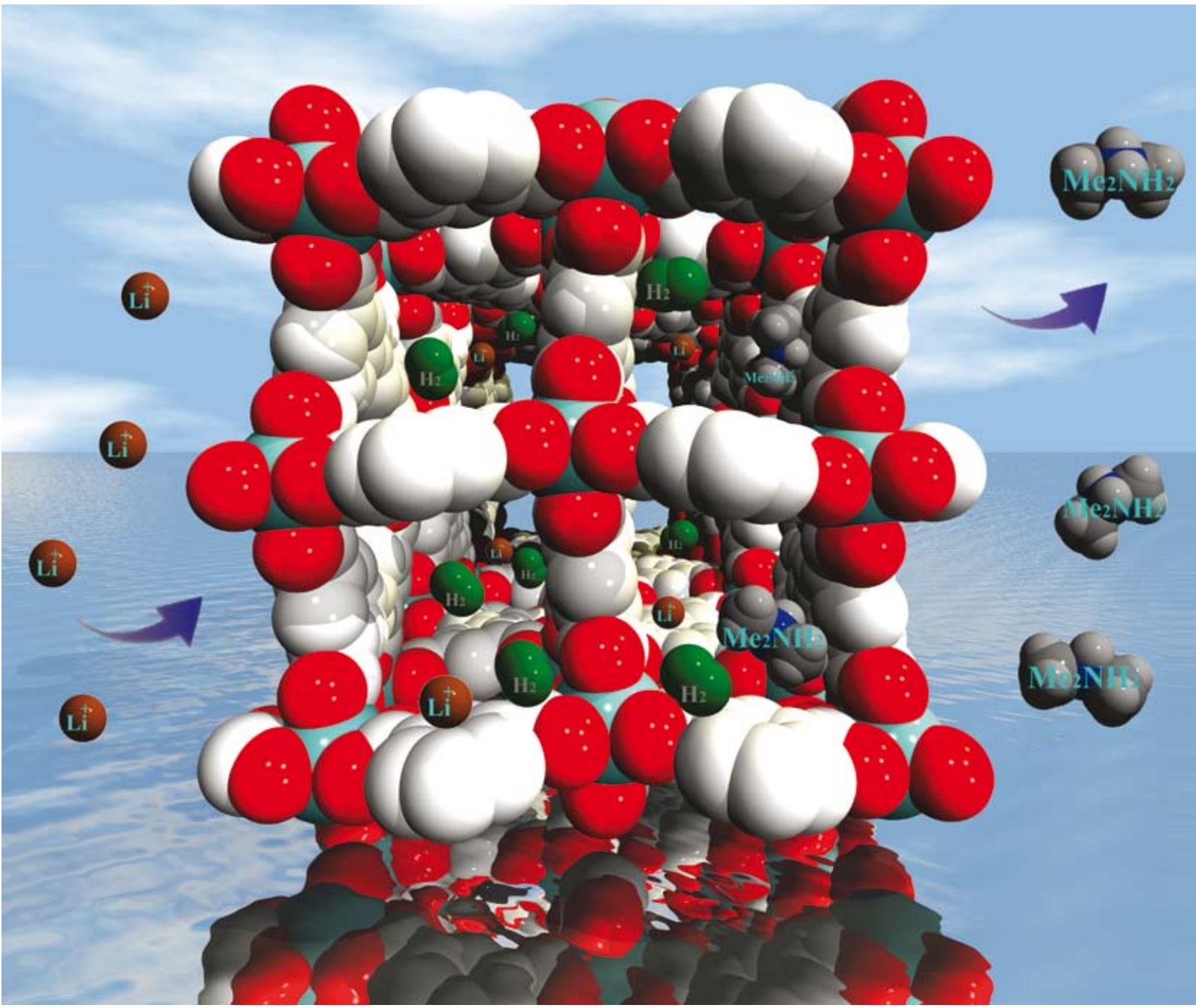
ChemComm

Chemical Communications

www.rsc.org/chemcomm

Number 46 | 14 December 2008 | Pages 6061–6248



ISSN 1359-7345

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1359-7345(2008)46;1-V

Enhancement of H_2 adsorption in Li^+-exchanged co-ordination framework materials†

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Received (in Cambridge, UK) 14th August 2008, Accepted 25th September 2008
First published as an Advance Article on the web 14th October 2008
DOI: 10.1039/b814155j

H_2 adsorption in (Me_2NH_2)[In(L)] is enhanced by exchange of $Me_2NH_2^+$ for Li^+ cations; the Li^+-exchanged material displays a lower isosteric heat for H_2 adsorption than the parent material, indicating that the increase in H_2 capacity is due to an increase in the accessible pore volume on cation exchange, while the lower adsorption enthalpy is consistent with increased pore size.

Hydrogen (H_2) is considered to be a promising candidate as an alternative to fossil fuels due to its high gravimetric energy capacity and its environmental benefits with reduced greenhouse emissions.[1] The design and production of materials that can efficiently and effectively store H_2 remain major challenges, and porous metal–organic framework materials, which are crystalline polymers composed of mononuclear or polynuclear metal centres and multi-dentate organic linkers, represent candidate materials of great current interest.[2–5] Sorption of H_2 in porous coordination polymers often displays excellent reversibility and fast kinetics, but the weak dispersive interactions that hold physisorbed H_2 molecules within a framework pore lead to low operating temperatures (often 77 K) and relatively high pressures (typically 20–90 bar).[5,6] Thus, in order to meet the US DoE criteria for use of H_2 in transportation at higher temperatures (6 wt% gravimetric and 45 g L^{-1} volumetric storage by 2010 with targets rising to 9.0 wt% and 81 g L^{-1} for 2015),[7] increasing the binding energy of H_2 in these materials above 15 kJ mol^{-1} is required.[8] Theoretical and modelling studies on co-ordination framework materials have suggested that introduction of light, non-transition metal ions such as Li^+, Na^+ or Mg^{2+} might afford non-dissociative H_2 binding, thus enhancing overall adsorption of H_2.[9–11] In particular, Li-doped materials appear to be especially interesting in this regard.[12–15] However, doping Li(0) into co-ordination framework materials is intrinsically problematic due to the reactivity of Li metal with metal cations and organic ligands that constitute the framework structure. Mulfort and Hupp have recently reported Li-doping of an interpenetrated metal–organic framework *via* chemical reduction with Li(0), and interestingly confirm improvements of both the isosteric heat and the overall H_2 adsorption uptake.[16] It remains unclear whether such an improvement is solely due to Li–H_2 interactions, or whether it can be accounted for by structural changes to the framework during the chemical reduction. An anionic co-ordination framework with large accessible voids affords an ideal platform to evaluate the effect of introducing Li^+ ions on H_2 uptake and adsorption enthalpy. We report herein H_2 uptake by an anionic co-ordination framework **1** based upon In(III), a metal ion rarely used in framework construction.[17] Framework **1** incorporates $Me_2NH_2^+$ cations and the Li^+-exchanged framework analogue **1-Li**$^+$ has been prepared to gain an insight into the effect of H_2 storage capacity.

Solvothermal reaction of H_4L (H_4L = biphenyl-3,3′,5,5′-tetracarboxylic acid[5]) with $In(NO_3)_3$ in a mixture of DMF–CH_3CN at 90 °C in the presence of two drops of 6 M HNO_3 solution affords the solvated framework complex $[Me_2NH_2][In(L)]$ (**1**). The counter-cation $Me_2NH_2^+$ is generated *via* decomposition of the DMF solvent. The composition of **1** was confirmed by single crystal X-ray diffraction, elemental analysis and IR spectroscopy, and, importantly, the phase purity of the bulk sample was confirmed by powder X-ray diffraction (PXRD) (see ESI†).

The crystal structure of **1** shows (Fig. 1) a three-dimensional (4,4)-connected topology constructed from mononuclear $[In(O_2CR)_4]$ nodes bridged by the tetracarboxylate ligand (L^{4-}). Each In(III) centre adopts an 8-co-ordinate geometry *via* binding to O-centres from four carboxylate groups to give a tetrahedral 4-connected node (Fig. 1a). Each ligand binds to four separate In(III) centres, and thus acts as square-planar 4-connected node. The framework in **1** has an overall PtS-type structure.

A view along the crystallographic *c*-axis (Fig. 1b) shows square-shaped channels running through the structure. The approximate diameter of the channel is 7.2 Å and is defined by the geometry of the $In(O_2CR)_4$ moiety and the span of the dicarboxylate phenyl linker of the isophthalate group on each terminus of the bridging ligand. These channels are interconnected by square windows composed of four In(III) centres and four ligands, which can be viewed along the crystallographic *a*- or *b*-axes (Fig. 1c). The solvent molecules within the pores in the as-prepared crystals are highly disordered and the void volume in **1** was estimated by PLATON/SOLV[18] to be 69%. However, this void contains the disordered $Me_2NH_2^+$ cations,

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† Electronic supplementary information (ESI) available: Experimental details, TGA plots, X-ray powder diffraction patterns, IR spectra, and simulation of the adsorption enthalpy. CCDC 698649. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814155j

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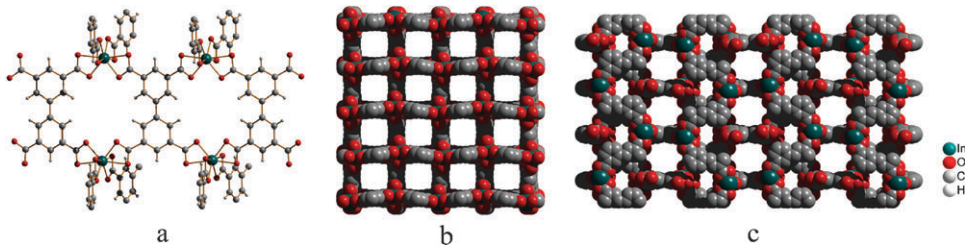

Fig. 1 (a) View of the structure of **1**, and views along the crystallographic *c*-axis (b) and *a*-axis (c).

and the actual volume available to solvent guest molecules is much smaller at ~56%.

The unco-ordinated solvent molecules in **1** can be readily exchanged for acetone and/or removed by heating at 180 °C either under a flow of N_2 gas or *in vacuo*. TGA measurements confirm that the as-synthesized sample **1** loses solvent slowly between 40 and 270 °C with a plateau observed from 270–390 °C indicating no further weight loss.

A Li^+-exchanged sample **1-Li**$^+$, in which $Me_2NH_2^+$ is replaced by Li^+, was prepared by immersing crystals of as-synthesized **1** in a saturated solution of LiCl in distilled water–acetone (v/v = 1 : 1). The crystals were soaked for ten days, and the LiCl solution refreshed daily. Upon decanting the metal chloride solutions, the cation-exchanged crystals of **1-Li**$^+$ were rinsed and soaked in distilled water–acetone (v/v = 1 : 1) for 3 days to remove residual free LiCl. PXRD of **1** and **1-Li**$^+$ clearly confirms that the structure of the framework remains intact after Li^+ exchange. The molar ratio between Li and In was determined by ICPMAS to be 0.5, which means half an equivalent of Li^+ and half an equivalent of H_3O^+ have replaced the $Me_2NH_2^+$ cation within the pores of the framework. This is confirmed by elemental analysis which confirms that no N is present in **1-Li**$^+$. **1-Li**$^+$ loses solvent rapidly between 20 and 170 °C, but undergoes no further significant changes below 390 °C. Above 390 °C both **1** and **1-Li**$^+$ decompose rapidly but the desolvated samples of **1** and **1-Li**$^+$ are stable in air and PXRD confirmed the structural stability of the framework (see ESI†).

The acetone-exchanged sample **1** or the Li^+-exchanged sample **1-Li**$^+$ was loaded into a Hiden Isochema IGA-003 instrument, and degassed at 180 °C and 10^{-10} bar for 24 h to give fully desolvated samples of **1a** or **1a-Li**$^+$. Both N_2 isotherms show typical Type-I adsorption behaviour confirming the retention of the microporous structures after the removal of solvents from the crystalline samples (Fig. 2a). The BET surface areas for **1a** and **1a-Li**$^+$ were estimated as 820 and 1024 $m^2\ g^{-1}$, respectively, indicating that the adsorption capacity of **1a** increases by *ca* 25% on Li^+-exchange. Applying Dubinin–Astakhov analysis to the isotherm data shows that the pore sizes are distributed widely around 5.8 Å for **1a**, and narrowly around 7.0 Å for **1a-Li**$^+$ (Fig. 2a). Interestingly, the pore size of **1a-Li**$^+$ is in good agreement with values (7.2 Å) calculated from the crystal structure of **1**. The pore volumes for **1a** and **1a-Li**$^+$ calculated from the maximum N_2 adsorption are 0.326 and 0.419 $cm^3\ g^{-1}$, respectively. These data clearly show that replacing the organic cation $Me_2NH_2^+$ by Li^+ produces a more porous material with a higher adsorption capacity.

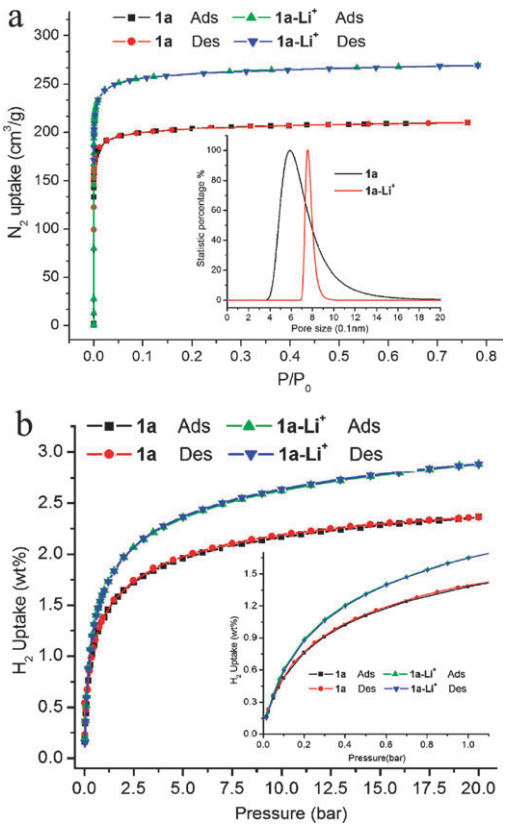

Fig. 2 (a) N_2 sorption isotherms and pore size distribution; (b) H_2 sorption isotherms (details of behaviour at low loading are depicted in the inset) for **1a** and **1a-Li**$^+$ at 78 K.

Gravimetric H_2 adsorption data were recorded over the range 0–20 bar at 78 K and at 88 K. All data were rigorously corrected for the buoyancy of system, samples and absorbates. All H_2 isotherms show good reversibility and an absence of hysteresis; furthermore, the kinetic data confirm that equilibrium is achieved rapidly within *ca.* 3 min of the isotherm pressure step. These results suggest a typical H_2 adsorption and exclude any significant effect due to the presence of impurities.

The H_2 adsorption isotherms at 78 K show a corresponding improvement in storage capacity on going from **1a** to desolvated **1a-Li**$^+$ (Fig. 2b). At 1 bar, H_2 capacity increases by 19.4%, from 1.39 wt% to 1.66 wt%, while at 20 bar, it increases by 22.0%, from 2.36 wt% to 2.88 wt%. These improvements are lower than the value of 75% achieved by doping an interpenetrated framework with Li(0).[16] Interestingly, in this latter study, although there is a large observed

enhancement of H_2 uptake, the BET surface area remains the same after framework doping and reduction. In contrast, the increase of BET surface area on going from **1a** to desolvated **1a-Li$^+$** (24.9%) is comparable to the observed increase in H_2 adsorption at 20 bar and 78 K, and is consistent with the relationship between BET free surface areas and pore volume.[19] By applying the Langmuir–Freundlich equation, the maximum H_2 uptake was estimated to be 2.7% and 3.3% for **1a** and **1a-Li$^+$**, respectively. The densities of the adsorbed H_2 at 20 bar with respect to pore volume from N_2 isotherms (assuming no distortion of the framework structure under pressure) were measured as 0.0724 and 0.0687 g cm^{-3} for **1a** and **1a-Li$^+$**, respectively. The density of H_2 in **1a** is formally slightly higher than that of liquid H_2 (0.0708 g cm^{-3}), suggesting that H_2 is highly compressed within the pores. Such high H_2 storage density has been confirmed by low temperature neutron diffraction experiments,[20] and a similar value (0.0762 g cm^{-3}) has been observed in a copper co-ordination framework material.[21]

The enhancement of porosity in this system most likely originates from the replacement of the $Me_2NH_2^+$ cation by smaller Li^+ and H^+. However, recent studies show that co-ordinatively unsaturated metal sites can provide a strong H_2 binding site directly to the metal sites with an overall enhancement of adsorption enthalpy.[19,22,23] Li^+-exchange in **1** to give **1-Li$^+$** might be expected to generate additional available metal sites. IR spectroscopic analysis of **1a-Li$^+$** suggests that the co-ordinated water on Li^+ in **1** is removed completely on heating under vacuum (see ESI†), which leaves Li^+ as a potentially non-dissociative binding centre for H_2 molecules. In this situation, a higher H_2 adsorption enthalpy might be expected for **1a-Li$^+$** compared to **1a**. The isosteric heats of the adsorption Q_{st} were determined by fitting a virial-type equation to the H_2 adsorption isotherms measured at 78 K and 88 K (see ESI†).[24,25] Analysis of the virial A_1 parameter shows that the adsorption enthalpies are at a maximum of 7.6 and 6.1 kJ mol^{-1} at zero surface coverage for **1a** and **1a-Li$^+$**, respectively, and decrease with increasing H_2 loading (see ESI†). Thus, the adsorption enthalpy of H_2 in **1a** is *higher* than in **1a-Li$^+$**. This suggests that the increase in H_2 capacity for **1a-Li$^+$** compared to **1a** arises from the replacement of $Me_2NH_2^+$ by smaller Li^+ and H^+ cations resulting in a larger apparent pore volume in the framework rather than by any increase in H_2 adsorption enthalpy.

The study reported herein involving exchange of $Me_2NH_2^+$ cations with Li^+ is not strictly comparable with those of Li-doping using Li metal[16] since the latter also involve reduction of the framework structure. In models reported by Blomqvist *et al.*,[11] Li binds to a phenyl ring with C–Li bonds and the sphere of Li^+ is completely exposed to H_2 molecules. This might be very different to the nature of Li^+ introduced by cation exchange in the current experiments. Although we have sought to desolvate the incorporated Li^+ centres, it would appear that the Li^+ centre in **1a-Li$^+$** is not accessible to H_2 molecules. It seems likely that the Li^+ centres are bound to the carboxylate O-donors within the anionic In(III)-framework structure. This notwithstanding, the present study establishes a new protocol for the increase in apparent accessible pore volume in anionic co-ordination polymers by changing the size and nature of the cations.[26] Identifying precisely the location and co-ordination environment of Li^+ in **1-Li$^+$** and **1a-Li$^+$** is currently under investigation.

We thank the EPSRC and the University of Nottingham for support, and the EPSRC-funded synchrotron crystallography service and its director Prof. W. Clegg for collection of single-crystal diffraction data at the Daresbury Synchrotron Radiation Source. MS gratefully acknowledges receipt of a Royal Society Wolfson Merit Award and of a Royal Society Leverhulme Trust Senior Research Fellowship. SY thanks Shell-EPSRC and DHPA for funding.

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