Zinc Metal-Organic Frameworks: the Advanced/Energy materials prepared from Terephthalic acid and Methyl imidazole by Solvothermal Method

Krishnamurthy G[a]* and Omkaramurthy B M[a]

[a] Department of Studies in Chemistry, Bangalore University, Central College Campus, Bangalore-560 001, E-Mail: gkmurthy_2005@yahoo.com

*** Corresponding Author:** Email: gkmurthy_2005@yahoo.com, Ph.+919449523166

Abstract

The Metal-organic frameworks (MOFs) are a class of porous materials in which organic poly functional ligands like 1,4-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic acid, etc., form coordination bonds with some specific transition metals to form extended polymeric structures.These materials have a high pore volume and a large surface area. Hence, these materials are being studied widely for the application in the fields such as Energy (hydrogen gas) storage, sensors, catalysis, separation, as carriers for nano-materials and drug delivery, etc.This paper describes the synthesis of Zn-BDC MOFs at relatively low temperature by solvothermal procedure. The reaction mixture containing zinc salt and benzene-1,4-dicarboxylic acid (BDC)also called terephthalic acid(TPA) and 1-methylimidazole (MI) in DMF was heated under solvothermal condition at 120°C. White colored powder obtained was characterized by FTIR, Powder XRD, Field emission scanning electron microscopy (FE-SEM) and BET surface area measurementtechniques. The XRD study has revealed the crystalline nature of Zn-MOFs. The FE-SEM images show the stacks of well-aggregated flake like crystals with attractive smooth surfaces. The dimensions of the particles include the width ranging from 0.4 m to 1 m and the length ranging from ranging from 0.8m to 3 m. From BET surface area measurements, the above Zn-MOFs samples found to exhibit the specific surface area of about 14.7764 m2/g and average pore diameter of about 36.065 Å. The nitrogen adsorption–desorption isotherm of MOFs was measured at 77 K by using a NOVA-1000 Surface area analyzer.

Keywords: Benzene-1,4-dicarboxylic acid, Metal-organic frameworks, Solvothermal reaction, Zinc, Hydrogen adsorption.

1. Introduction.

Metal-organic frameworks (MOFs) form a new class ofpolymericporous materials[1]with frameworks constructed by the organicligands and metal ions/clusters[2]havingunique features[3-5].The linkers are organic functionalligands that coordinate with multiple metal centres formingone, two, orthree dimensional polymeric structuresin accordance with their starting materials[7-9].

MOFs have attracted great attention over the past years. They have potential applications in many areas, including catalysis, sensors, and drug delivery, especially in gas separation and gas storage. MOFs are porous materials hving high surface area, tuneable pore sizes and topologies, which leads to flexible architectures and applications such as ion exchange, adsorption with a special importance on hydrogen gas storage[10]. According to the pore size, the porous materials are classified into: microporous (pore diameter 0.2–2.0 nm), mesoporous (pore diameter range up to 2.0–50.0 nm) and macro porous (pore sizes exceeding 50.0 nm). Microporous and macro porous materials are extensively used as adsorbents [11].

MOFs can be synthesized by hydrothermal, solvothermal, Microwave, etc., techniques. These methods involve normally elevated temperatures and pressures[12]. The synthesis of MOFs can be influenced by many factors such as the nature of metal ions and organicligands, solventsystem, pH counter ions, and temperature as well as

molecular interactions including hydrogen bonding [13–15].

In this work, we have focused onsynthesis conditions and the morphologiesof the conventional and novel metal-organicframework material using 1,4-benzenedicarboxylic acid of (H_2BDC),oxalic acid (OA), and 1-methylimidazole (MI) linkersrespectively.Several metals have been used for the synthesis of MOFS these metals are divided into two groups as nitratesandoxides of (Zn, Co, Cu, Cr, Fe,Mn, La, Ag)[16-18].These can be formed by heating a mixture of organic linker andmetal salt in a solvent system that usually contains *N,N*-dimethylformamide functional group[19,20].

2. EXPERIMENTAL

2.1 Materials and Apparatus

All chemicals such as Zinc nitrate hexahydrate, Terephthalic acid, Oxalic acid, N,N-dimethylformamide (DMF) etc.,used in this research work were of analytical grade, obtained from SDFCL (s d fine chem. Limited). 1-methyleimidazole and chloroform were obtained fromSpectrochem Pvt. Ltd. All of these were reagent grade chemicals and used as they received.

The reactors used were stainless steel autoclaves with Teflon liners of 60 ml capacity. The Mathri (Kerala) hot air oven was used for heating the autoclaves. Sonicator was used for uniform dispersion of the reaction solution.

2.2 Synthesis Procedure

A mixture of $Zn(NO_3)_2.6H_2O$ (2.0 gm), tetephthalic acid (i.e., 1,4-benzenedicarboxylic acid) of about 0.70 gmand oxalic acid(0.70 gm) were dissolved separately in 25 ml of DMF with mild stirring and then added about 0.5 ml of 1-methylimidazole to get a clear solution.The resulting solutions weretransferred to a Teflon-lined stainless steel autoclave and heated in a oven at 120°C for 72 h. Then the reaction system allowed to cool to room temperature. The content of the autoclave was filteredand the white colored crystalline materialobtainedwas washed repeatedlywith fresh DMF several times followed bychloroform. Finally, the productwasdried at room temperature for 24 hours.

2.3 Characterization Techniques

Theabove product was characterized by studying the vibrational properties of the functional groupson Shimadzu 8400S FTIR spectrophotometer using KBr pellets. Powder X-ray diffraction (PXRD) analysis was carried out using BrukerD8 Advance powder X-ray diffractometer with CuKα radiation, at λ= 0.1541874 nm to obtain the information on the purity, phase structure and nature (crystalline or amorphous) of the product. FE-SEM images were taken on the Zeiss field emission scanning electron microscope.The BET surface area measurements were made on Nova1000 instrument.

3. RESULTS AND DISCUSSION

3.1 FT-IR spectral analysis

Fig.1 is the FTIR spectrum of as synthesized compound. It comprises the major peaks at 3400, 3116, 2750, 1600, 1460, 1384, 1310, 1090, 1018, 952, 800, 889 cm^{-1}. Theabove-mentioned peaks can be identified as different regions in the spectrum. The first region is showing the peak 3400 cm^{-1} due to C-H stretching mode of benzene ring. The second region is having peaks in the region 2750 cm^{-1} because of C-H stretching in methyl ring. The third region is 1600 - 1460 cm^{-1} having intense bands due to asymmetric and symmetric modes of carboxylate at 1600 cm^{-1} and 1425 cm^{-1}. This region is also shows the characteristic peaks for aromatic benzene ring at ~ 1600 cm^{-1}(v), 1580 cm^{-1}(v), 1440 cm^{-1} due to benzene ring starching and C-H bending vibrations. The fourth region carrying peak in the region 1310 cm^{-1} is due to C-N stretching and C-H bending in the plane. The fifth region is 1090-1018 cm^{-1}, which is an indicative of aromatic substitution pattern and indicates 1,4 substitution. The same region also correspond to the peaks because of C=C and C=N stretching. The peaks in the sixth region (930 - 880 cm^{-1}) correspond to C-N-C bending in the plane. The next and the last region from 780 – 850 cm^{-1} associated with deformation of carbonyl substituent out of the

planeat 800 cm^{-1}. The shifting of the C=O of carboxylate and C-N vibrations indicate the formation of the bonding with the metal, Zn centrally with the ligandsterephthalicacid, Oxalic acid and 1- Methyl imidazole.

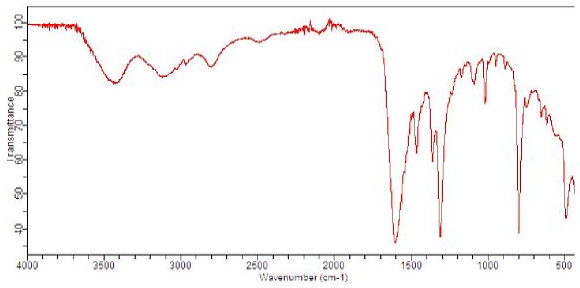


Fig1:FTIR spectrum forZn-bdc MOF compound

3.2 P-XRD analysis

Powder XRD pattern (Fig.2) for the product was obtained by employing the monochromatic high-intensity CuKα radiation (λ= 0.1541874 nm). The sharpness of the peaks in the pattern indicates thecrystalline nature of the product.The presence of prominent metallic peak at the 2č

Values at 10.6 and 12.5, 13.0 indicate the coordination of metal with the ligands to form complex. The pattern without much of noise and extra peaks hint us about the purity and purephase structure of the products obtained. The theoretical (simulated) PXRD pattern calculated from the single-crystal XRD data is in good agreement with the experimental pattern, confirming that the product is highly crystalline and phase-pure.

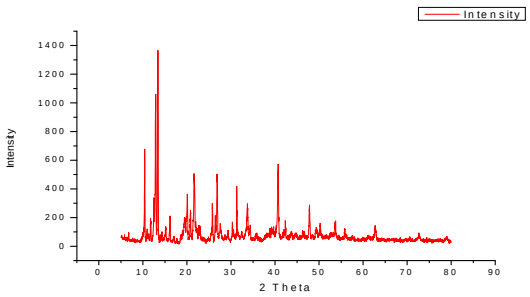


Fig.2:PXRD patterns for Zn-bdc MOF compound

3.3 FE-SEMAnalysis

FE-SEMimage of Zn-MOFis presented in Fig. 3. Scanning electron microscopy is a technique that enables the study of the microstructure and surface morphology of the products. The SEM micrographs show the distribution of particles in zinc MOF in a range of dimensionsas piles of flakes arranged as sheet-like clusters. The FE-SEM images viewed under different magnificationssuch as 2µm,1µm and 200nm. The images show the stacks of well-aggregated flake like crystals with attractive smooth surfaces. A high magnification image in Fig. 3, shows that these flakes-like particles are having a range of dimensions. The dimensions of the particles include the width ranging from 0.4 µm to 1 µm and the length ranging from ranging from 0.8µm to 3 µm. The externalmorphology of the zinc MOF is more explicit than that of the other MOFs.

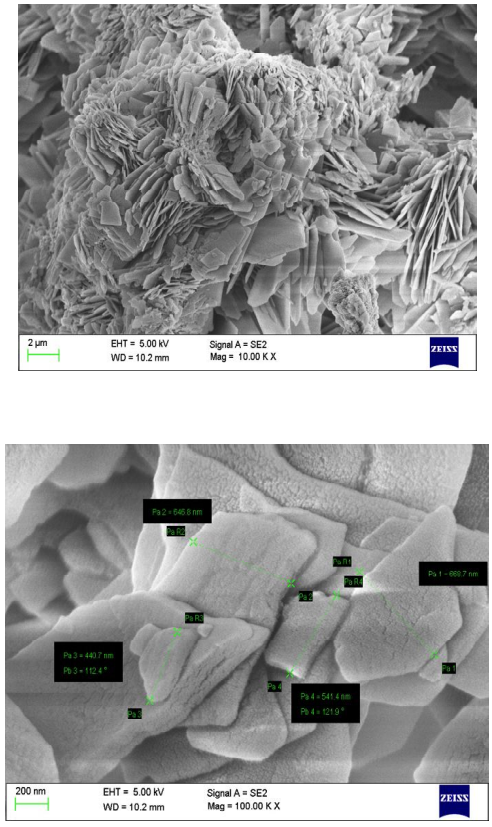
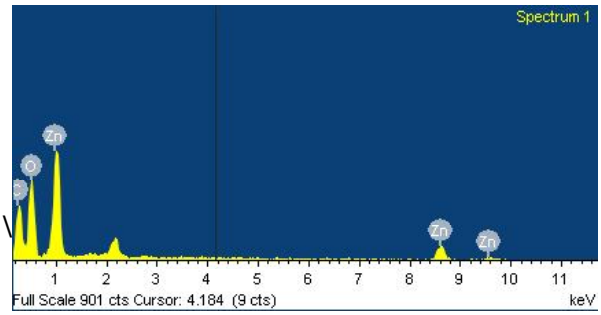


Fig. 3: Scanning electron micrograph (SEM) of metal organic framework of Zinc showing different magnifications

3.4 SEM-EDS Analysis

The chemical composition of zinc MOFs were studied by means of energydispersive spectroscopy (EDS). The EDS pattern of zinc MOF is presented in Figure 4 (a) and 4 (b) indicates Zn, C, O, Composition.The EDS pattern confirms the presence ofzinc, carbon and oxygen. The corresponding elemental compositions are given in the table.



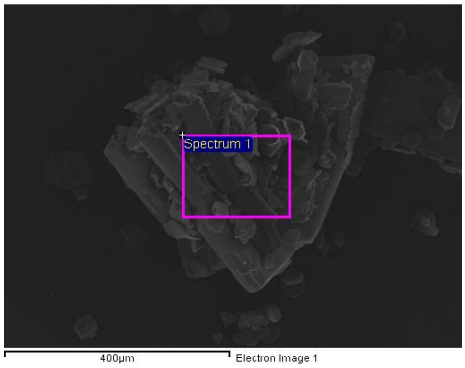


Fig.4 (a) **and**4 (b) **Energy dispersive spectroscopy (EDS) of metal organic framework of Zinc(bdc).**

Quantitative analyses of the EDS result shows theZn-MOFs on the other hand consists of 35.99% weightof carbon with atomic percentage of 53.85. Oxygen has a 33.66% weight and atomic percentage37.81 while zinc was found to have 30.35% weight and atomic percentage of 8.34.\

Table1. Element and atom percentage weight obtained from energy dispersive spectroscopy of zinc MOFs.

Element	Weight %	Atomic %
C K	35.99	53.85
O K	33.66	37.81
Zn L	30.35	8.34
Totals	100.00	100.00

3.5 BET surface area measurement

The surface area and pore volume of Zn-MOFs were evaluated via N_2 adsorption using a NOVA-1000BET surface area measurement instrument. Materials were degassed at180°C for 4 hours. Surface areas of Zn-MOFs were evaluated using nonlocal density functional theory (NLDFT). The pore textural properties, BET specific surface area,the Langmuir specific surface area, cumulative pore volumeand the adsorption average pore diameter for the compoundswere calculated. The sorption isotherms of obtained with nitrogen gas represent type I isotherm with no hysteresis, which demonstrates the presenceof microporous structure. The obtained BET surface area, 475 $m^2 g^{-1}$ represents the adsorption capacity of our compounds whichis reached at amount adsorbed = 14.77m^2/g^{-1} andthe average pore diameter = 36.065Åcorresponding to micropore volume =0.01332 cc/g.

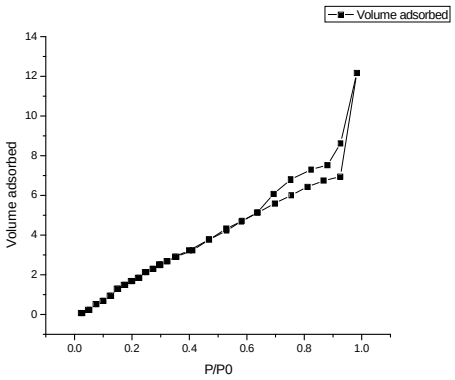


Fig. 5N_2 adsorption–desorption isotherms of Zn-bdc MOF sample

5. CONCLUSIONS

Zn-bdc, a well known MOF, has been successfullysynthesized by solvothermal methodat low temperature at about 120°C.Theaccelerated synthesis of crystals has been observed in solvothermal method and it could be due to the fastnucleation reaction whereas, in conventional heatingmethod, the nucleation takes place only on the walls ofthe reaction container. But solvothermal methodprovides a uniform nucleation environment for the crystalgrowth. The SEM images show the very attractive morphology of the product which includes the piles/ cluster of theflakes of MOF crystals. The dimensions, surface area and pore volumes of the MOFs prepared are quite significant.The successfulness of our method of synthesis lies in obtainingthe pure and crystalline product overhigh temperatureand time consuming conventional methods.

6. ACKNOWLEDGEMENTS

The authors like to acknowledge UGC and DST for their financial support for the Instruments and other facilities at our department premises to carryout this research work. We also like to acknowledgeBangalore University for thefellowship.

REFERENCES

1. Ferey, G. Some Suggested Perspectives for MultifunctionalHybrid Porous Solids. Dalton Trans.,**2009**, 23, 4400"4415.
2. Kuppler, R. J.; Timmons, D. J.; Fang, Q. R.; Li, J. R.; Makal, T. A.; Young, M. D.; Yuan, D. Q.; Zhao, D.; Zhuang, W. J.; Zhou, H. C.Potential Applications of Metal”Organic Frameworks. CoordChem.Rev, **2009**, 253 (23"24), 3042"3066.
3. Sun Y, Yu H, Wang L, Ding W, Ji J, Chen Y, Ren F, Tian Z, Zhao Y, Huang L, Ren P, Tong R. Synthesis of three coordination polymer microspheres and their application in hydrogen storage. J Alloys Compd.,**2014,** 585, 667–73.
4. Ferna´ndez-Zapico E, Montejo-Bernardo J, D’Vries R, Garcý´a JR, Garcý´a-Granda S, Rodrý´guez Ferna´ndez J, Pedro I, Blanco JA. Phase stability and magnetic properties of a new cobalt(II) coordination polymer based on 2-carboxyethylphosphonate and 1,100-phenanthroline. J Alloys Compd.,**2012**, 536,507–510.
5. Tabacaru A, Pettinari C, Masciocchi N, Galli S, Marchetti F, Angjellari M. Pro-porous coordination polymers of the 1,4- bis(3,5-dimethyl-1Hpyrazol-4-yl)-methyl)benzene ligand withlate transition metals. Inorg Chem.,**2011**, 50, 11506–13.
6. Kitagawa, S.; Kitaura, R.; Noro, S. Functional PorousCoordination Polymers. Angew. Chem., Int. Ed.,**2004,** 43 (18),2334"2375.
7. Yaghi OM, Li G. Selective binding and removal of guests in a microporous metal-organic framework. Nature.**1995,** 378,703–706.
8. Saha D, Zacharia R, Lafi L, Cossement D, Chahine R. Synthesis, characterization and hydrogen adsorption on metal-organic frameworks Al, Cr Fe and Ga-BTB. Chem Eng J.,**2011,**17,1517–1525.
9. Tanabe, K. K.; Cohen, S. M. Post synthetic Modification of Metal”Organic Frameworks A Progress Report. Chem. Soc. Rev.,**2011**, 40 (2), 498"519.
10. Tonigold, M.; Lu Y, Bredenkotter, B.; Rieger, B.; Bahnmuller, S.;Longstien, G.; Volkmer, D. Heterogeneous catalytic oxidation by MFU-1: a cobalt(II)-containing metal-organic framework. Angew. Chem. Int. Ed.,**2009**, 48, 7546–7550
11. Farha, O. K.; Hupp, J. T. Rational Design, Synthesis, Purification, and Activation of Metal”Organic Framework Materials. Acc. Chem.Res., **2010**, 43 (8), 1166"1175.
12. Wang L, Zhang L, Song T, Li C, Xu J and Wang L, Micropor Mesopor Mater.,**2012**,155, 281- 286

13. Furukawa, H.; Kim, J. H.; Ockwig, N. W.; O'Keeffe, M .; Yaghi, O. M. J. Am. Chem. Soc.,**2008,**130,11650

14. Opelt, S.; Türk, S.; Dietzsch, E.; Henschel, A.; Kaskel, S.; Klemm, E.Catal.Commun., **2008,**9, 1286

15. Clausen, H. F.; Bond, A. D.; Chevallier, M. S.; Iversen, B. B.;J. Solid. State.Chem., **2005,**178,3342

16. Christoph Janiak w and Jana K. ViethReceived (in Montpellier, France)New J. Chem., **2010**,34, 2366–2388

17. Czaja, A. U.; Trukhan, N.; Muller, U. Industrial Applications ofMetal"Organic Frameworks.Chem. Soc. Rev.,**2009**, 38 (5), 1284"1293.

18. Lupu, D.; Ardelean, O.; Blanita, G.; Borodi G.; Lazar, M. D.; Biris, A. R.; Ioan, C.; Mihet M, Misan I.; Popeneciu, G.Int J Hyd. Ene.,**2011,**36(5),3586-3592.

19. Fischer, M.; Hoffmann, F.; Fröba, M.J. Col. Surf A., Phys. Chem. Eng. Ass.,**2010**, 357, 35-42.

20. Tsao, C. S.;Yu, M. S.; Chung, T. Y.; Wu, H. C.;Wang C. Y.; Chang, K. S .; Chen, H. L.J. Am. Chem. Soc.,**2007,** 129(51), 15997-16004.

THE ELECTRO CHEMICAL SOCIETY OF INDIA DETAILS FOR MEMBERSHIP		
Category	**Admission Fee**	**Annual Subscription**
Member	**Rs. 2,000-00**	**Rs. 500-00**
Fellow	**Rs. 2,000-00**	**Rs. 1,500-00**
Life Members	**Rs. 6,500-00**	**Lifetime**
Patrons	**Rs. 30,000-00**	**Lifetime**
Donors	**Rs. 25,000-00**	**Lifetime**