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An adsorption study on STA-16(Co)

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ABSTRACT

Adsorption is considered a promising method for carbon capture. CO_2 adsorbents take a variety of forms, but one approach is the use of metal-organic frameworks (MOFs). In this study, the potential of STA-16(Co) to selectively adsorb and separate CO_2 is considered. Isotherms for CO_2 and N_2 were measured from 0 to 25 bar at temperatures between 25 and 105 °C to evaluate the potential application in high pressure separation processes. Low pressure CO_2 pseudo-isotherms were measured from 0 to 0.5 bar at temperatures between 25 and 105 °C, together with dry and wet cycling experiments, to determine the applicability of STA-16(Co) in a vacuum swing adsorption (VSA) process. The presence of 1% H_2O vapour during ten cycle experiments resulted in a decrease in CO_2 working capacity obtained under dry cyclic conditions of ~66% due to the high H_2O uptake. In contrast to the majority of MOFs, STA-16(Co) exhibited a good H_2O stability and maintained its CO_2 adsorption capacity after adsorption/desorption of H_2O vapour at 30 and 60% RH at 25 °C. However the treatment at 90% RH resulted in a small decrease in CO_2 adsorption capacity, apparently due to the formation of a different crystal structure.

1. Introduction

One of the major challenges that will have to be overcome in the 21st century is the increase in CO_2 emissions due to the combustion of coal, oil and natural gas [1–3]. In order to meet the high energy demand, fossil fuels will remain the backbone of worldwide electricity production for some time to come and therefore methods for the reduction of our CO_2 emissions are urgently required [4]. Carbon capture and storage (CCS) has been proposed as a promising strategy to reduce anthropogenic greenhouse gas emissions and thereby halt climate change and global warming. Traditional technologies capture CO_2 by using aqueous amines (e.g. MEA, DEA), which have been shown to have a high selectivity towards CO_2. The main disadvantages of aqueous alkanolamines are a high energy requirement for the regeneration of the absorbents, loss of effectiveness over time due to their low thermal stability, loss due to evaporation, the tendency to induce corrosion and the formation of heat stable salts, which decrease the efficiency of CO_2 capture [5–10].

The evaluation of adsorption as an alternative to amine-based absorption/stripping processes has received much attention during the past decade. The application of pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) processes in carbon capture is attractive due to the low energy requirement, which could result in a reduction of the capture costs [11]. Adsorbents are required that show a high thermal and hydrothermal stability, high CO_2 capacity, high selectivity towards CO_2 and good long term stability [4,12,13]. Zeolite 13X has shown great potential for post-combustion capture, with a CO_2 uptake of 20.7 wt% at 25 °C and 1 bar [14]. However, its low hydrothermal stability, energy intensive regeneration, due to the large heat of adsorptions, and its low selectivity are major drawbacks of this material [3,15,16].

Metal-organic frameworks (MOFs) are promising candidates for carbon capture due to their very high porosity and surface area, ordered and well characterized porous structure, and adjustable chemical functionality [17–19]. Coordinatively unsaturated sites (CUS) can induce strong local interactions with CO_2, resulting in higher binding energies, higher enthalpies of adsorption and a high selectivity towards CO_2 [12,20–22].

The majority of CO_2 adsorption studies to date have involved MOFs containing carboxylate, pyridine and polyazolate linker molecules. Very limited data are available on phosphonate MOFs [23–27]. One reason for this is the strong affinity and chelation of phosphonate groups to metal ions, which results in the formation of dense layered structures [28]. Phosphonate groups can bind to a variety of metal cations through one, two or three of the oxygen

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atoms [29]. Due to the small pore size (<0.6 nm) of most metal phosphonates, the reported CO_2 adsorption capacities are low. To be applicable for post-combustion capture, stability in the presence of H_2O vapour is also important. While most carboxylate MOFs decompose or undergo a phase change under high H_2O vapour pressure, MOFs containing phosphonate monoesters as organic linker molecules tend to be more hydrothermally stable [30].

The organic linker N,N′-4,4′-bipiperidinebis-(methylenephosphonic acid) tetrahydrate (H_4LL) contains two phosphonic acids, which are each capable of three states of protonation, as well as two amino nitrogen atoms capable of two protonation states [31]. The reaction of H_4LL and $Co(OAc)_2$ results in the formation of a phosphonate MOF with a pore diameter of 1.8 nm, which is known as STA-16(Co). The coordination of the Co(II) cations to four phosphonate oxygen atoms, one piperazinyl nitrogen atom and one oxygen atom of a H_2O molecule results in a distorted CoO_5N octahedron. A metal phosphonate spiral, which is built up by edge-sharing CoO_5N octahedra, is connected to three others in order to give a hexagonal array of channels (Fig. 1). One P=O bond from each phosphonate group projects into the hexagonal channels and can hydrogen-bond with lattice and coordinated H_2O molecules. The terminal H_2O ligands of the CoO_5N octahedra can be removed upon vacuum activation at 150 °C to give CUS [32,33].

Here we report the adsorption properties and hydrothermal stability of STA-16(Co). Its applicability as an adsorbent has been assessed in terms of low pressure CO_2 adsorption, single component adsorption of CO_2 and N_2 up to 25 bar and hydrothermal stability. The stability and regenerability of the material were determined by performing ten-cycle adsorption/desorption experiments under dry and wet conditions. The CO_2/N_2 selectivities and the applicability of STA-16(Co) as a CO_2 adsorbent at high pressure were determined by performing high pressure CO_2 and N_2 adsorption/desorption measurements. In order to evaluate the hydrothermal stability, H_2O sorption isotherms were measured to different relative humidities.

2. Experimental section

2.1. Chemicals

4,4′-bipiperidine dihydrochloride (99%, Alfa Aesar), cobalt(II) acetate tetrahydrate (≥98%, Sigma Aldrich), formaldehyde (40% w/v GR grade, Merck), hydrobromic acid (Merck), phosphorous acid (97% Alfa Aesar), potassium hydroxide (GR grade, Merck) argon (high purity, BOC and Air Liquide), CO_2 (Food grade, Coregas), helium (high purity, Air Liquide) and nitrogen (high purity, Air Liquide).

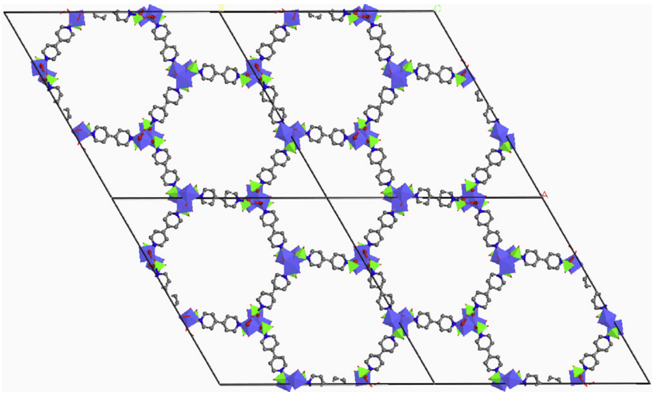

Fig. 1. The hexagonal array of channels in STA-16(Co) (Phosphonate tetrahedra: green, Co(II) octahedra: blue, C: grey, N: dark blue, O: red). The lattice H_2O molecules and the hydrogen atoms have been omitted [32]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

2.2. Synthesis of STA-16(Co)

The syntheses of H_4LL and STA-16(Co) were performed following the procedure described by Wharmby et al. [32,33].

In a typical synthesis, H_4LL was prepared using 4,4′-bipiperidine dihydrochloride, phosphorous acid, hydrobromic acid solution and formaldehyde in a Mannich reaction. 0.99 g of H_4LL were placed in a 100 mL Teflon lined autoclave and 44.7 mL of distilled H_2O were added. After the further addition of 5.7 mL of potassium hydroxide solution (1 M), the mixture was stirred until the majority of the ligand had dissolved. 1.36 g of cobalt(II) acetate tetrahydrate were added and the mixture was aged for 30 min at room temperature, then heated at 220 °C in a Teflon lined autoclave for 65 h. The purple powder was filtered and washed with distilled H_2O.

2.3. Characterization of STA-16(Co)

Powder x-ray diffractograms (PXRD) were measured on a Bruker D8 Focus powder diffractometer using CuK_α radiation ($\lambda = 1.5418$ Å). The module “Reflex Tools” in Materials Studio 6.0 was used to calculate the theoretical diffractogram [34].

SEM images and EDS analysis were performed on a JEOL 7001F field emission scanning electron microscope using an accelerating voltage of 15 kV.

A Perkin–Elmer Spectrum RXI Fourier-transform infrared spectrometer was used to obtain the IR spectrum on a KBr pellet in the spectral range 4000 to 400 cm^{-1}. The background correction, measured on a pure potassium bromide pellet, was performed automatically by the instrument control software.

Elemental analysis was performed in the Campbell Microanalytical Laboratory at the University of Otago, New Zealand.

Thermal behaviour was measured using the Setaram TAG 24 symmetrical thermoanalyser. The first step was the removal of volatile matter inside the pores at 110 °C for 30 min under Ar atmosphere. The gas composition was then changed from 100 vol% Ar to 50 vol% air and 50 vol% Ar to study the decomposition of the MOF in the presence of air and the temperature was held at 110 °C for a further 30 min. The sample was then heated to 900 °C with a heating ramp of 10 °C min^{-1} in the Ar/air mixture. After 15 min at 900 °C the air flow was switched off and after another 15 min the system was cooled to 20 °C.

2.4. Low pressure gas adsorption

Low pressure CO_2 isotherms at 25, 45, 75 and 105 °C were measured using a modified [35] Setaram TAG 24 symmetrical thermoanalyser. Prior to the experiment, the sample was activated under vacuum at 150 °C overnight. Approximately 20 mg of sample were used for each experiment. The first step of the TGA program was the pre-treatment at 150 °C under Ar (70 mL min^{-1}) for 1 h in order to remove moisture. The system was then cooled down under Ar until the adsorption temperature was reached. The thermoanalyser was allowed to equilibrate for 20 min before CO_2 flow was begun. The amount of CO_2 was increased in five steps (2.1, 5.2, 14.7, 29.7 and 49.8 vol%) allowing 20 min equilibration time for each step, then the desorption was started by decreasing the amount of CO_2 in the gas stream. The change in gas feed composition is able to mimic a vacuum swing adsorption process by varying the partial pressure of CO_2. After the last desorption step, the temperature was held constant for another 20 min. At the end of the experiment the MOF was heated to 150 °C in order to desorb the CO_2 completely. Fresh samples were used for each experiment.