

# 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<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub> at 30 bar and 298 K. The high CH<sub>4</sub> 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<sub>4</sub> over CO<sub>2</sub> (11.5) and H<sub>2</sub> (16.2), suggests that MIL-53-Cu is a effective adsorbent material for the separation of CH<sub>4</sub> 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<sub>x</sub>, SO<sub>x</sub>, CO<sub>x</sub>, 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<sub>2</sub>(4,4'bpy)<sub>3</sub>(NO<sub>3</sub>)<sub>4</sub>•4H<sub>2</sub>O}<sub>n</sub>, 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<sub>2</sub>, CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, SF<sub>6</sub> and Ar adsorption on MIL-101. At 5.3 bar and 283 k, the adsorption capacities for gases C<sub>3</sub>H<sub>8</sub>, SF<sub>6</sub>, CO<sub>2</sub>, CH<sub>4</sub> 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<sub>2</sub> and CH<sub>4</sub> adsorption on Mg-MOF-74 at 298 K and 1 bar, and

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the adsorption capacities for CO<sub>2</sub> and CH<sub>4</sub> 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<sub>4</sub>.

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<sub>2</sub>C-(C<sub>6</sub>H<sub>4</sub>)-CO<sub>2</sub>H] (TP), hydrofluoric acid-HF (38-40%) and Cu (NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O 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<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O, terephthalic acid, hydrofluoric acid and H<sub>2</sub>O 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. Then, the existing gas inside the system was swept out with helium. To de-gas the system, valves 9 and 11 were 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<sub>2</sub> adsorption – desorption isotherms of MIL-53-Cu at 77 K up to 1 bar. The N<sub>2</sub> 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<sup>2</sup>/g.

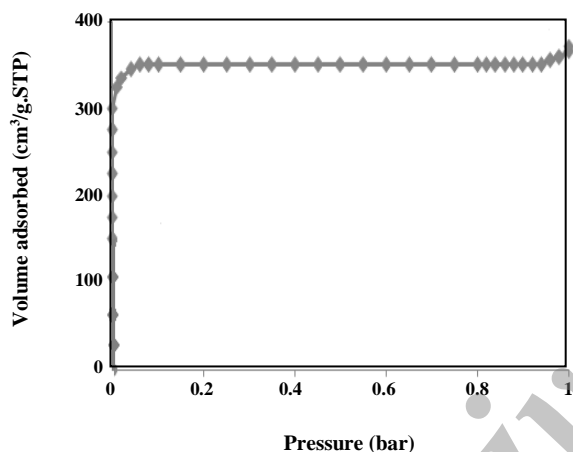
The absolute adsorption isotherms of CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub> on MIL-53-Cu at ambient temperature (298 K) and different pressures in the range 0-30 bar are shown in Fig. 2. MIL-53-Cu showed for CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub> adsorption capacities of 8.1, 0.7 and 0.5 m.mol.g<sup>-1</sup>, 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<sub>4</sub>>> CO<sub>2</sub>> H<sub>2</sub>. The high CH<sub>4</sub> 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<sub>4</sub> and other porous materials are given in Table 1. The adsorption selectivity for the CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub> were calculated from their adsorption isotherms. The adsorption selectivity of a gas A over gas B was calculated by using the equation. 1. [29].

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

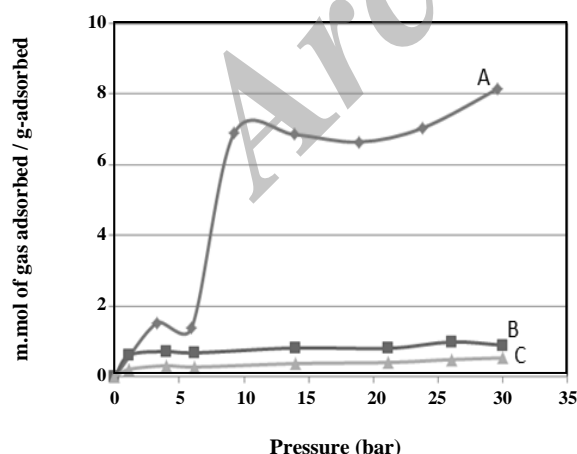
Where, V<sub>A</sub> and V<sub>B</sub> are the volumes of gas A and B respectively adsorbed at any given pressure P and temperature T. The order of adsorption selectivity towards CH<sub>4</sub> over CO<sub>2</sub> and H<sub>2</sub> is as follows: CH<sub>4</sub>/ H<sub>2</sub> > CH<sub>4</sub>/ CO<sub>2</sub>. MIL-53-Cu shows high selectivity towards CH<sub>4</sub> over CO<sub>2</sub> (11.5) and H<sub>2</sub> (16.2). The selectivity for

**Table 1: Comparison of the adsorption capacity of MIL-53-Cu for CH<sub>4</sub> and other porous materials at 298 K and 30 bar.**

Sample	CH <sub>4</sub> 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<sub>2</sub> adsorption-desorption isotherm of MIL-53-Cu.**



**Fig. 2: Adsorption isotherms of CH<sub>4</sub> (A), CO<sub>2</sub> (B) and H<sub>2</sub> (C) on MIL-53-Cu at 298 K up to 35 bar.**

CH<sub>4</sub> over CO<sub>2</sub> for MIL-53-Cu indicates its suitability for separation of CH<sub>4</sub> 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<sub>4</sub>>>CO<sub>2</sub>>H<sub>2</sub>. The high CH<sub>4</sub> 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<sub>4</sub> over CO<sub>2</sub> (11.5) and H<sub>2</sub> (16.2), suggests that MIL-53-Cu is a potential adsorbent material for the separation of CH<sub>4</sub> from gas mixtures and also the potential application of this adsorbent in ANG due to high methane adsorption capacity.

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