Synthesis of Metal-Organic Frameworks and Comparative Study of CO₂ and SO₂ Adsorption Properties

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In this work, porous aluminum-trimesate (MIL-96), one of the metal-organic frameworks, has been synthesized at 210 °C for 24 h. The MIL-96 adsorbs nitrogen readily at liquid nitrogen temperature to show permanent porosity ($S_{\text{BET}} = 507 \text{ m}^2/\text{g}$, $S_{\text{Langmuir}} = 668 \text{ m}^2/\text{g}$). The thermogravimetric analysis shows that the material is stable up to 350 °C. CO₂ and SO₂ are adsorbed over the synthesized MIL-96 in the pressure of 0-50 bar at 40 °C. The experimental results show that CO₂ saturated adsorption amount on MIL-96 at 40 °C is up to 5-25 mmol/g, is far superior to SO₂ on the same conditions. Adsorption experimental results of SO₂ on MIL-96 at various temperatures show that the adsorption capacity increases with temperature increases. Very interestingly, the saturated adsorption amount at 100 °C is less than the one at 80 °C, which may be explained that water vapour molecules hinder SO₂ adsorption.

Key Words: MIL-96, Synthesis, Adsorption properties, CO₂ and SO₂.

INTRODUCTION

Warming for the global environmental problem is recognized by the international community, CO₂ is the biggest greenhouse gas contributions to global warming¹. In the 1970-2004 periods, annual CO₂ 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 1950s². The average annual economic loss caused by extreme weather increased approximately \$400 billion in the 1990s from \$40 billion to in the 1950s³. With the rapid economic development, environment is becoming seriously in Guangxi Province, China. In 2009⁴, SO₂ emission in Guangxi Province is 890, 500 tons. And sulfur dioxide emissions increased by 13.68 in the first half of 2010⁵. Guangxi Province is one of the provinces of the growth of SO₂ emission in China. Therefore, CO₂ and SO₂ 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 CO₂ and SO₂.

EXPERIMENTAL

Aluminum nitrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], AR, Shanghai Chemical Reagent Company of China National Pharmaceutical

Group (SCRC)); 1,3,5-benzene tricarboxylic acid ($\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$, AR, Shanghai Notai Chemical Co. Ltd., noted H₃btc); trimethyl 1,3,5-benzenetricarboxylate ($\text{C}_6\text{H}_3(\text{CO}_2\text{CH}_3)_3$, AR, Shanghai Notai Chemical Co. Ltd., or Me₃btc); diluted hydrofluoric acid (HF, AR, SCRC); tetraethylortho silicate [$\text{Si}(\text{OC}_2\text{H}_5)_4$, AR, SCRC].

Synthesis: The reaction mixture containing the molar ratio: $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (3.5 mmol, 1.314 g)/0.14 1,3,5-benzene tricarboxylic acid (0.5 mmol, 0.105 g)/80 H₂O (278 mmol, 5 mL) was placed in a 23 mL Teflon-lined steel Parr autoclave at 210 °C 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.

CO₂ and SO₂ adsorption: The synthesized aluminium trimesate (MIL-96) was acted as adsorbent. The samples (*ca.* 0.1 g) were dehydrated at 150 °C under high vacuum (less than 1 μ 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 CO₂ and SO₂ adsorption isotherm in the pressure region from vacuum to 200 bar and in temperature region from 260 to 500 °C.

The nitrogen adsorption/desorption isotherms were obtained at -196°C with an adsorption analyzer (Micromeritics, USA, Tristar 3000) after evacuation at 150°C 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 $668\text{ m}^2/\text{g}$, 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°C . The second weight loss is attributed to the decomposition of the structure at 350 up to 580°C . The MIL-96 structure is stable upon water removal and collapsed at 350°C . 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°C is up to $5\text{--}25\text{ mmol/g}$. 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°C

SO_2 adsorption: Experimental results show that the adsorption of SO_2 on MIL-96 reaches saturation after 7 h at 40°C 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°C . It is less than the one at 80°C (5.15 mmol/g),

but the adsorption time at 100 °C is slightly longer than that at 80 °C. Because the water molecules are evaporated out from the surface of MIL-96 aperture and it is the water vapour molecules that are not conducive to adsorption of SO₂ molecules on the surface of MIL-96 aperture.

Conclusion

(1) The BET and Langmuir surface areas are around 507 and 668 m²/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 °C.

(3) On the same conditions the adsorption performance of CO₂ is far superior to SO₂. 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 °C is less than the one at 80 °C, which may be explained that water vapour molecules hinder SO₂ adsorption.

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