MWCNT@MIL-53 (Cr) Nanoporous Composite: Synthesis, Characterization, and Methane Storage Property

Mansoor Anbia*, Sara Sheykhi
and Roghaye Dehghan

Research Laboratory of Nanoporous Materials, Faculty of Chemistry, Iran University of Science and Technology, Farjam Street, Narmak, Tehran 16846-13114, Iran

(Received 2016.06.10, Accepted 2017.05.14)

Abstract

In this paper, porous metal–organic frameworks (MIL-53 [Cr^{III} (OH).{$O_2C-C_6H_4-CO_2$}.{$HO_2C-C_6H_4-CO_2H$}$_x$]) were hydrothermally synthesized and, then, a hybrid composite of these synthesized porous metal–organic frameworks (MOF) with acid-treated multi-walled carbon nanotubes (MWCNTs) was prepared. The materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer–Emmet–Teller (BET), and FT-IR analysis. The X-ray diffraction patterns showed that the structure of MWCNT@MIL-53-Cr nonoporous composite was not disturbed by incorporation of MWCNT in MIL-53-Cr. N_2 adsorption – desorption analysis showed that the MIL-53-Cr and MWCNT@MIL-53-Cr nanoporous composite had BET surface areas of $1500 m^2.g^{-1}$ and $1347 m^2.g^{-1}$, respectively. These materials were developed as adsorbents for methane storage at room temperature. The analysis showed about 50% increase in methane storage capacity (from 7.1 to 10.8 $mmol.g^{-1}$ at 298K and 35bar) for MWCNT@MIL-53-Cr composite. The increment in the CH_4 adsorption capacity of MWCNT@MIL-53-Cr nanoporous composite is attributed to the increase in micropore volume of MIL-53-Cr by MWCNT incorporation.

Keywords

Metal organic framework;
MIL-53-Cr;
MWCNT;
Acid-treated;
CH_4 storage.

1. Introduction

During the last few years, considerable efforts have been made to develop new fuels technologies to meet transportation energy demand and lower reliance on conventional petroleum-based gasoline. Among the possible fuels, natural gas (NG) is inexpensive and abundant worldwide. Methane, one of the major components of NG, has the highest energy density (per mass) among hydrocarbons because of having the highest hydrogen-to-carbon ratio [1, 2].

Two major classes of porous materials have been traditionally considered for methane storage: zeolites and porous carbon materials [3-6]. Na-

---

* Corresponding Author.
Tel.: +98 21 77240516 / Fax: +98 21 77491204
E-mail: anbia@iust.ac.ir (M. Anbia)

noporous materials have many applications [7-13]. In recent years, a new family of physisorptive materials, porous metal–organic frameworks (MOFs) or coordination polymers in a broader sense, have emerged as promising adsorbents for methane storage [14]. MOFs have been known to have the advantages of reversibility and fast kinetic ability in CH_4 storage behavior.

Recent efforts for the design and synthesis of MOFs with high CH_4 storage capacity at 298K have led to the development of numerous MOF families [15-20]. It is interesting that CH_4 storage at 298K of MOF families increases when they are mixed with activated carbons [21]. Much effort has been devoted to improve MOF gas storage capacities and adopt strategies such as high porosity with appropriate pore size, catenation, and inclusion of open metal sites [22].

It is worth mentioning that HKUST-1 [$Cu_3(btc)_2$, btc = 1,3,5-benzenetricarboxylate], an ionic MOF compound, has been studied by several groups and the methane storage capability of ~160cm^3(STP)cm^{-3} is reported [23]. Also, MIL53-Cr [Cr(OH)(bdc)], MOF compound by Férey's group, has exhibited the methane storage capability of 165cm^3(STP)cm^{-3} at 303K and 35bar [24]. These frameworks have Cr^{2+} sites that become available for interaction with other molecules after removal of H_2O in carbonyl complexes, and can also be easily rehydrated without change in the crystalline nature of the material after exposure to air [25].

In this study, we have prepared and tested CH_4 storage by incorporating multi-walled carbon nanotubes into the crystal system of MOFs. We have found that the newly synthesized hybrid composites exhibit significantly enhanced CH_4 storage capacity at 298K over a wide range of pressures.

2. Experimental Section

2.1. Materials

Chromium (III) nitrate ($Cr(NO_3)_3.9H_2O$) (Aldrich, 97%), terephthalic acid HO_2C-(C_6H_4)-CO_2H (Alfa 97%), and hydrofluoric acid (HF) (Prolabo, 40%) were used as such.

2.2. Synthesis of MIL-53-Cr

For synthesis of MIL-53-Cr, a mixture of chromium (III) nitrate, terephthalic acid, hydrofluoric acid, and H_2O in the molar ratio 1:1:1:280 at autogenous pressure was prepared. 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 493K for 3 days. The pH remained acidic (<1) during the course of the synthesis. A light purple powder together with traces of terephthalic acid was finally obtained. All attempts for getting crystals of MIL-53-Cr were not successful. Then, the MIL-53-Cr solid product was calcined at 300°C under air atmosphere.

2.3. Preparation of MWCNT@MIL-53-Cr

For synthesis of MWCNT@MIL-53-Cr, 10mg/10mL of MWCNTs/DMF with 30mL of DMF containing 4g of pre-dissolved $Cr(NO_3)_39H_2O$ and 1.164g of terephthalic acid were mixed. Then, the mixture was stirred for 24h at room temperature and heated to 220°C in a furnace for 72h without stirring. A purple powder was repeatedly washed with DMF and anhydrous chloroform, and soaked in anhydrous chloroform for 12h. Further steps were as described above for MIL-53-Cr.

2.4. Materials Characterization

The structure of MIL-53-Cr samples was studied by X- Ray diffraction on a Philips 1830 diffractometer with Cu-Kα radiation source. Fourier transform infrared (FT-IR) spectra of the adsorbents were recorded at room temperature on a DIGILAB FTS 7000 spectrometer equipped with an attenuated total reflection (ATR) cell. The nitrogen physical adsorption-desorption isotherms of the samples were measured at 77k using a micromeritics ASAP 2020 analyzer. Specific surface area was obtained using the BET method and pore size distribution was evaluated using the Barrett – Joyner – Halenda (BJH) method. SEM (PHILIPS XL30) was used to study the morphology of products.

2.5. CH_4 adsorption measurement

To investigate the MIL-53-Cr Methane adsorption capacity, volumetric method with the setup shown in Fig. 1 was used. At first, 0.5g 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, we opened the valves of 9, 11 and closed other valves and, then, turned on the vacuum pump and the system was vacuumed along with the heating temperature of 473K for 1.5h. 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, one could calculate the exact pressure decrease because of gas adsorption.

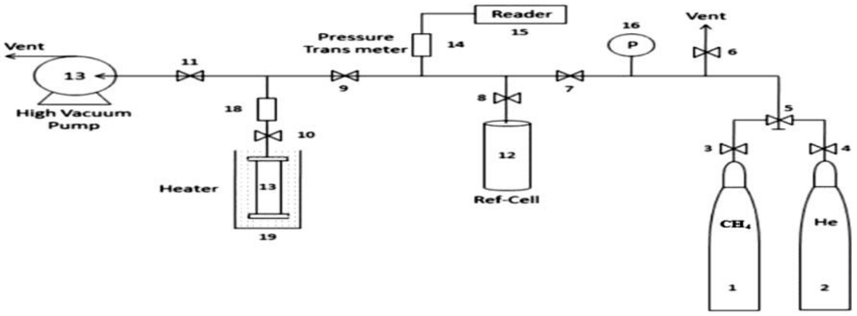

Figure 1. Setup for adsorption capacity test

3. Results and Discussion

3.1. Characterization of MIL-53-Cr

The powder X-ray diffraction patterns of MWCNT@MIL-53-Cr samples showed the same diffraction patterns as MIL-53-Cr (Fig. 2). These patterns were found to be in perfect agreement with earlier data on MIL-53-Cr [24]. This confirms that the structure of MIL-53-Cr was not affected by the MWCNT incorporation.

Fig. 3 shows the N_2 adsorption – desorption isotherms of MWCNT incorporated MIL-53-Cr composite material and MIL-53-Cr at 77K up to 1bar pressure. Both of them revealed a type I adsorption – desorption isotherm characteristic of microporous solids. Structural properties of MWCNT@MIL-53-Cr composite material and MIL-53-Cr are listed in Table 1. The corresponding surface area was estimated to be over $1500m^2.g^{-1}$ and $1347m^2.g^{-1}$ for MIL-53-Cr and MWCNT@MIL-53-Cr, respectively. Decrease in surface area could be due to the decrease in pore width and pore blocking by MWNCT in the pores of MIL-53-Cr.

The SEM images of MIL-53-Cr and MWCNT@MIL-53-Cr composite material are shown in Fig. 4. The morphology of MIL-53-Cr is homogeneous. SEM image of MWCNT@MIL-53-Cr reveals that the MWCNTs are indeed well admixed with MIL-53-Cr. These images indicate that MWCNTs are well incorporated into the MIL-53 crystalites.

4. Conclusions

A novel hybrid composite has been developed; we successfully synthesized a novel hybrid composite designated with CNT@MIL-53-Cr, which showed significant specific surface area enhancement and improvement in CH_4 storage capacity compared with MIL-53-Cr. The approach to incorporation of MWCNTs in high-surface-area metal-organic frameworks and subsequent utilization of the unutilized volume of MOFs presents new direction for achieving novel hybrid materials between two spotlighting materials, such as CNTs and MIL-53-Cr.

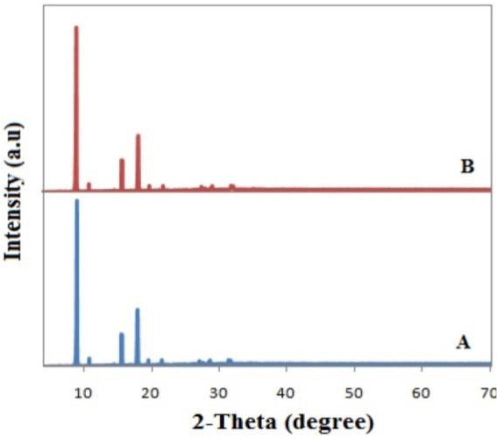

Figure 2. XRD patterns of the MIL-53-Cr (A) and MWCNT@MIL-53-Cr composite material (B)

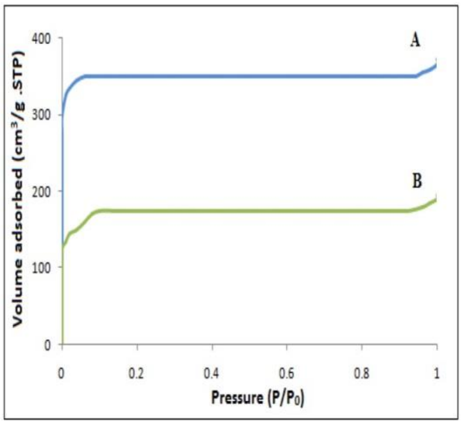

Figure 3. The N_2 adsorption – desorption isotherms of MIL-53-Cr (A) and MWCNT@MIL-53-Cr composite material (B) powders at 77K

Table 1. Textural properties of MIL-53-Cr and MWCNT@MIL-53-Cr composite material

Material	S_{BET}(m^2g^{-1})	S_L(m^2g^{-1})	Reference
MIL-53-Cr	1100	1500	This study
MWCNT@MIL-53-Cr	856	1347	This study

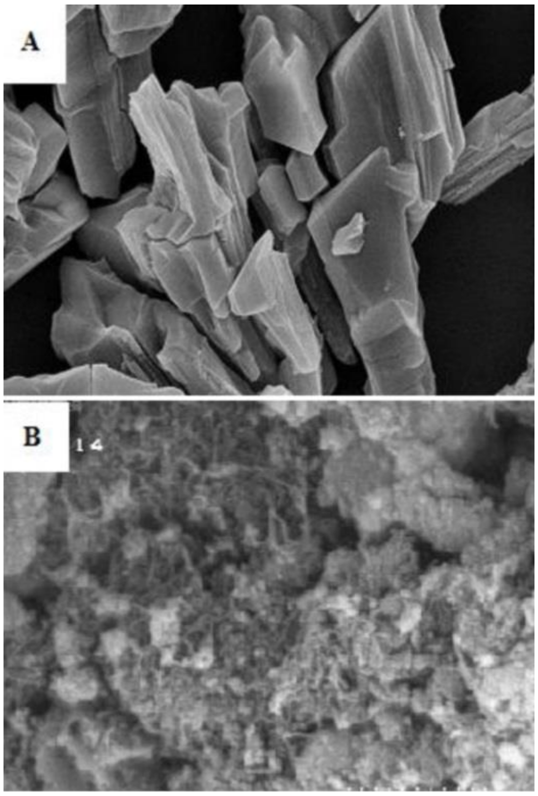

Figure 4. SEM images of MIL-53-Cr (A) and MWCNT@MIL-53-Cr composite material (B)

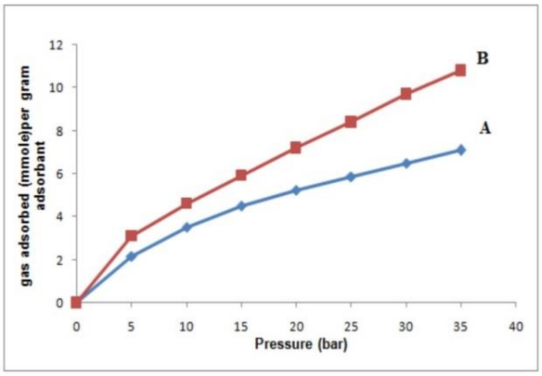

Figure 5. CH_4 adsorption isotherms in MIL-53-Cr (A) and MWCNT@MIL-53-Cr composite material (B) at 298K up to 35bar

Acknowledgment

This work was supported by the Research Laboratory of Nanoporouse Materials, Iran University of Science and Technology.

References

1. 1. Lozano-Castelló, D., Alcaniz-Monge, J., De la Casa-Lillo, M. A., Cazorla-Amorós, D. and

Linares-Solano, A . (2002). “Advances in the study of methane storage in porous carbonaceous materials.” *Fuel*, Vol. 81, pp.1777-1803.

2. 2. Yulong, W., Fei, W., Guohua, L., Guoqing, N. and Mingde, Y. (2008). “Methane storage in multi-walled carbon nanotubes at the quantity of 80 g.” *Materials Research Bulletin*, Vol. 43, pp.1431-1439.
3. Celzard, A. and Fierro, V. (2005). “Preparing a Suitable Material Designed for Methane Storage: A Comprehensive Report.” *Energy & Fuels*, Vol. 19, pp. 573-583.
4. ZareNezhad, B. (2009). “An investigation on the most important influencing parameters regarding the selection of the proper catalysts for Claus SRU converters.” *Journal of Industrial and Engineering Chemistry*, Vol. 15, pp. 143-147.
5. Menon, V.C. and Komarneni, S. (1998). “Porous Adsorbents for Vehicular Natural Gas Storage: A Review.” *Journal of Porous Materials*, Vol. 5, pp. 43-58.
6. Dong, J., Wang, X., Xu, H., Zhao, Q. and Li, J. (2007). "Hydrogen storage in several microporous zeolites.” *International Journal of Hydrogen Energy*, Vol. 32, pp. 4998-5004.
7. Erdogan, F.O. and Kopac, T. (2007). “Dynamic analysis of sorption of hydrogen in activated carbon.” *International Journal of Hydrogen Energy*, Vol. 32, pp. 3448-3456.
8. Anbia, M. and Lashgari, M. (2009). “Synthesis of amino-modified ordered mesoporous silica as a new nano sorbent for the removal of chlorophenols from aqueous media.” *Chemical Engineering Journal*, Vol. 150, pp. 555-560.
9. Anbia, M. and Moradi, S.E. (2009). “Removal of naphthalene from petrochemical wastewater streams using carbon nanoporous adsorbent.” *Applied Surface Science*, Vol. 255, pp. 5041-5047.
10. Anbia, M. and Moradi, S.E. (2009). "Adsorption of naphthalene-derived compounds from water by chemically oxidized nanoporous carbon.” *Chemical Engineering Journal*, Vol. 148, pp. 452-458.
11. Anbia, M. and Hoseini, V. (2012). “Enhancement of CO 2 adsorption on nanoporous chromium terephthalate (MIL-101) by amine modification.” *Journal of Natural Gas Chemistry*, Vol. 21, pp. 339-343.
12. Anbia, M., Hoseini, V. and Sheykhi, S. (2012). “Sorption of methane, hydrogen and carbon dioxide on metal – organic framework, iron terephthalate (MOF-235).” *Journal of Industrial and Engineering Chemistry*, Vol. 18, pp. 1149-1152.
13. Anbia, M., Mohammadi, N. and Mohammadi, K. (2010). “Fast and efficient mesoporous adsorbents for the separation of toxic compounds from aqueous media.” *Journal of hazardous materials*, Vol. 176, pp. 965-972.
14. Zhou, W. (2010). “Methane storage in porous metal – organic frameworks: current records and future perspectives.” *The Chemical Record*, Vol. 10, pp. 200-204.
15. Klontzas, E., Mavrandonakis, A., Tylianakis, E. and Froudakis, G. E . (2008). “Improving hydrogen storage capacity of MOF by functionalization of the organic linker with lithium atoms.” *Nano letters*, Vol. 8, pp. 1572-1576.
16. Kesanli, B., Cui, Y., Smith, M. R., Bittner, E. W., Bockrath, B. C. and Lin, W . (2005). “Highly interpenetrated metal – organic frameworks for hydrogen storage.” *Angewandte Chemie International Edition*, Vol. 44, pp. 72-75.
17. Zhou, W., Wu, H., Hartman, M. R. and Yildirim, T . (2007). “Hydrogen and methane adsorption in metal-organic frameworks: a high-pressure volumetric study.” *The Journal of Physical Chemistry C.*, Vol. 111, pp. 16131-16137.

18. Ma, S., Sun, D., Simmons, J. M., Collier, C. D., Yuan, D. and Zhou, H. C. (2008). “Metal – organic framework from an anthracene derivative containing nanoscopic cages exhibiting high methane uptake.” *Journal of the American Chemical Society*, Vol. 130, pp. 1012-1016.

19. Wang, X.-S., Ma, S., Rauch, K., Simmons, J. M., Yuan, D., Wang, X . and Zhou, H. C . (2008). “Metal – Organic Frameworks Based on Double-Bond-Coupled Di-Isophthalate Linkers with High Hydrogen and Methane Uptakes.” *Chemistry of Materials*, Vol. 20, pp. 3145-3152.

20. Wu, H., Zhou, W. and Yildirim, T. (2009). “High-capacity methane storage in metal – organic frameworks M2 (dhtp): The important role of open metal sites.” *Journal of the American Chemical Society*, Vol. 131, pp. 4995-5000.

21. Lee, J.S., Jhung, S. H., Yoon, J. W., Hwang, Y. K. and Chang, J. S . (2009). “Adsorption of methane on porous metal carboxylates.” *Journal of Industrial and Engineering Chemistry*, Vol. 15, pp. 674-676.

22. Rowsell, J.L. and Yaghi, O.M. (2005). “Strategies for hydrogen storage in metal – organic frameworks.” *Angewandte Chemie International Edition*, Vol. 44, pp. 4670-4679.

23. Senkovska, I. and Kaskel, S. (2008). “High pressure methane adsorption in the metal – organic frameworks Cu 3 (btc) 2, Zn 2 (bdc) 2 dabco, and Cr 3 F (H 2 O) 2 O (bdc) 3.” *Microporous and Mesoporous Materials*, Vol. 112, pp. 108-115.

24. Serre, C., Millange, F., Thouvenot, C., Noguès, M., Marsolier, G., Louër, D. and Férey, G . (2002). “Very Large Breathing Effect in the First Nanoporous Chromium (III)-Based Solids: MIL-53 or CrIII (OH)⊙{O2C-C6H4-CO2}⊙{HO2C-C6H4-CO2H} x⊙ H2O y.” *Journal of the American Chemical Society*, Vol. 124, pp. 13519-13526.

25. Prestipino, C., Regli, L., Vitillo, J. G., Bonino, F., Damin, A., Lamberti, C. and Bordiga, S . (2006). “Local structure of framework Cu (II) in HKUST-1 metallorganic framework: spectroscopic characterization upon activation and interaction with adsorbates.” *Chemistry of materials*, Vol. 18, pp. 1337-1346.