Synthesis of Nanoporous Metal Organic Framework MIL-53-Cu and Its Application for Gas Separation

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ABSTRACT: *MIL-53-Cu has been synthesized hydrothermally and has been used for the first time for gas separation. MIL-53-Cu shows adsorption capacities of 8.1, 0.7 and 0.5 m.mol/g, respectively, for CH_4, CO_2 and H_2 at 30 bar and 298 K. The high CH_4 adsorption capacity of MIL-53-Cu maybe attributed to the high pore volume and large number of open metal sites. The high selectivity for CH_4 over CO_2 (11.5) and H_2 (16.2), suggests that MIL-53-Cu is a effective adsorbent material for the separation of CH_4 from gas mixtures.*

KEY WORDS: *MIL-53-Cu, Gas separation, Hydrothermal, Methane.*

INTRODUCTION

Natural gas has attracted considerable attention as a fuel for vehicles because of several advantages (such as natural gas is inexpensive and abundant worldwide) compared with conventional fossil fuels [1]. Methane, the principle component of natural gas, is available in large quantities and is preferable to other hydrocarbon fuels because of its cleaner combustion [2]. Moreover methane has the highest hydrogen-to-carbon ratio, and therefore, has highest energy density (per mass) among hydrocarbons. Natural Gas (NG) can be regarded as a clean fuel compared with petroleum because of reduced emissions such as NO_x, SO_x, CO_x, benzene, particulate matters, etc [3-5].

Adsorbed Natural Gas (ANG) can be an alternative solution to store natural gas at relatively low pressure (35 bar) and at room temperature (298 K) if adequate adsorbent is developed [6]. Porous materials such as zeolites, carbons and mesoporous materials have been tried as potential adsorbents for ANG [6].

Many materials have been investigated for gas storage including zeolites, carbons and Metal Organic Framework (MOFs) materials [7-9]. MOF materials, which consist of organic linkers and inorganic joints, represent a new class of porous crystalline materials that provides very high surface area and controllable pore size for energy storage and gas separation applications. Generally, nanoporous materials have many applications [10-19].

Kitagawa et al. [20] have reported a coordination polymer compound $\{Co_2(4,4'bpy)_3(NO_3)_4 \bullet 4H_2O\}n$, which exhibits modest but encouraging gravimetric methane uptake of ~ 2.3 m.mol/g at 298 K and 30 bar.

Pradip et al. [21] have studied CO_2, CH_4, C_3H_8, SF_6 and Ar adsorption on MIL-101. At 5.3 bar and 283 k, the adsorption capacities for gases C_3H_8 , SF_6 , CO_2 , CH_4 and Ar were 13.4, 9.1, 8, 2.2 and 0.9 m.mol/g, respectively. *Bao et al.* [22] have also investigated CO_2 and CH_4 adsorption on Mg-MOF-74 at 298 K and 1 bar, and

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the adsorption capacities for CO_2 and CH_4 were 8.61 and 1.05 m.mol/g, respectively. Also, under these conditions zeolite 13X can only adsorb 0.38 m.mol/g of CH_4.

In the present study, the adsorption measurements of methane, carbon dioxide and hydrogen on metal organic framework Copper (II) terephthalate (MIL-53-Cu), have been made at 298 K up to 30 bar.

EXPERIMENTAL SECTION

Reagents and materials

All materials such as, terephthalic acid [HO_2C-(C_6H_4)-CO_2H] (TP), hydrofluoric acid-HF (38-40%) and Cu $(NO_3)_2.3H_2O$ were of analytical grade from E. Merck (Germany).

Synthesis of MIL-53-Cu

MIL-53-Cu was hydrothermally synthesized at autogenous pressure from a mixture of $Cu(NO_3)_2.3H_2O$, terephthalic acid, hydrofluoric acid and H_2O in the molar ratio of 1:1:1:280. Reactants were introduced in this order and stirred for few minutes before introducing the resulting suspension in a Teflon-lined steel autoclave, and the temperature was set at 493 K for 72 h. The green solid product was recovered by filtration, washed with deionized water and dried at room temperature. Finally, the solid product was calcined at 573 K under air atmosphere.

Characterization

The nitrogen physical adsorption-desorption isotherms of the sample was measured at 77 K using a micromeritics ASAP 2020 analyzer. Specific surface area was obtained using the BET method and pore size distribution was evaluated using the BJH (Barrett – Joyner – Halenda) method. Other methods were used from before study [23].

Gas adsorption measurement

To investigate the adsorption capacities of MIL-53-Cu for methane, carbon dioxide and hydrogen, volumetric method was used setup from before study [23]. At first, 1 g of a sample was loaded in the adsorption reactor (HP vessel) and attached to the system. Them, the existing gas inside the system was swept out with helium. To de-gas the system, valves 9 and 11were opened and other valves were closed, then, the vacuum pump was turned on and the system was vacuumed along with the heating temperature of 473 K for 1.5 h. After de-gassing, the system was cooled to ambient temperature. The test gas was adsorbed by opening the valves 7, 9 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, the exact pressure decrease because of gas adsorption was calculated.

RESULTS AND DISCUSSION

The powder X-ray diffraction patterns, SEM image and TGA profiles of MIL-53-Cu sample are shown in previous study [23].

Fig. 1. Shows the N_2 adsorption – desorption isotherms of MIL-53-Cu at 77 K up to 1 bar. The N_2 adsorption isotherm on MIL-53-Cu is of a typical type I isotherm, a signature characteristic of microporous materials. Structural properties of MIL-53-Cu, is listed in previous study [23]. The BET surface area of MIL-53-Cu was found to be 1283 m^2/g.

The absolute adsorption isotherms of CH_4, CO_2 and H_2 on MIL-53-Cu at ambient temperature (298 k) and different pressures in the range 0-30 bar are shown in Fig. 2. MIL-53-Cu showed for CH_4, CO_2 and H_2 adsorption capacities of 8.1, 0.7 and 0.5 $m.mol.g^{-1}$, respectively, at 30 bar and 298 K. At high pressure, the absolute adsorption capacity for an isotherm reaches to the saturation and then remains constant. The absolute adsorption capacities were found in order of CH_4>> CO_2> H_2. The high CH_4 adsorption capacity of MIL-53-Cu can be attributed to the high pore volume and large number of open metal sites. Comparison of the adsorption capacities of MIL-53-Cu for $CH_4$and other porous materials are given in Table 1. The adsorption selectivity for the CH_4, CO_2 and H_2 were calculated from their adsorption isotherms. The adsorption selectivity of a gas A over gas B was calculated by using the equation. 1. [29].

$$\alpha_{A/B} = [V_A/V_B]_{P,T} \quad (1)$$

Where, V_A and V_B are the volumes of gas A and B respectively adsorbed at any given pressure P and temperature T. The order of adsorption selectivity towards CH_4 over CO_2 and H_2 is as follows: CH_4/ H_2 >CH_4/ CO_2. MIL-53-Cu shows high selectivity towards CH_4 over CO_2 (11.5) and H_2 (16.2). The selectivity for

Table 1: Comparison of the adsorption capacity of MIL-53-Cu for CH_4 and other porous materials at 298 K and 30 bar.

Sample	CH_4 adsorption capacity (m.mol/g)
MOF-235	2.7
MIL-100-Cr	5.5
MIL-100-Fe	~5.1
Active carbon	~5.3
ZSM-5	2.8
Zeolite HY	3.1
MIL-53-Cu	8.1

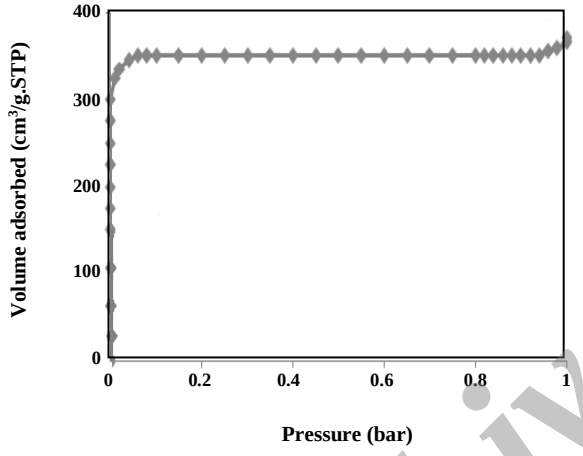

Fig. 1: The N_2 adsorption-desorption isotherm of MIL-53-Cu.

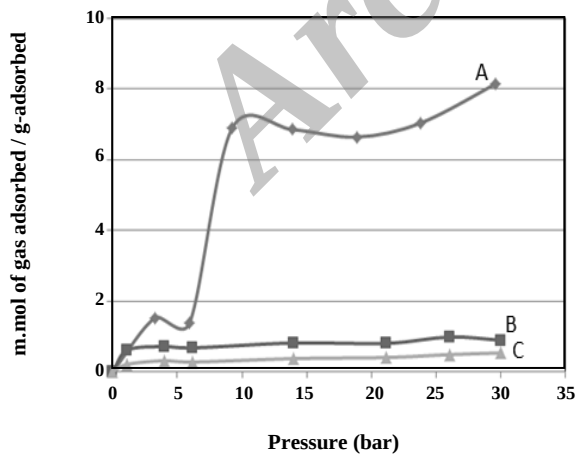

Fig. 2: Adsorption isotherms of CH_4 (A), CO_2 (B) and H_2 (C) on MIL-53-Cu at 298 K up to 35 bar.

CH_4 over CO_2 for MIl-53-Cu indicates it's suitability for separation of CH_4 from gas mixtures.

CONCLUSIONS

We have successfully synthesized metal organic framework MIL-53-Cu and have used it for the first time as an adsorbent for separation of methane, carbon dioxide and hydrogen. Gas adsorption capacity is measured by volumetric measurements at 298 K up to 30 bar. The absolute adsorption capacities is found in the order of CH_4>>CO_2>H_2. The high CH_4 adsorption capacity of MIL-53-Cu is attributed to the high pore volume and large number of open metal sites. The high selectivity for CH_4 over CO_2 (11.5) and H_2 (16.2), suggests that MIL-53-Cu is a potential adsorbent material for the separation of CH_4 from gas mixtures and also the potential application of this adsorbent in ANG due to high methane adsorption capacity.

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