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Hydrogen Storage

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Hydrogen Storage by Cryoadsorption in Ultrahigh-Porosity Metal–Organic Frameworks

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Limited fossil fuel resources and the environmental impact of their use require a change to renewable energy sources in the near future. Owing to the fluctuating supply of renewable energy, the key problem to be solved for this change is energy storage. For applications in transportation, in particular, an efficient energy carrier is needed that can be produced and used in a closed cycle. Presently, hydrogen is the only energy carrier that can be produced easily in large amounts and on an appropriate timescale. Electric energy, from either solar or wind power, or from future fusion reactors, can be used to produce hydrogen from water by electrolysis. The combustion of hydrogen in either an internal combustion engine or a fuel cell generates only water, and the cycle is closed (for a comprehensive overview see Ref. [1]).

Hydrogen has the highest gravimetric energy density of all chemical fuels; however, the volumetric density is very low since hydrogen is gaseous under normal conditions down to its boiling point at 20 K. An efficient and safe means of hydrogen storage is thus the bottleneck for the commercialization of fuel-cell-driven vehicles since storage in either liquid form or under high pressure has severe disadvantages. Ideal would be the storage of hydrogen in lightweight solids. There are two principal approaches: 1) the chemical bonding of hydrogen as a hydride, in other words, chemisorption, and 2) the adsorption of hydrogen molecules on surfaces, in other words, physisorption.

Owing to the formation of either metallic, ionic, or covalent bonds in hydrides, the interaction energy for chemisorbed hydrogen is typically quite high, leading to a high heat evolution during absorption, which limits fast refueling. Furthermore, hydrides are either too heavy or require high temperatures for hydrogen release.

The physisorption of hydrogen molecules is a rapid process; however, owing to the weak van der Waals forces, high storage capacities can be achieved only at low temperatures. Typically these are cryogenic temperatures between 60 and 120 K and, therefore, this kind of hydrogen storage by physically adsorbed hydrogen molecules on a porous material is called cryoadsorption. Nevertheless, from the viewpoint of reversibility and fast refueling times this cryoadsorption has great potential to be used in hydrogen-storage devices. One key to reaching high storage capacity by cryoadsorption is a high specific surface area. The maximum hydrogen uptake at low temperature was found to be linearly dependent on the specific surface area of carbonaceous materials.[2,3] The best of these carbonaceous materials are activated carbons with a surface area of slightly over 3000 $m^2 g^{-1}$. For a further improvement of the storage capacity, materials with even higher surface areas accessible for hydrogen molecules are needed.

Metal–organic frameworks (MOFs) are a new class of crystalline materials exhibiting extremely high porosity, which immediately attracted great attention as potential gas-storage materials. MOFs are crystalline solids composed of inorganic subunits, for example, metal oxide clusters, and rigid organic linkers. These building blocks can be used to design an almost infinite variety of frameworks with tunable and well-defined pore structures, extremely high specific surface areas, and no dead volume, in contrast to zeolites. Soon after the first synthesis of these novel porous materials, some high-surface-area MOFs were reported to display hydrogen-storage capacities similar to the best activated carbons. Two research groups independently found that also in the case of MOFs a linear correlation exists between the hydrogen uptake at 77 K and the specific surface area.[4,5] Therefore, one means of increasing the storage capacity is to generate larger specific surface areas. Last year the group of Kaskel succeeded in synthesizing a new mesoporous framework by joining $\{Zn_4O(CO_2)_6\}$ units through 4,4′,4″-benzene-1,3,5-triyl-tribenzoate (BTB) 2,6-naphthalenedicarboxylate (NDC) linkers; the new framework material, DUT-6, was named after the Dresden University of Technology.[6]

A recent publication by Yaghi et al. described a further step towards even higher specific surface areas.[7] They prepared a whole series of new mesoporous MOFs, including DUT-6 (renamed MOF-205). In this new series the highest Brunauer–Emmett–Teller (BET) specific surface area of 6240 $m^2 g^{-1}$ is exhibited by MOF-210, which is composed of $\{Zn_4O(CO_2)_6\}$ units and 4,4′,4″-(benzene-1,3,5-triyl-tris(ethyne-2,1-diyl))tribenzoate (BTE) and biphenyl-4,4′-dicarboxylate (BPDC) linkers. This extremely high surface area may be very close to the ultimate limit possible for porous structures. Therefore, MOF-210 shows the highest excess hydrogen uptake of 86 $mg g^{-1}$ ever observed for physisorption

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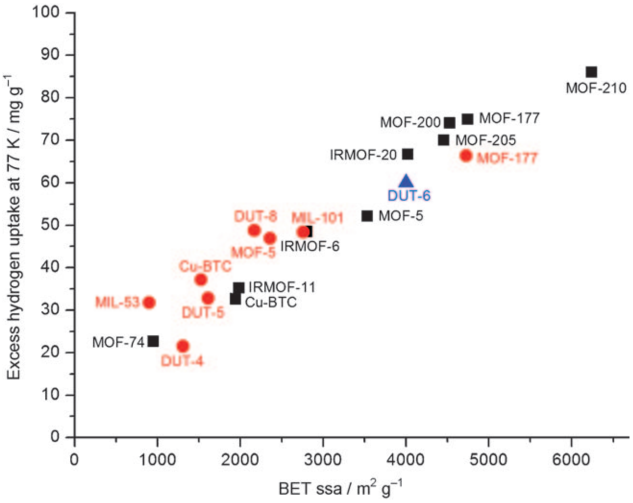

Figure 1. Excess hydrogen uptake at 77 K versus BET specific surface area (BET ssa) for various high-porosity MOFs. The symbols denote measurements conducted by different research groups (circles: at 20 bar by Hirscher et al.; triangles: at 60 bar by Kaskel et al.; squares: saturation values by Yaghi et al.).

at 77 K. The excess uptake still has linear correlation with the specific surface area (Figure 1).

For the characterization of porous solids usually the excess adsorption values are stated since these are easy to measure. However, for technical application the total uptake is relevant. The total uptake is the adsorbed gas layer plus the gas phase in the pores. For pores much larger than twice the kinetic diameter of the hydrogen molecule (> 0.6 nm), the gas phase adds quite an appreciable amount to the hydrogen stored by adsorption. Based on its single-crystal density, MOF-210 shows an extremely high value of 176 mg g^{-1} for the total storage capacity at 77 K and 80 bar; this value exceeds that of all complex aluminum hydrides and most borohydrides. The volumetric storage density based on the single-crystal density, 44 g L^{-1}, is acceptable; however, in applications the MOF is used as a powder, and the storage density thus depends on the packing density of the powder.

In conclusion, the low heat evolution during loading and the high gravimetric storage capacity of these newly synthesized MOFs with ultrahigh porosity represent a huge step forward to materials for hydrogen-storage systems based on cryoadsorption.

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