



Inelastic neutron scattering study of binding of para-hydrogen in an ultra-microporous metal–organic framework ^{☆☆}



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ABSTRACT

Metal–organic framework (MOF) materials show promise for H₂ storage and it is widely predicted by computational modelling that MOFs incorporating ultra-micropores are optimal for H₂ binding due to enhanced overlapping potentials. We report the investigation using inelastic neutron scattering of the interaction of H₂ in an ultra-microporous MOF material showing **low** H₂ uptake capacity. The study has revealed that adsorbed H₂ at 5 K has a liquid recoil motion along the channel with very little interaction with the MOF host, consistent with the observed low uptake. The low H₂ uptake is not due to incomplete activation or decomposition as the desolvated MOF shows CO₂ uptake with a measured pore volume close to that of the single crystal pore volume. This study represents a unique example of surprisingly low H₂ uptake within a MOF material, and complements the wide range of studies on systems showing higher uptake capacities and binding interactions.

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1. Introduction

Hydrogen (H₂) is a promising alternative energy carrier not only because it can potentially achieve zero-carbon emission at the point of use, but also because H₂ has a high energy density (33.3 kWh/kg) compared to hydrocarbons (12.4–13.9 kWh/kg) [1]. The major scientific challenge for on-board H₂ applications is that of inventing effective and efficient H₂ storage materials, and there is an ever-increasing worldwide interest in meeting the United States Department of Energy's (DoE) H₂ storage targets of 5.5 wt% gravimetric and 40 gL⁻¹ volumetric by 2017. It is important to note that the DoE targets refer to storage within the whole system rather than within the storage medium alone, with a target operating temperature of –40 to 60 °C and an operating pressure below 100 atm. Although solid-state H₂ storage based on chemisorption and physisorption has been extensively studied over recent years, so far no material is able to meet this DoE target thus presenting a major impediment for the realisation of the

“Hydrogen Economy”. Nevertheless, physisorption of molecular H₂ based upon the non-dissociative interaction in porous solids is an especially attractive option since it shows fast kinetics and favourable thermodynamics over multiple adsorption and release cycles [2]. Thus, enormous efforts have been focused on developing new porous solid materials for high capacity H₂ storage.

Metal–organic framework (MOF) complexes are a sub-class of porous solids which show great promise for gas storage and separation due to their high surface area, low framework density, and tuneable functional pore environment [3]. MOF materials are usually built up from metal ions or clusters bridged by organic linkers to afford 3D extended frameworks with the formation of cavities ranging from microporous to mesoporous region. Several members within this MOF family have achieved impressively high H₂ adsorption capacities (albeit at cryogenic temperatures, typically at 77 K) [4] with a record of ~16 wt% total uptake capacity observed in NU-100 [5] and MOF-200 [6]. However, these high uptake capacities drop dramatically with increasing temperature, and thus none is a practical material. There is thus particular emphasis on optimising the interactions between MOF hosts and adsorbed H₂ molecules, and the identification of specific binding interactions and properties of gases within confined space represents an important methodology for the development of better materials that may lead us to systems of practical use. *In situ* neutron powder diffraction (NPD) at below 10 K has been used previously to determine the locations of D₂ within a few best-behaving MOF materials incorporating exposed metal sites [7–12]. It has been found that D₂ can bind directly to vacant sites

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on metal centres, and that the adsorbed D_2 molecules have molecular separations comparable to that to D_2 in the solid state. These studies have provided invaluable structural rationale for their observed high gas adsorption capacities. Research has thus focused understandably on MOFs with high H_2 uptake capacities, while materials showing very low H_2 uptake and/or incorporate fully coordinated metal centres are often ignored for this study. Therefore, information on binding interactions within those low-uptake MOF systems is entirely lacking, but can still give important complementary data and potential understanding for the subsequent design and optimisation of hydrogen storage materials.

It is critical to the success of the NPD technique that the MOF complex adsorbs a significant amount of D_2 to boost the observed signal. This technique therefore has disadvantages when studying the binding interaction within MOFs with low uptakes. Furthermore, static crystallographic studies cannot provide insights into the dynamics of the adsorbed gas molecules. Thus, it is very challenging to probe experimentally the H_2 binding interactions within a porous host system which has very low gas uptake due to the lack of suitable characterisation techniques. We report herein the application of the *in situ* inelastic neutron scattering (INS) technique to permit direct observation of the dynamics of the binding interactions between adsorbed H_2 molecules and an aluminium-based porous MOF, NOTT-300, exhibiting moderate porosity, narrow pore window and very low uptake of H_2 . This neutron spectroscopy study reveals that adsorbed H_2 molecules do not interact with the organic ligand within the pore channels, and form very weak interactions with $[Al(OH)_2O_4]$ moieties *via* a type of through-spacing interaction ($Al-O \cdots H_2$). Interestingly, the very low H_2 adsorption has been successfully characterised as weak binding interactions and, for the first time, we have found that the adsorbed H_2 in the pore channel has a liquid type recoil motion at 5 K (below its melting point) as a direct result of this weak interaction to the MOF host.

2. Experimental

2.1. Synthesis

Synthesis of $[Al_2(OH)_2(C_{16}O_8H_6)](H_2O)_6$ (NOTT-300-solvate) and of the desolvated material NOTT-300 was carried out using previously reported methods [13].

2.2. Gas adsorption isotherms

H_2 sorption isotherm was recorded at 77 K (liquid nitrogen) on an IGA-003 system at the University of Nottingham under ultra-high vacuum from a diaphragm and turbo pumping system. H_2 gas used was ultra-pure research grade (99.999%) purchased from BOC. In a typical gas adsorption experiment, ~ 100 mg of NOTT-300 was loaded into the IGA, and degassed at 120 °C and high vacuum (10^{-10} bar) for 1 day to give fully desolvated NOTT-300.

2.3. Inelastic neutron scattering

INS spectra were recorded on the TOSCA spectrometer at the ISIS Neutron Facility at the Rutherford Appleton Laboratory (UK) for energy transfers between ~ -2 and 500 meV. In this region TOSCA has a resolution of $\sim 1\% \Delta E/E$. The sample of desolvated NOTT-300 (~ 2.5 g) was loaded into a cylindrical vanadium sample container and connected to a gas handling system. The sample was degassed at 10^{-7} mbar and 120 °C for 1 day to remove any remaining trace guest solvents. The temperature during data collection was controlled using the instrument built-in cryostat and electric heaters (5 ± 0.2 K). The loading of para- H_2 (99.5%) was performed

volumetrically at 40–50 K in order to ensure that H_2 was adsorbed into NOTT-300. Subsequently, the temperature was reduced to 5 K in order to perform the scattering measurements with the minimum achievable thermal motion for H_2 molecules.

3. Results and discussion

3.1. Crystal structural analysis and gas adsorption

NOTT-300 crystallises in a chiral space group $I4_122$ and has an open structure comprising infinite chains of $[AlO_4(OH)_2]$ moieties bridged by biphenyl-3,3',5,5'-tetracarboxylate ligands L^{4-} (Fig. 1(a)). The Al(III) ion in NOTT-300 has an octahedral coordination environment with six oxygen atoms, four of which are from carboxylate groups and two of which are hydroxyl groups, giving an $[AlO_4(OH)_2]$ moiety. These aluminium oxide moieties are further linked to each other *via* the corner-sharing hydroxyl groups μ_2 -OH. Al(III)-carboxylate MOFs are usually constructed from the 1D aluminium oxide chains linked by the carboxylate ligands (Fig. 1(c)) [14–19]. Two distinct types of aluminium oxide chains have been reported previously. The aluminium chain in MIL-120 is composed of $[AlO_2(OH)_4]$ octahedra linking to each other *via* a common edge defined by two μ_2 -(OH) groups [14]. The different positions of the common edge in the two crystallographically distinct Al sites induce a *cis-trans* connection mode of the octahedral units, and thus *zigzag* chains are generated. The aluminium oxide chains in MIL-53 and MIL-118 are composed of $[AlO_4(OH)_2]$ octahedra linked to each other *via* vertex-sharing μ_2 -(OH) groups [16–18]. In both case, the connections of the $[AlO_4(OH)_2]$ octahedra adopt *trans* configurations, generating straight, rod-like aluminium building blocks. Depending on the coordination mode of the carboxylate groups, the aluminium chains in MIL-53 and MIL-118 show small differences in linkage of the octahedral nodes. However, in NOTT-300 the corner-sharing $[AlO_4(OH)_2]$ octahedra in the aluminium oxide chains display a *cis* configuration, and in order to accommodate the hydroxide groups, adjacent $[AlO_4(OH)_2]$ octahedra are rotated by 90° with respect to each other, thereby generating 4₁ screw axes. This type of connection is distinct from the other two examples, and, therefore, represents a new type of aluminium oxide building block (Fig. 1(c)). The chirality of the NOTT-300 framework therefore arises from the formation of helical chains of $[AlO_4(OH)_2]$ octahedra induced by the *cis*-configuration of μ_2 -OH groups. This overall connectivity affords a porous extended framework structure with square-shaped 1D channels with hydroxyl groups protruding into them, endowing the pore environment with free hydroxyl groups over four different directions (Fig. 1(b)). The diameter of the channel window, taking into account the van der Waals radii of the surface atoms, is approximately 6–7 Å.

Desolvated NOTT-300 has a pore volume of 0.38 cc g⁻¹ and a BET surface area of 1370 m² g⁻¹ and so the general porosity of NOTT-300 is moderate within the family of MOF complexes. The H_2 isotherm (Fig. 2) at 77 K for NOTT-300 shows exceptionally low adsorption uptakes (26 cc g⁻¹ or 0.22 wt%), albeit NOTT-300 shows very high uptakes of CO₂ (3.30 Å) and SO₂ (4.11 Å), both of which have a larger kinetic diameter than that of H_2 (2.89 Å). The uptake of H_2 increases sharply in the low pressure region and reaches saturation at ~ 1 bar. By using the pore volume of NOTT-300 and the liquid density of H_2 at its boiling point (20.3 K), it is estimated that NOTT-300 can hold a maximum of 2.7 wt% H_2 (302 cc g⁻¹) at saturation. Surprisingly, the experimental uptake is 10 times lower than this estimation, suggesting that NOTT-300 has unusually weak binding interaction to H_2 molecules, even though the pore size of NOTT-300 (6–7 Å) is believed to be optimal to afford strong overlapping potential to H_2 molecules and thus

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