A flexible copper based microporous metal–organic framework displaying selective adsorption of hydrogen over nitrogen†

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Received 4th November 2010, Accepted 10th February 2011
DOI: 10.1039/c0dt01531h

A microporous metal–organic framework \([\text{Cu}_3(\text{ipO})_2(\text{pyz})_2]_n\), \((\text{ipO} = 2\text{-hydroxyisophthalic acid}, \text{pyz} = \text{pyrazine})\) was synthesized via an in situ ligand transformation reaction. The microporous framework displays helical arrays of ipO ligands holding the Cu atoms in 2D sheets, whilst the coordination of pyz molecules acts to arrange these sheets into a microporous 3D structure. Remarkable selective sorption behaviour (>5) for \(\text{H}_2\) over \(\text{N}_2\) is observed and explained with molecular dynamics simulations.

Metal–organic frameworks (MOFs) are novel porous crystalline materials consisting of metal ions or clusters interconnected by a variety of organic linkers and have attracted great attention because of their potential applications in gas separation,1 gas storage,2 ion exchange,3 catalysis,4 magnetism,5 and others. In addition to the above mentioned promising applications, their unique properties, such as their highly diversified structures, large range of pore sizes, very high surface areas, and even specific adsorption affinities, make MOFs excellent candidates for use in the construction of molecular sieves of superior performance.6 The preparation of MOF membranes for gas separation is rapidly becoming a major research focus. Unlike traditional porous zeolite materials whose pores are confined by tetrahedral oxide skeletons and are thus difficult to tune, the pores within MOFs can be systematically adjusted by the judicious choice of metal-containing secondary building units and/or bridging organic linkers.7 This superior feature is very important for developing novel microporous materials with selective sorption behaviours or molecular sieving attributes.8 Despite their importance, MOFs showing selective gas adsorption behaviours are currently not so common. In particular, MOFs that can selectively absorb \(\text{H}_2\) over \(\text{N}_2\) are very important because they have the potential to be applied in the separation of \(\text{H}_2\) enrichment from the \(\text{N}_2\)–\(\text{H}_2\) exhaust in ammonia synthesis. To the best of our knowledge, preferential adsorption of \(\text{H}_2\) over \(\text{N}_2\) by a coordination solid \(\text{Mn(HCO}_3)_2\), was first reported by Dybtsev et al., in 2004.9 In 2007, Chen et al., reported a zinc based interpenetrated microporous MOF for selective adsorption of \(\text{H}_2\) over \(\text{N}_2\).10 In addition, a number of attempts have been made to prepare supported-MOF membranes.11 Recently, supported MOFs were reported as molecular sieve membranes for high hydrogen selectivity over nitrogen.12 However, progress is very limited and there is a need to focus on developing materials better tuned for this process. Further control may be obtained by utilizing short bridging ligands to target small pores,13 also flexibility in the structure may help in allowing the gas molecules to enter through the pores. We expect that introduction of short carboxylates and bidentate pillar linkers will lead to the formation of 3D frameworks having small pores suited to the selective uptake of small molecules like hydrogen. Herein, we report the discovery of preferential adsorption of \(\text{H}_2\) over \(\text{N}_2\) in just such a copper based microporous 3D metal–organic framework, \([\text{Cu}_3(\text{ipO})_2(\text{pyz})_2]_n\), (1).

I was synthesized by the in situ ligand transformation in a hydrothermal approach. A mixture of \((\text{Cu(NO}_3)_2)_2\cdot2\text{H}_2\text{O} (242 \text{ mg}, 1 \text{ mmol}), 1,2,3\text{-benzene tricarboxylic acid} (\text{H}_3\text{btc} 123 \text{ mg}, 0.5 \text{ mmol}), \text{pyrazine} (40 \text{ mg}, 0.5 \text{ mmol}), \text{KOH} (112 \text{ mg}, 2 \text{ mmol}) \text{ and } \text{H}_2\text{O} (10 \text{ mL}) \text{ was stirred for } 10 \text{ min and sealed in a } 23 \text{ mL Teflon lined stainless steel autoclave, which was heated to } 220 \text{ °C and held at that temperature for } 3 \text{ days. After cooling to room temperature, green hexagonal plates of } I \text{ were recovered by filtration, washed, dried and picked out manually for further analysis. (yield: } 32\% \text{ based on } \text{Cu). The complex has previously been reported and our structural data is in close accord with Zheng et al. in 2009.14}

The microporous framework 1 consists of two crystallographically different types of copper centers (Cu1 and Cu2). The Cu1 centre is in a distorted square pyramidal geometry and is bridged to another Cu1 atom via the central oxygen atom of the hydroxyl group of the ipO ligand, to form a dimer. Each Cu2 is in a distorted octahedral geometry, coordinated with the four oxygen atoms from two ipO ligands in the equatorial plane and with two nitrogen atoms of pyz at the axial positions. The compound displays helical arrays of ipO ligands, which hold the Cu atoms in 2D sheets, whilst...
the coordination of pyz molecules acts to arrange these sheets into a microporous 3D structure, Fig. 1. The phase purity of the bulk sample was independently confirmed by powder X-ray diffraction (PXRD), Fig S1.†

Fig. 1 A view of the microporous framework I showing pores along the c-axis.

The microporous framework I shows remarkable preferential adsorption of H₂ over N₂. Given the lower adsorption enthalpies typically associated with hydrogen in comparison to nitrogen, this is all the more exceptional. Molecular dynamics simulations indicate that I has a flexible structure that is able to accommodate H₂ 15.8% of the time, but N₂ only on a sporadic basis <1.5% of the time.

The structure of the microporous framework I reveals a topology that includes small, microporous channels aligned to the c-axis (Fig. 1). Blue and grey channels in Fig. 4 indicate the accessible surface areas available within the structure. These channels are too small to include solvent from the synthesis, which were absent during both crystallographic investigations and thermal analysis (Fig. S3†). Gas adsorption was conducted on the material at 77 K with H₂ and N₂ adsorbents. The gas adsorption/desorption data is given in Table S1 of the ESI.†

Fig. 2 Plot of N₂ and H₂ adsorption/desorption isotherms at 77 K.

The selectivity for this adsorption process was calculated by fitting the Toth isotherm model¹⁵ to each adsorption branch, as shown in Fig. 3. At low pressures H₂ adsorbs in preference to N₂ at a selectivity of greater than 5, a value which decays at higher partial pressures. The nitrogen isotherm does not exhibit the type I behaviour expected of a microporous material, and shows very low adsorption levels. Whilst the measurement was performed at the longest possible equilibration times, there may be large timescale diffusion effects that inhibit the adsorption curve. These effects are likely due to the flexibility observed within the structure (vide infra), and there may also be a small contribution from surface adsorption. Nevertheless, the uptake is extremely low; the material is essentially non-porous to nitrogen. Analysis with other gaseous probes at higher temperatures did not reveal sufficient uptake for a reliable interpretation.

Further investigations were undertaken to determine the cause of the remarkable preferential adsorption of H₂ over N₂. The
accessible free volume has been outlined in Fig. 4 for a probe radius of 1 Å, using a commercial package, Materials Studio.46 The narrow pore channels oriented in 1-dimension are likely to be responsible for the limited storage capacity of small molecules over larger molecules, for example H$_2$ over N$_2$. As shown in Fig. 5, the pore size distribution, calculated geometrically with the open source package RASPA 1.0, indicates a channel size of 1.75 Å in diameter. Though this is smaller than the estimated kinetic diameter of hydrogen (2.89 Å, assuming single spherical entity),47 by considering structural flexibility the axially orientated gas molecules and the known axial acceptance diameter for H$_2$ into a pore of 2.27 Å and N$_2$ 2.92 Å,48 it is reasonable that these channels are capable of gas storage. Molecular dynamics of the unit-cell has been performed with Materials Studio using the Universal Forcefield49 and a microcanonical (NVE) ensemble over 1000 ps simulation time. Other simulation details include use of the Forcite module after an initial geometry optimization with an energy tolerance of 2 × 10$^{-5}$ kcal mol$^{-1}$. Molecular dynamics was then performed in a NVT ensemble with a time step of 0.5 fs. Total simulation time was 2.1 ps with 10$^5$ equilibration steps and 4 × 10$^5$ simulation steps. The temperature was held constant at 77 K using a Nose–Hoover thermostat.

During the course of the simulation of 1, an average measure of pore size fluctuation was determined, resulting in a standard deviation of 0.51 Å about the mean pore size of 1.75 Å. This means that the pore channel will expand to a size larger than 2.27 Å about 15.8% of the time and 2.92 Å < 1.5% of the time and as such, the structural flexibility of 1 is enough to allow hydrogen to penetrate the crystal at a higher rate than nitrogen. Additionally, the measured uptake at 0.9 atm. translates to 3 hydrogen molecules penetrate the crystal at a higher rate than nitrogen. Additionally, 1$_1^1$$_2$$_3$(IP$_2$)$_2$(pyz)$_2$, which is suitable for adsorption at 77 K using a Nose–Hoover thermostat.

Molecular dynamics simulations revealed that although the channels of 1 are too small for inclusion of hydrogen, the structure is flexible, and adopts more open topologies that account for the preferential adsorption. Such flexibility was also observed in the hysteretic nitrogen adsorption isotherm.

Thermo-gravimetric analyses were performed under nitrogen using a Mettler Toledo TGA/DSC 1 at a heating rate of 10 °C min$^{-1}$. PXRD data were recorded on a Philips X’Pert Multipurpose X-ray Diffractometer (Cu$_{\text{K}}$, $\lambda = 1.54056$ Å). Gas adsorption experiments were performed on a Micromeritics ASAP 2420 equipped with a micropore pressure transducer. Data points were regarded to be measured after less than 2% variance in pressure was recorded over 1200 s intervals (typical conditions: 5 s intervals with 5% variance).

Notes and references


16 Materials Studio v5.0 Accelrys, Inc. San Diego, CA, USA, 2009.


