Solvothermal Synthesis of $Cu_3(BTC)_2$ Metal Organic Framework

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Abstract

For the last two decades the research with Metal Organic Framework (MOF) is proving to be most fruitful, due to their crystalline-inorganic hybrid material with uniform porous structure, high environmental stability and tuneable matrices. With these unique properties of MOFs material have vast applications in storage, chemical separation, catalysis, drug delivery. In present investigation we have reported the chemical synthesis of copper benzenetricarboxylate. In Teflon-lined stainless-steel autoclave at 80ºC for 20hr. The resulting Copper benzenetricarboxylate (Cu-BTC) is further characterised by Fourier Transform Infrared Spectroscopy and X-ray diffraction (XRD)

Keywords: Metal organic framework (MOF), Fourier transform infrared (FTIR), X-Ray diffraction.

1. Introduction

The metal organic frameworks (MOFs) hybrid materials in which inorganic and organic materials forms crystalline structures where metal ions are linked together with organic bringing ligands, bivalent or trivalent aromatic carboxylic acids or N-containing aromatics are commonly used to form frameworks with zinc, copper, chromium, aluminium, Zirconium, and other elements[1]. most of the synthesis procedures are small-scale batch procedures, rare studies of reports production in the order of kg scale[2]. Many of the MOF synthesis methods requires expensive ligands or the use of costly and non-reusable solvents. MOFs have been synthesised by various methods, including Solvothermal[3], ultrasonic[4], microwave heating[5], diffusion or direct addition of amines[6], and growth on substrate[7], Solvothermal method is most used synthesis process, which do not require costly equipment and gives relatively fast growth of crystals with high level of crystallinity, phase purity and surface areas[8]. In the Cu-BTC MOF consist of Cu ions and 1, 3, 5-benzenetricarboxylate as a linker. It Possess crystallographic structure[9], the three-dimensional structure of Cu-BTC features pores with different sizes and shapes. Cu-BTC has many applications such as gas storage (hydrogen[10], methane, carbon dioxide[11]), gas separation[12], supercapacitors[13], catalysis[14] and sensors[15]. In the present investigation, we have synthesised the $Cu_3(BTC)_2$ MOF by Solvothermal method and the synthesised $Cu_3(BTC)_2$ is characterised spectroscopically and structurally by FTIR and XRD respectively.

2. Materials and methods

2.1. Synthesis of (Cu-BTC):

All chemicals and reagents used as it is as received from commercial sources. Cu $(NO_3)_2$, $3H_2O$ (10.7mmole) in the 30 ml of H_2O and in the separate flask dissolve the BTC (3.2mmole) in the 30 ml of ethanol solution. In the

H_3BTC solution the Cu $(NO_3)_2 \cdot 3H2O$ solution was added slowly with stirring for 30 min at room temperature. With the formation of precipitation, the solution became turbid. DMF (2ml) was added in the mixed solution with precipitate, then combination was transferred to the 100ml Teflon-lined autoclave and allowed to be react at 80 ºC for 20 hrs. After 20hrs allow to cool the autoclave and its contents to the room temperature, a crystalline solid $Cu_3(BTC)_2$, was collected and washed with deionised water and ethanol.

The synthesised Cu-BTC was further characterised by FTIR spectroscopy in the range of 500 cm^{-1} to 4000 cm^{-1}. From the X-ray diffraction pattern of Cu-BTC the interplanar spacing (d) between the crystal planes can be calculated and the lattice parameter of the Cu-BTC are determined by following equation,

$$d = \frac{a}{\sqrt{h2 + k2 + l2}} \quad \text{.... (1)}$$

3. Results and discussion

3.1 FTIR analysis:

The FTIR spectrum of H_3BTC shows the appearance of the peaks at 1720 cm^{-1}, 1180 cm^{-1}, 1270 cm^{-1} corresponds to stretching vibration and bending vibration of O-H, indicate the presence of carboxylic group[16]. The symmetric and antisymmetric stretching vibration O-C=O group were in the range of 1400-1620 cm^{-1} [16]. The FTIR spectrum of the Cu-BTC shows the appearance of peaks in the range of 1300-1600 cm^{-1} characterised for vibration of carboxylate group. Appearance of peaks near the 1710 cm^{-1} and near 1240 cm^{-1} corresponds to the vibration of C=O and O-H groups which confirms the $Cu_3(BTC)_2$ was synthesised successfully

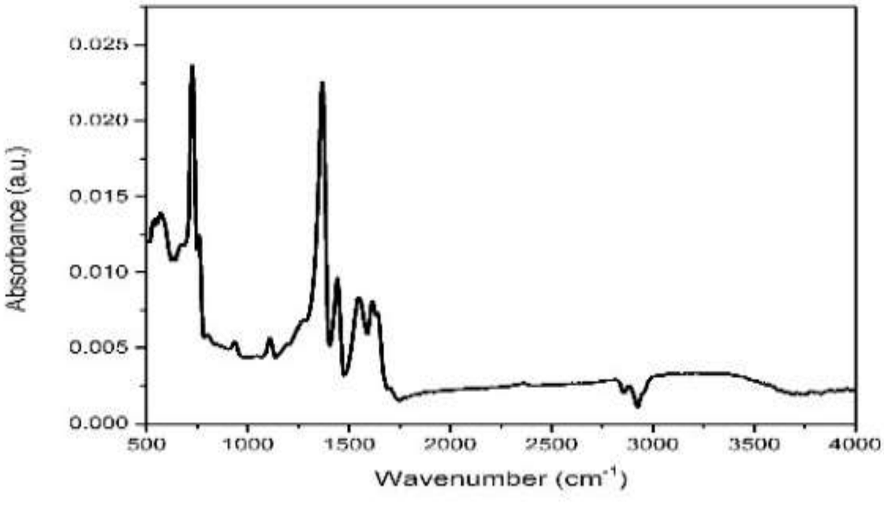

Fig-1: FTIR Spectrum of Synthesised Cu3(BTC)2

3.2 XRD analysis:

From the X-ray diffraction (XRD) analysis shows that the synthesised Cu-BTC has face-centered cubic structure, which identified from (hkl) planes derived from Braggs diffraction angle and the values of angles are , 2Ө: 11.6863, 13.4703, 19.1036, and 35.2980 and the corresponding crystal planes are (111), (200), (220) and (333) the hkl values derived from diffraction angle are either all odd or all even which confirms that the synthesised Cu-BTC material has face-centered cubic structure with approximate lattice constant 1.313 nm from equation (1)

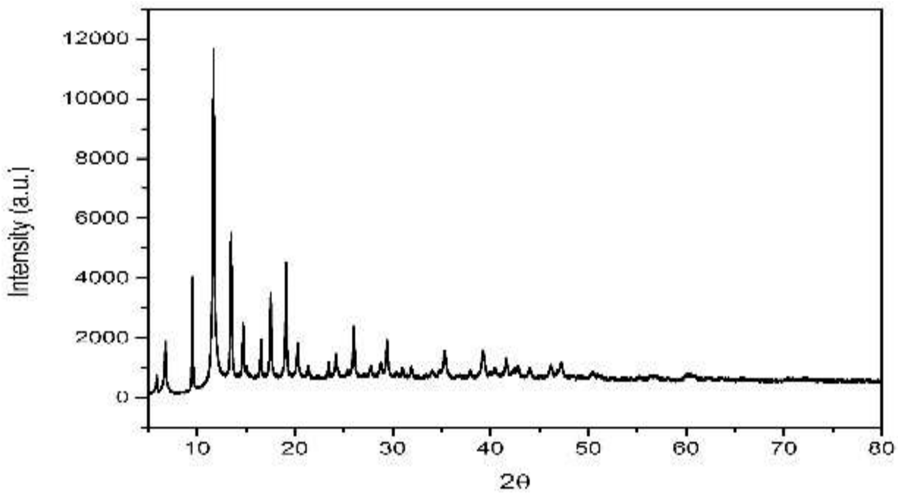

Fig-2: XRD Spectrum of Synthesised Cu3(BTC)2

4. Conclusions

The Cu-BTC was successfully synthesized in the Teflon-lined steel autoclave which is placed in oven at 80 ºC for 20hr by Solvothermal method. From FTIR spectra it confirms that the synthesized Cu-BTC the presence of O-C=O, C-O and O-H functional groups and from XRD analysis one can conclude that the Cu-BTC material has face-centered cubic structure.

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References

1. V. R. Remya, Manju Kurian., "Synthesis and catalytic applications of metal–organic frameworks: a review on recent literature", Springer International Nano Letters (2019) 9:17–29.
2. Debanjan Chakraborty, Aysu Yurdusen, Georges Mouchaham, Farid Nouar, and Christian Serre., "Large-Scale Production of Metal–Organic Frameworks", Adv. Funct. Mater. **2023**, 2309089.
3. Khaliesah Kamal, Mohamad Azmi Bustam, Marhaina Ismail, Denys Grekov, Azmi Mohd Shariff, Pascaline Pré., "Optimization of Washing Processes in Solvothermal Synthesis of Nickel-Based MOF-74", *Materials* **2020**, *13*, 2741; doi:10.3390/ma13122741.
4. Sepideh Bagheri, Farzane Pazoki, Akbar Haydari., "Ultrasonic Synthesis and Characterization of 2D and 3D Metal− Organic Frameworks and Their Application in the Oxidative Amidation Reaction", ACS Omega 2020, 5, 21412−21419.
5. Andrea Laybourn, Juliano Katrib, Rebecca S. Ferrari-John, Christopher G. Morris, Sihai Yang, Ofonime Udoudo, Timothy L. Easun, Chris Dodds, Neil R. Champness, Samuel W. Kingman and Martin Schro¨der., "Metal–organic frameworks in seconds via selective microwave heating", J. Mater. Chem. A, 2017, 5, 7333–7338 | 7333.

6. Isabel Abánades Lázaro, Ross S. Forgan, Francisco. G. Cirujano., "MOF nanoparticles as heterogeneous catalysts for direct amide bond formations", Royal Society of Chemistry Dalton Trans., 2022, 51, 8368–8376.
7. Monica L. Ohnsorg, Christopher K. Beaudoin, and Mary E. Anderson., "Fundamentals of MOF Thin Film Growth via Liquid-Phase Epitaxy: Investigating the Initiation of Deposition and the Influence of Temperature" American Chemical Society, Langmuir 2015, 31, 6114−6121
8. Stephen D. Worrall, Mark A. Bissett, Patrck I. Hill, Aidan P. Rooney, Sarah J. Haigh, Martin P. Attfield, Robert A.W. Dryfe., "Metal-organic framework templated electrodeposition of functional gold nanostructures", Electrochimica Acta, 222, 361-369 (2016)
9. Shiraz Ahmed Siddiqui, Alexander Prado-Rollerb, Hidetsugu Shiozawa., "Room temperature synthesis of a luminescent crystalline Cu–BTC coordination polymer and metal–organic framework", Royal Society of Chemistry. Mater. Adv., 2022, 3, 224–231
10. Anish Mathai Varghese, K. Suresh Kumar Reddy, Georgios N. Karanikolos, "An In-Situ-Grown Cu-BTC Metal−Organic Framework / Graphene Oxide Hybrid Adsorbent for Selective Hydrogen Storage at Ambient Temperature", Ind. Eng. Chem. Res. 2022, 61, 6200−6213
11. Mansoor Anbia *, Vahid Hoseini, Sara Sheykhi., "Sorption of methane, hydrogen and carbon dioxide on metal-organic framework, iron terephthalate (MOF-235)", Journal of Industrial and Engineering Chemistry 18 (2012) 1149–1152
12. Hilal Daglara, Sena Aydin, Seda Keskin., "MOF-based MMMs breaking the upper bounds of polymers for a large variety of gas separations", Separation and Purification Technology 281 (2022) 119811
13. Dennis Sheberla, John C. Bachman, Joseph S. Elias, Cheng-Jun Sun, Yang Shao-Horn, Mircea Dinca., "Conductive MOF electrodes for stable supercapacitors with high areal capacitance", NATURE MATERIALS | VOL 16 | FEBRUARY 2017
14. Jian Liu, Timothy A. Goetjen, Qining Wang, Julia G. Knapp, Megan C. Wasson, Ying Yan, Zha H. Syed, Massimiliano Delferro, Justin M. Notestein, Omar K. Farha, Joseph T. Hupp., "MOF-Enabled Confinement and Related Effects for Chemical Catalyst Presentation and Utilization", Chemical Society Reviews. CS-REV-10-2021-000968.R1
15. Leo J. Small, Susan E. Henkelis, David X. Rademacher, Mara E. Schindelholz, James L. Krumhansl, Dayton J. Vogel, Tina M. Nenoff., "Near-Zero Power MOF-Based Sensors for NO_2 Detection" Adv. Funct. Mater. 2020, 2006598
16. Nguyen Thu Phuong, Claudine Buess-Herman, Nguyen Thi Thom, Pham Thi Nam, Tran Dai Lan and Dinh Thi Mai Thanh., "Synthesis of Cu-BTC, from Cu and benzene- 1,3,5-tricarboxylic acid (H_3BTC), by a green electrochemical method", *Green process Synth*. **5,** 537-547 (2016).