Amino-functionalized Zr-MOF nanoparticles for adsorption of CO₂ and CH₄

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Amino-functionalized Zr-MOF (amino-Zr-MOF) was synthesized using 2-aminoterephthalic acid as an organic linker. The physicochemical properties of the material were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and N₂ adsorption to understand its crystalline structure, morphology, thermal stability, and porous structure. CO₂ adsorption isotherms on amino-Zr-MOF were obtained at 1 atm and at different temperatures. In addition, CO₂ and CH₄ adsorption at high pressure (up to 10 atm) was also measured. CO₂ adsorption capacity on amino-Zr-MOF was 9 mmol/g at 988 kPa, 0°C, while CH₄ adsorption capacity was 3.7 mmol/g at 900 kPa, 0°C. The heat of CO₂ adsorption on amino-Zr-MOF was estimated to be 29.4 kJ/mol. Continuous column tests of CO₂ adsorption were performed at different concentrations of CO₂ in nitrogen at 20 mL/min and 0.7 g adsorbent and total adsorbed amounts of CO₂ within the column during the breakthrough time were calculated to be 4.55, 5.26 and 4.37 mmol/g at 10%, 15% and 20% CO₂, respectively.

Keywords: Zr-MOF; amino-Zr-MOF; carbon dioxide; methane; adsorption

1. Introduction

Over the last few decades, carbon dioxide removal technologies from industrial emissions have been dependent on traditional methods, absorption and adsorption, which are very expensive and energy intensive due to low capacity and selectivity of materials [1]. Metal organic frameworks (MOFs) as new emerging porous materials have been investigated to be alternative adsorbents for various industrial and environmental applications [2]. The applications of MOFs have covered several areas, including gas purification and separation [3], gas storage [4], drug delivery [5], and catalysis [6,7]. Unprecedentedly, MOFs have many characteristics such as the ability to be designed with required specifications, high rigidity and flexibility to be functionalized, and exceptional low density [8]. The synthesis of MOFs can result in a robust extended framework with permanent porosity and these porosities may be fulfilled when the molecular building nets are connected by strong bonds [9,10]. Previously, some transition metals have been used in the synthesis of MOFs, but priority is given to Zn and Al [2,11].

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Zirconium oxide (ZrO$_2$) has stable properties and the nature of zirconium atom connection with oxygen [12] makes it attractive in the synthesis of MOFs. Moreover, it was observed that the synthesis of organic ligand of this framework could be controlled to get several Zr-MOFs (UiO-66, UiO-67, and UiO-68) [13]. Modification and application of Zr-MOFs have also been reported. Recently, Kandiah et al. [14] synthesized Zr-MOF (UiO-66) with different functional groups by using different linker ligands, such as H$_2$N–H$_2$BDC, O$_2$N–H$_2$BDC, and Br–H$_2$BDC. Silva et al. [15] used both UiO-66 and UiO-66–NH$_2$ as photocatalysts for hydrogen generation, while Vermmortele et al. [16] selected amino-UiO-66 for the cross-aldol condensation. These researchers used different procedures and molar ratios in the synthesis of amino-modified Zr-MOF. However, few investigations have been reported in Zr-MOF application for CH$_4$ and CO$_2$ adsorption [17].

In this work, an amino-functionalized Zr-MOF (amino-Zr-MOF) sample was synthesized by using a different precursor ratio and activation process at various temperatures. The main work focused on the characteristics of this material and its application for CO$_2$ and CH$_4$ adsorption. Carbon dioxide adsorption capacity was determined at both low and high pressures, while methane adsorption capacity was obtained at high pressure. Continuous column tests were also carried out for CO$_2$ adsorption.

2. Experimental

2.1. Chemicals

All chemicals including 2-aminoterephthalic acids (NH$_2$–BDC, 99%), terephthalic acid (BDC, 99.8%), zirconium chloride (ZrCl$_4$, 99.9%), dimethylformamide (DMF, 98%), methanol (CH$_3$OH, 99%) and chloroform (CHCl$_3$, 99.98%) were supplied by Sigma-Aldrich (Sydney, NSW, Australia) without further purification.

2.2. Synthesis and activation

Synthesis of Zr-MOF (UiO-66) follows a reported procedure [13]. In detail, 0.053 g of ZrCl$_4$ (0.227 mmol) and 0.034 g of 1,4-benzenedicarboxylic acid (H$_2$BDC, 0.227 mmol) were dissolved in 24.9 g of N,N-dimethylformamide (DMF, 340 mmol) at room temperature. The solution was placed in an autoclave of 45 mL and placed in a preheated oven at 120$^\circ$C for 24 h. The final product was activated by immersing in chloroform for 4 d and then dried and heated under vacuum at 190$^\circ$C overnight. This activation process was found to enhance the surface area and carbon dioxide adsorption [17].

In a typical procedure to synthesize amino-Zr-MOF (amino-UiO-66), 1.47 g (6.31 mmol) of ZrCl$_4$ was dissolved in 15 mL DMF solution and stirred for around 20 min. Meanwhile, 1.06 g (5.85 mmol) of NH$_2$–BDC was dissolved in 68 mL DMF solution and stirred for 30 min. Then, the two prepared solutions were mixed and placed in an autoclave of 125 mL. The sealed autoclave was then placed in an oven at 120$^\circ$C for 48 h. Finally, the greenish yellow crystalline product was extracted from the solution by vacuum filtration. The crystalline product was activated by immersing in methanol for 5 d, and then it was filtered, dried and heated under vacuum at 200$^\circ$C or 300$^\circ$C for 12 h. Methanol activation could remove the non-coordinated amino-BDC from the pores.

2.3. Characterization of materials

A Perkin-Elmer 100 FT-IR spectrometer was used to investigate functional groups of crystalline materials. Scans were conducted from 650 to 4000 cm$^{-1}$ with a resolution of
4 cm\(^{-1}\) using a universal ATR-Diamond/ZnSe as infrared (IR) detector. Hydrothermal stability of the crystalline structure was checked by a TGA instrument (TGA/DSC1 STAR\(^{\circ}\) system-METTLER TOLEDO, Columbus, OH, USA). A sample of 10 mg was loaded into an alumina pan and placed automatically in the TGA furnace for heating. Argon gas is then supplied into the furnace at a flow rate of 20 mL/min and the heating rate was 10\(^{\circ}\)C/min from 35\(^{\circ}\)C to 900\(^{\circ}\)C. X-ray powder diffraction patterns were measured on an X-ray diffractometer (D8 Advanced Bruker Axs, Karlsruhe, Germany) with a transmission mode using Cu \(K\alpha\) radiation at \(2\theta = 5–70\^\circ\) to evaluate the stability of the crystalline structure. \(N_2\) physisorption measurements were carried out on a Quantachrome instrument (Autosorb-1, Boynton Beach, FL, USA) at \(-196\^\circ\)C. The surface area was obtained by the Brunauer-Emmett-Teller (BET) method and pore size distribution was determined by the Barrett-Joyner-Halenda (BJH) method. In general, 15 mg of samples were degassed at 200\(^{\circ}\)C under vacuum for 6 h and then the sample was used for adsorption/desorption measurement on the same instrument. The morphology of materials, including the shape and the size of crystals, was determined by a SEM (Zeiss NEON 40 EsB CrossBeam, North Billerica, MA, USA) with high resolution.

2.4. Adsorption at low pressure

A static volumetric technique with an apparatus of Micromeritics (Gemini I-2360, Norcros, GA, USA) was used to determine the adsorption isotherm of CO\(_2\) (99.995\%) at 0\(^{\circ}\)C and 23\(^{\circ}\)C, respectively, under pressure up to 100 kPa. In each test, about 0.3 g of amino-Zr-MOF was degassed by Vacprep 061 (Micromeritics, Norcros, GA, USA) overnight at 200\(^{\circ}\)C under vacuum. The heat of CO\(_2\) adsorption was calculated from the Clausius–Clapeyron equation relying on the data of adsorption isotherms that were measured at different temperatures by the Gemini I-2360.

2.5. Adsorption at high pressure

A Micromeritics-ASAP2050 was used to measure the adsorption isotherms of carbon dioxide (99.995\%) and methane (99.995\%) at high pressure up to 1000 kPa. A sample was first degassed on the same instrument by increasing the temperature to 100\(^{\circ}\)C at a heating rate of 10\(^{\circ}\)C/min and held at this temperature for 2 h. Then, the temperature was increased again at the same heating rate to 200\(^{\circ}\)C under vacuum (up to 0.4 kPa) and held at these conditions for 8 h. Finally, the degassed sample was used for the analysis at 0\(^{\circ}\)C.

2.6. Breakthrough experiments of CO\(_2\) adsorption

CO\(_2\) capture in a continuous column was tested by setting up breakthrough experiments. A mixture of N\(_2\) (99.999\%) and CO\(_2\) (99.995\%) at different molar concentrations (10, 15, and 20 mol\% of CO\(_2\)) was used. A total flow rate of 20 mL/min during all breakthrough tests was maintained and controlled by calibrated mass flow controllers (GFC17-CO\(_2\) and GFC-N\(_2\), AALBORG, Orangeburg, NY, USA). The stainless steel adsorption column has a length of 150 mm and an inside diameter of 4 mm. In each run, 0.7 g of amino-Zr-MOF (particle size ranged from 0.1 to 1 \(\mu\)m) was packed in the column with quartz wool on the ends of the column to avoid suspension of packed materials. A gas chromatograph instrument (GC-17A, Shimadzu, Kyoto, Japan) was used to measure the concentration of carbon dioxide effluent from the column by a thermal conductivity detector (TCD) using He as a carriage gas.
3. Results and discussion

3.1. Characterization of amino-Zr-MOFs

Figure 1 shows FTIR spectra of as-synthesized amino-Zr-MOF activated by methanol and heated at various temperatures. In Figure 1a, the bands of 1400–1767 cm\(^{-1}\) are referred to as carboxylic functional groups [18]. The carboxyl groups from free aromatic carboxylic acid were observed at 1656 cm\(^{-1}\) [19] on the as-synthesized sample; however, the peak was removed after heat activation, due to solvent extraction and heat treatment. For the as-synthesized samples activated at 200\(^{\circ}\)C, the band of 1430–1533 cm\(^{-1}\) was observed, indicating the presence of aminocarboxylate compounds that were coordinated with zirconium metal center by –CO\(_2\) asymmetrical stretching with the peaks at 1497 and 1564 cm\(^{-1}\) or –CO\(_2\) symmetrical stretching with the peaks at 1385 and 1424 cm\(^{-1}\) [18,20,21]. In the magnification part of the spectrum of as-synthesized amino-Zr-MOF (Figure 1b), two peaks that appear at 3376 and 3457 cm\(^{-1}\) with much lower intensities were related to primary amines, –NH\(_2\), on the organic linker. Low intensities of these peaks before heat activation may be attributed to the strong bonding between the amino groups in the coordinated acid, with C=O groups of free NH\(_2\)–BDC inside the pores.

Figure 1. FTIR spectra of amino-Zr-MOFs (a) and magnification of the band at 2600–3800 cm\(^{-1}\) of as-synthesized amino-Zr-MOF (b).
and bridging OH groups in the metal center (bridging OH groups can interact with amino groups on the organic linker by hydrogen bonding) [22,23]. In addition, the amino group of organic linker was affected by moisture from the surroundings by hydrogen bonding interaction. After activation at 200°C, a small shift in the position of amino group stretching can be observed and the primary amines, –NH₂, on the organic linker can be clearly seen at 3394 and 3480 cm⁻¹, referring to symmetric and asymmetric vibrations of NH₂ groups, while the bridging OH group can be observed at 3675 cm⁻¹ [21].

In the spectrum of amino-Zr-MOF after heating at 300°C, it was found that the intensities of peaks at 1564, 1497, 1424 and 1384 cm⁻¹ were reduced. In addition, the width of the band 1479–1785 cm⁻¹ was reduced, indicating the collapse of the structure. This can be confirmed by TGA profiles of amino-Zr-MOF (Figure 2), which showed a broad weight loss process at 350°C on amino-Zr-MOF treated at 300°C, due to breakup of the interconnection between the functional groups and oxygen of metal center inside the pores. Meanwhile, the weight loss profile of amino-Zr-MOF treated at 200°C showed two weight loss processes at 350–550°C, suggesting the presence of the interconnection binding. By breaking this interconnection, the whole structure of Zr-MOF will be collapsed and most of the pores will be blocked. In a previous report, such a weight loss was not found [14], due to a different activation process.

XRD patterns of amino-Zr-MOFs are illustrated in Figure 3. The profiles of the as-synthesized amino-Zr-MOF and amino-Zr-MOF activated at 200°C were similar and show a similar pattern of UiO-66 as reported in the previous investigation [13]. However, the sample XRD after activation at 300°C was totally different. The XRD profile presented a broad peak at 2θ = 7.5°, suggesting amorphous structure due to the collapse of crystalline structure. This further confirmed the FTIR and TGA results.

The nitrogen isotherms and pore size distributions of amino-Zr-MOFs are presented in Figure 4. It can be seen that amino-Zr-MOF activated at 200°C presented a highly developed microporous structure with much higher N₂ adsorption than the sample after heating treatment at 300°C. The pore size distribution of amino-Zr-MOF activated at 200°C showed two peaks centered at 1.5 and 3.3 nm, respectively. However, amino-Zr-MOF activated at 300°C showed a shift of pore size to larger pore range. The two peaks were changed to 2.4 and 4.4 nm, respectively.

![Figure 2. TGA profiles of amino-Zr-MOF activated by methanol and heating under 200°C and 300°C.](image-url)
Figure 3. XRD patterns of amino-Zr-MOFs activated at different temperatures.

Figure 4. N₂ adsorption isotherm and pore size distributions of amino-Zr-MOFs activated at different temperatures.

The BET surface area of amino-Zr-MOF activated at 200°C was 1220 m²/g, while the Langmuir surface area was 1395 m²/g. The average pore radius was 0.99 nm and the total pore volume was 0.611 cm³/g. The surface area of this sample is similar to the result reported by Zlotea et al. [24]. However, the BET surface area of the sample activated at 300°C was significantly reduced to 180 m²/g, reflecting the destruction of porous structure. A comparison of amino-Zr-MOF with other MOFs shows that amino-Zr-MOF still has high porosity (Table 1). These above results suggested that the activation of as-synthesized amino-Zr-MOF could only be done below 300°C. Above 300°C, the crystalline structure of amino-Zr-MOF could be destroyed to produce amorphous phase.
Table 1. BET surface area of different amino-functionalized MOFs.

| Sample                | \(S_{\text{BET}} \) (m\(^2\)/g) | Reference |
|----------------------|-----------------------------------|-----------|
| MIL–125(Ti)          | 1130                              | [24]      |
| UiO-66(Zr)–NH\(_2\)  | 1206 \( (1280) \)              | [24]      |
| IRMOF–3 DEF          | 3683                              | [25]      |
| Amino-MIL–53(Al)     | 675                               | [25]      |
| Amino-MIL–101(Al)    | 2100                              | [26]      |
| Amino-Zr-MOF         | 1220                              | This work |

Figure 5. SEM photograph of activated amino-Zr-MOF.

Figure 5 shows SEM photograph of amino-Zr-MOF. As seen, amino-Zr-MOF presented as symmetrical crystals with triangular base pyramid shape and the particle size was about 200 nm.

3.2. Adsorption study

Figure 6 displays \(\text{CO}_2\) adsorption isotherms on amino-Zr-MOF at 0°C and 23°C. Amino-Zr-MOF showed good adsorption of \(\text{CO}_2\) and the capacity depended on temperature. At 1 atm, 0°C, \(\text{CO}_2\) adsorption was 4.46 mmol/g, which was higher than that on Zr-MOF (3.52 mmol/g) [17]. This could be attributed to the presence of basic amino groups in porous structure. In addition, the adsorption of \(\text{CO}_2\) at 23°C was reduced and the capacity was determined as 2.86 mmol/g. Heat of adsorption was calculated using the Clausius–Clapeyron equation \((\Delta \text{H})/T = \Delta \text{H}/RT^2\) and an average value from different \(\text{CO}_2\) coverages on amino-Zr-MOF was obtained as 29.4 kJ/mol. Table 2 presents the heat of \(\text{CO}_2\) adsorption on various amino-functionalized MOFs. The value of amino-Zr-MOF is reasonable in comparison with other amino-functionalized MOFs [27]. The relatively higher values of the heat of \(\text{CO}_2\) adsorption are due to amino groups, which could create an electric field inside the pores against more polarizable adsorbates [28]. In addition, the free primary amine present in amino-Zr-MOF would form a carbamate with the \(\text{CO}_2\) resulting in high energy.

Amino-Zr-MOF was also tested at high pressure up to 980 kPa at 0°C for \(\text{CO}_2\) and \(\text{CH}_4\) adsorption and the adsorption isotherms are presented in Figure 7. As seen, \(\text{CH}_4\) and
Figure 6. CO$_2$ adsorption on amino-Zr-MOF at different temperatures.

Table 2. Heat of CO$_2$ adsorption on different amino-functionalized MOFs.

| Sample                 | CO$_2$ heat of adsorption (kJ/mol) | Reference |
|------------------------|-----------------------------------|-----------|
| IRMOF–3 DEF            | 20                                | [25]      |
| Amino-MIL–53(Al)       | 38                                | [25]      |
| Amino-MIL–101(Al)      | 28                                | [26]      |
| Zr-MOF                 | 28                                | [29]      |
| Amino-Zr-MOF           | 29.3                              | This work |

Figure 7. CO$_2$ and CH$_4$ adsorption on amino-Zr-MOF and ideal selectivity.

CO$_2$ adsorption increased with increasing pressure and CO$_2$ adsorption was higher than CH$_4$. The adsorption values were 9.04 and 3.73 mmol/g for CO$_2$ and CH$_4$, respectively, at 980 kPa. The ideal selectivity of CO$_2$ to CH$_4$ was obtained based on the ratios of the equilibrium adsorption at various pressures and is shown in Figure 7. It is seen that the ideal selectivity of CO$_2$/CH$_4$ on amino-Zr-MOF decreased with increasing pressure and it ranged from 4.5 to 2.35 over the range of pressure between 0.3 and 9 atm, 0°C.
In adsorption column tests shown in Figure 8, it was proved that this material had a good capacity to adsorb carbon dioxide in real conditions. The breakthrough times changed with the variations in CO2 concentrations. They were 40, 31, 20 min at 10%, 15% and 20% CO2, respectively, in CO2–N2 gas mixture passing through the adsorption column. From the breakthrough curve, it was shown that the slope of the curve increased sharply with increase in CO2 concentration, suggesting no diffusion limitations in the material during the adsorption. In addition, the high slope of these curves may refer to the possibility of adsorbent regeneration directly after reaching saturation, which can be a good indication toward reducing the cost of gas regeneration [30]. By the integration of the curves, the total adsorbed amounts of CO2 within the column during the breakthrough time could be calculated as around 4.55, 5.26 and 4.37 mmol/g at 10%, 15% and 20% CO2, respectively.

The adsorption capacities obtained at dynamic tests at 10% and 20% CO2 are in good agreement with the value obtained from the static volumetric adsorption (4.46 mmol/g), whereas the value is higher at 15% CO2. The high CO2 adsorption obtained at 15% CO2 was probably attributed to the dynamic exchange equilibrium of CO2 with N2. Before CO2 adsorption, Zr-MOF column was saturated with N2. A lower CO2 concentration, the exchange of N2 by CO2 may take longer time, resulting in a fast effluent of CO2 and overestimation of CO2 adsorption at 15% CO2.

4. Conclusion

An amino-Zr-MOF was synthesized with methanol activation and heating treatment at temperature below 300°C. It was found that activating temperature played an important role for the porous structure of amino-Zr-MOF. The amino-Zr-MOF exhibited higher thermal stability and higher CO2 adsorption than CH4. The CO2/CH4 ideal selectivity decreased with increasing pressure. Static isothermal measurement and column tests showed that CO2 adsorption at 1 atm was around 5 mmol/g. At higher pressure of 10 atm, CO2 adsorption was 9 mmol/g.

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