Applying benzene tetracarboxylic acid as a linker in the synthesis a porous Ba(II)-based MOF by Ultrasonic method

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Abstract

Metal−organic frameworks (MOFs) which are inorganic-organic hybrid porous materials, prepared from metal ion/clusters and multidentate organic ligands have evolved to be next generation utility materials because of their usability in diverse applications. [1] MOFs as a class of interesting materials have attracted great attention due to their controllable pore size and elaborately designed pore structure. In the past two decades, MOFs have exhibited versatile potential applications such as gas storage, gas separation, heterocatalysis, sensors, and luminescence. [2] Most of the research works so far are focused on MOFs based on transition metal ions or rare-earth ions. However, the main group alkaline earth metals are receiving increasing attention recently. [3] In this review, a porous Ba(II)-based MOF was synthesized by ultrasonic method using benzene-1,2,4,5-tetracaboxylic acid as an organic linker; which was characterized by X-Ray Diffraction, Fourier Transform Infrared spectroscopy and Scanning Electron Microscopy methods.

Keywords: Metal-Organic Framework, Barium ion, Benzene-1,2,4,5-tetracaboxylic acid

1. Introduction

Metal−organic frameworks (MOFs), created by organic linkers and metal clusters; and they have attracted much attention as a growing class of porous materials. [4] The unique characteristics of MOFs include high surface area, good thermal stability, uniform structured nanoscale cavities, uniform but tunable pore size, controllable particle dimensions and morphology, accessible cages and tunnels, specific adsorption affinities, and the availability of in-pore functionality and outer surface modification. [5] One of the exceptional properties of MOFs relies on their ability to adapt their pore openings to accommodate guest species, and different modes of flexibility have been described. This “breathing” effect and swelling can produce a dramatic increase or decrease in cell volume without a loss of crystallinity or bond breaking. These materials (MOFs) have shown great potential in gas adsorption, gas separation,

catalysis, lithium storage [7], drug delivery [4] and biomedical imaging [5]. Among many, alkali earth metal-organic frameworks have been of great interest attributable to their variable structural architectures and their subsequent properties. [8] Alkaline earth metals are very reactive and show a wide range of coordination, which makes them excellent candidates to construct a range of functional materials with specified structure and properties. [9]

2. Experimental

2.1. Reagents and Instrumentation

All the chemical agents are commercially available and employed without further purification. The infrared spectra were recorded on Shimadzu Transform IR, Shimadzu spectrometer in the range 400-4000 cm^{-1} using the KBr disk technique. X-ray powder diffraction (XRD) measurements were performed using a Bourevestnik Dron Poh-8 (V=40.00 Kv, Current=20.08 mA) diffractometer with monochromated Cu-k_α radiation (λ=1.54056Å). Scanning Electron Microscopy Tscan Vega was used for getting micrographs of the MOF.

2.2. Preparation of MOF

To the best of our knowledge, this method of synthesis has not been previously reported and has been used because it is an easy and low-risk method.

A mixture of 2 mmol $Ba(NO_3)_2$ (261.337 g/mol), 0.2 mmol benzene-1,2,4,5-tetracaboxylic acid 254.15 g/mol and 150 ml CH_3CN:H_2O (v:v = 1:1) were placed in a completely isolated container in an ultrasonic bath for 6 hours. The temperature was slowly increased from room temperature to 80 ° C, and finally the formed MOF was cooled slowly and the white precipitate was washed with deionized water.

According to a previous sources, it was expected that a 3-dimensional 3D network will occur in the structure. [10]

3. Results and Discussion

3.1. X-Ray Diffraction

The phase purity of MOF by powder XRD is shown in Fig. 1; the conformity of the main peaks in the 2theta: 10, 20, 25, 28, 30, 40, 45 and 50 regions, but with less intensity, indicates the formation of the title material. The differences in intensity may be attributed to the preferred orientation of the powder sample.

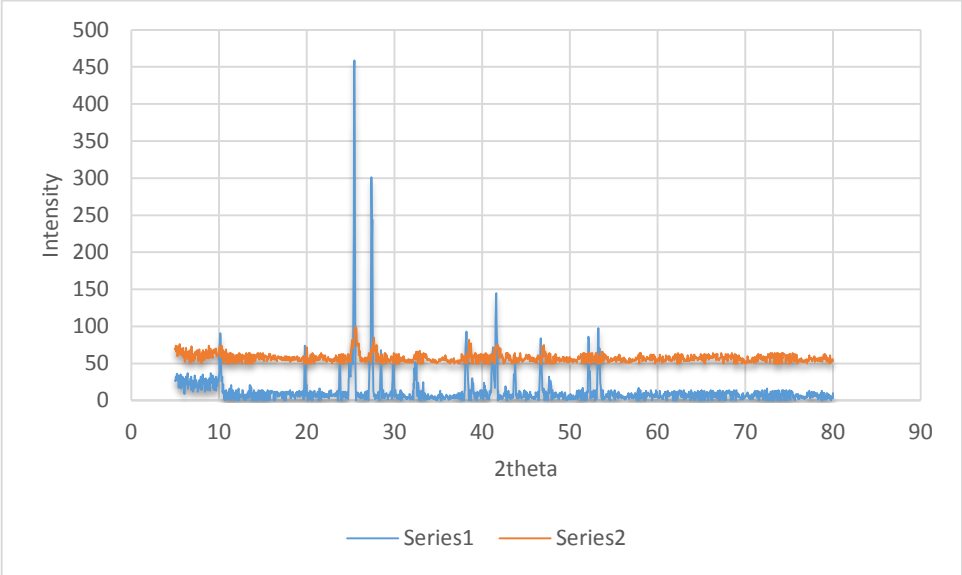

Fig. 1. XRD Patterns for $\{[Ba_2(H_2btec)\cdot H_2O]\cdot 0.5H_2O\}_n$ (series 1: Simulated, series 2: Experimental)

3.2. FTIR spectra

The FT-IR spectrum of the title MOF in the range of 4000–400 cm^{-1} was investigated. The strong peaks in the range of 3400 cm^{-1} are related to the O−H stretching vibration of water molecules, 1690-1605 cm^{-1} and 690-900 cm^{-1} can be ascribed to asymmetric stretching vibrations of carboxyl group and C−H aromatic ring, respectively.

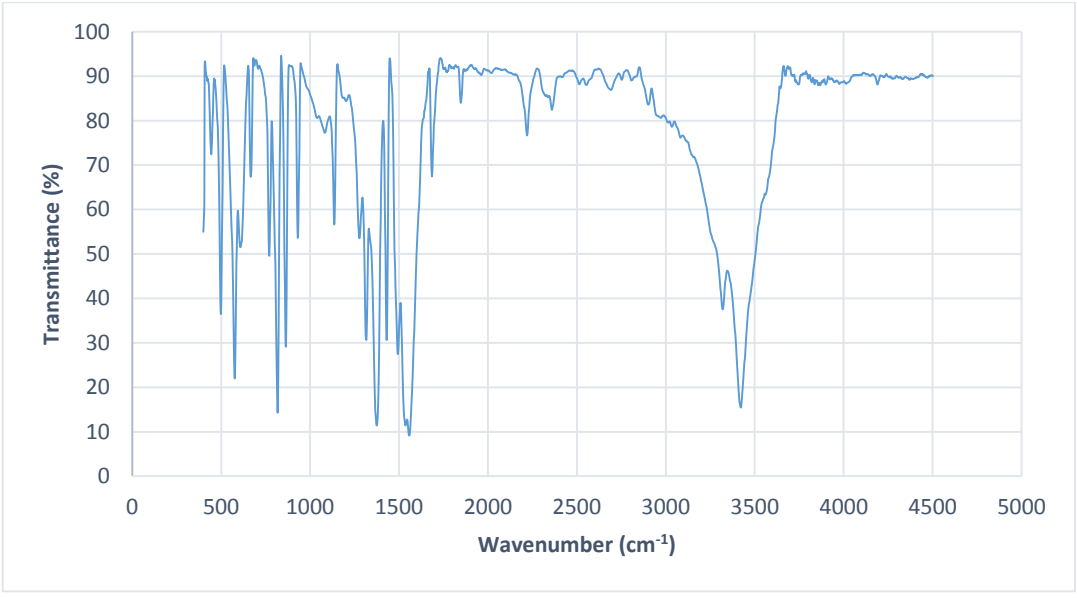

Fig. 2. The FT-IR spectrum of $\{[Ba_2(H_2btec)\cdot H_2O]\cdot 0.5H_2O\}_n$ Framework

3.3. SEM analysis

SEM Gives excellent images of very small, rough particles of the material under investigation. Therefore, from the SEM analysis according to Fig. 3 was used to identify the structural morphology of the material.

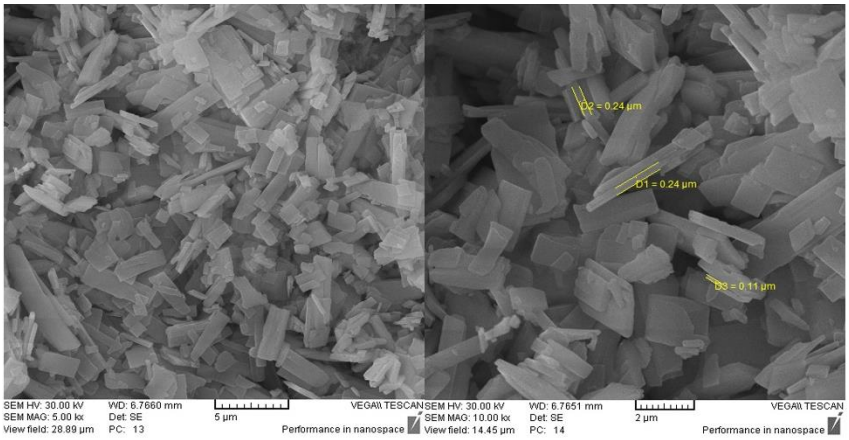

Fig. 6. SEM images of the metal-organic framework $\{[Ba_2(H_2btec)\cdot H_2O]\cdot 0.5H_2O\}_n$

4. Conclusions

In summary, a three-dimensional framework based on Ba(II) and benzene-1,2,4,5-tetracaboxylic acid ligand was synthesized by ultrasonic method. X-Ray Diffraction, Fourier Transform Infrared spectroscopy and Scanning Electron Microscopy analyzes were used to identify this material

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