

Nanoporous Polymers for Hydrogen Storage

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INTRODUCTION

Developing safe and reliable hydrogen storage technologies that meet performance and cost requirements is critical to achieving a future hydrogen economy. Hydrogen storage will be needed for both vehicular applications and off-board uses such as for stationary power generation and for hydrogen delivery and refueling infrastructure. However, before this vision can be realized, a number of very significant technological hurdles need to be overcome including safe, compact, and high capacity storage systems for hydrogen. The current focus of the US Department of Energy (DOE) Hydrogen Storage activities is to create a system enabling to carry about 4 kg hydrogen on-board a vehicle affording a driving range of at least 250 miles. The current target set by DOE requires the development of materials able to store 6 wt% of hydrogen by the year 2010. A wide variety of approaches including carbon nanostructures,¹ graphite and activated carbon,² metal/carbon nanostructures,³ carbon aerogels,⁴ metal-organic frameworks,⁵ and high-capacity metal hydrides,⁶ are explored within the framework of this project.

In contrast to the approaches mentioned above, very little has been published about the use of synthetic polymers in this application. Several polymers were prepared from 5,5',6,6'-tetrahydroxy-3,3',3',3'-tetramethyl-1,1'-spirobisindane copolymerized in bulk with tetrafluoro-terephthalonitrile, hexachlorohexaazatriphenylene, and cyclotricatechylene to afford materials with "intrinsic porosity" exhibiting a surface area ranging from 760 to 830 m²/g.⁷ The best of these materials afforded a hydrogen storage capacity of 1.43 wt% at 0.1 MPa, with a capacity at saturation of 1.7 wt%. More recently, a triptycene-based polymer, Trip-PIM was prepared which adsorbs 2.7 wt% hydrogen.⁸

More than three decades ago, Davankov described the preparation of very high surface area materials based on crosslinking of swollen chloromethylated polystyrene via Friedel-Crafts alkylation reaction and called them hypercrosslinked resins.⁹ Despite their large surface area, they have never been used for the adsorption of gases. Only very recently, two papers, one published by Cooper's group¹⁰ and another published by ourselves,¹¹ demonstrated the use of hypercrosslinked porous polymers for hydrogen storage. The former group prepared their porous polymer adsorbent having a N₂/BET specific surface area of 1466 m²/g from precursor polystyrene beads crosslinked with 2% divinylbenzene. This porous polymer reversibly adsorbed 1.28 wt.% H₂ at a pressure of 0.1 MPa and 77.3 K.¹¹ This value was close to the capacity of 1.55 wt.% that we found for our best polymer exhibiting N₂/BET specific surface area of 1930 m²/g.¹²

In this communication we show the direct relationship between specific surface area and low pressure hydrogen adsorption and report the effect of substitution of hypercrosslinked nanoporous polymers on hydrogen storage at low pressure. We also present our results with hydrogen adsorption at high pressure.

EXPERIMENTAL

Preparation of Hypercrosslinked Polystyrene. The precursor, poly(vinylbenzyl chloride) beads crosslinked with 2.5% divinylbenzene, was prepared via suspension polymerization of a mixture consisting of 0.65 g divinylbenzene, 20.54 g vinylbenzyl chloride, and 226 mg 2,2'-azobisisobutyronitrile in 20 mL of aqueous 2% poly(vinyl alcohol) solution. The hypercrosslinking reaction was carried out using 1.70 g polymeric beads pre-swollen for 2 h in 20 mL 1,2 dichloroethane. The Friedel-Crafts catalyst (0.94 g FeCl₃) was then added to the slurry cooled in an ice bath. After allowing the catalyst to homogeneously disperse in the mixture, and the mixture to come to room temperature, the crosslinking reaction was allowed to proceed at 80°C for 24 h.¹²

Bromination of Hypercrosslinked Polystyrene. Hypercrosslinked polystyrene (6.5 g) was placed in a flask, which was rinsed with N₂ for 30 minutes. Then 47.3 g of bromine, 100 mL of dichloromethane and 1.6 g of FeCl₃ were mixed together and added to the polymer. The flask was kept under N₂, and heated at 35 °C in the dark. After 3 h, 3 mL dichloroethane saturated with FeCl₃ and an additional 50 mL dichloromethane were added. The reaction was allowed to continue for 2 days. The particles were rinsed with dichloromethane and extracted consecutively in a Soxhlet apparatus with chloroform, dichloro-methane, and acetone. The resulting material was stored in the dark.

Nitration of Hypercrosslinked Polystyrene. 20 mL of sulfuric and 10 mL of nitric acid were combined in an ice bath. Hypercrosslinked polystyrene (1.01 g) was added and the slurry mixed and allowed to react overnight. The slurry was then placed in a new ice bath, rinsed with methanol and extracted with water in a Soxhlet apparatus.

Determination of Hydrogen Storage Capacity. Adsorption/desorption experiments were carried out at the temperature of liquid nitrogen (77.3 K). To remove adsorbed materials from the surface, the polymers were first heated in a sample tube under vacuum at a temperature of 140°C until the pressure in the manifold reached 1.07 kPa (8 mmHg) or less and kept at that pressure and temperature for at least 30 min. Samples were transferred between manifolds in sample tubes sealed with transeals in nitrogen at a pressure of 107 kPa (800 mmHg). Nitrogen adsorption/desorption isotherms were measured using an ASAP 2010 surface area and porosimetry analyzer (Norcross, GA). Hydrogen adsorption/desorption isotherms were measured using a Micromeritics ASAP 2020 and 99.999% pure H₂. Free space was measured using helium (99.9999% purity).

Hydrogen adsorption isotherms at higher pressures were measured using a PCT-PRO 2000 instrument (Hy-Energy, LLC, Newark, CA) by Southwest Research Institute, which has been designated as the US Department of Energy Carbon-based Hydrogen Storage Center of Excellence.

RESULTS AND DISCUSSION

It has already been shown that hydrogen adsorption onto porous sorbents at low pressures is a function of surface area.¹²

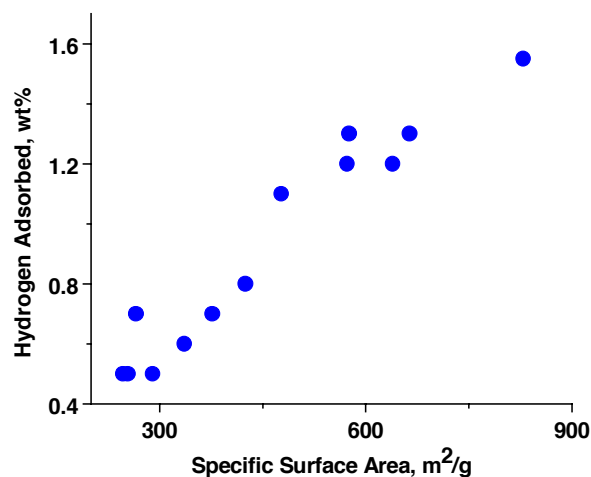


Figure 1. Hydrogen adsorption of a variety of porous styrenic polymers specified in ref.¹¹ measured at 77 K and 0.12 MPa and plotted as a function of specific surface area calculated from the hydrogen adsorption isotherm using the Langmuir equation.

Figure 1 shows that this linear relationship between adsorption capacity and the specific surface area calculated from the hydrogen adsorption isotherm using the Langmuir equation applies for a wide range of styrene-based porous polymers we tested.

Studies concerning mechanism of hydrogen adsorption in systems containing conjugated π -bonds indicate that the adsorption is controlled by H_2 - π interactions¹³ and suggest that the addition of electron donating or withdrawing substituents may affect their ability to store hydrogen.¹⁴ To demonstrate this effect, we modified our hypercrosslinked polystyrene with a series of electron withdrawing groups and measured adsorption of hydrogen. Table 1 shows that modification of our nanoporous polymer with electron withdrawing groups decreases the extent of hydrogen adsorption calculated per single aromatic ring.

Table 1. Hydrogen adsorption onto functionalized hypercrosslinked aromatic porous polymers

Substituent	Degree of substitution ^a		H ₂ ^b
	mmol/g	% of arom. rings	
None	-	0	0.8
- Br	4.7	62	0.4
- NO ₂	4.6	86	0.6

^a Calculated from carbon/bromine and carbon/nitrogen ratios based on elemental analysis; ^b Hydrogen molecules adsorbed per aromatic ring at 77 K and 0.12 MPa

Polymers with electron withdrawing bromo- and nitrogroups adsorb significantly less hydrogen than the original polymers. Although the possibility of adsorption to groups attached to the polymer cannot be excluded, these results suggest that adsorption to aromatic rings significantly contributes to the overall adsorption capacity of these materials and that the electron density in the aromatic rings is a critical parameter for hydrogen storage.

Earlier, we reported¹¹ that hypercrosslinked polystyrene with a specific surface area of 1930 m²/g and a mean pore size of 1.8 nm can store 1.55 wt% H₂ at 0.12 MPa.

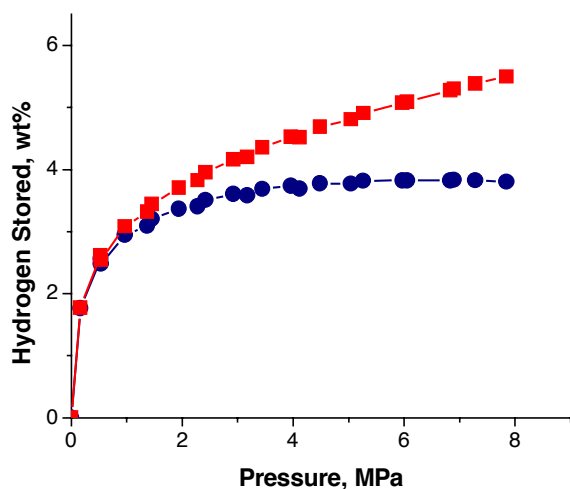


Figure 2. Total (squares) and excess (circles) hydrogen adsorption in hypercrosslinked poly(chloromethylstyrene-co-divinylbenzene) at 77K.

We have extended this study and measured adsorption at higher hydrogen pressures. One of these measurements shown in Figure 2 revealed that our hypercrosslinked poly(chloromethylstyrene-co-divinylbenzene) can store rather high 3.8 wt% excess hydrogen at 4.5 MPa and 77 K. The total, completely reversible adsorption

characterizing this material is 5.5 wt% H₂ at a pressure of 8 MPa and 77 K.

CONCLUSIONS

This study clearly demonstrates that hypercrosslinked nanoporous polymers with high hydrogen adsorption capacity are good candidates for use in future hydrogen storage systems. The major advantages of nanoporous polymers are light weight, and rapid complete adsorption and desorption with no appreciable hysteresis. Using a variety of well known reaction, these synthetic polymers can be easily modified and their adsorption ability further tuned.

ACKNOWLEDGEMENTS

Work at the Molecular Foundry was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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