Hydrogen adsorption in microporous hypercrosslinked polymers

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

Department of Chemistry, University of Liverpool, Crown Street, Liverpool, United Kingdom.

Supporting Information: Figures S1–S6

Figure S1 Plot showing reproducibility of gravimetric H₂ sorption measurements.

Figure S2 Detailed gravimetric H₂ adsorption / desorption isotherms up to 1 bar.

Figure S3 Plot showing H₂ uptake versus apparent BET surface area for various microporous polymers and MOFs at 77 K and 10 bar.

Figure S4 Effect of sample buoyancy correction on adsorption isotherms.

Figure S5 BET plot used to calculate polymer surface area.

Figure S6 Electron microscope image of hypercrosslinked polymer beads.
**Figure S1** Gravimetric H$_2$ adsorption isotherm data (77 K) for the hypercrosslinked polymer demonstrating measurement reproducibility (filled symbols = adsorption; open symbols = desorption). Only one desorption run is shown for clarity (corresponding to the adsorption isotherm represented by filled circles; max. pressure = 15 bar). Note that the three adsorption isotherms overlay very precisely despite being obtained in separate measurement runs.
Figure S2  Gravimetric H₂ adsorption/desorption isotherms (77 K) for the hypercrosslinked polymer up to 1 bar (filled symbols = adsorption; open symbols = desorption).
Figure S3  Hydrogen uptake as a function of apparent BET surface area at 77 K and 10 bar for a series of materials including (a) polymers of intrinsic microporosity (PIMs, red symbols, Angew. Chem., Int. Ed., 2006, 45, 1804); (b) metal organic frameworks (MOFs, blue symbol, Science, 2004, 306, 1012; green symbols, J. Am. Chem. Soc., 2006, 128, 3494) and hypercrosslinked polymer (HCP, black/yellow symbol, this work). In general, the H$_2$ uptake at this temperature and pressure scales with the apparent BET surface area for this set of samples. Please note that this figure was not generated from an exhaustive literature review, but was drawn from recent reports where comparable analysis conditions were used (77 K, 10 bar). As such, we do not imply here that H$_2$ sorption for all porous materials will fall on a common surface area “master curve” and this is very unlikely to be the case; see for example Nijkamp et al., Appl. Phys. A, Mater. Sci. Proc., 2001, 72, 619.
Figure S4  (a) Gravimetric H₂ adsorption isotherms (77 K) for the hypercrosslinked polymer as calculated using four different polymer densities for the buoyancy correction (1.05, 1.15, 1.25 & 1.5 g/cm³). A density of 1.34±0.02 g/cm³ was used to calculate the isotherms shown in Figs. 4 & 5 as determined by helium pycnometry. It is relatively challenging to accurately measure the true (or “absolute”) density for microporous, non-crystalline organic polymers of this type. The technique of helium pycnometry is problematic because of the difficulties involved in adequately purging high surface area sorbents in the pycnometer (see for example J. Mater. Sci., 2005, 40, 747). We were able to overcome this by loading the sample while still hot after thorough degassing and allowing the sample to cool in the pycnometer under a flow of helium. In this way we achieved good reproducibility for the true density measurement. In fact, plot (a) shows that the sensitivity of the isotherm to the inputted sample density is only significant at higher pressures (>10 bar), and even then the effect is relatively small. (b) Influence of polymer density correction on total H₂ uptake at 15 bar. Given the relative insensitivity to this buoyancy correction, even at 15 bar H₂ pressure, we are confident that we are not significantly underestimating or overestimating the H₂ uptake as a result of small errors in the true density measurement.
Figure S5  BET plot for hypercrosslinked polymer. Apparent BET surface area = 1466 m$^2$/g. Micropore volume P/P$_0$ = 0.053 determined as 0.48 cm$^3$/g.
Figure S6  Electron microscope image of hypercrosslinked polymer beads (sample sputter coated with gold before analysis). Note that these polymers are somewhat brittle and a proportion of the beads are fragmented into smaller particles during the hypercrosslinking reaction and washing/drying process.