Recent Studies in Materials for Hydrogen Storage

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Hydrogen is the most abundant element in the universe and on the earth. However, most of it is in the form of water, and less than 1% exists as molecular hydrogen.[1, 2] Hydrogen is an important potential alternative fuel because it has many attractive properties, such as non-toxicity, clean combustion, and high energy density.[2] The chemical energy per mass of hydrogen is at least three times larger than that of liquid hydrocarbons.[1, 2] However, there are some problems in using hydrogen as a fuel. The most crucial one is to develop safe and efficient storage for it. The U.S. Department of Energy has set the target capacity for storage units as 6.5 % hydrogen by mass and 62 kg H_2 m^{-3} for cars using fuel cells.[1, 2] High-pressure containers and liquid-hydrogen containers conventionally used for hydrogen storage have some dangerous parts and can lose some hydrogen.[1] Also, the capacity for these storage units is only about 4 % hydrogen by mass.[1] Thus, many researchers have tried to find better methods for hydrogen storage.

Many metals and alloys have been studied and show the ability of adsorbing hydrogen.[1,3-5] Well-known metals and alloys are enlisted in Table 1.[1,3] Generally, however, metal hydrides have low mass density and sometimes show unfavorable kinetics which are inappropriate for hydrogen storage.[1,6] Light-metal hydrides show high hydrogen capacity, such as 7.4 wt% hydrogen for $NaAlH_4$.[7] However, the light-metal hydrides generally produce the hydrogen at high temperature, above about 200 °C. Bogdanovic et al. showed that the desorption temperature can be decreased by doping $NaAlH_4$ with Ti catalysts.[6-11] They also demonstrated the reversibility for several adsorption and desorption cycles.[9,11] However, they have not discovered the identity and mechanism of the Ti catalyst in the reaction, which will have to be known for further progress.[6]

Table 1. Metal hydrides and their hydrogen-storage properties

Type	Metal	Hydride	Mass%	Peq, T
Elemental	Pd	$PdH_{0.6}$	0.56	0.02 bar, 298 K
Elemental	Mg	MgH_2	7.66	5 bar, 620 K
AB5	$LaNi_5$	$LaNi_5H_6$	1.37	2 bar, 298 K
AB2	ZrV_2	$ZrV_2H_{5.5}$	3.01	10^{-8} bar, 323 K
AB	FeTi	$FeTiH_2$	1.89	5 bar, 303 K
A2B	Mg_2Ni	Mg_2NiH_4	3.59	1 bar, 555 K
Body-centered cubic	TiV_2	TiV_2H_4	2.6	10 bar, 313 K

Yaghi et al. synthesized MOF-5 in 1999, consisting of $[OZn_4]^{6+}$ groups assembled into the cubic lattice by the organic connectors, BDC(1,4-benzenedicarboxilate), as shown in Figure 1.[12-14] They designed and synthesized various isoreticular MOFs by changing the organic connectors.[15] MOF-5 showed 4.5 wt% at 78 K and 1.0 wt % at 298 K and 20 bar in hydrogen capacity.[13,14] MOF-5 has two different hydrogen-binding sites: one is the $[OZn_4]^{6+}$, and the other is an organic connector, BDC.[13] Yaghi et al.

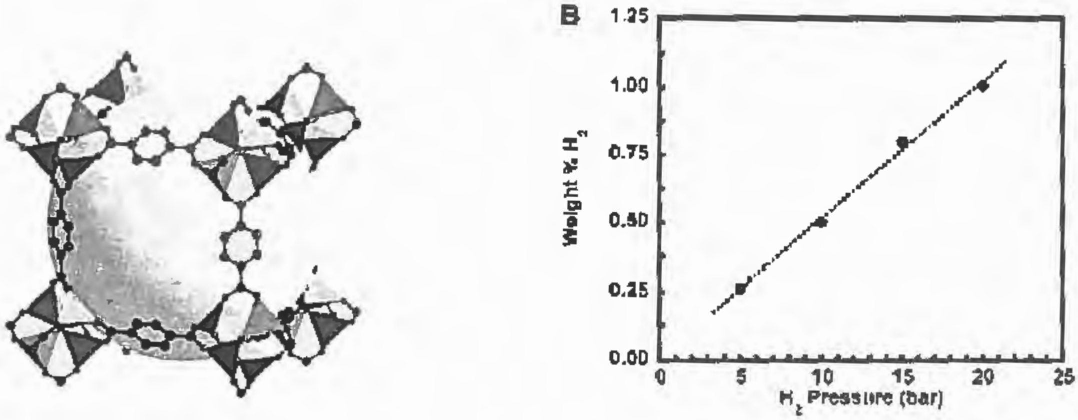

Figure 1. MOF-5 structure and hydrogen-gas adsorption isotherm at 298 K

demonstrated that organic connectors in MOFs play an important role in determining hydrogen-uptake level. Experimental data showed that the MOFs having different organic connectors had different hydrogen capacities.[13]

Carbon nanotubes, found by Iijima in 1991,[16] were expected to be good for hydrogen storage due to low specific weight and their structure, which is microporous and contains capillaries.[16] Dillon et al. estimated the hydrogen-storage capacity of carbon nanotubes to be 5-10 wt% based on their experimental results.[17] After that, many researchers studied in this area and produced much experimental data. However, this data showed large differences in hydrogen capacity, from 0.01 to 10 wt% for the same material, single-walled carbon nanotubes.[17-19] In some cases, the controversy is caused by non-reliable characterization of the carbon nanotubes used in the experiments, as well as improper analytical methods.[17,19] Some groups claimed that hydrogen-storage capacity of carbon nanostructures is proportional to the specific surface area by 1.5 wt% per 1000 m^2/g.[17] Also, many theoretical calculations have been performed for understanding adsorption processes and maximum possible storage capacity for carbon nanotubes. By theoretical calculation, the maximum capacity is 4.2 wt% for physisorption and about 14 wt% for chemisorption of hydrogen.[20,21]

In conclusion, light-metal hydrides and metal organic frameworks showed promising results. Further research of carbon nanotubes is needed to establish whether they are suitable materials for hydrogen storage.

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