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Adsorption of CH_4 and CO_2 on Zr-metal organic frameworks

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ABSTRACT

Zirconium-metal organic frameworks (Zr-MOFs) were synthesized with or without ammonium hydroxide as an additive in the synthesis process. It was found that addition of ammonium hydroxide would change the textural structure of Zr-MOF. The BET surface area, pore volume, and crystal size of Zr-MOF were reduced after addition of ammonium hydroxide. However, the crystalline structure and thermal stability were maintained and no functional groups were formed. Adsorption tests showed that Zr-MOF presented much higher CO_2 adsorption than CH_4. Zr-MOF exhibited CO_2 and CH_4 adsorption of 8.1 and 3.6 mmol/g, respectively, at 273 K, 988 kPa. The addition of ammonium hydroxide resulted in the Zr-MOF with a slight lower adsorption of CO_2 and CH_4, however, the selectivity of CO_2/CH_4 is significantly enhanced.

1. Introduction

Carbon dioxide (CO_2) and methane (CH_4) are major greenhouse gases. In the past decades, the level of CO_2 and CH_4 in the atmosphere has significantly increased. Capture of CO_2 and CH_4 from their emission sources is important to control their emissions into the atmosphere. In some cases, separation of CO_2 and CH_4 is also important in their utilization [1–3]. The coexistence of CO_2 with CH_4 in natural gas processing can produce pipeline problem. Landfill gas also contains mainly CO_2 and CH_4. Thus, separation of CO_2 from CH_4 is critical for the application of CH_4.

Metal organic frameworks (MOFs) have been increasingly attracted as novel microporous materials in applications of adsorption, separation, and catalysis [4–8]. It has been generally believed that MOFs are formed due to the coordination bonds between metal salt and multidentate ligands. This reaction relies on the reagents and the synthesis parameters such as solvent composition, temperature, pressure, additives, and pH [9,10]. In the past decades, a lot of MOFs have been designed and synthesized; however, most of MOFs suffer from low hydrothermal stability.

Recently, a Zr-MOF (UiO-66) was synthesized by Cavka et al. [11] and it exhibits high hydrothermal stability up to 773 K. Several other researchers have further investigated the modification and functionalization of UiO-66 [12,13]. Chavan et al. [12] reported an insertion of (arene) $Cr(CO)_3$ species in UiO-66 and its photoinduced reactivity. Kandiah et al. [13] reported a synthesis of tagged UiO-66 using three different linker ligands, $H_2N–H_2BDC$, $O_2N–H_2BDC$, and $Br–H_2BDC$. The results demonstrated that incorporating active functional groups into the UiO-66 structure would not affect thermal and chemical stability. However, few investigations of UiO-66 in gas adsorption have been reported.

We have investigated the synthesis of UiO-66 using solvent exchange activation process to enhance porous structure and its application in H_2 and CO_2 adsorption [14]. In this paper, we report the synthesis of Zr-MOF with addition of ammonium hydroxide in synthesis solution and the effects of the additive on the structure and adsorption behavior in CH_4 and CO_2 adsorption.

2. Experimentals

2.1. Synthesis of Zr-MOFs

All chemicals including DMF (Dimethylformamide 99%), BDC (Benzene-1,4-dicarboxylic acid, 98.9%), chloroform (99%), NH_4OH (24%), and $ZrCl_4$ were supplied by Sigma–Aldrich, Thermo Fisher Scientific, and Perth Scientific and were used without further purification.

Zr-MOF was synthesized following the procedure reported by Cavka et al. [11] with some amendments. Generally, 2.27 mmol of $ZrCl_4$, 2.27 mmol of BDC were mixed together in 405.38 mmol of DMF for 30 min, then the homogenous mixture was placed inside a Parr PTFE-lined digestion vessel of 45 mL. The autoclave was placed in an oven preheated to 120 °C for 24 h.

In preparation of NH_4OH modified Zr-MOF, the solvent (DMF) was divided into two parts at 202.69 mmol each. In the first solution, BDC was added in and stirred for 15 min, then 0.4 mmol NH_4OH was added in dropwise under stirring. The second DMF solution was mixed with $ZrCl_4$ for stirring about 30 min. Then the two solutions were mixed together and stirred for 20 min.

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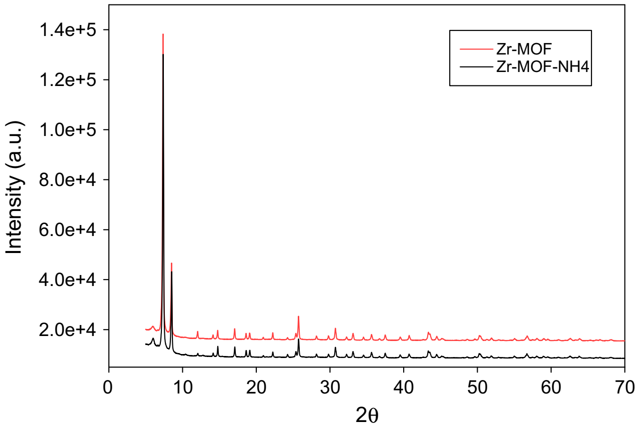

Fig. 1. XRD patterns of Zr-MOF and Zr-MOF-NH4 samples.

The resulted solution was placed in the autoclave at 393 K for 24 h. This Zr-MOF was referred as Zr-MOF-NH4.

After synthesis, the above crystalline materials were immersed inside chloroform solution for 5 d and then the solids were filtered and dried in vacuum. Finally, these materials were heated in an oven at 463 K overnight.

2.2. Characterizations of Zr-MOFs

Thermal stability of Zr-MOFs was checked by a thermogravimetric analysis (TGA) instrument (TGA/DSC1 STAR^{e} system-METTLER TOLEDO). Zr-MOF samples were loaded into a pan and heated to 1173 K at a rate of 5 K/min. The air gas flow rate was maintained at 10 mL/min. FTIR spectra (Spectrum 100-FT-IR Spectrometer, Perkin-Elmer) were obtained to check the stability of the functional groups on the organic ligands. The spectrum was scanned from 600 to 4000 cm^{-1} with a resolution of 4 cm^{-1} by using an attenuated total reflectance (ATR) technique.

SEM analysis (Zeiss NEON 40 EsB CrossBeam) was used to capture and determine the morphologies of the crystalline Zr-MOF samples. X-ray powder diffraction patterns were obtained with an X-ray diffractometer (D8 Advance-Bruker aXS) using Cu Kα radiation (λ = 1.5406 Å), with accelerating voltage and current of 40 kV and 40 mA, respectively. A Quantachrome instrument (Autosorb-1) was used to determine N$_2$ isotherms as well as the

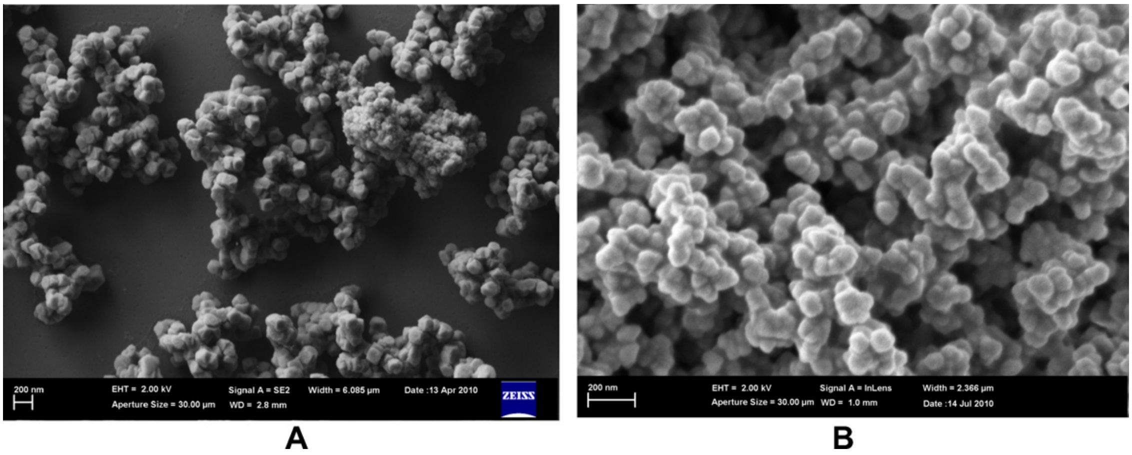

Fig. 2. SEM Images of Zr-MOF synthesized without additives (A) and with NH$_4$OH as an additive (B).

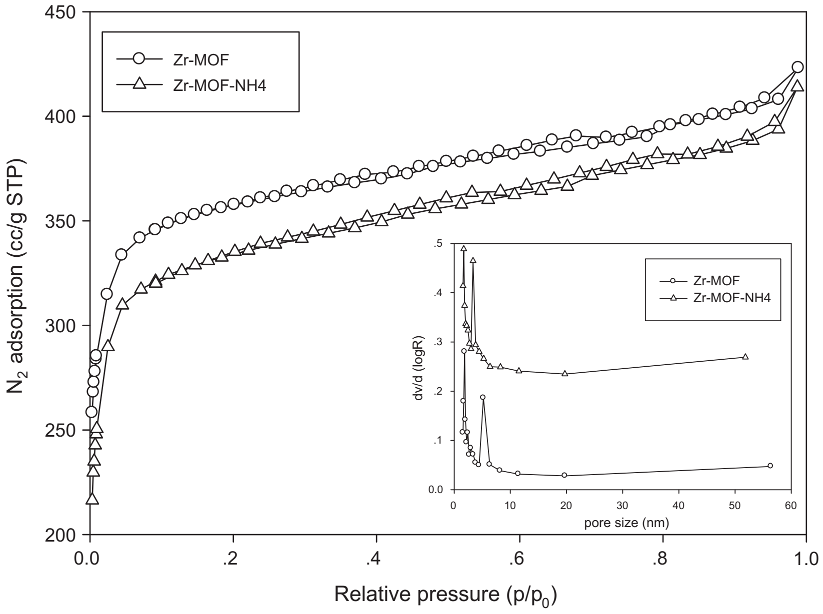

Fig. 3. N$_2$ adsorption and pore size distribution of Zr-MOF samples.