High Surface Area Nanoporous Polymers for Reversible Hydrogen Storage

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Hydrogen adsorption using a series of nanoporous synthetic polymers has been studied. Promising results were obtained during the screening of commercially available porous polymer beads; of the polymers considered, hypercrosslinked Hypersol-Macronet MN200 resin exhibited the highest adsorption capacity for hydrogen. This initial success triggered the development of our own high surface area hypercrosslinked materials. Subjecting gel-type and macroporous vinylbenzyl chloride-based precursors swollen in dichloroethane to a Friedel−Crafts reaction catalyzed by iron trichloride afforded beads with surface areas of 1 930 and 1 300 m^2/g, respectively, as calculated using the BET equation. The former polymer reversibly stores up to 1.5 wt % H_2 at a pressure of 0.12 MPa and a temperature of 77.3 K. The initial heat of adsorption of hydrogen molecules onto this polymer is 6.6 kJ/mol.

Introduction

The use of hydrogen as a fuel and the development of a hydrogen economy have been suggested as means to decrease our dependency on petroleum products worldwide. However, before this vision can be realized, a number of very significant technological hurdles needs to be overcome. One such hurdle is the development of safe, compact, and high capacity storage systems for molecular hydrogen. The current target set by the U.S. Department of Energy requires the development of materials able to store 6 wt % of hydrogen by the year 2010.[1]

Several materials including carbon nanotubes,[2−5] metal−organic frameworks,[6−8] metal hydrides,[9,10] graphite and activated carbon,[11,12] and metal/carbon nanostructures[13] exhibit promise as potential materials for hydrogen storage. Surprisingly, very little has been published about the use of synthetic polymers in this type of application. Cho et al. have claimed that up to 8 wt % hydrogen can be stored on pellets of commercial polyaniline and polypyrrole.[14] However, other groups have been unable to repeat these results.[15] Alcohol-based polymers synthesized from 1-butanol via a plasma-induced process have also been suggested for the storage of hydrogen.[16,17] However, since only very small quantities of this polymer have been synthesized, the quantification of their hydrogen storage capacity has not been achieved. Recently, three polymers have been prepared from 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane copolymerized in bulk with tetrafluoroterephthalonitrile, hexachlorohexaazatrinaphthylene, and cyclotricatechylene to afford materials with intrinsic porosity having BET surface areas ranging from 760 to 830 m^2/g.[18] The best of these materials afforded a hydrogen storage capacity of 1.4 wt % at 0.1 MPa, with a capacity at saturation of 1.7 wt %.

In this paper, we for the first time report the use of porous polymers based mostly on simple styrenic monomers for hydrogen storage. These materials are typically produced in a porous form via the suspension polymerization of a monomer mixture containing a high percentage of the cross-linker and a porogenic solvent. They have been used as adsorption resins and matrixes for the manufacture of ion-

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Table 1. List of Commercial Resins, Their Properties, and Their Ability to Store Hydrogen

trade name	composition	surface area (m^2/g)[a] a	surface area (m^2/g)[a] b	H_2 capacity (wt %)[b]
Amberlite XAD4	poly(styrene-*co*-divinylbenzene)	1060	425	0.8
Amberlite XAD16	poly(styrene-*co*-divinylbenzene)	770	336	0.6
Hayesep N	poly(divinylbenzene-*co*-ethylenedimethacrylate)	460	247	0.5
Hayesep B	polydivinylbenzene modified with polyethyleneimine	570	290	0.5
Hayesep S	poly(divinylbenzene-*co*-4-vinylpyridine)	510	254	0.5
Wofatit Y77	poly(styrene-*co*-divinylbenzene)	940	573	1.2
Lewatit EP63	poly(styrene-*co*-divinylbenzene)	1206	664	1.3
Lewatit VP OC 1064	poly(styrene-*co*-divinylbenzene)	810	377	0.7
Hypersol-Macronet MN200	hypercrosslinked polystyrene	840	576	1.3
Hypersol-Macronet MN100	amine functionalized hypercrosslinked polystyrene	600	477	1.1
Hypersol-Macronet MN500	sulfonated hypercrosslinked polystyrene	370	266	0.7

[a] Calculated from nitrogen adsorption using the BET equation (a) and hydrogen adsorption using the Langmuir equation (b). [b] Hydrogen storage capacity at a pressure of 0.12 MPa.

exchange resins for almost half a century.[19] In addition, Davankov has developed an approach based on crosslinking of swollen chloromethylated polystyrene via Friedel−Crafts alkylation[20,21] that leads to polymers with very high surface areas. Since one of the prerequisites for useful physisorption of hydrogen is a large surface area, we tested a series of commercial and in-house synthesized polymers possessing very high surface areas for their potential in hydrogen storage.

Experimental Procedures

Materials. Commercial porous polymer beads Amberlite XAD-4 and Amberlite XAD-16 (Rohm and Haas, Philadelphia, PA), Hypersol-Macronet MN200 (Purolite Company Philadelphia, PA), HayeSep S (Hayes Separations, Bandera, TX), Lewatit EP63 and VP OC (Bayer, Leverkusen, Germany), and Wofatit Y77 (Chemie AG, Bitterfeld-Wolfen, Germany) were extracted in a Soxhlet apparatus with methanol and diethyl ether for 24 h and dried in vacuo at room temperature. Poly(vinyl alcohol) (87−89% hydrolyzed, average MW 85 000−146 000), divinylbenzene (80%, technical grade), vinylbenzyl chloride (mixture of 3- and 4-isomers, 97%), and 2,2′-azobisisobutyronitrile (98%) were purchased from Aldrich (St. Louis, MO). Monomers were distilled before use to remove inhibitors. Ferric chloride was purchased from Fischer.

Preparation of HyperCrossLinked Polymers. High surface area polymers were prepared from two precursors using a procedure reported by Ahn et al.[22] The first precursor, poly(vinylbenzyl chloride) crosslinked with 2.5% divinylbenzene, was prepared via suspension polymerization of a mixture consisting of 0.65 g of divinylbenzene, 20.54 g of vinylbenzyl chloride, and 226 mg of 2,2′-azobisisobutyronitrile. The mixture was loaded into a 100 mL Multiplant reactor (Chemspeed, Monmouth Junction, NJ), and 20 mL of aqueous 2% poly(vinyl alcohol) solution was added. The polymerization system was heated to 80 °C and stirred for 24 h. The resulting polymer beads were decanted several times in methanol and water, then extracted with methanol and diethyl ether in a Soxhlet apparatus and dried. The particle size estimated via imaging in an electron microscope was about 20−40 μm. No classification was attempted.

Macroporous 50 mol% crosslinked beads were prepared in suspension from a polymerization mixture comprised of 10.82 g of divinylbenzene, 12.65 g of vinylbenzyl chloride, 42 mL of toluene, and 950 mg of 2,2′-azobisisobutyronitrile. A 250 mL Buchi reactor was charged with 82 mL of 2 wt % aqueous poly(vinyl alcohol) solution. The organic phase was added, and the contents of the reactor were purged with nitrogen for 10 min. After stirring for 10 min at room temperature, the stirred mixture was heated to 70 °C for 24 h. The purification procedure was identical with that described previously. The particle size range of these beads was about 40−60 μm. No classification was attempted.

The post-crosslinking reaction was carried out using 1.70 g of polymeric precursor pre-swollen for 2 h in 20 mL of 1,2-dichloroethane. The Friedel−Crafts catalyst (0.94 g of $FeCl_3$) 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 The hypercrosslinked polymer was separated and washed with methanol, 0.5 mol/L HCl in acetone, and again with methanol before drying.

Methods. 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 μmHg) or less and was 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 either a Micromeritics ASAP 2020 or 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 H_2. Free space was measured using helium (99.9999% purity). Heat of adsorption was determined using hydrogen adsorption isotherms obtained at the temperatures of both liquid nitrogen (77.3 K) and argon (87.2 K).

Calculations using density functional theory (DFT) were carried out using the Tarazona DFT portion of the DFT Plus software (Micromeritics) with the regularization set to 0.01000.

Results and Discussion

Screening of Commercial Resins. Ease of manufacture and ability to perform a large number of fast adsorption and desorption cycles are two of the many requirements placed on hydrogen storage materials that should easily be met by nanoporous polymers. To evaluate their ability to adsorb hydrogen, we screened a number of commercial porous resins prepared by both direct copolymerization and postcrosslinking. Table 1 lists only those polymers that had a surface area exceeding 500 m^2/g as calculated from nitrogen adsorp-

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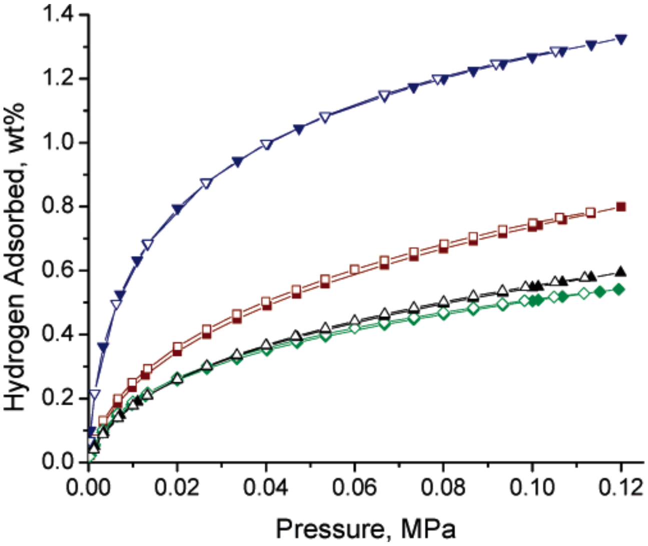

Figure 1. Hydrogen adsorption (filled symbols) and desorption (open symbols) isotherms measured using commercial resins Amberlite XAD4 (squares), HayeSep S (diamonds), Hypersol-Macronet MN200 (inverted triangles), and Amberlite XAD16 (triangles) at 77.3 K in the pressure range of 0−0.12 MPa.

tion using the BET equation. Figure 1 shows the adsorption and desorption of hydrogen for four selected resins at pressures up to 0.12 MPa. It is worth noting that the stored hydrogen is completely desorbed. The hydrogen storage capacity of these materials varies within a broad range with the highest value measured for Hypersol-Macronet MN200 resin reaching 1.3 wt %. This value is on par with that measured for a wide variety of other materials that are being considered for hydrogen storage. In evaluating the various commercial polymers, we also observed that the storage capacity was not directly related to the BET surface area of the material analyzed. For example, a poly(styrene-*co*-divinylbenzene) resin Amberlite XAD4 with a BET N_2 surface area of 1060 m^2/g adsorbed only 0.8 wt % hydrogen at 0.12 MPa, while a hypercrosslinked polystyrene-based Hypersol-Macronet MN200 with a lower surface area of 840 m^2/g adsorbed 1.3 wt % at the same pressure.

The most common method of evaluating the apparent surface area of porous materials involves the use of the Brunauer−Emmett−Teller (BET) equation to data obtained from nitrogen adsorption isotherms measured at 77.3 K.[23,24] However, this approach is known to afford inflated values for materials that contain small pores.[25] In addition, it has been suggested that hypercrosslinked polymers swell in liquid nitrogen. Although it cannot be ascertained whether swelling occurs during the portion of the adsorption cycle that is used for determination of the BET surface area, it might distort the apparent surface area obtained from nitrogen adsorption isotherms.[26] Such deficiencies have rekindled interest in methods of surface characterization that rely on adsorption of gases in their supercritical state.[27−29] Surface characterization methods based on adsorption of supercritical gases perform best when a near-monolayer is adsorbed on the substrate surface with very little found in additional layers. The desired monolayer formation occurs when the adsorbed gas is well above its critical point as is the case when hydrogen is adsorbed at 77.3 K. Therefore, we have used a simple method for assessing the apparent surface area in nanoporous materials that relies on the hydrogen adsorption isotherm measured at 77.3 K and calculations involving the Langmuir equation. This method largely avoids the problem of overcounting of nanopores that is associated with determination of surface area from nitrogen adsorption. The significant difference between the surface areas calculated using the BET (N_2 isotherm) and Langmuir (H_2 isotherm) equations is also shown in Table 1. For example, Amberlite XAD4 exhibits a specific surface area of only 425 m^2/g as calculated from hydrogen adsorption, while Hypersol-Macronet MN200 exhibits a surface area of 576 m^2/g. Although the small difference in surface areas between these two adsorbents may not fully account for the rather large difference in hydrogen adsorption, the results appear qualitatively more reasonable since the resin with a higher apparent surface area absorbs more hydrogen.

Hypercrosslinked Polystyrene Gel. Given the results obtained in the screening of commercial resins suggesting that hypercrosslinked polymers are better suited for hydrogen storage than crosslinked copolymers, a further study of hypercrosslinked materials was carried out. However, because the surface areas of current commercial resins is far lower than the maximum value these polymers can achieve (ca. 2000 m^2/g as measured by BET),[22] we prepared hypercrosslinked beads with a surface area significantly higher than that of the commercial polymers using the procedure shown schematically in Figure 2. The two-step process includes first the preparation of poly(vinylbenzyl chloride) precursor beads using a typical suspension polymerization process. This is followed by a second step in which the beads are swollen in dichloroethane and an $FeCl_3$ catalyzed Friedel−Crafts crosslinking reaction is carried out. During this step, the polymer chains become fixed in their solvated state, thus forming pores that persist even after the solvent is removed.[30] Table 1 shows that the specific surface

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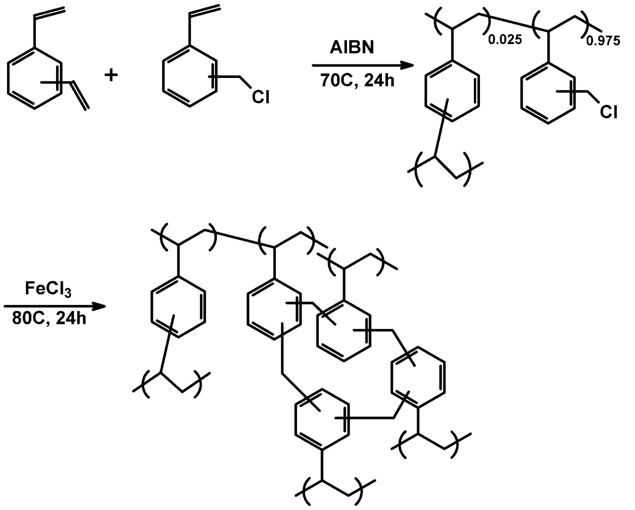

Figure 2. Reaction scheme for the synthesis of a hypercrosslinked polymer prepared from gel poly(chloromethylstyrene-*co*-divinylbenzene). The final polymer is a crosslinked polystyrene in which most aromatic rings have attachments to a polymer backbone plus two crosslinks.

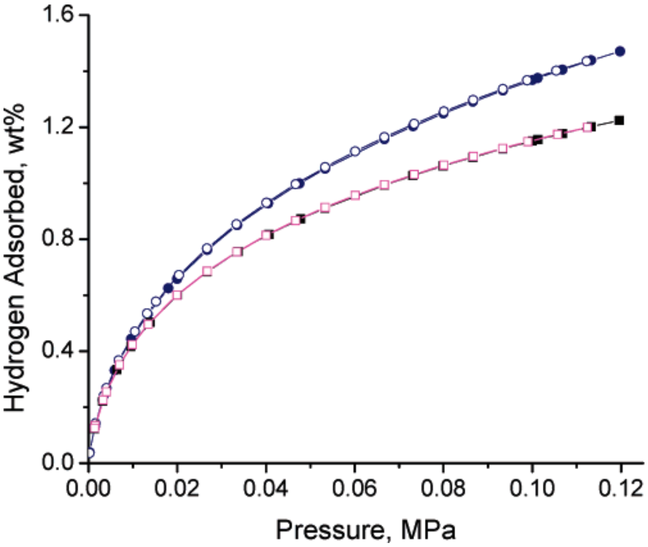

Figure 3. Hydrogen adsorption (filled symbols) and desorption (open symbols) isotherms measured using hypercrosslinked polymers prepared from gel (circles) and macroporous (squares) poly(chloromethylstyrene-*co*-divinylbenzene) at 77.3 K in the pressure range of 0−0.12 MPa.

area of an optimized polymer reaches values as high as 1930 and 829 m^2/g as calculated from nitrogen and hydrogen adsorption, respectively. As shown in Figure 3, this material adsorbs 1.55 wt % hydrogen at a pressure of 0.12 MPa. Application of the Langmuir equation reveals that only about 68% of the available surface is covered with hydrogen at a pressure of 0.12 MPa. Extrapolation using the Langmuir equation indicates that coverage to 95% of the monolayer capacity would be reached at a reasonable pressure of 1.2 MPa, thus affording a respectable hydrogen adsorption capacity of 2.2 wt % at that pressure.[31]

The nitrogen adsorption isotherm of this material measured at 77.3 K is shown in Figure 4. The type 1 isotherm indicates that the polymer contains large numbers of very small pores.[32] An incremental surface area distribution calculated using the Tarazona DFT method[33,34] and shown in Figure 5 reveals that pores with a size of about 2 nm contribute most to the overall surface area. The presence of pores of this size has also been observed for similar porous polymers.[22]

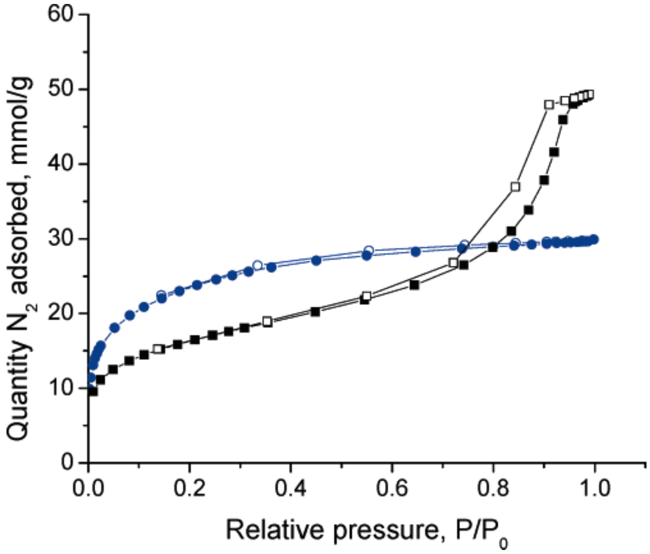

Figure 4. Nitrogen adsorption (filled symbols) and desorption (open symbols) isotherms determined at 77.3 K for hypercrosslinked polymers prepared from gel (circles) and macroporous (squares) poly(chloromethylstyrene-*co*-divinylbenzene).

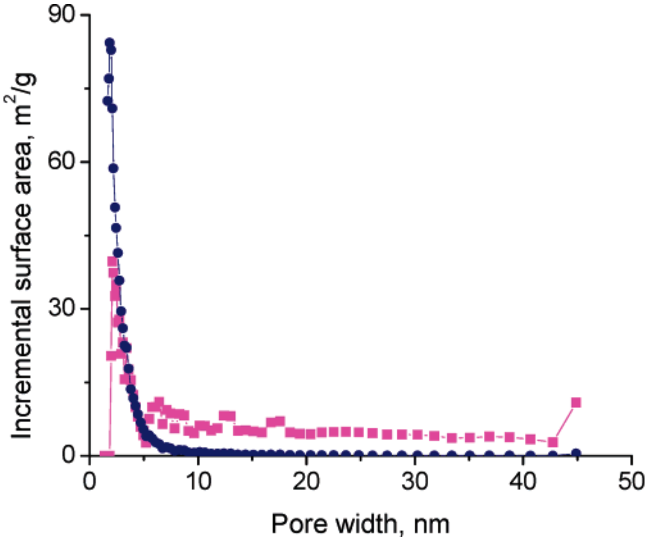

Figure 5. Incremental surface area for hypercrosslinked polymers prepared from gel (circles) and macroporous (squares) (chloromethylstyrene-*co*-divinylbenzene)calculated using the Tarazona DFT method.

Figure 6 shows an SEM image of the internal structure of the hypercrosslinked bead. This structure is rather featureless since the size of the nanopores is much smaller than the resolution of the microscope. The micrometer-sized bubble-like pores visible in the image result from the internal restructuring of the morphology during post-crosslinking. The presence of these voids decreases the effective length scale of mass transport into macroscopic polymer particles.

Hypercrosslinked Macroporous Polymer. As noted previously, upcoming hydrogen storage systems must exhibit increased capacity. In addition, the rate at which hydrogen can be stored should be fast with a current DOE goal of 1.5

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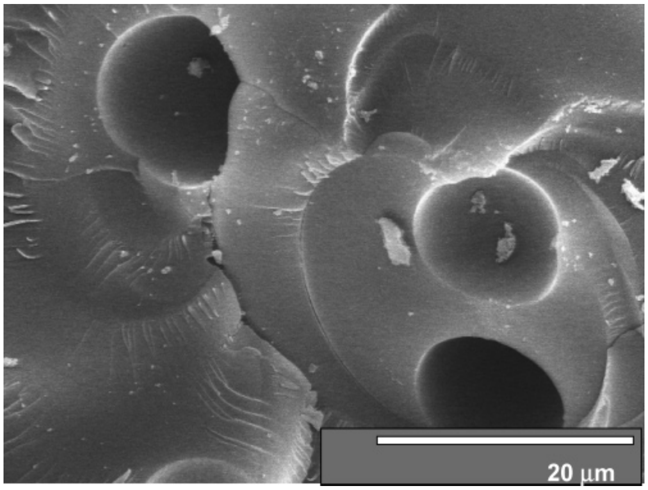

Figure 6. SEM micrograph (15.0 kV, magnification 2500×) of crushed hydrogen adsorbing porous polymers prepared from gel (chloromethylstyrene-*co*-divinylbenzene).

kg H_2/min in 2010. Despite the high diffusion rate of the small hydrogen molecule, small pore size and a long distance through kilograms of material are likely to limit this fueling rate. In contrast to classical hypercrosslinked polymers featuring large numbers of nanopores, their macroporous counterparts enable fast mass transport through the much larger pores. However, typical macroporous polymers exhibit surface areas that only reach a few hundreds of m^2/g. Sherrington recently demonstrated the preparation of hypercrosslinked polymers from a polymer precursor containing a high percentage of divinylbenzene.[22] Despite the general perception that these highly crosslinked polymers do not swell to a significant extent, they prepared beads with a dual pore size distribution including the original macropores and newly formed small pores.

Using this concept, we prepared 50 mol% crosslinked porous poly(vinylbenzyl chloride-*co*-divinylbenzene) beads using toluene as a porogen. These beads exhibit a specific surface area of 310 and 176 m^2/g determined using nitrogen and hydrogen, respectively. Because of its relatively low surface area, the hydrogen storage capacity of the macroporous precursor is only 0.4 wt %. After applying the same hypercrosslinking process as used previously, we formed a nanoporous polymer with an almost 4-fold higher surface area (measured as 1300 and 639 m^2/g using nitrogen and hydrogen, respectively). This significant increase is not very surprising taking into account the unfavorable reactivity ratios for monomers we used. Since the divinyl monomer polymerizes faster, the remaining monomer mixture becomes significantly richer in the monovinyl monomer as the polymerization reaction approaches completion. This mixture then affords only slightly crosslinked chains attached to the surface of highly crosslinked microglobular scaffolds. After filling the pores with a thermodynamically good solvent such as dichloroethane, this surface polymer layer swells. The presence of such swellable layers in various highly crosslinked polymers was confirmed long ago by Jerabek et al. utilizing size exclusion chromatography.[35,36] Once swollen, this layer can be crosslinked via the Friedel−Crafts reaction to create the desired network of nanopores that significantly increases the surface area.

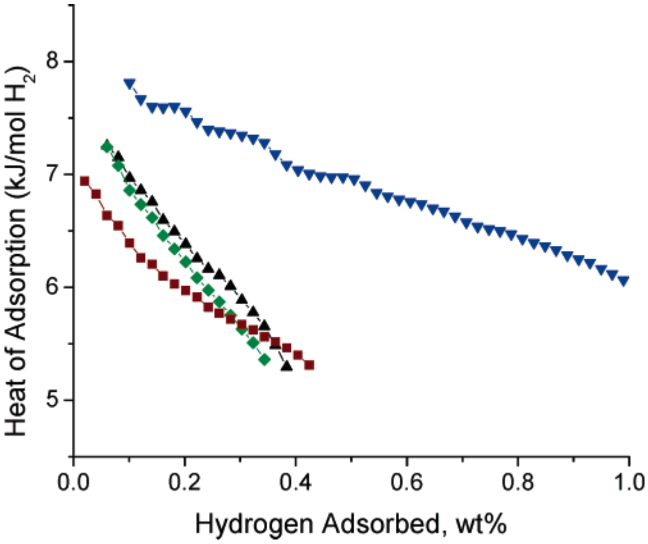

Figure 7. Heat of adsorption of hydrogen onto commercial resins Amberlite XAD4 (filled squares), HayeSep S (diamonds), Hypersol-Macronet MN200 (inverted triangles), and Amberlite XAD16 (triangles).

This hypercrosslinked macroporous polymer affords a respectable capacity of 1.2 wt % for hydrogen at 0.12 MPa (Figure 3). The smaller surface area limits the useful hydrogen storage capacity of the polymer, as calculated using the Langmuir equation, to 1.7 wt % H_2. The nitrogen adsorption isotherm of this porous polymer shown in Figure 4 is different from that of the hypercrosslinked gel and can be classified as type 4, which indicates a material with relatively large pores. The calculated incremental surface area distribution shown in Figure 5 suggests that a significant fraction of the pore surface area still originates from pores with a size of 2 nm. However, this fraction is notably smaller that that observed for hypercrosslinked gel beads. In contrast, a significant proportion of the surface area in the macroporous/nanoporous hybrid polymer originates from pores larger than 5 nm.

Heat of Adsorption. Hydrogen adsorption isotherms measured at 77.3 and 87.2 K enable a calculation of heat of adsorption for several resins used in this study. As shown on a few examples in Figures 7 and 8, the heat of adsorption decreases rapidly with saturation of the surface. This finding suggests that the surface available for hydrogen adsorption is rather heterogeneous.

Conclusion

This study clearly demonstrates that hypercrosslinked porous polymers with a hydrogen adsorption capacity in the same range as most of the other currently tested materials can be synthesized and are good candidates for use in future hydrogen storage systems. The promising results obtained with macroporous beads suggest a potential for the application of another format of macroporous materials: monoliths. In contrast to beads that fill available space to about 60% with the remainder represented by interstitial voids, monolithic structures can occupy all of the available space. Our

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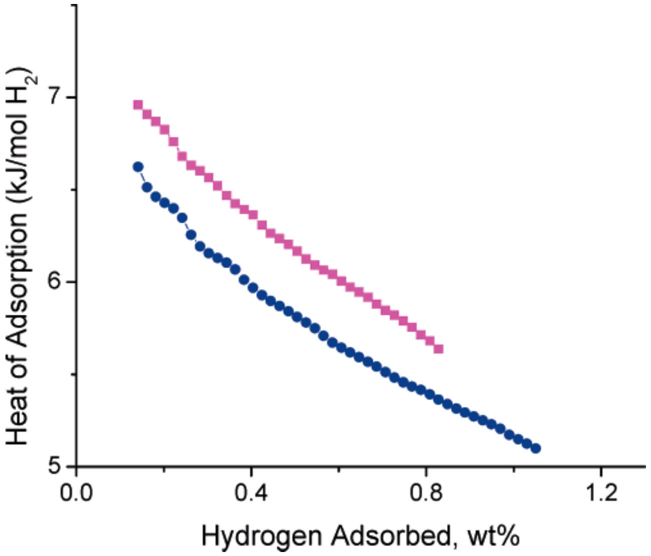

Figure 8. Heat of adsorption of hydrogen onto hypercrosslinked polymers prepared from gel (circles) and macroporous (squares) (chloromethylstyrene-*co*-divinylbenzene). Temperature 77.3 K and a pressure range of 0−0.12 MPa.

previous studies have confirmed that these structures are quite permeable to gases.[37] However, two major challenges remain to be addressed. First, the storage capacity needs to be increased to meet the goal for 2010, and second, the heat of adsorption must be increased to enable adsorption at higher temperatures.

Since it is unlikely that these problems can be solved using approaches based solely on increasing the already large surface area of the best porous polymers, new surface chemistries must also be introduced. Since modification of synthetic polymers is a well-charted field, a number of reactions leading to a variety of different functionalities is currently being tested to determine their effect on hydrogen adsorption. The ease with which hydrogen adsorbing or other functional moieties can be attached to these polymers is one of their primary advantages. With 8.5 mmol/g mostly accessible aromatic rings, the ability of these lightweight polymers to be used as a scaffold for other hydrogen adsorbing moieties is significant. Another approach, which we are pursuing, includes the coating of the pore surface with a nanolayer of a metal suitable for the hydrogen adsorption.

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