Ethylendiamine (EDA) loading on MOF-5 for enhanced carbon dioxide capture applications

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Abstract. Reducing carbon dioxide levels in atmosphere presents greatest challenge in controlling global climate change. Each stage of Carbon Capture and Storage (CCS) strategy requires specialized materials. Metal–organic framework, being highly porous and crystalline materials are captivating vast scientific attention for exploring their potential in gas adsorption applications. This research work presents an attempt to synthesis post amine modified MOF materials for enhanced carbon dioxide capture applications. Thermogravimetric studies reveal that EDA MOF-5 is far more thermally stable then MOF-5; moreover synthesis can be performed successfully with recycled solvent (DMF). Carbon dioxide adsorption studies represents better carbon dioxide capture tendency for MOF-5 and EDA MOF-5 i.e., 5 mmol/g and 3.9 mmol/g respectively at 0°C.

1. Introduction
Among various greenhouse gases listed under Kyoto Protocol; carbon dioxide is labeled as major contributor in global warning. Carbon dioxide absorbs and emits radiant energy within the thermal infrared range, thus raising global temperatures. CO₂ has the highest positive radiative forces of all the human-influenced climate drivers compared by the IPCC. After a pulse of CO₂ is emitted into the atmosphere, 40% will reside in the atmosphere for 100 years and 20% will remain for 1000 years, while the final 10% will take 10,000 years to turn over [1].

Metal–organic frameworks (MOFs) are advanced class of crystalline solid nanomaterials reinforced by metal coordination sites coupled with organic molecules [2–4]. Resulting organic/inorganic hybrid 3-D networks formed contains well-defined porosity, high surface area, and tunable chemical functionalities having versatile applications in catalysis [5, 6], Separations [7], and gas storage [8]. Owing to gas storage ability, a lot of research work has been done to capture carbon dioxide gas. Nevertheless, mostly MOFs adsorb carbon dioxide by weak physiosorption interactions so adsorption at low gas pressure and N₂/CO₂ selectivity is very low [9].

Amine sites being acidic in nature have affinity towards carbon dioxide and are known to be highly effective for CO₂ adsorption and to be amenable to use under dry or humid conditions. [10-13]. This research work is an effort to incorporate ethylenediamine molecules within MOF-5 molecule using post-synthesis modification and study potential effects on its carbon dioxide gas adsorption capacity.
2. Experimental section

All the chemicals were purchased from Sigma Aldrich and Merck. The reactions that require heating were conducted in 23 ml Parr bombs in oven. To test purity of reagents PXRD data for reagents was collected and verified prior to the synthesis.

2.1. Synthesis: MOF-5 synthesis

Synthesis Equimolar quantities (1:1) of Zn (NO$_3$)$_2$.6H$_2$O 189.36 mg (1 mmol) and 166 mg of terephthalic acid (1 mmol) were dissolved in 10 ml DMF in a 50 ml beaker. Dissolved contents were ultra-sonicated at 100°C for 2 hours then solution was transferred to 23 ml Teflon vials. Parr bombs were sealed and heated in oven at 100°C for 6 hours to yield white crystals. The reaction mixture was then decanted (and saved for recycling); crystals obtained were washed thrice with DMF then with THF thrice. Crystals were dried overnight at room temperature. Sample was activated in vacuum oven at 130°C for 6 hours before further analysis.

2.2. EDA MOF-5 synthesis

Prepared MOF-5 crystals were modified using ethylenediamine. 500 mg of MOF-5 was added to 15 % ethylenediamine solution in methanol. Contents were allowed to react under reflux with vigorous stirring for 6 hours. The product obtained was filtered and then washed with DI water and ethanol to remove any unreached ethylenediamine from sample. Sample was dried overnight at room temperature to collect a pale colored crystals of EDA-MOF-5. Crystals were activated in vacuum oven at 130°C for 6 hours before further analysis. Reaction scheme for EDA MOF-5 is given in Figure 1.

![Figure 1. Reaction Scheme for EDA MOF-5 synthesis](image)

3. Characterization

PXRD for synthesized MOF samples was collected at room temperature on an XPertpro panalytical Chiller 59 diffractometer using Copper Kα radiation. Activated samples were mounted onto zero-background silicon for PXRD analysis. Morphology of crystals was studied using scanning electron microscopy. TGA was performed using a Perkin Elmer Pyris 1 thermo-gravimetric analyzer. The samples were heated from 25°C to 700°C under a flow of air (20 ml min$^{-1}$), using a heating rate of 5°C min$^{-1}$. SHIMADZU IR Affinitit-1S spectrometer was used to obtain IR data. Elemental analysis for EDA MOF-5 samples was performed to confirm presence of amine in prepared material, using FlashSmart NC ORG elemental analyzer with Thermal conductivity detector.

4. Results

To check the synthesis of MOF-5 and EDA MOF, powder X-ray diffraction (XRD) studies were carried out. PXRD patterns of MOF-5 and EDA MOF-5 prepared in this study are shown in Figure 2. Fourier transform infrared spectra (FTIR) collected for prepared materials confirm the presence of representative functional groups indicative of MOF-5 formation (Figure. 3). Two sharp peaks were obtained at 1589 cm$^{-1}$ and 1375 cm$^{-1}$ in MOF-5 sample is representative of symmetric and asymmetric stretching of C-O bonded to Zn, respectively [11]. Various small peaks in the range of 1200 to 910 cm$^{-1}$ represents to the in-plane bending of the C-H group present in the benzene ring of the linker [10-11].
addition to MOF-5 typical peaks, EDA MOF-5 sample illustrates some new peaks. Typical peaks at 2845 and 2845 cm$^{-1}$ are ascribed to stretching vibration of C-H bonds introduced by ethylenediamine molecules [14].

![Figure 2. PXRD pattern for MOF-5 and EDA MOF-5](image)

Thermogravimetric analysis (TGA) was performed to study thermal behaviors of prepared MOF materials (Figure 4). For both MOFs there is no significant weight loss observed below 170°C, indicating there was no surface adsorbed moisture, THF and solvent molecules in prepared materials. Initial weight loss in both samples from 170°C to 320°C (approx 12 %) represents degradation of surface adsorbed DMF molecules [3]. For MOF-5 decomposition of carboxylic linker started at 381°C, while in EDA MOF-5 linker degradation initiated at a bit higher temperature, i.e. 445°C then onwards there is rapid degradation in both materials. No further weight loss was observed as the temperature continued to rise leaving behind residual zinc oxide above 503°C for MOF-5 and 517°C for EDA MOF-5 [5,6].

![Figure 3. FTIR pattern for MOF-5 and EDA MOF-5](image)
Figure 4. TGA graph for MOF-5 and EDA MOF-5

Scanning electron microscopy images of prepared MOF 5 sample are illustrates in Figure 5. It is observed that prepared MOF-5 has cubic crystals, supported by literature [4].

Figure 5. SEM images for MOF-5 at (a) 1µm (b) 3 µm and (c) 20µm

Elemental analysis results (Table.1) shows elemental composition for EDA MOF-5. Results clearly indicate significant amount of nitrogen (6.76 - 6.83) representing presence of ethylenediamine in the sample.

|                      | % Carbon | % Hydrogen | % Nitrogen |
|----------------------|----------|------------|------------|
| Elemental analysis   | 45.01-45.07 | 4.85-4.77 | 6.76-6.83 |

4.1 Solvent recovery and recycling


The absence of any alien peaks in Batch II MOF material PXRD results is indicative of the high purity MOF-5 and EDA MOF-5 production using recycled DMF. Solvent recovery and re-utilization is a clear indicator for cost advantage for this MOF synthesis.

5. CO₂ adsorption capacities of MOF-5 and EDA MOF-5

The CO₂ adsorption capacity for both MOF materials was evaluated by monitoring pseudo equilibrium adsorption uptakes using Quantarchrome Isorb-HP100 volumetric type sorption analyzer. Initially samples were degassed 130°C for 12 hours using a heating rate of 5°C min⁻¹. 200 mg of each sample was used for three consecutive adsorption-desorption cycles at 0°C and 25°C with adsorbate pressure ranging between 1 to 14 bar. The CO₂ capacities calculated at 0 °C and 14 bar pressure were 3.9 and 5 mmol/g for MOF-5 and EDA MOF-5, respectively. This trend found consistent with adsorption capacities calculated at 25°C (Figure 6).

On the contrary, silica based surface-grafted amine based sorbents shows enhanced stability under dry conditions, illustrating relatively high values of CO₂ uptake with same number of adsorption cycles tested, with only a negligible adsorption decrease. Here we observed that initial CO₂ uptake for MOF 5 was higher for initial adsorption cycles at both 0° C and 25 °C, however, adsorption capacity declined considerably under successive cycles. This fact implies that MOF-5 demands more energy input for its regeneration then applied in this work, possibly making a CO₂ capture process with this adsorbent significantly more energy-intensive. In contrast, EDA MOF-5 indicated complete regenerability under the moderate desorption conditions used here, showing negligible CO₂ adsorption capacities decline over successive test cycles. These observations suggest that newly synthesized robust EDA MOF-5 material is more stable adsorbent compared to the parent MOF-5.

6. Conclusion

In summary, we report that or MOF-5 production, ultrasonication at 100°C for 2 hours prior to solvothermal reaction; can significantly reduce synthesis time from 24 hours to 6 hours. Characterization results confirmed good quality MOF-5 crystals synthesis with this method. Synthesis cost can further be reduced for both MOFs synthesis using recycled solvent (DMF). This work demonstrates simple modification of MOF-5, with ethylenediamine to substantially improve its thermal stability and CO₂ adsorption properties. Thermogravimetric studies reveal that EDA MOF-5 prepared is more thermally stable than MOF-5; moreover, carbon dioxide adsorption studies for these samples reveal better carbon
dioxide capture tendency i.e., 5 mmol/g and 3.9 mmol/g respectively at 0°C. The modified MOF, EDA
MOF-5, indicate enhanced stability/regenerability, being cycled three times with identical adsorption
capacities. Future studies are needed to address EDA MOF-5 long-term adsorption cycle studies, stability
to contaminants and oxidation.

Figure 7. CO₂ adsorption mmol/g for MOF-5 and EDA MOF-5 MOF at 0°C and 25°C

7. References
[1] Farha O and Hupp J 2010 Acc. Chem. Res. 43 pp 1166–1175.
[2] Meek S, Greathouse J and Allendorf M 2011 Adv. Mater. 23 pp 249–267.
[3] Ferey G 2008 Chem. Soc. Rev. 37 pp 191–214.
[4] Yaghi O, Keefee O, Ockwig N, Chae H, Eddaoudi M and Kim J 2003 Nature. 423 pp 705–714.
[5] Lee J, Farha O, Roberts J, Scheidt K, Nguyen S and Hupp J 2009 Chem. Soc. Rev. 38 pp 1450–1459.
[6] Ma L and Lin W 2010 SpringerVerlag 293 p 175.
[7] Tran U, Le K and Phan N 2011 ACS. Catal. 1 pp 120–127.
[8] Miralda C, Macias E, Zhu M, Ratnasamy P and Carreon M 2012 ACS. Catal. 2 pp 180–183.
[9] Bae Y and Snurr R 2011 Angew. Chem. Int. 50 pp 11586–11596.
[10] Alessandro D, Smit B, Long J 2010 Chem. Int. 49 pp 6058–6082.
[11] Coates J 2000: Encyclopedia of Analytical Chemistry, Meyers, R.A. John Wiley and Sons Ltd.,
New York. 3 pp 10815-10837.
[12] Sabouni R, Kazemian H and Rohani H 2010 Chem. Eng. J. 165 pp 966-973.
[13] Stevens J, Huang A, Peng H, Chiang W, Khabashesku V, Margrave L 2003 Nano. Lett. 3 pp 331.
[14] Jia-lin Y, Gui-jiao C, Jun C, Wei Y, Bang-hu X, Ming-bo Y 2012 New. Carbon. Mater. 27 370.
[15] Eddaoudi M, Kim J, Rosi N, Vodak D, Wachter J, Keeffe M and Yaghi O 2002 Science. 295 pp 469-472.
[16] Rosi N, Eckert J, Eddaoudi M, Vodak D, Kim J, Keeffe M and Yaghi O 2003 Science. 300 pp 1127-1129.

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