Enhanced dehydrogenation of $LiBH_4$ catalyzed by carbon-supported Pt nanoparticles†

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The catalytic dehydrogenation of $LiBH_4$ doped with exceptionally low quantities of carbon-supported Pt nanoparticles can be improved significantly, and smaller Pt nanoparticles result in greater enhanced catalytic dehydrogenation of $LiBH_4$ than do larger Pt nanoparticles.

Hydrogen is widely considered as an ideal energy carrier because its combustion product is water, a zero pollutant. However, safe and efficient hydrogen storage as well as hazards associated with transportation are difficult challenges that must be overcome in order for hydrogen to play a key role in meeting humankind's future energy needs.[1] Presently, hydrogen is available mainly as a high pressure gas in cylinders, as liquid hydrogen in cryogenic tanks, and as adsorbed hydrogen in alloy and carbon materials.[2] The safety of pressurized cylinders is an issue of concern, especially in highly populated regions, and the low critical temperature for cryogenic storage is a harsh requirement. Also, the amount of adsorbed hydrogen in alloy materials and carbon nanotubes is currently too low for practical applications.[3] Consequently, extensive efforts have been directed at developing new hydrogen storage materials.[4]

Because of its high storage capacity of 18.5 wt%, $LiBH_4$ may be considered as a good candidate for on-board applications that are dependent on total weight. However, extraction of hydrogen from $LiBH_4$ suffers because of its thermal stability, requiring a temperature of ~400 °C to desorb hydrogen at a pressure of 0.1 MPa.[5] As a result, recent research efforts have focused on the catalyzed dehydrogenation and rehydrogenation of $LiBH_4$, in order to lower the H_2 evolution temperature and to increase the hydrogen desorption capacity.

Doping with catalyst has been widely studied as a means of destabilizing $LiBH_4$. When $LiBH_4$ is doped with, for example, SiO_2 powder, with a mass ratio of 1 : 3, the temperature of hydrogen desorption is lowered to 240 °C, and about 9 wt% of H_2 can be released below 400 °C.[6] Further addition of TiF_3 into a mixture of $LiBH_4$ and SiO_2 shows that the ternary mixture $LiBH_4 + 0.2SiO_2 + 0.3TiF_3$ could release hydrogen from 70 °C and desorbed 8.3 wt% H_2 below 500 °C.[7] The reaction of $LiBH_4$ with $LiNH_2$ leads to the formation of a quaternary hydride that can desorb 10 wt% H_2 above 300 °C.[8] Also, it has been qualitatively verified that $LiBH_4$ doped with disordered mesoporous carbon, to a mass ratio of 1 : 1, gives rise to a large amount of hydrogen at 332 °C.[9] The ball milled mixture of $LiBH_4$ and MgH_2 with a mass ratio of 1 : 4 gives rise to a decrease in dehydrogenation temperature and the formation of a Li–Mg alloy.[10] More recently, carbon nanotubes have been used for doping $LiBH_4$. Onset of hydrogen desorption starts at 250 °C and the majority of the hydrogen can be released below 600 °C.[11]

Although catalysts efficiently decrease the dehydrogenation temperature and increase the dehydrogenation capacity, the requisite loading of dopant is too large, leading to an unfavorable weight ratio. Here, we report a doping strategy to improve the dehydrogenating properties of $LiBH_4$ that involves the addition of small quantities of carbon-supported Pt nanoparticles (Pt/C). We observe that the dehydrogenation properties of $LiBH_4$ are significantly improved, even for exceptionally low catalyst content.

The mixture of $LiBH_4$ and Pt/C was prepared through a ball milling method, as described in the ESI.† We have found that the trace of Fe species was introduced into the mixture (*cf.* Tables S1, S2 and S3 in ESI†). Fig. 1 shows mass spectra (MS) of pure $LiBH_4$ and $LiBH_4$ doped by 10 wt% catalysts of two different particle sizes: *ca.* 4.7 and 16.0 nm; the Pt mean particle sizes of two Pt/C catalysts were determined from TEM images, as shown in Fig. S1 in ESI.† The MS profile of pure $LiBH_4$ in Fig. 1(a) exhibits four hydrogen desorption peaks: corresponding to the structural transition (80–110 °C), melting reaction (280–310 °C) and dehydrogenation reactions

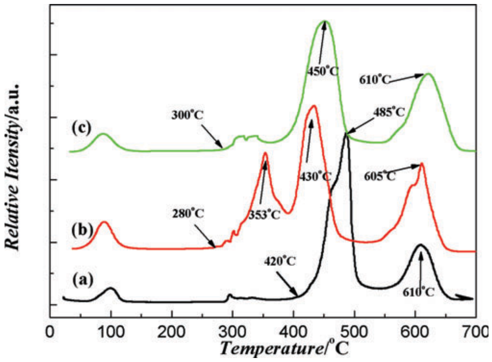

Fig. 1 MS profiles of dehydrogenation reactions of pure $LiBH_4$ (a) and $LiBH_4$ doped with 10 wt% Pt/C catalyst with Pt particle sizes of 4.7 (b) and 16.0 nm (c).

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(420–510 and 560–650 °C).[5,12] The main hydrogen desorption reactions start at 420 °C, with peak values at 485 and 610 °C. However, by adding 10 wt% of as-purchased Pt/C catalyst (with a particle size of *ca.* 4.7 nm) to the $LiBH_4$ compound, the dehydrogenation temperature of $LiBH_4$ is significantly reduced, as shown in Fig. 1(b). The first major dehydrogenation peak starts at *ca.* 280 °C, resulting in *ca.* 2.2 wt% of hydrogen released from $LiBH_4$, which is quite different from pure $LiBH_4$, where only a minor dehydrogenation of 0.6 wt% occurs between 280 and 310 °C. Also, in comparison to pure $LiBH_4$, the other main dehydrogenation peaks of the Pt/C doped $LiBH_4$ shift to lower temperatures, with an increased total weight loss of 16.3 wt%, determined from curve b in Fig. S3.† These results clearly demonstrate that dehydrogenation of $LiBH_4$ is significantly improved by doping small amounts of carbon-supported Pt nanoparticles into $LiBH_4$.

A similar conclusion is reached when doped with 5 wt% catalyst (*cf.* Fig. S4†). Our studies indicate that the temperature for the onset of dehydrogenation decreases even at a catalyst doping loading that would be considered very low in comparison with recently reported results.[6,11,12] On the other hand, in the case that $LiBH_4$ doped with 10 wt% catalyst with a mean particle size of 16.0 nm, the temperature for initial hydrogen desorption is found at *ca.* 300 °C, with two major desorption peaks at 450 and 610 °C, and a hydrogen released amount of 14.1 wt%, as shown in Fig. 1(c) and Fig. S3c.† Generally, the shape, particle size and surface area of the catalyst may have an influence on the hydrogen storage properties of $LiBH_4$. As reported, the shape of the metal catalyst could have a significant influence on the hydrogen storage properties.[13] However, in this work, no change in the shapes of Pt nanoparticles was found after heat treatment at 400 °C. Obviously, the onset temperature increases and the dehydrogenation capacity decreases with increase in Pt particle size, indicating an important role of Pt nanoparticle size in dehydrogenation performance of $LiBH_4$. Since the Pt surface area of the Pt catalysts is inversely proportional to the particle size of Pt nanoparticles (*cf.* Fig. S5†), thus, the improved dehydrogenation properties of $LiBH_4$ doped with Pt/C may be partly relevant to the change in Pt surface area.

The thermal hydrogen desorption curves of $LiBH_4$ doped with as-purchased catalyst at different doped amounts are presented in Fig. S6;† while the detailed data are listed in Table S4.† With increase in catalyst loading (up to 50 wt%), the onset dehydrogenation temperature approaches 280 °C, however the two main desorption peaks from $LiBH_4$ shift to lower temperatures and the total dehydrogenation capacity increases. The dehydrogenation capacity of $LiBH_4$ doped with 50 wt% catalyst is found to be 18.4 wt%, very close to the theoretical value of *ca.* 18.5 wt%. Hence, one observes that with increase in Pt/C content in mixtures of Pt/C and $LiBH_4$, there is apparently a remarkable increase in the contact area between Pt/C and $LiBH_4$, which leads to an improved dehydrogenation of $LiBH_4$.

The question of recovering $LiBH_4$ after dehydrogenation, in order to develop a reversible H_2 storage and release system, important for practical applications, is now dealt with. To this end, a mixture of Pt/C and $LiBH_4$ with a mass ratio of 1 : 9 that had been dehydrogenated under a vacuum up to 600 °C was rehydrogenated at 600 °C for 24 h under 3 MPa hydrogen pressure. Fig. 2 shows comparisons, respectively, of MS (curves a and c) and TG (curves b and d) for the first dehydrogenation (curves a and b) and the fourth dehydrogenation (curves c and d) after recharging with H_2. The onset temperature for hydrogen desorption for the sample that had not experienced a prior dehydrogenation is *ca.* 280 °C, while the three main desorption peaks are located at 353, 430 and 605 °C, and the weight loss corresponds to 16.3 wt%. After three cycles, the initial dehydrogenation temperature is still at *ca.* 280 °C, but only two main dehydrogenation peaks (at 405 and 575 °C) are observed as shown in Fig. 2(c). For cycling measurements, the capacity shown in Fig. 3 is the dehydrogenation capacity of the mixture. After 30 cycles, the capacity was still kept at *ca.* 6.1 wt%, indicating that the system can reversibly store *ca.* 6.1 wt% hydrogen, which could meet the US DOE target for automobile application, although the dehydrogenation temperature is still high. Furthermore, the measured mean thermal conductivity for the 10 wt% Pt/C doped $LiBH_4$ is *ca.* 2.2 W m^{-1} K^{-1}, which is higher than that of pure $LiBH_4$ with a value of *ca.* 1.4 W m^{-1} K^{-1}.[14] Moreover, from the DSC results in Fig. S7,† the endothermic enthalpy of the dehydrogenation reaction of pure $LiBH_4$ is *ca.* 67.9 kJ mol^{-1} H_2, which is close to the previously reported result.[15] However, for the 10 wt% Pt/C doped $LiBH_4$, the endothermic reaction enthalpy in the dehydrogenation process is *ca.* 36.3 kJ mol^{-1} H_2, which is much lower than that of pure $LiBH_4$.

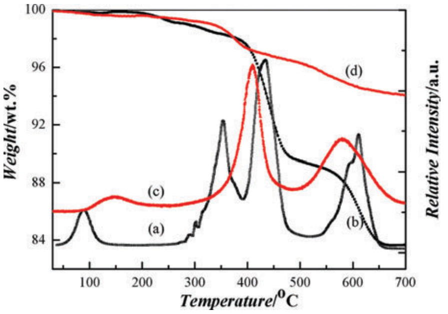

Fig. 2 MS (a, c) and TG (b, d) profiles for the mixture of Pt/C and $LiBH_4$ with a mass ratio of 1 : 9. The first dehydrogenation (a, b) and the fourth dehydrogenation after recharging H_2 (c, d).

As discussed in the literature, the utilization of carbon nanotubes and mesoporous carbon at high catalyst content (50 wt%) results in enhanced dehydrogenation of $LiBH_4$.[9,11] To clarify the possible roles of carbon and Pt nanoparticles in

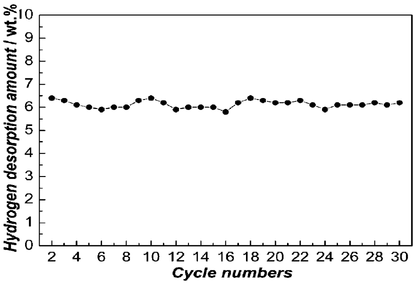

Fig. 3 Dehydrogenation cycling of the 10 wt% Pt/C doped $LiBH_4$.

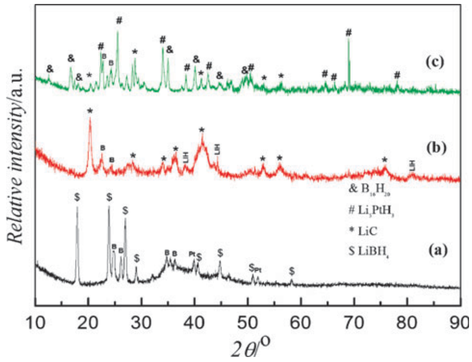

Fig. 4 XRD patterns of 10 wt% Pt/C doped $LiBH_4$ before the first dehydrogenation (a), after the first dehydrogenation at 600 °C for 5 h (b), and after the fourth rehydrogenation at 600 °C for 24 h (c).

catalyzed dehydrogenation of $LiBH_4$, a comparison of the dehydrogenation behaviors of $LiBH_4$ doped with 20 wt% XC-72 carbon and 50 wt% Pt/C catalyst (corresponding to a carbon content of 20 wt%) is shown in Fig. S8.† We conclude that Pt nanoparticles rather than carbon play the crucial role in the catalyzed dehydrogenation of $LiBH_4$. The improved catalytic efficiency when C and Pt are both present is likely attributable to increased contact area between Pt nanoparticles and $LiBH_4$ during ball-milling process for forming the composite material.

To explore any possible structural change during the dehydrogenation/rehydrogenation process, XRD patterns of $LiBH_4$ doped with 10 wt% Pt/C before and after the initial dehydrogenation, and the sample after the third dehydrogenation at 600 °C for 5 h and then rehydrogenation at 600 °C for 24 h were acquired, as shown in Fig. 4. Only $LiBH_4$, Pt and boron diffraction peaks are observed for the mixture before the first dehydrogenation (curve a), indicating that the ball milled product is a physical mixture of Pt/C and $LiBH_4$; the appearance of boron peaks may result from slight decomposition of $LiBH_4$ during the ball milling process. However, no XC-72 carbon peaks were observed, probably due to its low amount and amorphous structure. After the first dehydrogenation at 600 °C for 5 h, the $LiBH_4$ phase disappears, and LiC, LiH and B phases are identified. The possible dehydrogenation reaction may be described as $LiBH_4 \rightarrow LiH + B + 1.5H_2$ and $LiBH_4 + C \rightarrow LiC + B + 2H_2$,[11] catalyzed by carbon-supported Pt nanoparticles. In the case of the rehydrogenated sample (curve c), no $LiBH_4$ is reformed, but many new diffraction peaks are clearly seen, with the exception of the LiC and B peaks. A careful comparison of the XRD pattern of the rehydrogenated sample with the JCPDS cards (*i.e.* 21-0104 and 42-1097) indicates that these new diffraction peaks can be assigned as the corresponding $B_{16}H_{20}$ and Li_5PtH_3 phases. Thus, we deduce that the possible catalytic rehydrogenation approaches may be represented as follows: $5LiH + 32B + 19H_2 + Pt \rightarrow Li_5PtH_3 + 2B_{16}H_{20}$. Based on this equation, a mixture of the newly formed Li_5PtH_3 and $B_{16}H_{20}$, in the stoichiometric ratio of 1 to 2, respectively, might reversibly store *ca.* 7.0 wt% of hydrogen, which is close to the experimentally reversible hydrogen released amount of *ca.* 6.1 wt%.

In summary, we have found that Pt nanoparticles play a crucial role in the catalyzed dehydrogenation of $LiBH_4$, and that by using carbon-supported Pt nanoparticles as catalyst, the dehydrogenating properties of $LiBH_4$ can be improved significantly even at very low catalyst contents. We also report a Pt particle size effect on the catalytic dehydrogenation of $LiBH_4$ that smaller Pt nanoparticles result in greater enhanced catalytic dehydrogenation of $LiBH_4$ than do larger Pt nanoparticles. A key finding is that the mixture of Li_5PtH_3 and $B_{16}H_{20}$ with a theoretical hydrogen capacity of *ca.* 7.0 wt% is likely formed during the rehydrogenation/dehydrogenation process. Also, a reversible rehydrogenation/dehydrogenation capacity of *ca.* 6.1 wt% has been shown, which is close to the theoretical hydrogen capacity of newly formed mixture of Li_5PtH_3 and $B_{16}H_{20}$. It is to be noted that although Pt is expensive, it can be readily recycled in practical applications through hydrolyzation reaction, and our results may open a new and promising way for the nanocatalytic dehydrogenation of $LiBH_4$.

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