Asian Journal of Chemistry; Vol. 25, No. 2 (2013), 1137-1139

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13743

Synthesis of Metal-Organic Frameworks and Comparative Study of CO_2 and SO_2 Adsorption Properties

YU-PING HU[1,2], CHUN-PING TAN[3], SHUANG-FEI WANG[1,*] and XIAO-BO MENG[2]

[1]Institute of Light Industry and Food Engineering of Guangxi University, Nanning, P.R. China
[2]Guangxi University for Nationalities, Guangxi Key Laboratory of Chemistry and Biological Transforming Process, University of Guangxi, Guangxi Key Laboratory of Chemical and Engineering of Forest Products, Nanning, P.R. China
[3]Yongjiang University, Nanning, P.R. China

*Corresponding author: Fax: +86 771 3264900; Tel: +86 771 2173625; E-mail: yphu2001@163.com

(*Received*: 16 March 2012; *Accepted*: 31 August 2012) AJC-12060

In this work, porous aluminum-trimesate (MIL-96), one of the metal-organic frameworks, has been synthesized at 210 ºC for 24 h. The MIL-96 adsorbs nitrogen readily at liquid nitrogen temperature to show permanent porosity (S_{BET} = 507 m^2/g, $S_{Langmuir}$ = 668 m^2/g). The thermogravimetric analysis shows that the material is stable up to 350 ºC. CO_2 and SO_2 are adsorbed over the synthesized MIL-96 in the pressure of 0-50 bar at 40 ºC. The experimental results show that CO_2 saturated adsorption amount on MIL-96 at 40 ºC is up to 5-25 mmol/g, is far superior to SO_2 on the same conditions. Adsorption experimental results of SO_2 on MIL-96 at various temperatures show that the adsorption capacity increases with temperature increases. Very interestingly, the saturated adsorption amount at 100 ºC is less than the one at 80 ºC, which may be explained that water vapour molecules hinder SO_2 adsorption.

Key Words: MIL-96, Synthesis, Adsorption properties, CO_2 and SO_2.

INTRODUCTION

Warming for the global environmental problem is recognized by the international community, CO_2 is the biggest greenhouse gas contributions to global warming[1]. In the 1970-2004 periods, annual CO_2 emission is from 21 billion tons to 38 billion tons. Since the mid-20th century, the frequency of occurrence of extreme weather is increased 70 in the 1990s from 10 in the 1950s[2].The average annual economic loss caused by extreme weather increased approximately $400 billion in the 1990s from $40 billion to in the 1950s[3]. With the rapid economic development, environment is becoming seriously in Guangxi Province, China. In 2009[4], SO_2 emission in Guangxi Province is 890, 500 tons. And sulfur dioxide emissions increased by 13.68 in the first half of 2010[5]. Guangxi Province is one of the provinces of the growth of SO_2 emission in China. Therefore, CO_2 and SO_2 capture has become one of the focus of attention of governments and researchers in China.

The authors try to control the synthesis of new metal-organic frameworks materials by the method of proliferation and use the material as an efficient scavenger of CO_2 and SO_2.

EXPERIMENTAL

Aluminum nitrate [$Al(NO_3)_3{\cdot}9H_2O$], AR, Shanghai Chemical Reagent Company of China National Pharmaceutical Group (SCRC)); 1,3,5-benzene tricarboxylic acid ($C_6H_3(CO_2H)_3$, AR, Shanghai Notai Chemical Co. Ltd., noted H_3btc); trimethyl 1,3,5-benzenetricarboxylate ($C_6H_3(CO_2CH_3)_3$, AR, Shanghai Notai Chemical Co. Ltd., or Me_3btc); diluted hydrofluoric acid (HF, AR, SCRC); tetraethylortho silicate [$Si(OC_2H_5)_4$, AR, SCRC].

Synthesis: The reaction mixture containing the molar ratio: $Al(NO_3)_3{\cdot}9H_2O$ (3.5 mmol, 1.314 g)/0.14 1,3,5-benzene tricarboxylic acid (0.5 mmol, 0.105 g)/80 H_2O (278 mmol, 5 mL) was placed in a 23 mL Teflon-lined steel Parr autoclave at 210 ºC for 24 h. The pH of synthesis was 1. After the hydrothermal treatment, a powdered product was obtained, which was filtered off, washed with deionized water and dried in air at room temperature.

CO_2 and SO_2 adsorption: The synthesized aluminium trimesate (MIL-96) was acted as adsorbent. The samples (*ca.* 0.1 g) were dehydrated at 150 ºC under high vacuum (less than 1μ Torr) and purified before adsorption. Then the samples were put into the sample cell in the protection of inert gas of high-pressure gas adsorption and desorption analyzer (PCTPro2000, Setaram). The apparatus used for experiments is able to measure both CO_2 and SO_2 adsorption isotherm in the pressure region from vacuum to 200 bar and in temperature region from 260 to 500 ºC.

The nitrogen adsorption/desorption isotherms were obtained at -196 ºC with an adsorption analyzer (Micromeritics, USA, Tristar 3000) after evacuation at 150 ºC for 18 h. The surface area was calculated from nitrogen adsorption isotherms using the BET and Langmuir equations. Thermogravimetric analysis pattern of MIL-96 was obtained under the air flow using the thermogravimetric analyzer (Mettler Toledo, TGA/DSC1).

RESULTS AND DISCUSSION

The surface area (Fig. 1) illustrates the nitrogen adsorption and desorption isotherms obtained at liquid nitrogen temperature. The isotherms show a typical type-I pattern, confirming the microporosity of the MIL-96. The BET and Langmuir surface areas, calculated from the adsorption isotherm, are around 507 and 668 m^2/g, respectively, illustrating the permanent porosity of MIL-96. The absence of hysteresis between adsorption and desorption isotherms confirms that nitrogen desorbs very readily.

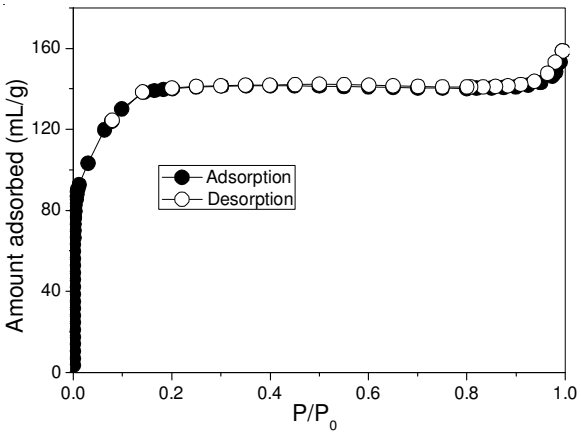

Fig. 1. 77.3 K Nitrogen adsorption and desorption isotherms of the synthesized MIL-96

The thermogravimetric analysis pattern shows a two-step weight loss. The first event is assigned to the continuous removal of water. It corresponds to 20 % at 200 ºC. The second weight loss is attributed to the decomposition of the structure at 350 up to 580 ºC. The MIL-96 structure is stable upon water removal and collapsed at 350 ºC. It is similar to the reported one 6.

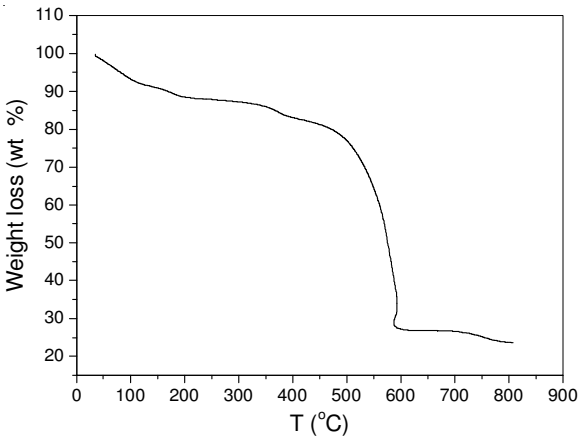

Fig. 2. Thermogravimetric analysis curves of the synthesized MIL-96

Comparison of CO_2 and SO_2 adsorption: As shown in Fig. 3, the adsorption performance of CO_2 is far superior to SO_2 on the same conditions. The experimental results show that CO_2 adsorption capacity on MIL-96 at 40 ºC is up to 5-25 mmol/g. The above-mentioned behaviour can be explained by the very small apertures of the pores. Carbon dioxide may be able to enter the apertures due to its smaller molecular. The adsorption of SO_2 is partly hindered by its dimension is close to that of the pore apertures.

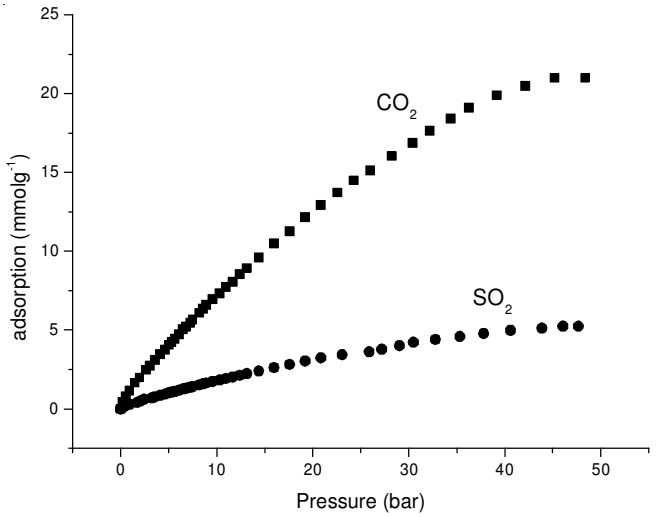

Fig. 3. Isotherms obtained for the adsorption of CO_2 and SO_2 on MIL-96 at 40 ºC

SO_2 adsorption: Experimental results show that the adsorption of SO_2 on MIL-96 reaches saturation after 7 h at 40 ºC and the saturated absorption amount is 2.31 mmol/g. However, it only takes 4 h to reach saturation, the amount increase 5.15 mmol/g. The results can be explained that, as the temperature increased, velocity of SO_2 molecular becomes faster. Thus, as temperature increases, the adsorption rate increases, the adsorption capacity increases and time-consuming to reduce.

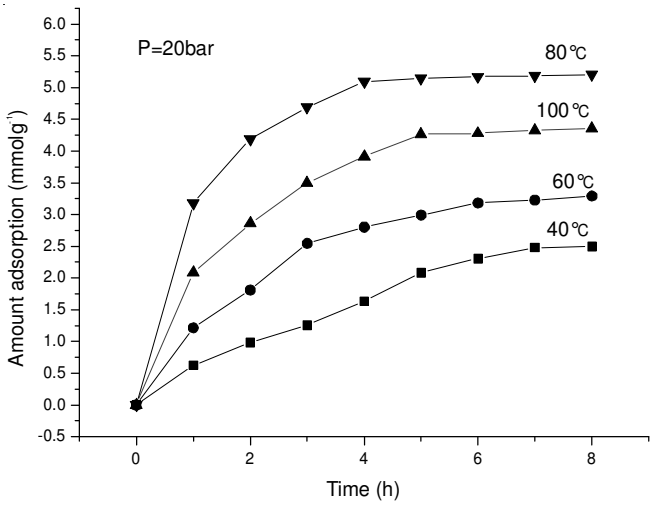

Fig. 4. Adsorption amount of SO_2 on MIL-96 at various temperatures

Interestingly, the saturated adsorption amount is 4.27 mmol/g at 100 ºC. It is less than the one at 80 ºC (5.15 mmol/g),

but the adsorption time at 100 ºC is slightly longer than that at 80 ºC. Because the water molecules are evapourated out from the surface of MIL-96 aperture and it is the water vapour molecules that are not conducive to adsorption of SO_2 molecules on the surface of MIL-96 aperture.

Conclusion

(1) The BET and Langmuir surface areas are around 507 and 668 m^2/g respectively from the nitrogen adsorption isotherm.

(2) The thermogravimetric analysis (TGA) pattern shows that the MIL-96 structure is stable upon water removal and collapsed at 350 ºC.

(3) On the same conditions the adsorption performance of CO_2 is far superior to SO_2. Because carbon dioxide may be able to enter the apertures due to its smaller molecular.

(4) The adsorption capacity increases with temperature increases. Interestingly, the saturated adsorption amount at 100 ºC is less than the one at 80 ºC, which may be explained that water vapour molecules hinder SO_2 adsorption.

ACKNOWLEDGEMENTS

This research is supported by the Research Foundation of Guangxi University for Nationalities (2011MDYB041), the Research Foundation of University of Guangxi Province (201203YB061) and National Natural Science Foundation of China (21267003).

REFERENCES

1. United Nations Intergovernmental Panel on Climate Change (IPCC), Climate Change, Comprehensive Report, (2007).
2. http://www.mnp.nl/en/dossiers/Climatechange/moreinfo/Chinanownol in CO_2 emission susain second position.html.
3. United Nations Intergovernmental Panel on Climate Change (IPCC), Climate Change, Impacts, Adaptation and Vulnerability, (2001).
4. http://www.gxepb.gov.cn/xxgkml/ztfl/hjzljc/hjzkgb/201006t20100612_930134.html
5. http://www.gxepb.gov.cn/xxgkml/ztfl/hjzljc/hjzkgb/201106/t20110603_4376.html
6. T. Loiseau, L. Lecroq, C. Volkringer, J. Marrot, G. Ferey, M. Haouas, F. Taulelle, S. Bourrelly, P.L. Llewellyn and M. Latroche, *J. Am. Chem. Soc*., **128**, 10223 (2006).