF exhibits selective CO₂ adsorption at low temperature and pressure.

Credit Author Statement

Experimental part, data analysis, manuscript writing was done by the corresponding author R. A. Agarwal. Minor part of introduction and catalysis was written by D. De.