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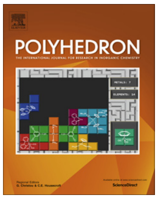

Improved CO_2 capture and separation performances of a Cr-based metal–organic framework induced by post-synthesis modification of amine groups

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ABSTRACT

A composite adsorbent based on a metal–organic framework MIL-101 ($Cr_3F(H_2O)_2O(BDC)_3$; BDC: terephthalic acid) loaded with N,N′-dimethylethylenediamine (dmeda) was synthesized by post-synthesis modification method, and the crystal structure and thermal stability of MIL-101 were maintained. The composite is shown to enhance capacity and selectivity for post-combustion carbon dioxide capture, even if its BET specific surface area decreases by 52% compared to MIL-101. At 273 K and 298 K under 1 bar, dmeda-MIL-101 exhibited 8.7% and 18.7% increase in CO_2 capacity respectively (from 2.30 mmol/g of MIL-101 to 2.50 mmol/g at 273 K, and from 1.35 mmol/g of MIL-101 to 1.59 mmol/g at 298 K). At 273 K and 298 K under a 0.15 bar CO_2/0.75 bar N_2 mixture, the CO_2/N_2 selectivities of MIL-101 and dmeda-MIL-101 were calculated by Ideal Adsorbed Solution Theory (IAST), according to single-component gas sorption experiment data. The improved capacity and selectivity are consequences of the higher isosteric heat of CO_2 adsorption (33.9 kJ/mol at zero coverage), which is due to the interaction between amines and CO_2.

1. Introduction

Nowadays, energetic needs are mainly met by fossil fuels with concomitant pollutant emissions responsible for global warming. The removal of CO_2 from flue gas at low pressures, applicable to post-combustion carbon capture, has been extensively studied in porous solids [1–4]. Generally, a flue gas mixture consists of nitrogen (70–75%), carbon dioxide (10–15%), water vapor, oxygen and minor components. The selective capture of low-concentration CO_2 from N_2-rich streams has more important practical significance and value.

Solid adsorbents are being investigated as alternatives to the aqueous amine scrubbers traditionally used to effect CO_2 removal from a mixed gas stream [1,5–7]. As a new porous solid material, metal organic framework (MOF) materials possess promising application prospect in gas adsorption and separation, catalysis, biomedicine, optics and magnetic in considering of the unique adjustable open-framework structure, chemical diversity of composition and soft synthesis conditions [8–13]. In 2008, Adam J. Matzger prepared Mg_2(dobdc) (named as Mg-MOF-74) with the unsaturated Mg^{2+} centers in the structure, and the Mg-MOF-74 can capture as high as 6.1 mmol/g of CO_2 at 0.15 bar CO_2 pressure and 298 K, which is the CO_2 capture record holder in MOFs at same conditions [14]. In addition, different polarizing and alkaline functional groups have been be rationally introduced into the pore walls of MOFs to enhance the enthalpy and improve the selectivity to CO_2 owing to the polarizability and quadrupole moment (-1.4×10^{-35} Cm) of acidic oxide CO_2 molecule [15–18]. The method of incorporating functional groups into MOFs is an effective way to balance low regeneration energy because of physisorption onto porous materials and high selectivity to CO_2.

MIL-101 ($Cr_3F(H_2O)_2O(BDC)_3 \cdot nH_2O$; BDC: terephthalic acid; $n \sim 25$) is an ultrastable MOF possessing a very high surface area and large pore sizes, and physicochemical stability is very important for practical applications [19–21]. MIL-101 has a three-dimensional network featuring two types of giant cages with diameters of 29 and 34 Å, and the exposed Cr^{3+} centers have been shown in the previous reports to serve as Lewis acid sites to facilitate the anchoring of amine groups after activation of MIL-101 [16,22]. There is still enough free space for CO_2 movement inside the cages, even if amine groups modification occupies a part of pore volume of MIL-101. Therefore, the incorporation of amine groups at higher loadings is expected to further increase the performance of CO_2

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capture and separation. However, the toxicity of chromium is a problem to be considered, and more attention should be pay to other environmental-friendly metal-based MOFs in the future.

In this work, we prepared a composite adsorbent based on MIL-101 loaded with N,N′-dimethylethylenediamine (dmeda) by post-synthesis modification method. The resultant dmeda-MIL-101 is shown to enhance capacity and selectivity for post-combustion carbon dioxide capture due to the interaction between amines and CO_2, despite a ~50% decrease in BET specific surface area and pore volume. Therefore, the MOF-based porous composites with functional groups modification have great potential applications in the field of carbon dioxide capture and separation.

2. Experimental

2.1. Synthesis of MIL-101

MIL-101 was prepared by a previously reported procedure [20]. A mixture of chromium nitrate nonahydrate (10 mmol) and H_2BDC (10 mmol) in 50 mL deionized water followed by stirring for 5 min. 0.5 mL of a 4 M hydrofluoric acid solution was added to the mixture which was then stirred and sonicated for 10 min. The reaction was heated to 493 K for 10 h in a Teflon-lined 80 mL parr pressure vessel. After filtration, the as-synthesized MIL-101 product was refluxed in water, ethanol, and NH_4F solution, each for 12 h, and then washed with hot water. The resultant product was activated at 433 K under vacuum overnight.

2.2. Synthesis of dmeda-MIL-101

A sample of MIL-101 (480 mg, 0.66 mmol) was suspended in 35 mL of anhydrous hexane under nitrogen, and 431.2 μL (4 mmol, 2 equivalents per unsaturated Cr^{3+} site) of dmeda was added via micropipette with stirring. The suspension was heated at reflux for 24 h under nitrogen. The solid was collected by filtration and washed with successive aliquots of hexane (5 × 50 mL) to remove unreacted dmeda. The solid was then dried under vacuum to remove hexane [23].

The experimental details of structure characterization and performance testing were included in the Supplementary material.

3. Results and discussion

3.1. Structure characterization

The power X-ray diffraction (PXRD) spectra of MIL-101 and dmeda-MIL-101 are shown in Fig. 1. The good agreement between the pattern of MIL-101 and the one reported in the literature demonstrated a successful synthesis procedure [20]. The two IR bands at 1597 and 1398 cm^{-1} of MIL-101 are attributed to the asymmetric and symmetric stretching vibrations of –COO, which clearly shows the presence of the framework –(O—C—O)– groups of the dicarboxylate within MIL-101 (Fig. S1) [20]. Both PXRD patterns and IR spectra indicate that post-synthesis modification of dmeda did not affect the crystal structure of MIL-101.

In addition, according to the results of elemental analysis (Table S1), the ratio of Cr^{3+} ions to dmeda in dmeda-MIL-101 is 4:3, which means a high concentration of dmeda molecules appended on the surface of pores.

3.2. Gas adsorption analysis

To evaluate the porosity of the materials, nitrogen adsorption measurements were carried out at 77 K, and the isotherms are plotted in Fig. 2. Table 1 lists the BET specific surface areas of MIL-101 and dmeda-MIL-101, as determined from N_2 adsorption isotherms. The significant decreases of surface area (−52.3%) and pore volume (−51.8%) reveal the successful tethering of dmeda inside the cages.

In general, the higher internal surface areas of MOFs can achieve larger CO_2 high-pressure adsorption capacities, owing to the efficient packing and close approach of the guest molecules on the pore surface. However, the low-pressure (<1 bar) adsorption capacities for MOFs at ambient temperatures are predominantly

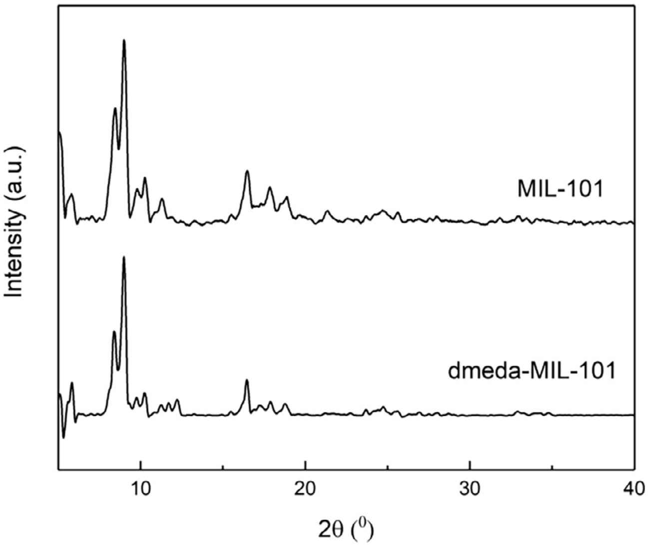

Fig. 1. PXRD patterns of MIL-101 and dmeda-MIL-101.

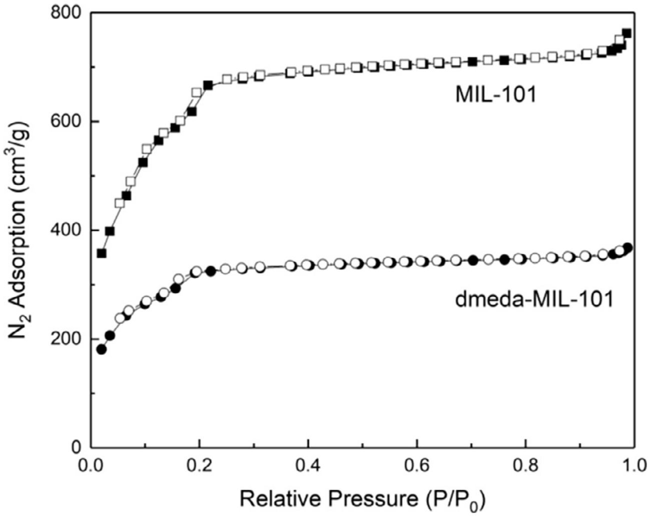

Fig. 2. N_2 adsorption (solid) and desorption (hollow) isotherms for MIL-101 and dmeda-MIL-101 at 77 K.

Table 1
Gas adsorption properties of MIL-101 and dmeda-MIL-101.*

Materials	S_{BET} (m^2/g)	V_t (m^3/g)	CO_2 uptake (mmol/g)	
			273 K	298 K
MIL-101	2132	1.179	2.30	1.35
dmeda-MIL-101	1018	0.5685	2.50	1.59
Results	−52.3%	−51.8%	+8.70%	+17.8%

[*] CO_2 uptake at 1 bar for different temperatures.