



Adsorption of methane on porous metal carboxylates

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ABSTRACT

Porous metal carboxylates such as MIL-101 (Cr-terephthalate), MIL-100-Cr (Cr-trimesate) and MIL-100-Fe (Fe-trimesate) with very high porosity have been tested as potential adsorbents for methane storage materials. The MIL-101 shows one of the highest adsorption capacities for methane. The adsorption capacity per weight increases with increasing BET surface area or micropore volume irrespective of the structure, type of metal ions such as Cr³⁺ and Fe³⁺. This result suggests that the porous adsorbent for methane should have high porosity rather than special adsorption sites or structures.

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1. Introduction

Recently, natural gas (NG) has attracted considerable attention as a fuel for vehicles because of several advantages compared with conventional fossil fuels [1–3]. NG is inexpensive and abundant worldwide. Methane, one of the major components of NG, has highest hydrogen-to-carbon ratio and, therefore, has highest energy density (per mass) among hydrocarbons. Moreover, NG can be regarded as a clean fuel compared with petroleum because of reduced emissions such as VOCs, SO_x, CO_x, NO_x, benzene, particulate matters, etc. [1–3]. However, the energy density of NG per volume is very low to have just 0.11% of gasoline. Therefore, suitable storage method is necessary to use NG as vehicular fuel. Several storage methods, including liquefied NG (LNG) and compressed NG (CNG), have been considered to increase the energy density. However, the storage as LNG or CNG has drawbacks to be used commercially. Even though LNG has high energy density (about 70% of gasoline), liquefaction needs low temperature and is energy-intensive process because of low critical temperature of methane (191 K). LNG needs specialized container and temperature should be maintained low for storage. Moreover, periodic venting is necessary because of pressure buildup in a cryogenic fuel tank. CNG is NG stored at room temperature as a compressed supercritical fluid (200–250 bar). Even though CNG is commercially used with energy density of about 25% of gasoline, CNG has drawbacks of heavy pressure vessel and multi-stage compression. Adsorbed NG (ANG) can be an

alternative solution to store NG at relatively low pressure (35–40 bar) and at room temperature if adequate adsorbent is developed [1–3]. Porous materials such as carbons, zeolites and mesoporous materials have been tried as potential adsorbents for ANG [1–3].

Recently, hybrid inorganic–organic materials called metal–organic frameworks (MOFs) are extensively studied because of high porosity, versatile structures and possibility of structural design [4–6]. These MOFs are also tested as potential candidates for ANG because of high porosity and hydrophobicity of MOFs. Cu-containing MOF [Cu(O₂CRCO₂) 0.5 triethylenediamine]_n (R: 4,4'-C₆H₄C₆H₄ or trans-C₆H₄CH=CH), showed high adsorption capacity [7]. The adsorption capacity (per weight) of an MOF called IRMOF-6 (Zn-1,2-dihydrocyclobutanebenzene-3,6-dicarboxylate) was high even though the volumetric adsorption capacity was relatively low because the density of IRMOF-6 is low [8]. By using computational methods, Düren et al. suggested some imaginary MOF structures for methane storage [9]. Very recently, some of us have reported that chromium terephthalate (MIL-101-Cr) and chromium trimesate (MIL-100-Cr) adsorb very large amount of methane [10].

In the present study, the adsorption of methane on MIL-100 and MIL-101 has been investigated in more detail because the studies on methane storage using MOFs are only now beginning [11]. The effect of porosity and type of metals has been investigated because MIL-100 can be synthesized from a few metal ions such as chromium and iron [12,13]. This work has the purpose to suggest the necessary properties of MOFs for methane storage or ANG.

2. Experimental

MOFs such as MIL-100 [12,13] and MIL-101 [14,15] have been synthesized following the reported methods. MIL-101 was treated

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with hot ethanol and aqueous NH_4F solution to remove occluded terephthalic acid [10]. Active carbon (Darco, Aldrich), HY (Zeolyst, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) and HZSM-5 (Zeolyst, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$) were used as received.

Nitrogen adsorption isotherms were obtained with Tristar-3000 adsorption unit (Micromeritics Corp.) to measure surface area and micropore volume. Surface area and micropore volume were calculated by using BET equation and t -plot, respectively. The adsorption isotherms for methane were obtained with high pressure volumetric adsorption unit (HPVA-100, VTI Corp.) at room temperature. Before nitrogen and methane adsorption, the samples were dehydrated at 300°C for 6 h under vacuum.

3. Results and discussion

It has been reported that the porosity (BET surface area and micropore volume) of a carbon or zeolite plays a dominant role to increase the storage capacity of methane [1–3]. Fig. 1 shows the nitrogen adsorption isotherms of the MIL-100s and MIL-101 materials. All of the MOFs show type-I isotherms without hysteresis (data not shown). The BET surface areas and micropore volumes of each MOF are summarized in Table 1. From Fig. 1 and Table 1, it can be understood that the porosity of MIL-100 does not rely much on the type of metal ions of MOFs. The porosity of active carbon, HY and ZSM-5 are also shown in Table 1.

As shown in Fig. 2, the adsorption capacity of methane increases with pressure for MIL-100s, MIL-101 and active carbon. However, the adsorption capacity saturates at relatively low pressure for ZSM-5 and HY zeolites due to small pore size (especially for ZSM-5). The adsorption–desorption isotherms do not show any hysteresis (the desorption isotherms are shown only for the zeolites and carbon samples), suggesting the potential applications of MOFs in ANG due to high delivery. Moreover, the adsorption capacity on MIL-101 shows the highest value based on the weight of adsorbent [8,9].

Fig. 3 illustrates the adsorption capacity (at 50 bar) depending on the BET surface area and the micropore volume. Both plots show quite good linear relationships irrespective of the structure, chemical composition and pore size. However, the relationship is relatively good for the plot with BET surface area. Moreover, the type of materials (such as MOF, zeolite and carbon) do not have noticeable effect on the methane adsorption capacity.

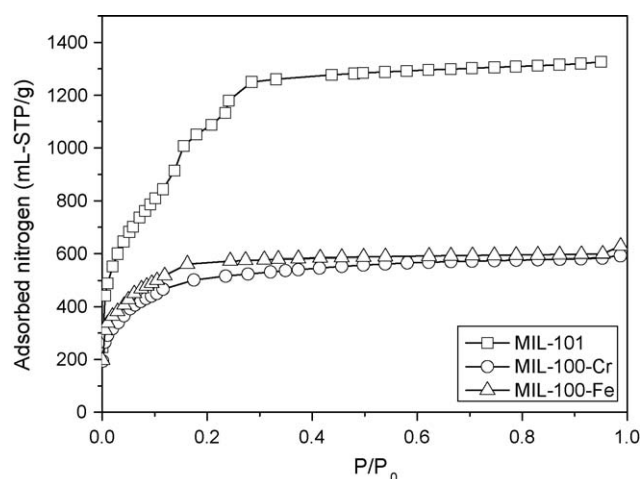


Fig. 1. Nitrogen adsorption isotherms over the adsorbents.

Table 1

Textural properties and methane adsorption capacities of the porous materials used in the study.^a

Sample	Sample type	S_{BET} (m^2/g)	PV_μ (ml/g)	V_{ads} (CH_4) (ml/g) ^b	Remarks
Active carbon	Carbon	1697	1.03	146	
HY	Zeolite	780	0.22	75	$\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$
HZSM-5	Zeolite	425	0.21	64	$\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$
MIL-101	MOF	4183	1.92	282	
MIL-100-Cr	MOF	1767	0.87	174	
MIL-100-Fe	MOF	1942	0.9	158	

^a S_{BET} : BET surface area; PV_μ : micropore volume.

^b Measured at 50 bar.

The metal ions such as Cr^{3+} and Fe^{3+} in MIL-100 [12,13] do not have dominant role in the adsorption isotherms and capacities as illustrated in Figs. 2 and 3. This may be due to the relatively high adsorption pressure of 50 bar. It has been reported that heat of adsorption (or chemical interaction), BET surface area and pore volume are important for hydrogen storage at low, medium and high pressure, respectively [16–20]. Therefore, it may be assumed that the chemical species or interaction are not important for methane storage at 50 bar. From the results, it can be suggested that high porosity of MOFs is vital for the methane storage irrespective of chemical composition and structure similar to the results over carbons and zeolites [1–3].

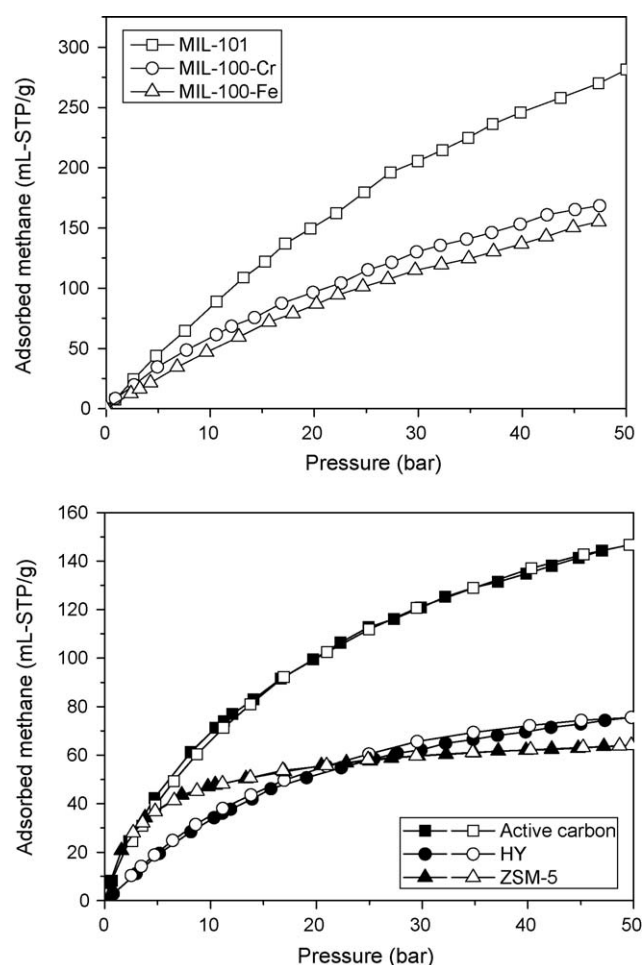


Fig. 2. Methane adsorption isotherms over the adsorbents. Upper figures and lower figures show the adsorption isotherms on MOFs and zeolites (and active carbon), respectively. The lower figures also show the desorption isotherms (filled symbols).

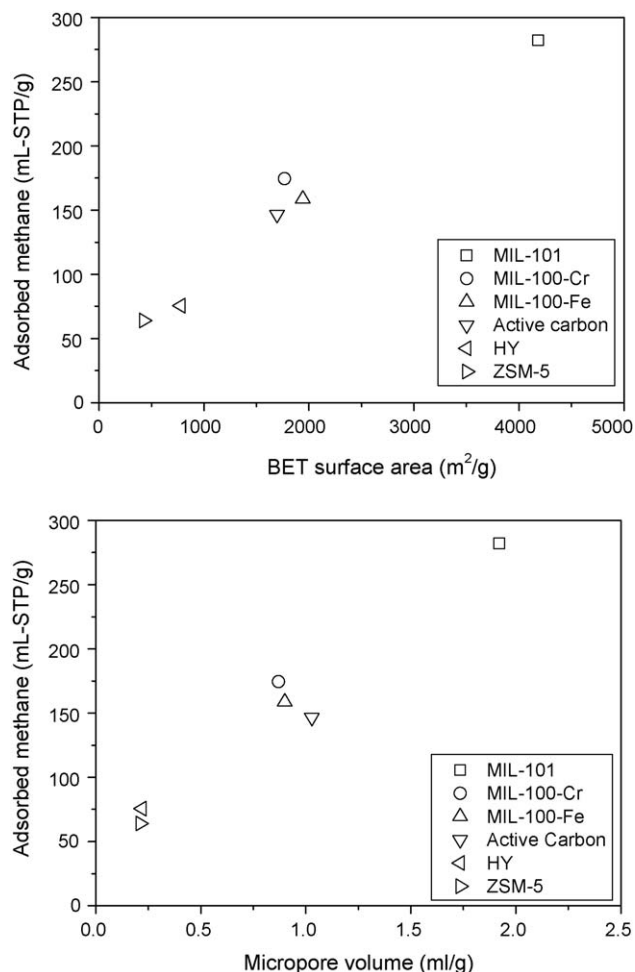


Fig. 3. Dependences of methane adsorption capacities on the BET surface area (upper figure) and micropore volume (lower figure) of the MOFs, zeolites and carbon.

4. Conclusion

Methane adsorption was carried out at high pressure (up to 50 bar) on various MOF materials such as MIL-100-Cr, MIL-100-Fe and MIL-101. The adsorption capacity (at 50 bar) was analyzed based on BET surface area and micropore volume, and following conclusions can be derived from this study.

- Porosity of MOFs such as surface area and pore volume has a dominant role in determining the methane adsorption capacity.
- The chemical composition and structure of MOFs are not important to increase the methane adsorption capacity.
- Therefore, MOFs should have high porosity in order to be applied as commercial adsorbents for natural gas storage via adsorption (ANG).

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