

An Amine-Functionalized MIL-53 Metal–Organic Framework with Large Separation Power for CO₂ and CH₄

Sarah Couck,[†] Joeri F. M. Denayer,^{*,†} Gino V. Baron,[†] Tom Rémy,[†] Jorge Gascon,[‡] and Freek Kapteijn[‡]

Department of Chemical Engineering, Vrije Universiteit Brussel, Belgium, and Catalysis and Engineering, Delft University of Technology, The Netherlands

Received January 23, 2009; E-mail: Joeri.Denayer@vub.ac.be

This work demonstrates that functionalizing the MIL-53(Al) metal–organic framework with amino groups increases its selectivity in CO₂/CH₄ separations by orders of magnitude while maintaining a very high capacity for CO₂ capture.

Adsorption and separation of CO₂ using porous, solid adsorbents as an alternative for amine-based absorption/stripping processes has received much attention during the past decade. Zeolites, mesoporous silicas, active carbons, hydrotalcites, and polymer-based adsorbents have been tested for their CO₂ adsorption behavior.¹ More recently, it was demonstrated that metal–organic frameworks (MOFs) have interesting properties with respect to CO₂ storage and separation.² Large CO₂ adsorption capacities were reported for several members of this family.³ Grafting of amines onto surfaces of porous materials to enhance adsorption of the acidic CO₂ molecule is another strategy that has been applied for silica-based sorbents and zeolites.⁴ To date, several types of MOFs containing amino groups have been described in the scientific and patent literature.⁵ Arstad et al.^{5f} reported CO₂ adsorption isotherms on three new types of amine-functionalized MOFs. Adsorption capacities of up to 60 wt % were obtained. An amine-functionalized MIL-53(Al) MOF was recently synthesized, and its basic properties were tested in Knoevenagel condensation reactions.⁶ The parent, nonfunctionalized MIL-53 has an adsorption capacity close to 40 wt % for CO₂.^{7a} The MIL-53 framework shows an extraordinary flexibility; the quadrupole moment of the adsorbing CO₂ molecules results in a strong interaction with the corner-sharing hydroxyl groups of the MIL-53 framework, which in turn induces a contraction of the framework, reducing the free pore diameter from 1.30 to 0.79 nm.⁷ Additional adsorption of CO₂ at higher pressure reopens the framework, resulting in a two-step adsorption isotherm. Adsorptive separation experiments with equimolar CH₄/CO₂ mixtures indicated a separation factor of ~7 at atmospheric pressure; CH₄ is still adsorbed to a significant extent.^{3c}

The present work discusses adsorption and separation of CO₂ and CH₄ on amine-functionalized MIL-53(Al). Amino-MIL-53(Al) was synthesized using 2-aminoterephthalic acid as a linker, according to a method described elsewhere⁶ (see the Supporting Information). The good agreement between the experimental and simulated X-ray diffraction (XRD) patterns demonstrated the formation of the amino-MIL-53(Al) phase (Figure S1 in the Supporting Information). The resulting material is built up of AlO₄(OH)₂ octahedra held together by the dicarboxylate groups of the 2-aminoterephthalate linkers. A 3D microporous framework with diamond-shaped 1D channels is formed (Figure S2).⁶ Diffuse-reflectance infrared spectroscopy (DRIFTS) analysis of the evacuated sample showed bands corresponding to the symmetric and asymmetric stretching of primary amines (3370 and 3490 cm⁻¹) (Figure S3), demonstrating that the amino groups are free

for interaction. The main absorption in the 3500–2500 cm⁻¹ range is due to hydroxyl groups perturbed by NH₂ groups, forming hydrogen bonds of medium strengths.⁸ The hydroxyl chains in the chains of trans corner-sharing AlO₄(OH)₂ octahedra give rise to only one $\nu(\text{OH})$ band at 3700 cm⁻¹ with a shoulder near 3660 cm⁻¹, in contrast with the two $\nu(\text{OH})$ bands reported for the nonfunctionalized MIL-53(Al) but in agreement with the spectrum reported for MIL-53(Cr) (Figure S3) (shifted 50 cm⁻¹ to lower wavenumbers). These results strongly suggest that amino and OH groups are present in the structure and that interactions between them take place. Absence of solvent within the pores after activation was demonstrated by thermogravimetric analysis (TGA) (Figure S6).

Zero-coverage adsorption properties of methane, ethane, propane, and CO₂ were determined using pulse chromatography. Under these conditions, at a very low degree of pore filling, the pores are expected to adopt the open form.^{7b} At 30 °C, CH₄, with a retention time of <5 s, was nearly nonadsorbed, certainly in comparison to CO₂, which had a retention time of 5.65 min (Table S2 in the Supporting Information). This yielded a separation factor larger than 60 at very low surface coverage, which is significantly larger than the factor of ~5 for the parent MIL-53(Al). Zero-coverage adsorption enthalpies were calculated using the van't Hoff equation (Figure S7). Because of the very small retention of CH₄, no accurate value for the adsorption enthalpy could be determined, but on the basis of data for ethane and propane, this value is estimated to be less than 20 kJ/mol. The zero-coverage adsorption enthalpy of CO₂ (38.4 kJ/mol) is significantly larger than those of methane, ethane, and propane (Table S2). Contrarily, on the parent MIL-53(Al), the zero-coverage adsorption enthalpy and Henry constant of CO₂ are smaller than those of ethane (Figure S8, Table S2). Functionalization with amino groups results in an increase in CO₂ zero-coverage adsorption enthalpy from 20.1 to 38.4 kJ/mol (Table S3). This points to a strong interaction between CO₂ and the amino groups in the pores, as demonstrated by in situ DRIFTS analysis (Figure S4), evidencing the formation of electron donor–acceptor complexes between CO₂ and the amino and OH groups of the MOF structure.⁶

At pressures below 5 bar, the adsorption isotherm of CO₂ reaches a first plateau at ~2.3 mmol/g (10 wt %) (Figure 1). A drastic increase in the amount adsorbed occurs at significantly higher pressure. At the onset of the second step in the isotherm, ~0.5 CO₂ molecules are adsorbed per amino group. This also corresponds to a configuration with one CO₂ molecule in the cross section of the pore. In earlier work, it was shown that strong adsorption of CO₂ in MIL-53(Al) results in framework contraction.⁷ A similar mechanism is also expected to prevail with amino-MIL-53. The position of this step in the isotherm is temperature-dependent. At 15 °C, the step occurs at 9 bar, whereas 13 bar of CO₂ is needed to induce reopening of the pores and further CO₂ uptake at 30 °C. On the nonfunctionalized MIL-53(Al) at 30 °C, the second step in the isotherm occurs at 5 bar.^{7a} The stronger

[†] Vrije Universiteit Brussel.

[‡] Delft University of Technology.

interaction of CO₂ in amino-MIL-53(AI), as indicated by in situ DRIFTS and the large adsorption enthalpy, stabilizes the closed structure to a greater extent than in MIL-53(AI), explaining the higher pressure needed to reopen the pore structure.

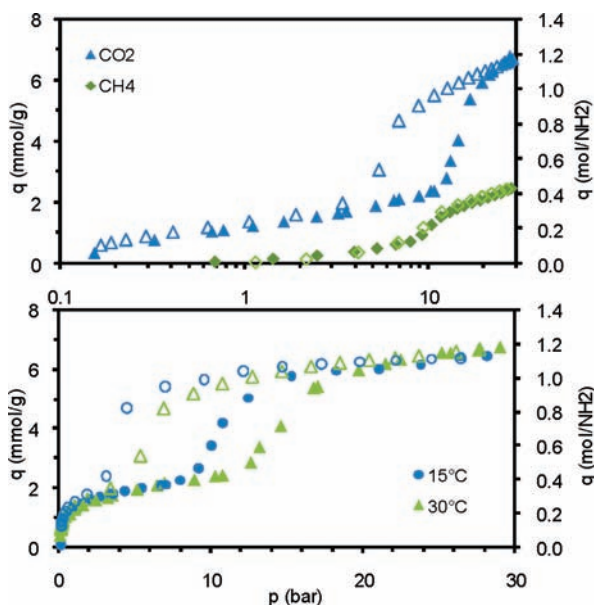


Figure 1. (top) Adsorption isotherms of CO₂ and CH₄ at 30 °C on amino-functionalized MIL-53. (bottom) Adsorption isotherms of CO₂ at 15 and 30 °C. Closed and open symbols show adsorption and desorption, respectively.

In the second plateau, a capacity of 6.7 mmol/g or 30 wt % CO₂ is reached. In contrast to CO₂, CH₄ is essentially nonadsorbed at pressures below 2 bar. This differentiates amino-MIL-53(AI) from MIL-53(AI), which adsorbs significant amounts of CH₄ at low pressure.^{7c} The presence of amino groups on the aromatic ring of the linker in the framework of amino-MIL-53(AI) reduces the number of apolar adsorption sites, leading to reduced CH₄ uptake. The CH₄ isotherm also shows a nonclassical shape: a weak and almost linear increase is followed by a small step at a pressure of 8 bar. For $p > 13$ bar, the amount adsorbed increases even more weakly with pressure to reach a capacity of only 2.4 mmol/g at 30 bar. It should be noted that whereas the CO₂ isotherm shows pronounced hysteresis, the adsorption and desorption branches coincide for CH₄ under the present experimental conditions.

The separation performance of amino-MIL-53 was tested in breakthrough experiments at 30 °C using an equimolar CO₂/CH₄ mixture (Figure 2). CH₄ elutes rapidly from the column, whereas CO₂ is strongly retained. A remarkable feature of the breakthrough profile is the occurrence of a second step in the CH₄ concentration profile right before CO₂ breakthrough occurs. To the best of our knowledge, such an effect has not been previously reported. This can be rationalized as follows. As CH₄ is not selectively adsorbed, it travels rapidly through the column, weakly adsorbing in the pores without causing framework contraction. CO₂, which travels more slowly because of strong adsorption, adsorbs in the still open pores and replaces preadsorbed CH₄ molecules. Beyond a certain CO₂ intrapore concentration, pore contraction occurs, resulting in a rapid elimination of excess CH₄ molecules from the pores, explaining the bump at the end of the CH₄ breakthrough profile. A mass-balance calculation shows that under the present conditions, essentially no CH₄ was globally adsorbed while 0.83 mmol of CO₂ was adsorbed per gram of adsorbent. This almost infinite selectivity at 1 bar is a very large improvement relative to MIL-53(AI), which shows a selectivity of ~ 7 at 1 bar.^{3c}

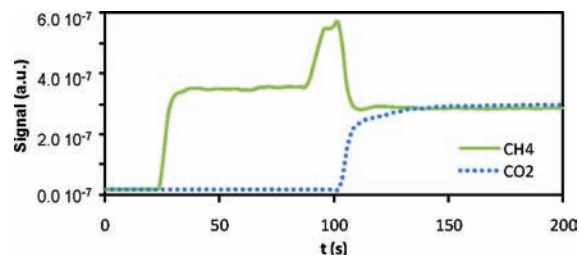


Figure 2. Separation of an equimolar CO₂/CH₄ mixture at atmospheric pressure and 30 °C.

In conclusion, it has been demonstrated that metal–organic frameworks can be effectively functionalized with amino groups. The presence of such functional groups together with the OH groups of the MIL-53 drastically enhances the affinity for CO₂, resulting in a very large selectivity in CO₂/CH₄ separations.

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Supporting Information Available: Experimental methods, material synthesis, characterization data (XRD, elemental analysis, DRIFTS, TGA), and results from pulse chromatography. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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