Hydrogen adsorption in microporous hypercrosslinked polymers†

Jun-Young Lee, Colin D. Wood, Darren Bradshaw, Matthew J. Rosseinsky and Andrew I. Cooper*

Received (in Cambridge, UK) 30th March 2006, Accepted 2nd May 2006
First published as an Advance Article on the web 19th May 2006
DOI: 10.1039/b604625h

A microporous hypercrosslinked polymer resin was synthesized and shown to adsorb 3.04 wt.% hydrogen at 77 K and 15 bar; this represents the highest level of hydrogen adsorption yet observed for an organic polymer.

The widespread use of hydrogen as a fuel is limited presently by the lack of a convenient, safe, and cost-effective method of H_2 storage.[1] A large number of materials have been investigated as physisorptive H_2 adsorbents including carbon,[2] zeolites,[3] and metal–organic frameworks (MOFs).[4–6] None of these materials meets the current criteria of size, recharge kinetics, cost, and safety required for use in transportation systems. The storage of hydrogen in porous materials by physisorption is very challenging because of the fundamentally weak interactions which exist between gas and sorbent at temperatures well above the critical temperature for H_2 (-240.17 °C). This has prompted researchers to develop MOFs with extremely high internal surface areas[4,6] or which exhibit kinetic trapping behaviour.[5]

During the course of this study, it was reported that organic "polymers of intrinsic microporosity" (PIMs) adsorb around 1.5–1.7 wt.% H_2 at 77 K and 10 bar.[7] While this is far from the US Department of Energy target of 6.5 wt.% by mass, organic polymers may prove to be attractive as H_2 adsorbents because, like "covalent organic frameworks",[8] they can be composed entirely of light elements. There are also a number of well-developed routes to produce organic polymers with high thermal and chemical stabilities. An additional advantage associated with organic polymers—for example, with respect to carbon[2]—is the very broad scope for synthetic variation of both chemical functionality and structural topology. A significant challenge, however, is the relatively limited number of synthetic routes to access organic polymers with high surface areas (> 1000 m^2/g) and pores in the micropore (ideally ultramicropore) range. PIMs form microporous solids with internal surface areas in the range 500–900 m^2/g as a result of their rigid and contorted molecular structures.[7,9] Hypercrosslinked polymers represent another class of predominantly microporous organic materials which can exhibit high surface areas.[10] Unlike solution-processable PIMs, the permanent porosity in hypercrosslinked materials is a result of extensive crosslinking reactions which prevent the polymer chains from collapsing into a dense, non-porous state. The most well-studied hypercrosslinked materials are "Davankov-type" resins[10,11] which are prepared by post-crosslinking of polystyrenic networks. These materials can exhibit apparent BET surface areas as high as 2090 m^2/g [12] and have been used as sorbents for organic vapours,[13] for the recovery of organic compounds from water,[14] and in chromatography.[15]

In our study, a hypercrosslinked polystyrene material was synthesized by suspension polymerisation of vinylbenzyl chloride followed by a Friedel–Crafts-type post-crosslinking in dichloroethane at 80 °C using $FeCl_3$ as the catalyst (Fig. 1).‡[16]

The hypercrosslinked polymer was recovered in the form of spherical beads with diameters in the range 50–200 μm. The apparent Brunauer–Emmett–Teller (BET) surface area for the polymer was found to be 1466 ± 11 m^2/g, as measured by nitrogen adsorption at 77 K (Langmuir surface area = 2138 m^2/g).§ The apparent BET value is high for an organic polymer[7] but somewhat lower than the highest surface area (2090 m^2/g) described thus far for Davankov-type resins.[12] Fig. 2 shows the nitrogen adsorption and desorption isotherms for the polymer. The adsorption isotherm can be classified as Type 1B and is consistent with a material which is substantially microporous.[17]

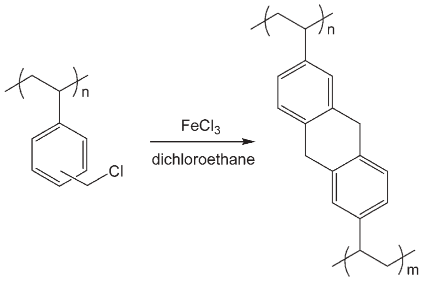

Fig. 1 Preparation of hypercrosslinked styrenic polymer from poly(vinylbenzyl chloride) gel-type resin precursor. This highly simplified scheme shows a "double" crosslink formed by internal electrophilic addition;[12] a variety of crosslink structures will exist in the actual material.

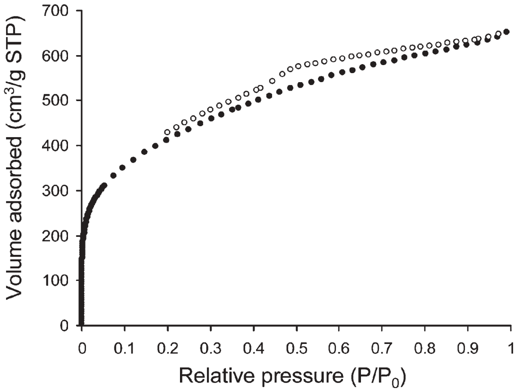

Fig. 2 Nitrogen adsorption isotherm (filled symbols) and desorption isotherm (open symbols) at 77 K.

Department of Chemistry, University of Liverpool, Crown Street, Liverpool, UK. E-mail: aicooper@liv.ac.uk; Fax: +44 151 7942304; Tel: +44 151 7943548

† Electronic supplementary information (ESI) available: Experimental details; H_2 adsorption/desorption isotherms; reproducibility studies; BET plot; electron micrographs. See DOI: 10.1039/b604625h

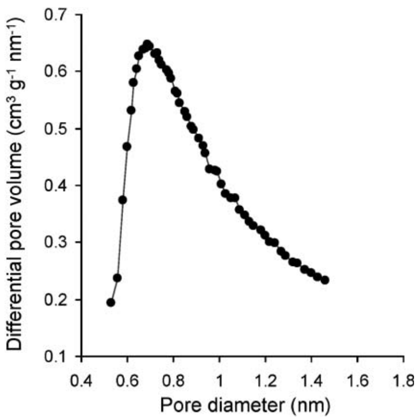

Fig. 3 Micropore size distribution for the hypercrosslinked polymer calculated by the Horvath–Kawazoe method (carbon-slit pore model).

Fig. 3 shows the apparent micropore size distribution for the sample as calculated by the Horvath–Kawazoe method (carbon slit-pore model).[18] The hypercrosslinked polymer has a median pore diameter of 0.789 nm and a relatively broad micropore size distribution. The micropore volume for the hypercrosslinked polymer at a nitrogen partial pressure (P/P_0) of 0.053 was determined as 0.48 cm^3/g – that is, substantially higher than most classes of porous organic polymers but somewhat lower than the micropore volume that can be achieved in certain carbons[2,19] and MOFs.[4–6]

The hydrogen sorption properties of this polymer at 77 K were investigated by gravimetric analysis (Hiden Isochema IGA).§ Given the significant scope for misleading measurement errors in H_2 sorption measurements, the analysis was repeated several times over a variety of pressure ranges. The H_2 sorption analyses for the hypercrosslinked polymer were also interspersed with analyses of samples of known H_2 sorption capacity (*e.g.*, activated carbon) to ensure that the system was operating correctly. Repeat determinations showed that the H_2 sorption measurement for the polymer was very reproducible (see Fig. S1). Fig. 4 shows the H_2 adsorption isotherms (filled symbols) and desorption isotherms (open symbols) for two separate samples of the hypercrosslinked polymer at 77 K, up to a maximum H_2 pressure of 15 bar.

At a pressure of 15 bar, the polymer was found to adsorb 3.04 wt.% H_2 at 77 K. In comparison with the PIM materials reported recently,[7] this hypercrosslinked polymer adsorbs significantly larger quantities of H_2 at 77 K, particularly at pressures of > 5 bar. For example, at 10 bar the hypercrosslinked polymer adsorbs around 2.75 wt.% H_2 in comparison with 1.70 wt.% reported for the highest sorbing PIM material (sample CTC).[7] At a pressure of 1 bar, however, the difference is small; the hypercrosslinked polymer adsorbs 1.28 wt.% H_2 whereas PIMs were reported to adsorb 1.04–1.43 wt.%.[7] The desorption isotherms shown in Fig. 4 show a weak hysteresis which was found to be reproducible and inherent to the hypercrosslinked polymer sample. In principle the hysteresis could be due to sample contamination (*e.g.*, sorption of less volatile molecules such as H_2O) but control experiments suggested that this was not the case.¶ Extensive washing and Soxhlet extraction of the sample also failed to eliminate the hysteresis, suggesting that it does not arise from contamination of the sample with, for example, entrained iron salts arising from the $FeCl_3$ catalyst. This weak hysteresis might be explained by the tortuosity and pore size distribution of the micropores in the polymer network, although no such observation was made for PIM samples[7] which, presumably, also possess a relatively broad distribution of tortuous micropores.

Fig. 5 shows a comparison of the gravimetric H_2 sorption data for the hypercrosslinked polymer, an activated carbon (AC) sample, and a large-pore MOF (C) material of framework composition $Ni_3(btc)_2(3\text{-pic})_6(pd)_3$ (where btc = 1,3,5-benzenetricarboxylate, 3-pic = 3-picoline and pd = 1,2-propanediol).[5,20] In general, the sorption capacities for the three materials appear to scale broadly with the apparent BET surface areas, although the total adsorption of AC up to 5 bar is somewhat higher than the hypercrosslinked polymer (see also Fig. S3 for comparison with other materials).

The H_2 sorption capacity measured for the hypercrosslinked polymer at 1 bar is comparable with that reported for active carbon samples of equivalent surface area; for example, a Norit Darco KB sample with an apparent BET surface of 1462 m^2/g and a micropore volume of 0.42 cm^3/g was reported to adsorb 1.32 wt.% H_2 (146 cm^3 (STP)/g) at 77 K and 1 bar[19] in comparison with 1.28 wt.% H_2 for the hypercrosslinked polymer (1466 m^2/g; micropore volume = 0.48 cm^3/g). These two carbon-based materials have very similar BET surface areas and micropore

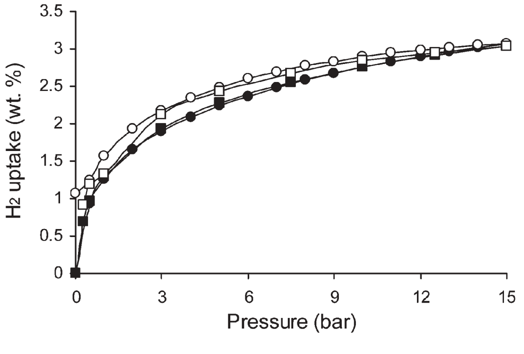

Fig. 4 Gravimetric H_2 adsorption isotherms (filled symbols) and desorption isotherms (open symbols) at 77 K for hypercrosslinked polymer. Datasets represented by square and circle symbols correspond to fresh samples measured on separate occasions to demonstrate reproducibility, see also Fig. S1.

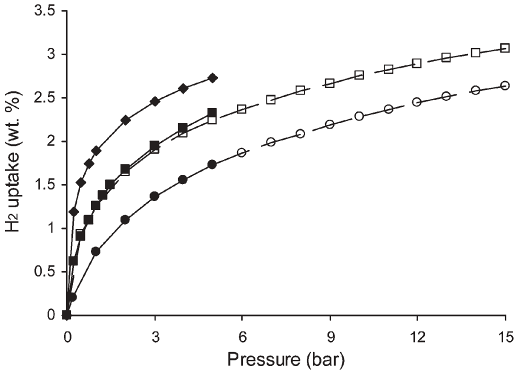

Fig. 5 Gravimetric H_2 adsorption isotherms at 77 K for large pore MOF (circles, BET SA = 930 m^2/g),[5] hypercrosslinked polymer (squares, BET SA = 1466 m^2/g) and activated carbon (diamonds, BET SA = 1348 m^2/g). Closed and open symbols for MOF and hypercrosslinked materials represent independent repeat analyses to 5 bar and 15 bar, respectively.

volumes and this appears to be reflected by the H_2 sorption capacities. Our results also suggest that hypercrosslinked polymers sorb similar quantities of H_2 in comparison with MOF materials of comparable BET surface areas, at least at 77 K. For example, the MOF sample IRMOF-13 reported recently[21] adsorbs around 2.75 wt.% H_2 at 15 bar and 77 K. IRMOF-13 has a similar BET surface area (1551 m^2/g)[22] to our hypercrosslinked polymer, the latter of which adsorbs 3.04 wt.% H_2 under equivalent conditions. An advantage of the MOF route is the very high surface area which can be achieved in these materials (*e.g.*, apparent BET surface areas of 3409 m^2/g for sample IRMOF-20).[21,22] Our preliminary data suggest that the H_2 sorption capacity per unit BET surface area for hypercrosslinked polymers is comparable with MOFs, and that similar storage densities might be achievable if strategies can be devised to tailor the surface area and pore dimensions in these polymers.

In summary, our results indicate that hypercrosslinked organic polymers could represent a promising new class of H_2 sorbent. We have shown that a hypercrosslinked polystyrene material can adsorb 2.75 wt.% H_2 at 77 K and 10 bar which is about 60% higher than the best-performing organic polymer reported thus far.[7] Hypercrosslinked polymers and PIMs are, as yet, a long way from meeting the US Department of Energy target of 6.5 wt.% sorption by mass. Nonetheless, the synthetic methodology for hypercrosslinked polymers is extremely versatile:[10] for example, one can envisage designing microporous networks based around a very broad range of aromatic molecules. It should therefore be possible to access new, high surface area microporous materials *via* this route which are composed entirely of light elements (C, H, N, O, *etc.*). The investigation of alternative carbon-based structures is timely, not least because recent theoretical analysis suggests that it may be extremely difficult to achieve practical levels of H_2 delivery using carbon itself (including carbon nanotubes) as a sorbent.[23] We are currently attempting to introduce custom-designed molecular sorption sites for H_2 (and other gases such as CH_4) into these materials in order to significantly enhance the potential gas delivery capacity.

We acknowledge EPSRC for funding (EP/C511794/1) and the Royal Society for a University Research Fellowship (to AIC) and a Wolfson Merit Award (to MJR).

Notes and references

‡ (i) Synthesis of gel-type precursor:[16] The gel-type precursor resin was obtained by free radical suspension polymerisation. The monomer phase consisted of vinylbenzyl chloride (VBC, Aldrich, 30 : 70 w/w mixture of *p*-VBC and *m*-VBC isomers, 98 wt.%, 39.10 g), divinylbenzene (DVB, Aldrich, 80% grade, 2 wt.%, 0.80 g), and 2,2′-azobis(isobutyronitrile) (AIBN, 0.5 wt.% based on monomers). The aqueous phase consisted of distilled water (1000 cm^3), poly(vinyl alcohol) (7.5 g, 88% hydrolyzed, M_w = 88,000 g/mol) and sodium chloride (33 g). The organic phase was suspended in the aqueous phase at 80 °C and stirred at 425 rpm under N_2 using a rotary impeller. After 6 h, the beads were filtered, washed three times with water, methanol, and diethyl ether, and dried under reduced pressure for 24 h at 50 °C. (ii) Hypercrosslinking reaction: The DVB–VBC gel-type precursor resin (2.5 g) was swollen in 1,2-dichloroethane (DCE, 40 cm^3) under N_2 for 1 h. Ferric chloride ($FeCl_3$, 2.61 g) in DCE (40 cm^3) was added to the solution which was then heated at 80 °C for 18 h. The resulting hypercrosslinked beads were filtered and washed three times with water, methanol and diethyl ether followed by drying for 24 h at 50 °C.

§ (i) Polymer surface areas and pore size distributions were measured using the BET method with a Micromeritics ASAP 2010 nitrogen adsorption analyzer. Samples were outgassed for 3 h at 120 °C under a N_2 flow before analysis. (ii) H_2 sorption studies were carried out using a Hiden Isochema (Warrington, UK) Intelligent Gravimetric Analyser (IGA) equipped with a micro-gram balance and 2, 100 and 20000 mbar barotron pressure transducers. Hydrogen gas of purity 99.9995% (N5.5) was obtained from BOC gases, and passed through a liquid-nitrogen trap prior to admittance into the IGA sample chamber. All admittance pipe work was thoroughly decontaminated under high vacuum for a minimum of 20 h prior to the admission of any gas into the system. All isotherm data points were fitted by the IGASwin systems software v.1.03.84 (Hiden Isochema 2002) using a linear driving force model, and all data corrected for buoyancy effects using the true density for the polymer as measured by helium pycnometry (1.34 ± 0.02 g/cm^3; see Fig. S4 for discussion). The samples were activated by outgassing under high dynamic vacuum (10^{-7} mbar) at 160 °C until a constant mass had been reached, typically overnight.

¶ No such hysteresis was observed for activated carbon samples which were interspersed between sorption measurements for the hypercrosslinked polymer, nor did the hysteresis decrease after prolonged activation of the polymer sample at 150 °C/10^{-7} mbar. The hysteresis was much less pronounced for adsorption/desorption runs up to lower pressures (1 bar, see Fig. S2), perhaps supporting the hypothesis that it is kinetic in origin.

1 L. Schlapbach and A. Zuttel, *Nature*, 2001, **414**, 353.

2 B. Panella, M. Hirscher and S. Roth, *Carbon*, 2005, **43**, 2209; X. B. Zhao, B. Xiao, A. J. Fletcher and K. M. Thomas, *J. Phys. Chem. B*, 2001, **105**, 10619; A. Zuttel, C. Nutzenadel, P. Sudan, P. Mauron, C. Emmenegger, S. Rentsch, L. Schlapbach, A. Weidenkaff and T. Kiyobayashi, *J. Alloys Compd.*, 2002, **330**, 676.

3 A. Zecchina, S. Bordiga, J. G. Vitillo, G. Ricchiardi, C. Lamberti, G. Spoto, M. Bjorgen and K. P. Lillerud, *J. Am. Chem. Soc.*, 2005, **127**, 6361; J. Weitkamp, M. Fritz and S. Ernst, *Int. J. Hydrogen Energy*, 1995, **20**, 967.

4 N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127; J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670.

5 X. B. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw and M. J. Rosseinsky, *Science*, 2004, **306**, 1012.

6 G. Ferey, M. Latroche, C. Serre, F. Millange, T. Loiseau and A. Percheron-Guegan, *Chem. Commun.*, 2003, 2976; G. Ferey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble and I. Margiolaki, *Science*, 2004, **309**, 2040.

7 N. B. McKeown, B. Ghanem, K. J. Msayib, P. M. Budd, C. E. Tattershall, K. Mahmood, S. Tan, D. Book, H. W. Langmi and A. Walton, *Angew. Chem., Int. Ed.*, 2006, **45**, 1804.

8 A. P. Cote, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166.

9 P. M. Budd, N. B. McKeown and D. Fritsch, *J. Mater. Chem.*, 2005, **15**, 1977; P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib and C. E. Tattershall, *Chem. Commun.*, 2004, 230.

10 V. A. Davankov and M. P. Tsyurupa, *React. Polym.*, 1990, **13**, 27.

11 V. A. Davankov, S. V. Rogozhin and M. P. Tsyurupa, US Patent 3,729,457, 1971.

12 J. H. Ahn, J. E. Jang, C. G. Oh, S. K. Ihm, J. Cortez and D. C. Sherrington, *Macromolecules*, 2006, **39**, 627.

13 V. V. Podlesnyuk, J. Hradil and E. Kralova, *React. Funct. Polym.*, 1999, **42**, 181.

14 A. M. Li, Q. X. Zhang, G. C. Zhang, J. L. Chen, Z. H. Fei and F. Q. Liu, *Chemosphere*, 2002, **47**, 981.

15 N. A. Penner, P. N. Nesterenko, M. M. Ilyin, M. P. Tsyurupa and V. A. Davankov, *Chromatographia*, 1999, **50**, 611.

16 N. Fontanals, J. Cortes, M. Galia, R. M. Marce, P. A. G. Cormack, F. Borrull and D. C. Sherrington, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 1718.

17 *Adsorption by powders and porous solids*, F. Rouquerol, J. Roquerol and K. Sing, Academic Press (London), 1999.

18 G. Horvath and K. Kawazoe, *J. Chem. Eng. Jpn.*, 1983, **16**, 470.

19 M. G. Nijkamp, J. Raaymakers, A. J. van Dillen and K. P. de Jong, *Appl. Phys. A: Mater. Sci. Process.*, 2001, **72**, 619.

20 D. Bradshaw, T. J. Prior, E. J. Cussen, J. B. Claridge and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2004, **126**, 6106.

21 A. G. Wong-Foy, A. J. Matzger and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 3494.

22 J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304.

23 S. K. Bhatia and A. L. Myers, *Langmuir*, 2006, **22**, 1688.