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Synthesis and Characterization of $Zn_3(BTC)_2$ Nanoporous Sorbent and its Application for Hydrogen Storage at Ambient Temperature

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Abstract

Metal organic frameworks (MOFs) are considered an interesting option for hydrogen storage. These materials show an exceptional H2 uptake. Here, $Zn_3(BTC)_2$ as MOF was synthesized with a solvothermal method. The phase stability and microstructure of the $Zn_3(BTC)_2$ was characterized in terms of their properties and structures, using a number of analytical techniques including FT-IR, XRD, SEM, BET and TGA. The analyses confirmed that the product has a conical shape structure with a Langmuir specific surface area of over 257m²/g. This MOF has shown to have a hydrogen storage capacity of 0.8 wt% at room temperature and 13 bar.

***Keywords**: Hydrogen adsorption, Metal-organic framework, $Zn_3(BTC)_2$, Solvothermal method.*

Introduction

The search for alternate energy sources is now one of the most demanding needs of global society. Energy requirements worldwide are growing, along with the environmental problems caused by energy resources based on fossil fuels [1]. Hydrogen is the future fuel and energy carrier; it is carbon free and hence environmentally friendly. Hydrogen is considered a clean and efficient energy carrier, since its combustion only produces water as by product [2]. In April 2009, the DOE set the new targets for on-board hydrogen storage systems: 0.045 kg kg^{-1} for system gravimetric capacity and 0.028 kg L^{-1} for system volumetric capacity by the year 2010, and 0.055 kg kg^{-1}

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and 0.040 kg L^{-1} by 2015 (Table 1) [3] at an operating temperature of 233–333 K under a maximum delivery pressure of 100 bar [4]. Main challenge in developing this technology is hydrogen storage [3].

In the area of hydrogen storage, physical storage methods such as compressed hydrogen gas and liquid hydrogen, and chemical storage methods such as metal hydrides and chemical hydrides are well known [5]. An optimum hydrogen storage material must have some the following characteristics: (1) such as high volumetric/gravimetric hydrogen storage capacity, (2) fast absorption kinetics, (3) near room temperature and ambient pressure operation, (4) light weight materials, and (5) low cost materials and so on [6]. Porous metal–organic framework (MOF) compounds, which consist of metal oxide/nitride clusters connected by rigid or semi-rigid organic linkers, are promising materials that provide very high surface area and controllable pore sizes for energy storage [7]. MOFs have the highest specific surface area reported to date for porous materials (up to 6200 m^2 g^{-1}) and large internal pore volumes with well defined pore sizes and apertures [8].

Another interesting feature of MOFs involves the great variety of cations, which can participate in the framework [9]. MOFs have shown great potential in gas storage, separation, chemical sensing, drug delivery, and heterogeneous catalysis applications [10]. In 2003, Yaghi and coworkers reported the first MOF-based hydrogen storage result. Since then, MOFs have attracted worldwide attention in the area of hydrogen energy, particularly for hydrogen storage [3]. These materials store hydrogen in molecular form at low temperatures. Within the micropores the hydrogen is effectively compressed to a high density, resulting in an increase in the volumetric density of the hydrogen in comparison with free gas at the same temperature and pressure [11].

In this study, $Zn_3(BTC)_2$ as a MOF material was prepared using a novel solvothermal method, and then the amount of hydrogen adsorbed was measured. To date, most studies that report hydrogen adsorption in MOFs are performed at cryogenic temperatures. As a result, only very few ambient temperature hydrogen storage data are available [11]. Since the on-board storage of hydrogen at room temperature is most relevant for practical applications, we have systematically investigated hydrogen adsorption of $Zn_3(BTC)_2$ MOF material at ambient temperature and elevated pressures.

Experimental

Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2{\bullet}2H_2O$, 99.5%), trimesic acid (Benzene-1,3,5-tricarboxylic acid (H_3BTC,95%), Dimethyl formamide (DMF, 99.8%) ethanol (96%,) were from E. Merck(Germany).

Synthesis of $Zn_3(BTC)_2$

$Zn_3(BTC)_2$ sample was prepared using a novel solvothermal method based on the reported procedure [12]. In a typical experiment, Zinc acetate dihydrate 1.2 g (5.4 mmol) was dissolved into 25 mL ethanol. It was followed by the addition of trimesic acid (Benzene-1,3,5-tricarboxylic acid, 0.315g (1.5 mmol) in a 5 mL of Dimethylformamide, and mixed thoroughly until it was completely dissolved. The resultant solution mixture was transferred into a 250 mL teflon-lined stainless steel autoclave. It was kept at 100°C 373 K for 12 h in oven to yield small crystals. Then the autoclave was cooled down to room temperature naturally, and the white crystals were isolated by filtration. The suspension was washed with the mixture of Dimethylformamide and ethanol (10:20) several times and then dried at 100°C and 45 min. The phase stability and microstructure of the $Zn_3(BTC)_2$ sample was characterized in terms of their properties and structures, using a number of analytical techniques including X-ray diffraction (XRD; BRUKER D8A,Germany, Cu-Kα radiation, 20-70) and scanning electron microscopy (SEM; Hitachi model SEM3500, Japan) equipped with energy dispersive spectroscopy (EDS). The porosities and specific surface areas were measured with a Micromeritics ASAP 2020 gas sorption and porosimetry apparatus using nitrogen gas at -196°C 77 K. Before the measurements, the samples were heated at 120°C under vacuum for 1.5 h. The hydrogen adsorption measurement (volumetric method) was measured at 25°C 298 K and 13 bar pressure using the same gas sorption apparatus. Before the hydrogen-uptake measurement, the samples were heated at 120°C in a vacuum for 1.5 h.

Results and discussion

The phase stability was examined with XRD method. Figure 1 shows XRD patterns of $Zn_3(BTC)_2$ sample. The main peaks and the corresponding crystal planes are identified. The main peaks of the pattern of $Zn_3(BTC)_2$ sample appeared at $2\theta=10.1$.

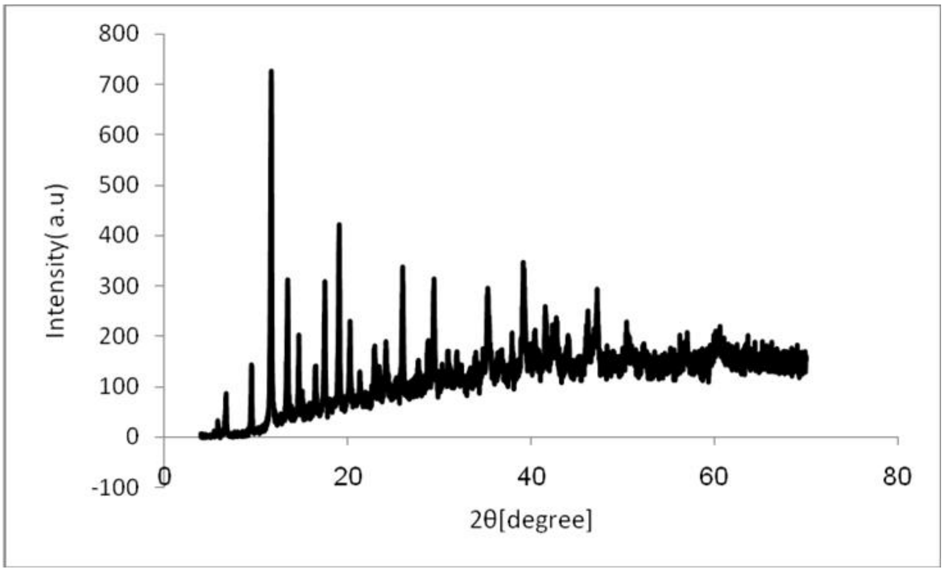

Figure 1. X-ray diffraction pattern of $Zn_3(BTC)_2$.

Scanning electron microscopy (SEM) images of the $Zn_3(BTC)_2$ sample showed the presence of well-shaped, high quality conical shaped crystals and their particle size is about 500 nm (Figure 2).

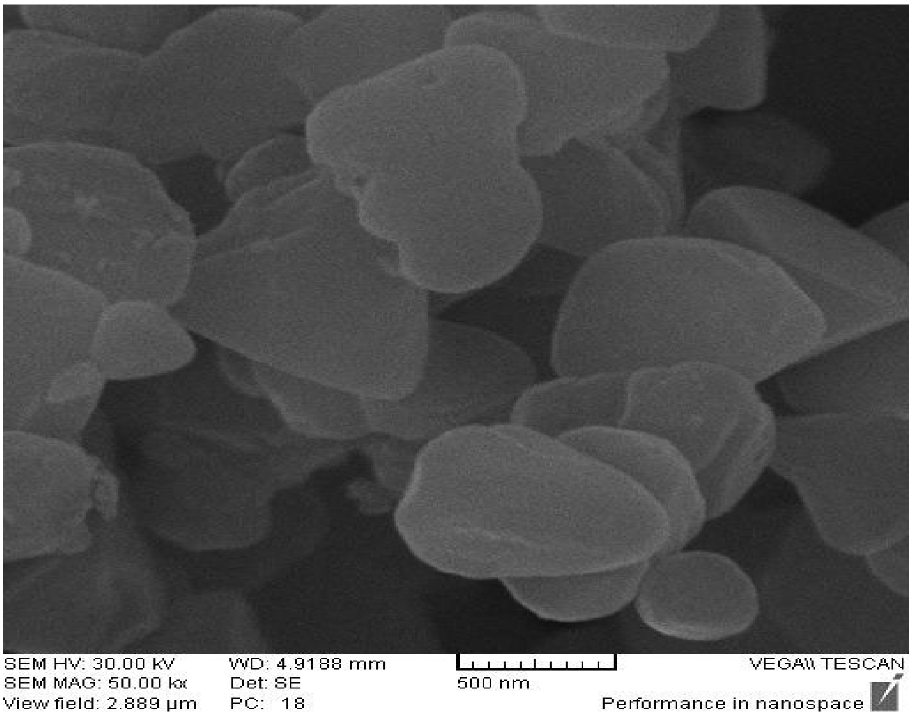

Figure 2. Surface morphology of $Zn_3(BTC)_2$.

The FT–IR spectra (4600–360 cm^{-1}) were obtained with a resolution of 4 cm^{-1} at room temperature with a shimadzu model of 8400S spectrometer, fitted with a DLATGS detector. The samples were previously prepared as KBr mixtures. Figure 3 shows the spectrum of $Zn_3(BTC)_2$ sample. According to presence possibility of metal-organic frameworks, sharp and strong bands in the range of 1400-1600 cm^{-1} refer to stretching vibrations band related to C=C bound in the aromatic ring. The presence of a weak band at 3070 cm^{-1} is related to C-H and is an evidence for the aromatic ring.

The presence of aromatic ring indicates that organic ligand used in the final sorbent structure have remained and not destroyed. The band around 1560-1650 cm^{-1} can be assigned to vibration of C=O group and the broad bands around 2400-3400 cm^{-1} can be associated to OH of ethanol. The FT–IR spectrum in this figure is similar to previous reports [13] and no certain change in the position and shape of the bands has been found, which indicates the structure of the compound is preserved.

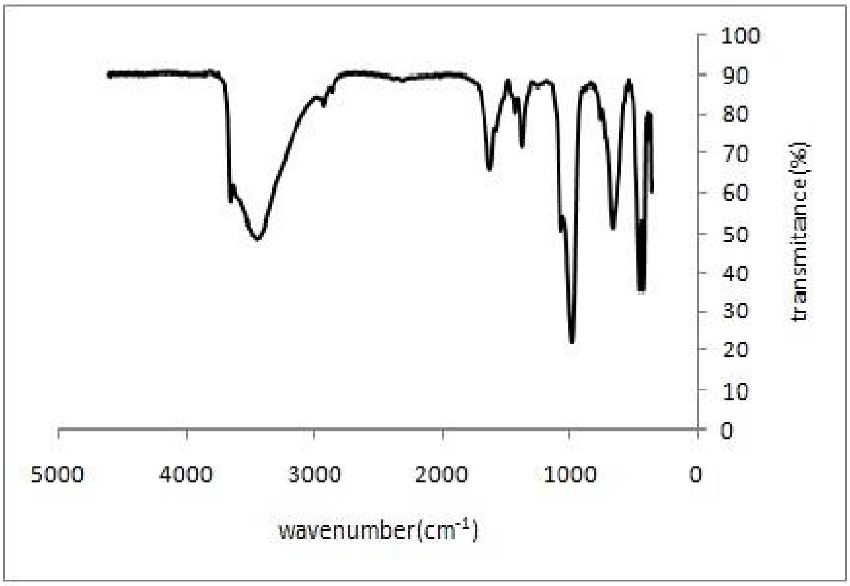

Figure 3. IR spectrum of $Zn_3(BTC)_2$.

The thermal behavior of $Zn_3(BTC)_2$ sample (Figure 4), shows that the initial weight loss up to 100°C is due to the loss of ethanol and other guest molecules from the framework. A sudden weight change (around 37.72 wt.%) is observed at 440°C due to the total damage of BTC linker and the remained product is ZnO. This higher thermal stability of $Zn_3(BTC)_2$ sample is favorable to use it in various applications, such as hydrogen gas storage unit integrated to a fuel cell processor.

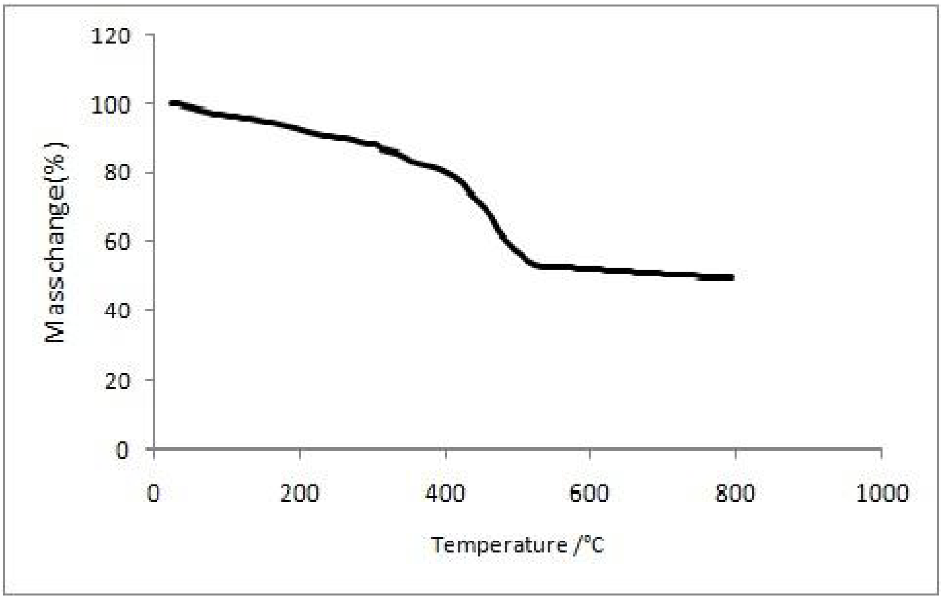

Figure 4. TGA plot of $Zn_3(BTC)_2$.

The pore size distribution, number of pores, and exposed surface area were calculated by using the results of N_2 adsorption measurements performed on an ASAP 2020 analyzer with built-in software. The N_2 adsorption/desorption isotherms of $Zn_3(BTC)_2$ sample at -196°C 77 K is shown in a type I curve (Figure 5) [13]. The BET surface area, pore volumes and pore size of the $Zn_3(BTC)_2$ sample are summarized in Table 1.

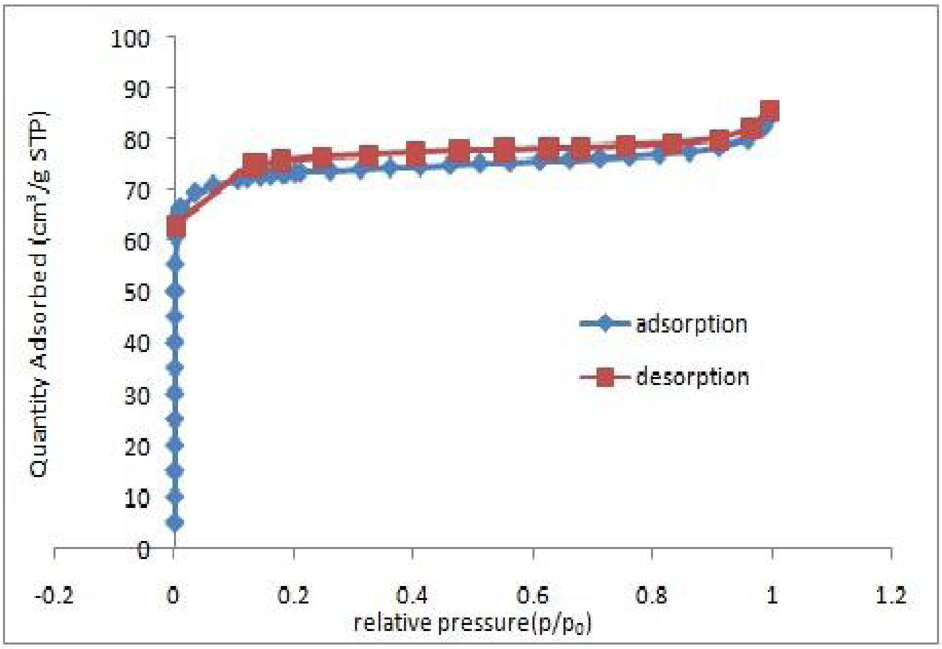

Figure 5. Comparison of N_2 adsorption (blue symbols) and desorption (red symbols) isotherms at -196°C 77 K of $Zn_3(BTC)_2$.

Table 1. Textural Properties of $Zn_3(BTC)_2$.

Material	BET Surface area (m^2 g^{-1})	BJH Pore volume (cm^3g^{-1})	t-Plot micropore volume (cm^3 g^{-1})	Mean pore diameter (nm)
$Zn_3(BTC)_2$	257.0083	0.026866	0.100435	3.9195

A homemade setup (Figure 6) was used for the $Zn_3(BTC)_2$ sample hydrogen storage capacity measurement. The volumetric method for hydrogen uptake measurement is extensively adopted because of its simplicity, low-cost, and easy assemblage [14]. At first, 1 g of a sample was loaded in the adsorption reactor (13) and attached to the system. Then, the existing gas inside the system was swept out with helium. To degas the system, the valves 8, 9, 11 and 18 was opened, and other valves closed. Then the vacuum pump was turned on, and the system was vacuumed along with the heating temperature of 200°C 473 K for 1.5 h (without any loss of crystallinity under the given thermal conditions). After degassing, system was cooled to ambient temperature. The hydrogen was adsorbed by opening the valves 3, 4, 5, 7, 8, 9 and 10, and closing all other valves. The pressure of HP vessel decreased due to some dead volume in the reactor (including hollow space and the connected tubes) and some adsorption. By measuring the dead volumes, one could calculate the exact pressure decrease due to hydrogen adsorption.

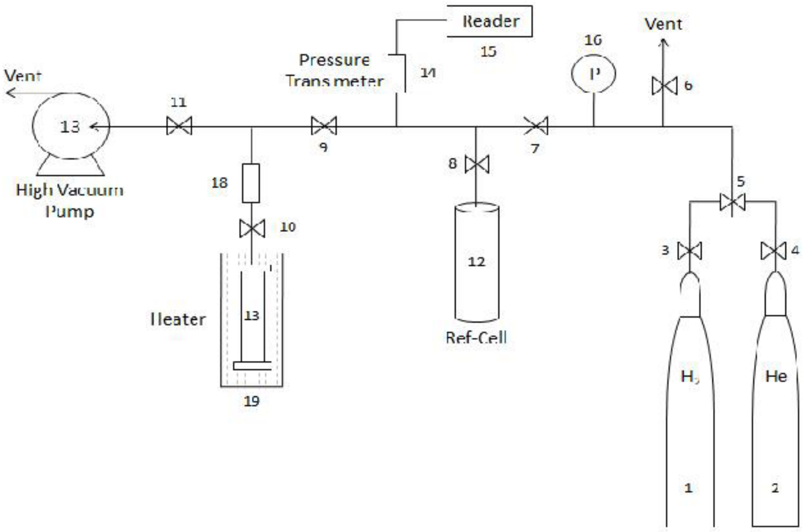

Figure 6. Setup for sorption/desorption capacity test.

The isotherm of hydrogen adsorption on $Zn_3(BTC)_2$ sample is presented in Figure 7 Hydrogen adsorption has been studied on it at 25°C 298K and 15 bar. The results show that an increase in adsorption is observed to 15 bar and this material in comparison with its relatively low surface area has higher adsorption. This indicates that surface area is not the only factor for measuring adsorption but hydrogen interaction sites with nominated material, pore type and pore size are affecting the amount of adsorption.

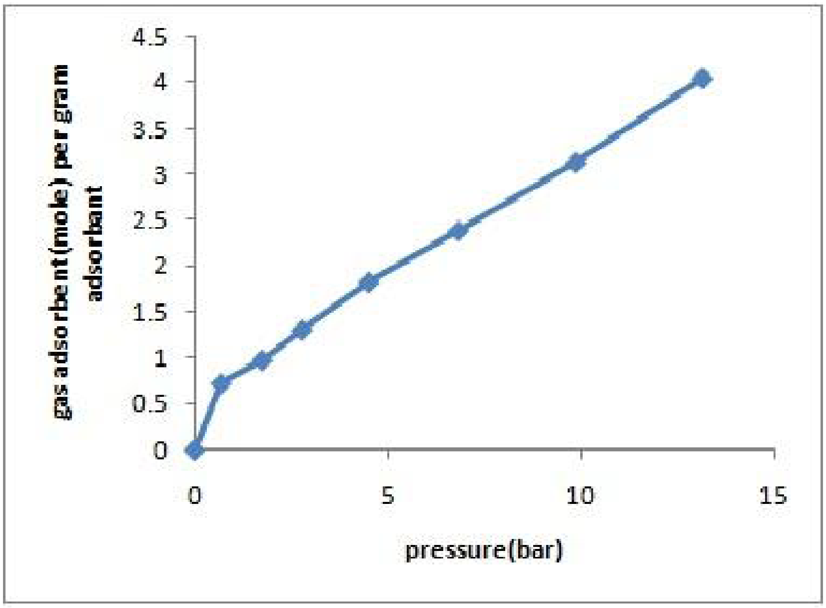

Figure 7. Hydrogen adsorption isotherms of $Zn_3(BTC)_2$.

Conclusions

Metal-Organic Frameworks (MOF) are porous hydrogen adsorbents with unusually high surface area. In this study $Zn_3(BTC)_2$ sample was synthesized from readily available and low cost raw materials using a simple procedure. The results showed that this material has a good adsorption at ambient temperature so that, this adsorption in comparison with surface area is high at ambient conditions, and this good adsorption may be due to Van der Waals and charge-quadrupole interactions with gas molecules. According to low cost, simplicity and high adsorption performance of the proposed adsorbent, it can be a good candidate for hydrogen storage at room temperature.

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