

Sorption of Methane and Carbon Dioxide on Nano Porous Zinc Carboxylate Metal-Organic Framework

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Received 7 Sep. 2015;

Revised 19 Feb. 2016;

Accepted 24 Feb. 2016

ABSTRACT: Zinc (II) tricarboxylate (Zn-BTC) with metal-organic framework (MOF) has been synthesized for the first time under solvothermal conditions and has been tested as an adsorbent for methane and carbon dioxide at standard temperature and pressure. The adsorbent was characterized by means of X-ray diffraction (XRD), Brunauer-Emmet-Teller (BET), Fourier transform infrared (FT-IR) and scanning electron microscopy (SEM). Sorption capacity of the methane and carbon dioxide on Zn-BTC in the range of pressure 1-20 bar and at 298 K was investigated by volumetric measurement. This result shows that Zn-BTC has higher sorption capacity methane at 20 bar compared to carbon dioxide. The high sorption capacity of this adsorbent for methane is attributed to large number of open metal site and the appropriate pore diameter of framework that caused higher interaction for the methane at between methane and carbon dioxide, suggests that (Zn-BTC) is a potential adsorbent for the separation of methane from gas mixtures.

Key word: Methane, Metal organic framework, Carbon dioxide, Adsorption, Solvothermal

INTRODUCTION

Methane is available in large quantities and preferable to other hydrocarbon fuels because this gas has the highest hydrogen/carbon ratio and higher octane number than other fuels also it is the essential component of natural gas. Therefore this is a clean fuel and is used in transport and power plants to generate electricity (Wu et al., 2010; Konstas et al., 2012). The main problem is the ability to store methane at ambient temperature. It cannot be converted to liquid phase by applying pressure only because the critical temperature of methane is low (191 K). The methane usually is stored as compressed natural gas (CNG) at 207 bar in vessels (J. J. Wozniak, 1995), moreover methane is stored in a porous solid at ambient pressure as adsorbent (ANG) (Rodgers, 2000). Carbon dioxide is a trace gas comprising 0.039% of the atmosphere that results from the burning of fossil fuels in automobiles and plants (Lee et al., 2006). Three types of gas mixtures are more important for separation and in capture technologies: the components of natural gas (CH₄/CO₂), fuel gases (CO₂/N₂) and pre-combustion gas mixture that contains H₂ (Hedin et al., 2010). The efficient storage of CH₄ is one of the main problems for its widespread application. Accordingly, the development of more efficient approaches for CO₂ capture and CH₄ storage is critically important. Since year 2000, the United

State of America, department of energy (DOE) has set the target for adsorbent of methane, storage at 180 cm³ (STP)/cm³ at 298 K and 35 bar (the standard temperature and pressure (STP) equivalent volume of methane per volume of the adsorbent material at temperature 298 K and pressure 1-35 bar.) (Min Wang et al., 2002; Ma et al., 2008). Recently porous metal-organic framework (MOFs) compounds have been used in drug delivery (Horcajada et al., 2006; Ferey, 2008) gas storage (Anbia & Hoseini, 2012; Anbia & Hoseini, 2012; Anbia et al., 2012; Anbia & Sheykhi, 2012; Anbia & Sheykhi, 2013) separation (Ma et al., 2007), catalysts (Farrusseng et al., 2009; Lee et al., 2009), sensor technology (Beauvais et al., 2000; Halder et al., 2002). These compounds are formed of cluster and rigid organic linker that have one, two or three dimension structure. For the first time, in 1997, the compound with formula [Co₂(4,4-bpi)₃(NO₃)₄·4H₂O]_n used as adsorbent for methane that showed gravimetric methane adsorption of 52 cm³ (STP)/g at 298 K and 30 bar (Kondo et al., 1997). The high surface area, high porosity and high volume are appropriate properties of MOFs. These properties can be changed with changing conditions (Kim et al., 2012). The solvothermal, hydrothermal (Anbia & Sheykhi, 2012), at room temperature (Tranchemontagne et al., 2008), microwave

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radiation (Lu et al., 2010) and ultrasonic irradiation (Son et al., 2008) are different methods of synthesis for MOFs. In this study, we have synthesized Zinc (II) tricarboxylates under solvothermal conditions with increased yield. The adsorption measurements of methane and carbon dioxide on Zn-BTC have been studied at 298 K up to 20 bars. This framework has shown higher capacity for sorption of methane at 20 bar pressure compared with CO₂. The potential use of Zn-BTC as an adsorbent for separation of CH₄ from gas mixtures is discussed.

MATERIALS & METHODS

Benzenetricarboxylic acid (H₃BTC) (Merck, >98%), Ethanol (Merck, 99.9%) and Zn (NO₃)₂·6H₂O (Merck) were obtained from E. Merck (Germany) and used without purification.

For synthesis of MOF, first benzenetricarboxylic acid ((H₃BTC)) (0.315 g, 0.150 mmol) and zinc (II) nitrate hexahydrate (0.90 g, 9.00 mmol) were transferred to 30 ml of absolute ethanol, then for several minutes this mixture was stirred until completely dissolved and the solution was added to a Teflon-lined steel autoclave, and the temperature was set at 393 K for 12h. The white solid product was recovered by filtration, washed with ethanol and dried at room temperature.

The structure of (Zn-BTC) was identified by X-ray diffraction on a Philips 1830 diffractometer with Cu-K_α radiation source. Fourier transform infrared (FT-IR) spectrum of the adsorbent was recorded at room temperature on a DIGILAB FTS 7000 spectrometer equipped with an attenuated total reflection (ATR) cell. Thermo gravimetric analysis was used to determine the thermal stability of the material which was carried out from room temperature to 350 °C using a TGA/DTA (Mettler Toledo 851) analyzer at a heating rate of 5 °C/min under air atmosphere. SEM (PHILIPS XL30) was used to study the product morphology.

To investigate the adsorption capacity of (Zn-BTC) for methane, we have used the volumetric method and a setup as shown in Fig. 1. At first, 0.5 g of a sample was loaded in the adsorption reactor (HP vessel) and attached to the system. Then, the existing gas inside the system was swept out with helium. To degas the system, we opened the valves 3 and 4 and closed other valves, then turned on the vacuum pump and the system was vacuumed at the heating temperature of 473 K for 1.5 h. After degassing, it was cooled to ambient temperature. The test gas was absorbed by opening the valves 2 and 3 and closing all other valves. The pressure of HP vessel decreased due to some dead volume in reactor (including hollow space and the connected tubes) and some adsorption. By measuring the dead volumes, one can calculate the exact pressure

decrease because of methane adsorption.

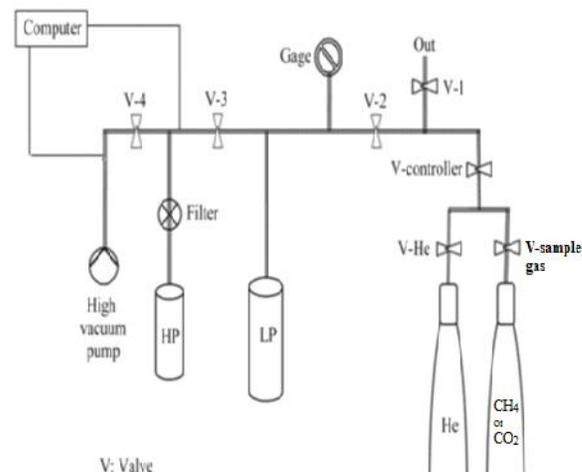


Fig.1. Setup for adsorption capacity test

RESULTS & DISCUSSION

FT-IR spectrum of (Zn-BTC) is shown in Fig. 2. It exhibits vibration bands in the region of Benzenetricarboxylic acid (1552 and 1435 1/cm), a hydrogen-bonded water and ethanol (3400 and 3194 1/cm), and nitrate (1377-1577 1/cm). Also it shows no absorptions for any protonated BTC (1730-1690 1/cm), indicating the complete deprotonation of Benzenetricarboxylic acid under synthesis conditions.

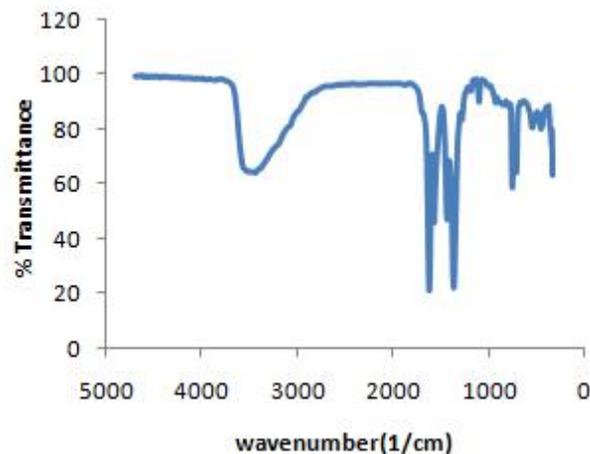


Fig.2. FT-IR spectrum of (Zn-BTC)

The powder X-ray diffraction pattern (XRD) of (Zn-BTC) is shown in Fig. 3. The location of peaks (such as; 2θ:10.12) refers to pattern of MOF that had been synthesized under room temperature conditions (Yaghi et al., 1997). This confirms that (Zn-BTC) has been synthesized. The absence of peaks due to BTC and Cu (NO₃)₂·6H₂O in the XRD pattern of (Zn-BTC) suggests its removal from the cavities of MOF.

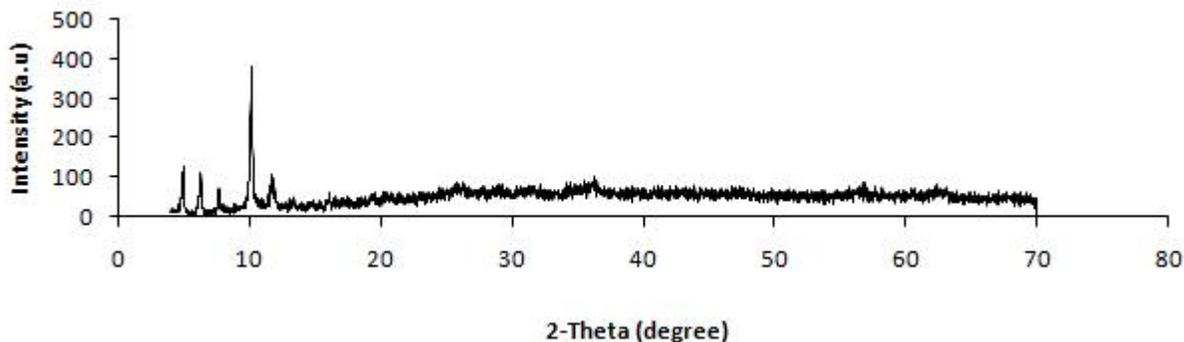


Fig.3. XRD patterns of the (Zn-BTC)

Scanning electron microscope (SEM) image of (Zn-BTC) is shown in Fig. 4. As can be seen in the image of metal-organic framework synthesized, that it has spherical morphology. As shown in Fig. 5, the morphology of (Zn-BTC) was homogeneous.

The N_2 adsorption-desorption isotherms is used to determine the specific surface area and pore diameter of (Zn-BTC). The N_2 adsorption and desorption isotherm of the adsorbent is shown in Fig. 5. The isotherm of the (Zn-BTC) is of type I that confirm (Zn-BTC) is microporous compound. The (Zn-BTC) showed BET surface area of $120.225 \text{ m}^2/\text{g}$ and pore volume of $0.5406 \text{ cm}^3/\text{g}$. Fig. 6 shows the pore size distribution of (Zn-BTC). The pore distribution of the adsorbent is 2.71 nm .

The adsorption isotherm of CH_4 and CO_2 on (Zn-BTC) at ambient temperature (298 K) and different pressures in the range of 0-20 bar is shown in Fig. 7. (Zn-BTC) shows the CH_4 and CO_2 adsorption capacities of 5.296 and 2.79 mmole/g at 20 bar and 298 K respectively. The adsorption isotherm of CH_4 and

CO_2 on this MOF at 298 K follows the type I isotherm, characteristic of microporous solids.

The high sorption capacity of (Zn-BTC) is attributed to the large number of open metal sites caused by removal of the ethanol from structure. It is executable via heating the HP vessel of the adsorption setup. Also pore diameter of the MOF caused higher interaction between CH_4 and adsorbent compared with CO_2 because the kinetic diameter of the methane is higher. Sorption capacity of the methane by porous materials such as MOFs has a strong correlation with the surface area, pore size and pore volume. Surface area is less strongly correlated with methane uptake (Llewellyn & Maurin, 2005) but pore size and pore volume are effective in interaction between MOF and CH_4 (C. E. Wilmer, 2012). Open metal site is drastic in sorption of the methane. Sorption capacity of the methane not increases by interchange of the chemical composition of metal organic frameworks (Zhou *et al.*, 2007). Comparison of CH_4 adsorption capacities of (Zn-BTC) and other porous materials are shown in Table 1.

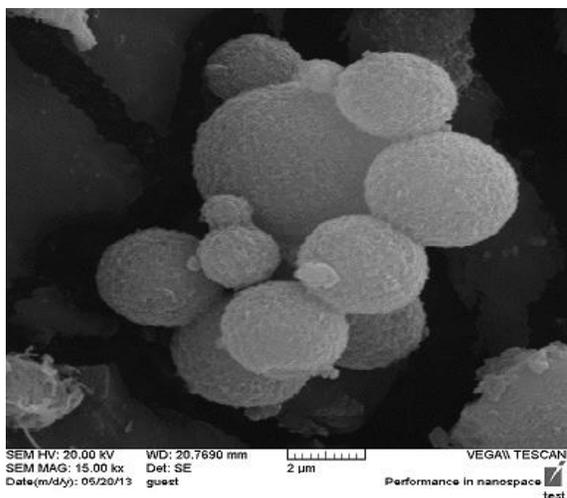


Fig.4. SEM image of (Zn-BTC)

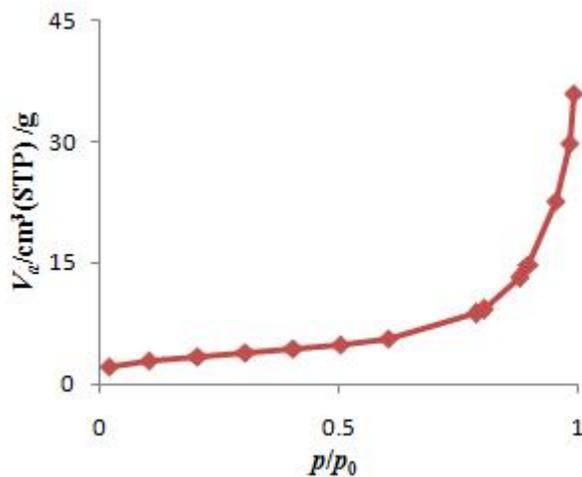


Fig.5. N_2 adsorption-desorption isotherms of (Zn-BTC)

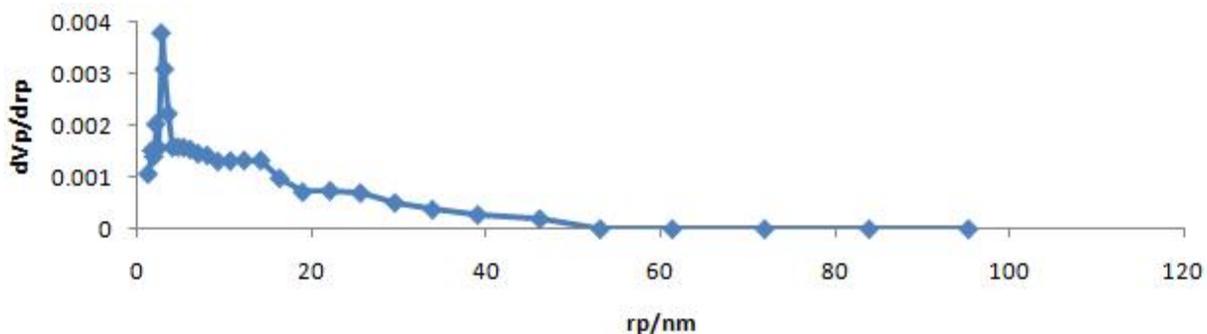
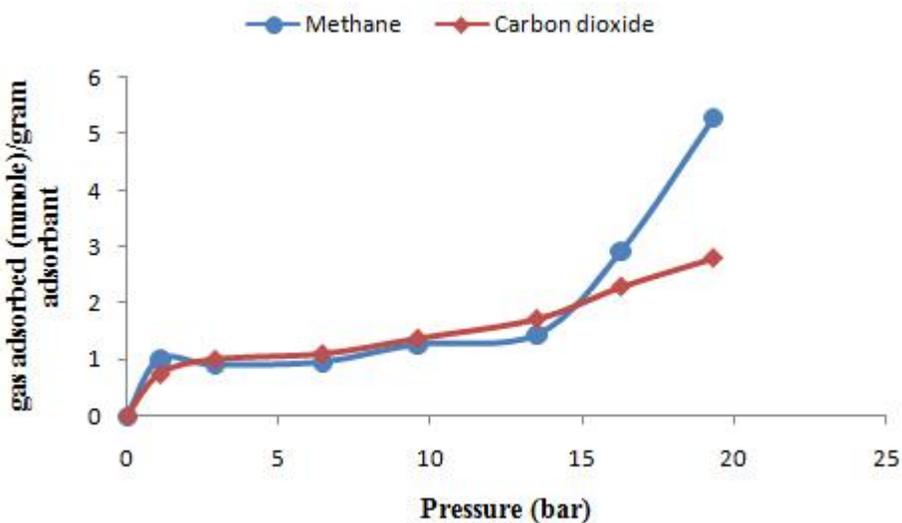


Fig.6. Pore size distribution of (Zn-BTC)

Fig.7. CH₄ and CO₂ adsorption capacity of (Zn-BTC) at different pressures and at 298 KTable 1. Comparison of CH₄ adsorption capacity of (Zn-BTC) with other adsorbents at different pressures and at 298 K

Samples	CH ₄ adsorption capacity (mmole/g)	Reference
MIL-101 Cr ₃ FO(bdc) ₃	14.2 (125 bar)	(Senkovska & Kaskel, 2008)
PCN-11 Cu ₂ (sbtc)	14.1 (35 bar)	(Wang <i>et al.</i> , 2008)
MIL-53(Cr) Cr(OH)(bdc)	10.2 (35 bar)	(Bourrelly <i>et al.</i> , 2005)
Co ₂ (4,4-bipy) ₃ (NO ₃)	3.6 (30.4 bar)	(Kondo <i>et al.</i> , 1997)
Zn ₄ O(R ₆ -bdc) ₃ IRMOF-6	4.7 (36.5 bar)	(Hofman <i>et al.</i> , 2002)
CuSiF ₆ (4,4-bipy) ₂	9.4 (36.5 bar)	(Noro <i>et al.</i> , 2000)
MCM-41	4.06 (18 bar)	(Yun <i>et al.</i> , 2002)
Cu ₂ (pzdc) ₂ (pia)	3.9 (31.4 bar)	(Kondo <i>et al.</i> , 1999)
Zn-BTC	5.29 (20 bar)	This work

CONCLUSIONS

Zinc metal organic framework synthesized by solvothermal method shows high yield and has been used as an adsorbent for gas adsorption studies. This MOF has been characterized by FT-R, XRD, SEM and BET. Zn-BTC adsorbed the methane 5.29 mmole/g which is higher compared sorption of the carbon dioxide. High sorption capacity of this adsorbent for methane is due to open metal sites created by removal of ethanol from the structure creating appropriate pore diameter.

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