Hydrogen Adsortion in Periodic Mesoporous Organic– and Inorganic–Silica Materials at Room Temperature

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The capacities of hydrogen storage at room temperature under moderate presure amounted to 0.9 and 0.4 wt %, for periodic mesoporous organic– and inorganic–silica materials, respectively.

Hydrogen has received much interest as an energy source for the replacement of fossil fuels in fuel-cell vehicles and portable electronics due to its clean combustion and high heating value. The development of fuel-cell vehicles and portable electronics will require new materials that can store large amounts of hydrogen at ambient temperature and relatively low pressures while possessing a small volume, low weight, and fast kinetics for recharging.[1] However, no practical means for hydrogen storage and transportation have yet been developed.[2] Various materials including metal hydride, chemical hydride, carbon nanostructures, and metal–organic frameworks (MOFs) have been employed for hydrogen storage.[3] This area has been dominated by announcements of high-storage capacities in carbon nanostructures over the past few years.[4] However, a critical review shows that at room temperature and moderate pressure carbon nanostructures cannot store the amount of hydrogen required for automotive applications.[5] Recently, MOFs have received much attention as a new approach for preparing porous materials because it allows more flexible and rational design of such materials.[6] However, a serious shortcoming of these materials has been the framework's instability, such as the collapse of the framework upon guest molecule removal.

One candidate for a hydrogen-storage medium is based on a certain type of periodic mesoporous organic–silica material that appears to have the potential to store hydrogen under conditions of room temperature and moderate pressure.[3,7] These materials possess the high surface area and porosity of carbon nanotubes and MOFs that may be important for adsorption of hydrogen. In view of their excellent properties, we chose to examine the porosity and hydrogen-storage properties of the mesoporous organic–silica (benzene–silica) material. We have also examined the hydrogen-adsorption capacities of the mesoporous inorganic–silica material in the absence of the benzene moieties, which play an important role in hydrogen uptake, as a comparison. Herein, we first report the adsorption of hydrogen at 78 K and room temperature under moderate pressure by the novel periodic mesoporous organic– and inorganic–silica materials with ordered open channels.

The mesoporous organic–silica material was synthesized as described previously.[8] The synthesis of the mesoporous inorganic–silica material was similarly performed following the procedure of Stucky and co-workers, as detailed in the Electronic Supporting Information.[9]

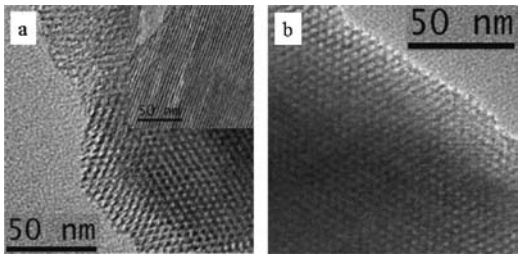

Figure 1. TEM images of (a) the mesoporous organic–silica material obtained in the channel direction [insert: TEM image obtained perpendicular to the channel direction] and (b) the mesoporous inorganic–silica materials obtained in the channel direction.

Figure 1 shows TEM images of periodic mesoporous organic– and inorganic–silica materials employed for hydrogen storage and clearly shows the formation of ordered mesostructures with a hexagonal arrangement of mesoporous channels. In the powder X-ray diffraction (PXRD) patterns (Supporting Information), the low-angle X-ray diffraction peaks also revealed that these materials possess hexagonal mesostructures with *d* spacing of 4.8 nm for the mesoporous organic–silica material and 4.2 nm for the mesoporous inorganic–silica material (Supporting Information: Figure S1). The high-angle diffraction peaks of the mesoporous organic–silica material indicated a periodic crystal-like structure along the pore channel axis with a *d* spacing of 0.75 nm (Supporting Information: Figure S1a, inset).

The nitrogen adsorption isotherms and Barrett–Joyner–Halenda (BJH) pore diameters of the periodic mesoporous organic– and inorganic–silica materials are shown in Figure S2 (Supporting Information). The mesoporous organic–silica material had a Brunauer–Emmett–Teller (BET) surface area of 34 m^2/g, a Langmuir surface area of 1548 m^2/g, and a pore volume of 0.66 cm^3/g. The mesoporous inorganic–silica material had a BET surface area of 142 m^2/g, a Langmuir surface area of 234 m^2/g, and a pore volume of 1.4 cm^3/g. Both materials contained narrow BJH pore diameters of 3.5 nm for the mesoporous organic–silica material and 3.1 nm for the mesoporous inorganic–silica material.

We measured the hydrogen-adsorption capacities of the mesoporous organic–silica material at both 78 K over a pressure range covering 0–600 Torr and room temperature over a pressure range covering 0–35 atm (see Supporting Information). Adsorption–desorption cycles were performed using identical experimental conditions. The hydrogen-storage capacity remained almost unchanged over several cycles of adsorption–desorption.

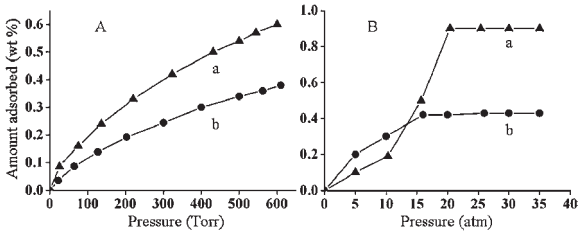

Figure 2. Hydrogen adsorption isotherms of the mesoporous organic–silica material (curve a) and the mesoporous inorganic–silica (curve b) (A) at 78 K and (B) at room temperature.

The calculated hydrogen-adsorption capacity at 600 Torr and 78 K was around 0.6 wt % (Figure 2A, curve a). Interestingly, this material showed an increased hydrogen-adsorption capacity of 0. 9 wt % at 20 atm and room temperature (Figure 2B, curve a). This result clearly indicates that the mesoporous organic–silica material was very effective as a hydrogen-storage material even at room temperature and moderate pressure.

Yaghi and co-workers recently reported for MOF-5 an initial sharp increase of the storage capacity at room temperature with a linear increase up to 20 bar and a storage capacity of 1 wt %.[1] However, Hirscher and Panella also measured the hydrogen uptake of MOF-5 under the same conditions and found it is nearly 20 times less, 0.05 wt %, than the previously reported value.[10] Therefore, the exceptional results initially reported could not be confirmed. Although several hydrogen uptake materials are now known, they are not useful for practical applications of hydrogen-storage due to the necessity for rather extreme temperature and pressure conditions. Therefore, we believe that periodic mesoporous organic-materials should be considered as a hydrogen-storage material.

We also measured the hydrogen uptake for the mesoporous inorganic–silica material in the absence of benzene rings using the same conditions as a comparison. We initially suspected that the organic moieties played an important role in hydrogen uptake. Hydrogen-storage values at both 78 K and room temperature were only around 0.4 wt % as was expected (Figures 2A and 2B, curve b). The accessible volume of the mesoporous inorganic–silica material was 2.1 times that of the mesoporus organic–silica material. Conversely, the hydrogen capacity of the mesoporous inorganic–silica material at 20 atm and room temperature was 2.2 times less than that of the mesoporous organic–silica material. These results strongly suggest that pore volume was not the sole factor that determined the amount of hydrogen adsorbed. The increased hydrogen capacity was likely due to the preferred adsorption of hydrogen on carbon. In addition, the polarizable π-electron clouds of the benzene rings in the mesoporous organic–silica material would be expected to have some affinity for hydrogen.[11]

We calculated the hydrogen-adsorption energy to get a positive evidence for the role of the benzene rings (Supporting Information for detail calculation method). We optimized the position of a hydrogen molecule above a small piece of the hexagonal lattice built from three benzene rings (Figure 3). The position with the highest exothermic energy (0.8 kcal/mol) for the hydrogen molecule was 3.71 Å above a carbon atom of the benzene ring. Thus, the hydrogen adsorption on carbon atoms of benzene rings is thermodynamically feasible. Meanwhile, hydrogen adsorption around an oxygen atom of silica moieties is energetically unstable with endothermic energy of 0.4 kcal/mol. These results clearly indicates that the amount of hydrogen storage is governed by the number accessible carbon atoms of benzene rings in the mesoporous organic–silica material.[12]

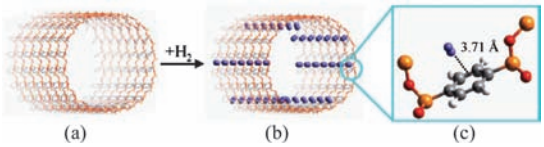

Figure 3. (a) PW91 optimized structure of the mesoporous organic–silica (Atoms are displayed as a stick model). (b) The schematical structure of the pore surface with adsorbed H_2 where the hydrogen molecules are represented as a ball model. (c) The B3LYP optimized structure model of the mesoporous organic–silica material. Oxygen, carbon, and silicon atoms are shown in red, gray, and orange, respectively. The hydrogen atoms bonded with carbon atoms are shown in white color, and the adsorbed hydrogen atoms are shown in blue color.

In summary, we prepared periodic mesoporous organic– and inorganic–silica materials by the co-assembly of surfactant and silica. We measured the hydrogen-storage capacities of these materials at 78 K and room temperature under moderate pressure. Remarkably, we observed a maximum hydrogen uptake of 0.9 wt % in the mesoporous organic–silica material at room temperature and 20 atm. The benzene moiety in organic silica acted as a driving force to high amount of hydrogen adsorption. We anticipate that further increases in performance can be achieved with new modified mesoporous organic–silica materials.

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