Enhancement of Methane Adsorption by Lithium Doping into Metal-Organic Framework Cu-BDC

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Abstract

Copper (II) carboxylate, (Cu-BDC), metal-organic-framework (MOF) has been synthesized undersolvothermalconditions and used as a new adsorbent for the methane. The Lithium doping intoCu-BDC, (Li-Cu-BDC), is made by impregnating Cu-BDC with an ethanol solution of$LiNO_3$, followed by heat treatment in vacuum. The adsorbent was characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Thermogravimetric analysis (TGA). Inductively coupled plasma atomic emission spectrometry (ICP-AES) and Brunauer-Emmet-Teller (BET) technique. The Sorption capacity of the methane on Cu-BDC and Li-Cu-BDC range of pressure 1-20 bar and at 298 K was investigated by volumetric measurement. This work shows that Li-Cu-BDCCompared with Cu-BDC has higher sorption capacity for CH_4.

***Keywords*:** *Sorption, Methane, Metal Organic Framework, Solvothermal, Lithium doping.*

Introduction

Methane, the principle component of natural gas, has the highest hydrogen/carbon ratio therefore its products least pollution. It is an abundant fuel which is cleaner burning than gasoline [1, 2]. The ability to store methane in a safe, cheap, and convenient manner at ambient temperature is a significant problem. Usually changing the methane to liquid (Liquefied Natural Gas (LNG) is a good technique for storing of the CH_4, but is limited to systems where the use of large scale cryogenic storage vessel is economically feasible[1]. Moreover methane stored as compressed natural gas at 207 bar in vessels and adsorbed natural gas (ANG) that methane stored in a porous solid at ambient pressure as adsorbent[3, 4]. Zeolites and porous

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carbon materials are used as adsorbent for the methane as sorption capacity of porous carbon materials nearly is higher than zeolites [5-7]. Recently porous metal-organic framework (MOFs) compounds have been used in drug delivery [8, 9] gas storage [10, 11] separation [12], catalysts [13, 14], sensor technology [15, 16].These compounds have two sections which may include cluster and rigid organic linker. Appropriate properties (pore volume, pore size, surface area) of the Metal Organic Frameworks (MOFs) are regarded as very promising host systems for methane storage [17]. Today much research in the area of MOFs is devoted to strengthening the gas interaction energies and to increasing gas adsorption and storage capacity to significant levels at or around room temperature. To enhance the sorption capacity for gases, many improvements have been proposed, such as catenation/interpenetration in the pores of the framework [18, 19],incorporation of multi walled carbon nanotube [11], replacing of atoms in the linker molecules (IRMOF-992), chemical function of MOF material (PEHA-MIL-101)[20] and metal doping of the MOFs with electropositive metals. Lan et al. [21] by multi scale simulations indicate that Li is the best surface modifier for gas adsorption among a series of metals(Li, K, Na, Be, Ca, Mg and Ti). There are several methods for doping metal in MOFs such as chemical reduction[22], cation exchange [23] and

metal doping into MOF through thermal decomposition of anion species[24].In this paper, we report the synthesis Copper (II) carboxylate under solvothermal conditions. This framework has show unsuitable sorption capacity for methane at pressure of 20 bar. The next step for enhancement of the methane sorption Lithium is doped into Cu-BDC. The Li-Cu-BDC has shown higher sorption capacity than Cu-BDC.

Experimental

Materials

Benzene-1, 2-dicarboxylic acid(H_2BTC), Lithium nitrate ($LiNO_3$), N,N-Dimethylformamide (DMF) and ($Cu(NO_3)_2$ $.3H_2O$) were from E. Merck (Germany) and used without further purification.

Synthesis of MOF

For synthesis of MOF, first benzene-1,2-dicarboxylic acid (H_2BTC) (0.362 g, 0.0021 mmol) and Copper (II) carboxylate (0.526 g, 0.0021 mmol) were transferd to 44 ml of absolute DMF, then for several minutes this mixture was stirred until completely dissolved. Then this solution was added to a Teflon-lined steel autoclave and the temperature was set at 383 K for 36 h. The green solid product was recovered by filtration and washed with deionized water and dried at room temperature. Then, the solid product was calcined at 493 K under air atmosphere for 24h.

Preparation of Li-Cu-BDC

Lithium doping into MOF was performed by the thermal decomposition of anion species method[24].The Cu-BDC was activated at 473 K in vacuum for 4 h. The activated Cu-BDC was immersed in a 0.1 M $LiNO_3$/ethanol solution with stirring at room temperature for 24 h. After filtration, LiNO3doped Cu-BDC ($LiNO_3$- Cu-BDC)) was obtained by drying at 333 K for 24h. For the removal of nitrate anions, LiNO3-MIL-53(Al) was heated at 573 K for 2 h in vacuum to give Li-doped MIL-53 (Li- Cu-BDC).

Characterization

The structure of (Cu-BDC) was identified by X-ray diffraction on a Philips 1830 diffractmeter with Cu-Kα radiation source. Inductively coupled plasma atomic emission spectrometry (ICP-AES) measurement was performed using a S7000 (SHIMADZU) for the quantitative analysis of Li and Cu species. 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^{-1} under air atmosphere. SEM (PHILIPS XL30) was used to study the product morphology.

Adsorption experiment

To investigate the adsorption capacity of (Cu-BDC) and Li-Cu-BDC for methane, we have used the volumetric method and a setup is shown in Figure 1. At first, 0.5 g of a sample was loaded in the adsorption reactor (HP vessel) and was 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.
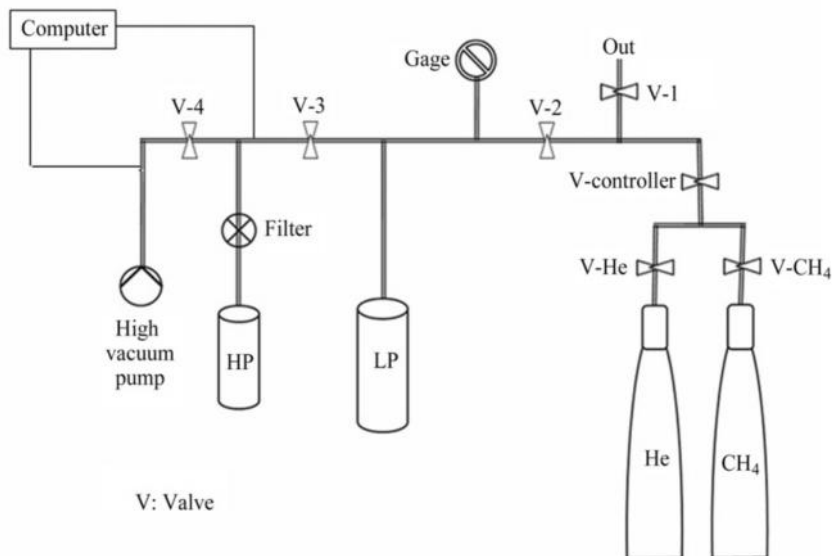
Figure 1. Setup for adsorption capacity test.

Results and Discussion

FT-IR spectrum of (Cu-BDC) is shown in Figure 2. In spectrum of the metal-organic framework (Cu-BDC), there is a sharp peak of high intensity in the range of 1623-1396 cm^{-1} that could be related to the C = C bond stretching vibrations of aromatic rings. It is clear that the aromatic rings of the organic ligands used in the final structure of the sorbent, have not been destroyed. The absence of peaks in the area of 1700 cm^{-1} show that the BDC was not released in the final structure. Two peaks appear at 1664 cm^{-1} and 1105 cm^{-1} which are associated to C = O stretching vibrations and C-O, respectively. Moreover 568 cm^{-1} and 756 cm^{-1} peaks, indicate that the substitutes are in the benzene ring.
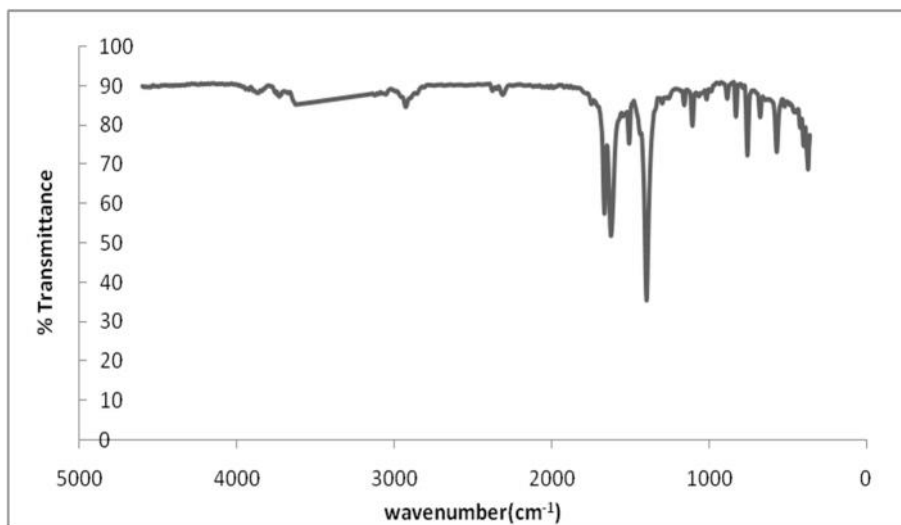

Figure 2. FT-IR spectrum of (Cu-BDC).

The powder X-ray diffraction pattern (XRD) of (Cu-BDC) is shown in Figure 3. The location of peaks (2θ:10.12) are similar to pattern of MOF that had been synthesized by terephthalic acid [25]. This confirms that (Cu-BDC) has been synthesized. The absence of peaks due to BDC and Cu $(NO_3).3H_2O$ in the XRD pattern of (Cu-BDC) suggests its removal from the cavities of MOF.
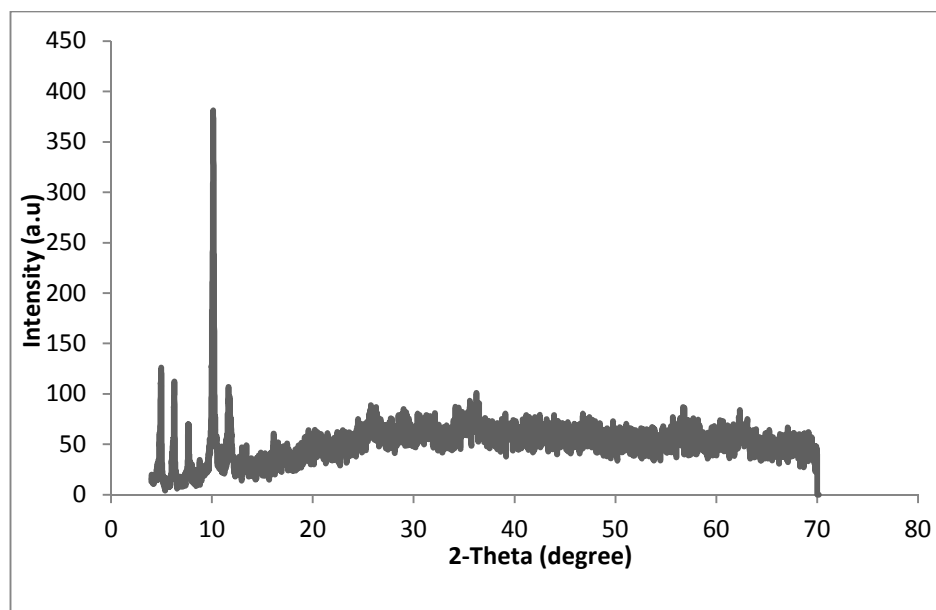

Figure 3. XRD patterns of the (Cu-BDC).

Scanning electron microscope (SEM) image of (Cu-BDC) is shown in Figure 4. As can be seen in the image of metal-organic synthesized framework, it has cubic morphology. As show in Figure 4, the morphology of Cu-BDC was homogeneous.
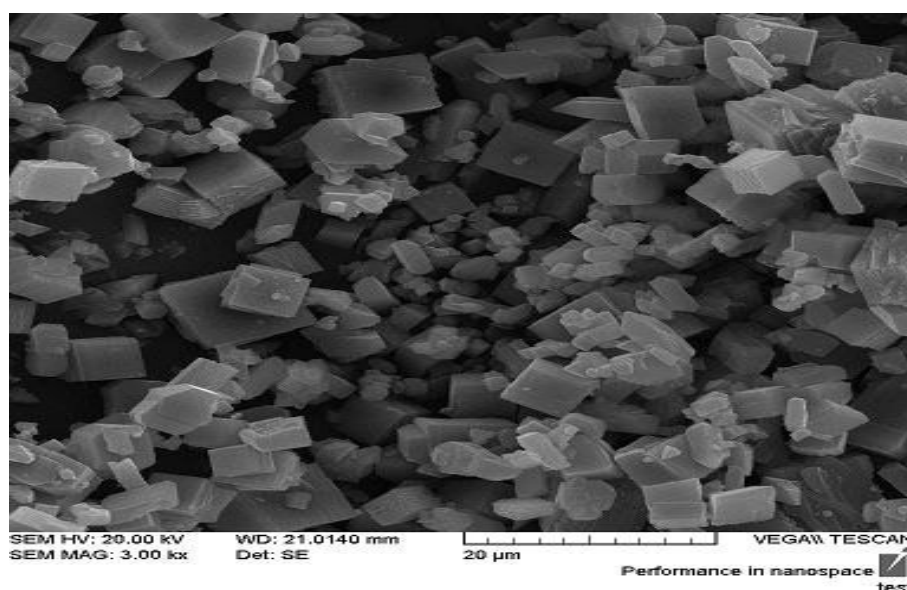

Figure 4. SEM image of (Cu-BDC).

The thermal behavior of (Cu-BDC) is shown in Figure 5. The thermogravimetric profile shows two clear weight-losses. The initial weight loss below 200∘C is due to the loss of

DMF molecules from the framework and the second weight loss step (200 <T>500 ∘C) is attributed to the elimination of acid.
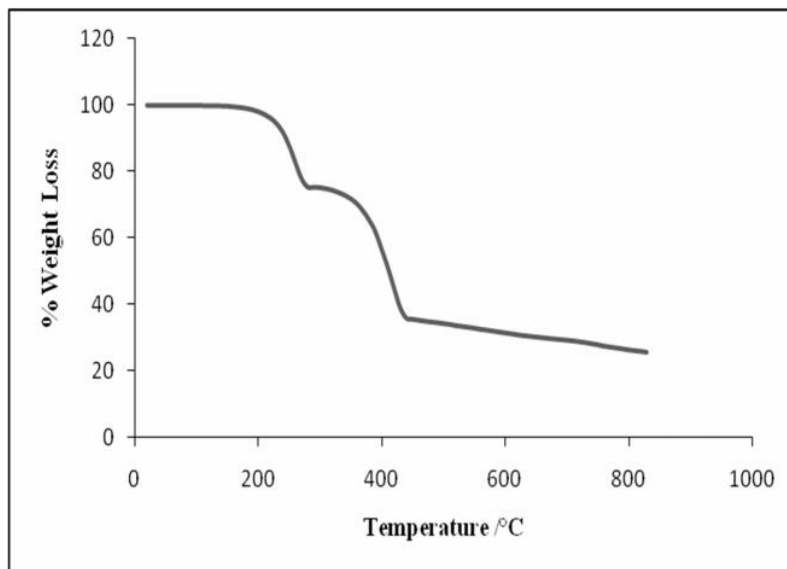
Figure 5. TGA plot of (Cu-BDC).

The N2 adsorption–desorption isotherms is used to find the specific surface area and pore diameter of Cu-BDC. The N2 adsorption and desorption of the adsorbent is shown Figure 6. The isotherm of the Cu-BDC is of type I which confirms that the Cu-BDC is microporous

compound. The Cu-BDC showed BET surface area of 642.14 m2/g and pore volume of 0.222376 cm³/g. Figure 7 shows the pore size distribution of Cu-BDC. The pore distribution of the adsorbent is 4.17 nm.
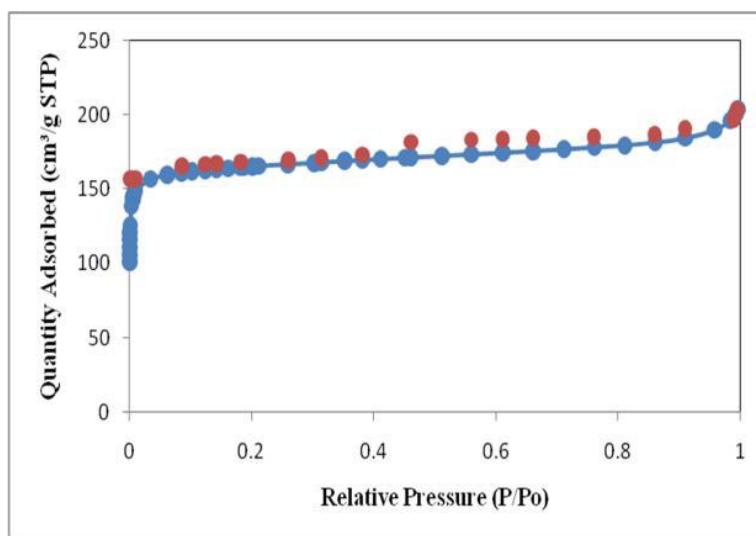
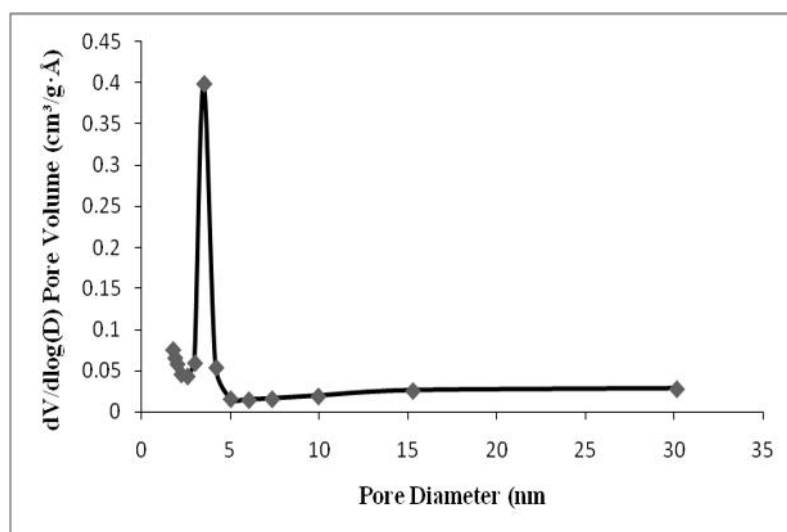**Figure 6.** N$_2$ adsorption–desorption isotherms of (Cu-BDC).

Figure 7. Pore size distribution of (Cu-BDC).

The adsorption isotherm of CH_4 on Cu-BDC and Li-Cu-BDCat ambient temperature (298 K) and different pressures in the range of 0−20 bar is shown in Figure 8. The Cu-BDC and Li-Cu-BDC show CH_4 adsorption capacities of 11.78 and 12.67 mmol g^{-1} respectively at 20 bar and 298 K. The adsorption isotherm of CH_4 on this MOFs at 298 K follows the types IV and II isotherm characteristic of microporous solids.
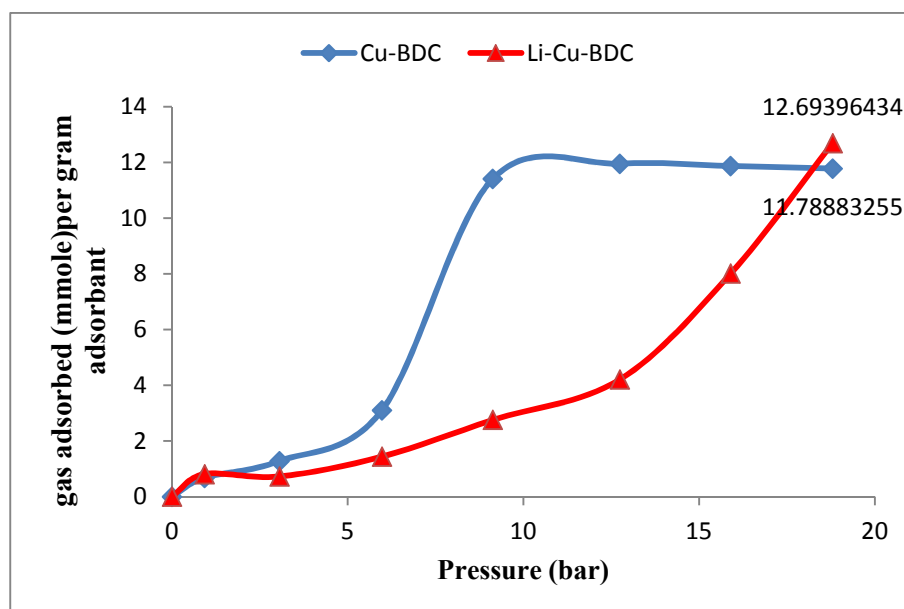

Figure 8.CH4 adsorption capacity of (Cu-BDC)and (Li-Cu-BDC) at different pressures and 298 K.

High sorption capacity of Cu-BDC was attributed to the large number of open metal sites that caused by removal from the DMF of structure [26-28]. It is executable via heating the HP vessel of the adsorption setup. Moreover high sorption capacity can be

attributed to the appropriate pore diameter of the framework. The Kinetic diameter of the methane is 0.38 nm which increases the interaction between CH_4 and Cu-BDC. Enhancement of sorption capacity of the Li-Cu-BDC is due to lithium cations which act as the additional adsorption site with an affnity to CH_4 molecules. The effect of the amount of lithium on methane sorption was examined by changing the concentration of the $LiNO_3$/ethanol solution for impregnation. 0.1 M is the optimum concentration of the $LiNO_3$/ethanol solution for the enhancement of methane sorption of Cu-BDC. The quantitative analysis was performed by ICP-AES which shows that Li/Cu ratio is 0.21587.Increase in lithium concentration decreases absorption of methane which is due to the filling of pores of the Cu-BDC by lithium. The 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 [29] but pore size and pore volume are effective in interaction between MOF and CH4 [30]. Open metal site is drastic for sorption of the methane. Sorption capacity of the methane does not increase by interchange of the chemical composition of metal organic frameworks [31].

Conclusion

Copper metal organic framework has been synthesized by solvothermal method. This adsorbent characterized is by BET, XRD, FT-IR, SEM and ICP analysis. It has a median pore width about 4.17 nm and a BET specific surface area of 642.14 m^2/g. The lithium is doped into adsorbent by heat treatment. The sorption capacity of the methane is measured by volumetric method. This MOF adsorbent has a methane sorption capacity of $12.67mmg^{-1}$. This high sorption capacity is due to open metal sites appropriate pore diameter and additional adsorption sites which is caused by lithium doping into of the framework and increases interaction between CH_4 and adsorbent.

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