Supplementary Information

Enhanced Dehydrogenation of $LiBH_4$ Catalyzed by Carbon-Supported Pt Nanoparticles

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Experimental section

Commercially acquired $LiBH_4$ (95% purity, J&K Chemical Ltd, Sweden), carbon-supported Pt nanoparticles (Pt/C, with a Pt loading of 60 wt. %, Hispec9000, Johnson Matthey Inc., U. K.), and Vulcan XC-72 carbon (with a specific surface area of 254 m^2g^{-1}) were used as received.

The particle size distribution and morphology of the as-purchased Pt/C and heat-treated Pt/C catalysts were analyzed by transmission electron microscopy (TEM) using a Technai G2 20 s-Twin Microscope (FEP Inc., USA).

X-ray diffraction (XRD) measurements utilized a Rigaku D/MAX-2000 diffractometer using Cu Kα radiation. Diffraction patterns were collected at a scanning rate of 2 ^{o} min^{-1} and with a step of 0.02 ^{o}. The mean particle size was calculated from the (220) plane using the Scherrer equation.

The BET surface areas of the as-purchased Pt/C and heat-treated Pt/C catalysts were determined by BET surface analyzer (ASAP 2010, Micromeritics, USA).

The mixture of $LiBH_4$ and Pt/C was prepared through a ball milling method: 1g of $LiBH_4$ and Pt/C mixture with various mass ratios was mechanically milled for 1.5 h (Planetary QM-1SP2) under argon atmosphere at room temperature. The ball-to-power weight ratio was 30:1 at 580 rpm using stainless steel balls of 10 mm diameter.

To investigate if the ball-milling process introduced impurity into samples, the element contents of $LiBH_4$ samples before and after the ball-milling process, and of the 10 wt. % Pt/C doped $LiBH_4$ were determined by inductively coupled plasma-atomic emission spectrometer (TCAP6300, USA).

Thermal conductivity measurement was performed using the hot wire method.[1] The 10 wt.% Pt/C doped $LiBH_4$ sample was packed in a tailor-made cell and tested using a quick thermal conductivity meter (QTM-500, Japan).

Hydrogen releasing property measurements were performed using a Netzsch STA449C TG-DSC thermoanalyzer coupled with a Balzers Thermostar Quadrupole Mass Spectrometer. The heating rate was 10 °C min^{-1} and a pressure of 1 atm argon flowing at a purging rate of 20 cm^3min^{-1}. Typical sample quantity used was ca. 5~10 mg. Unless stated otherwise, the hydrogen capacity is calculated based only on the mass of $LiBH_4$.

Results and discussion

The element contents of the $LiBH_4$ samples before and after the ball-milling process, and of the 10 wt.% Pt/C doped $LiBH_4$ are listed in Tables S1, S2 and S3, respectively. As can be seen, Na and K elements coexist within these three samples and the trace of Fe species appears in the ball-milled samples. Therefore, it can be concluded that Na and K elements come from the raw $LiBH_4$ and that the trace of Fe species was introduced into the ball-milled samples.

Table S1. Element contents of as-purchased $LiBH_4$

Element Name	Element Content (wt.%)
Li	29.69
B	46.81
Na	0.68
K	0.28

Table S2. Element contents within the $LiBH_4$ sample after the ball-milling process

Element Name	Element Content (wt.%)
Li	29.45
B	46.58
Na	0.66
K	0.27
Fe	0.04
Co	<0. 01
Ni	<0. 01

Table S3. Element contents of the 10 wt.% Pt/C doped $LiBH_4$ sample

Element Name	Element Content (wt.%)
Li	27.36
B	42.51
Pt	5.98
Na	0.63
K	0.27
Fe	0.03
Co	<0. 01
Ni	<0. 01

Note: C and H can not be determined by this method.

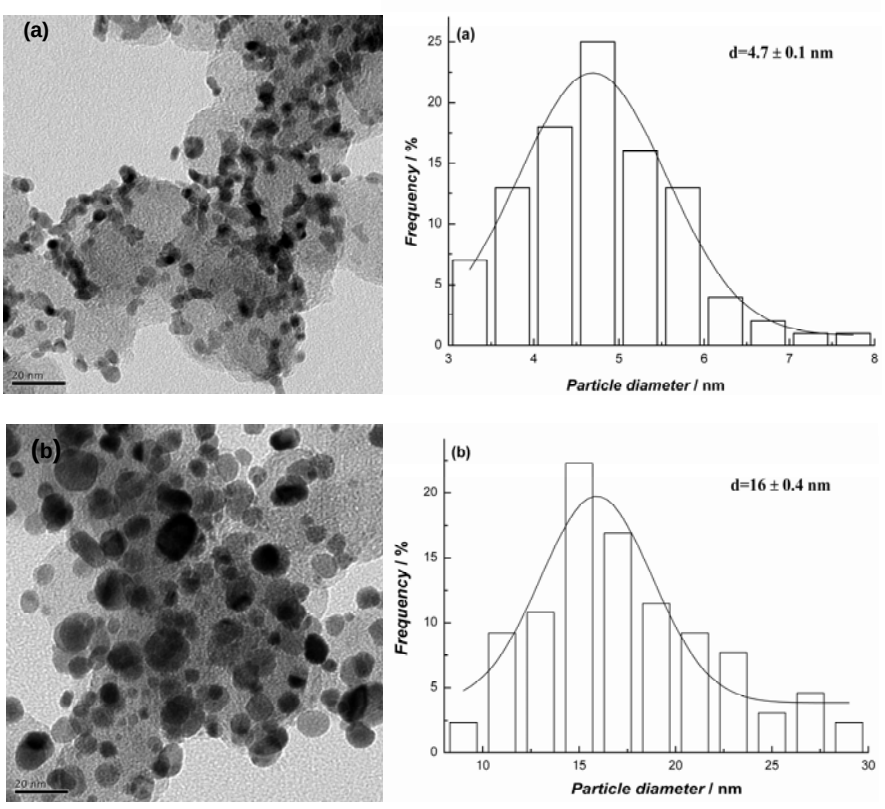

Figure S1. TEM images and the corresponding particle size distribution histograms of (a) the as-purchased Pt/C and (b) the Pt/C heat-treated under argon at 400 ^{o}C for 2 h.

Figure S1 presents TEM images of two Pt/C catalysts and their corresponding particle size

distribution histograms based on the observation of more than 500 nanoparticles. As can be seen, the mean Pt particle size of as-purchased catalyst is ca. 4.7 nm. After heat treatment at 400 ^{o}C for 2 h, the mean Pt particle size increases to ca. 16.0 nm. However, no change in the morphology of Pt nanoparticles was observed.

Figure S2 shows XRD patterns of the as-purchased Pt/C and the Pt/C heat-treated at 400 ^{o}C under argon for 2 h. By simple heat treatment under argon, Pt/C catalysts of large particle sizes were easily obtained. The Pt particle sizes of two Pt/C catalysts were ca. 3.4 and 16.0 nm, as calculated from the (220) plane using the Scherrer equation, which are in fairly good agreements with the TEM results.

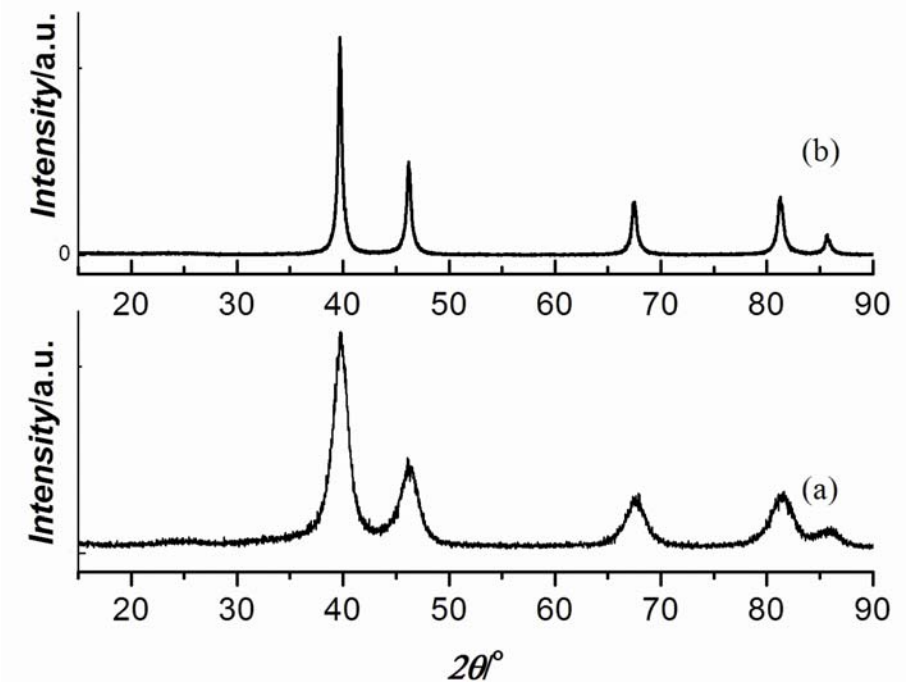

Figure S2. XRD patterns of (a) the as-purchased Pt/C and (b) the Pt/C heat-treated under argon at 400 ^{o}C for 2 h.

Figure S3 shows thermogravimetric (TG) curves 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 total amount of hydrogen released from pure $LiBH_4$ is ca. 10.7 wt.%, as shown in curve a of Figure S3, indicating that the available complement of hydrogen is released from pure $LiBH_4$ only when the temperature reaches 700 ^{o}C. By adding 10 wt.% of as-purchased Pt/C catalyst (with a

particle size of ca. 4.7 nm) to $LiBH_4$ compound, an increased total weight loss of 16.3 wt.% was observed from curve b of Figure S3. In the case that $LiBH_4$ doped with 10 wt. % catalyst with a mean Pt particle size of 16.0 nm, the total hydrogen released amount is ca. 14.1 wt.%, as shown in curve c of Figure S3.

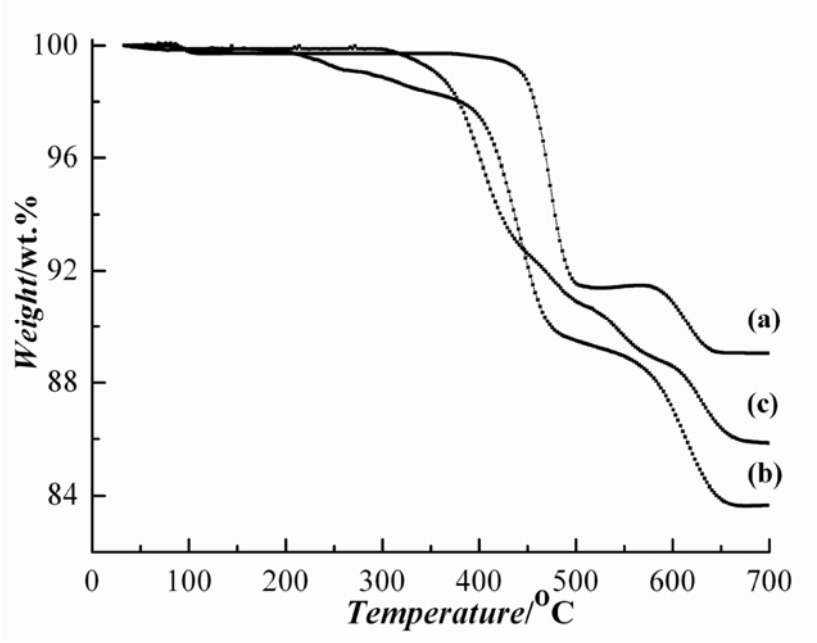

Figure S3 TG curves of dehydrogenation reactions of (a) pure $LiBH_4$, and $LiBH_4$ doped with 10 wt.% Pt/C catalyst with Pt particle sizes of (b) 4.7 nm and (c)16.0 nm.

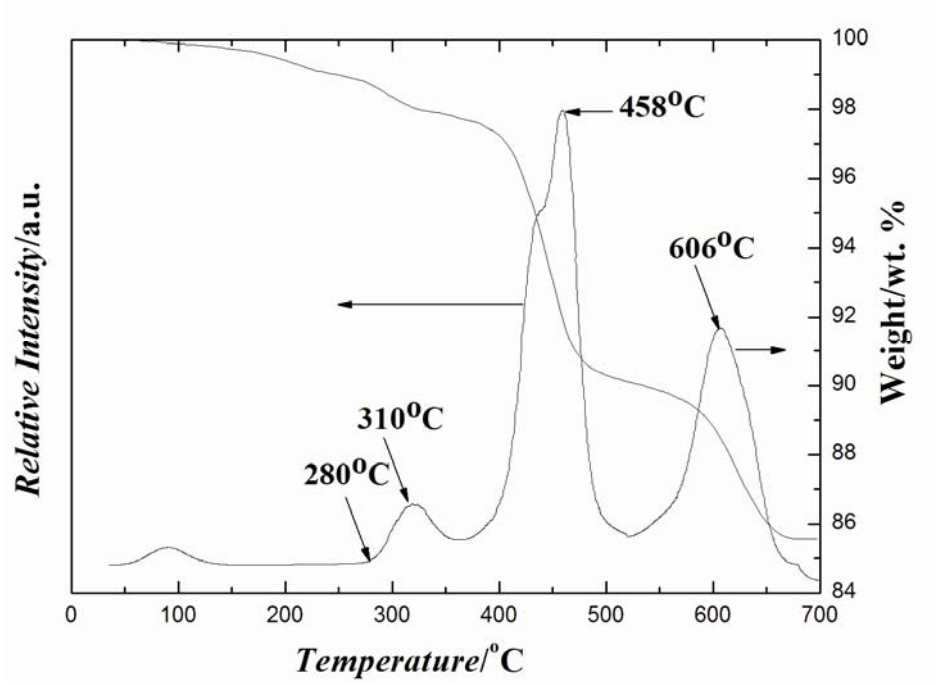

Figure S4. MS and TG profiles for the mixture of Pt/C and $LiBH_4$ with a mass ratio of 5:95.

Figure S4 shows MS and TG results for a mixture of Pt/C and $LiBH_4$ with a mass ratio of 5:95. The initial temperature for hydrogen desorption decreases to ca. 280 °C, which is similar to that for 10 wt.% Pt/C doped $LiBH_4$. Three main desorption peaks are found at 310, 458 and 606 °C, with a greatly increased weight loss of 14.5 wt. %. These results show that the dehydrogenation properties of $LiBH_4$ can be significantly improved by doping, even for very low catalyst loading within $LiBH_4$.

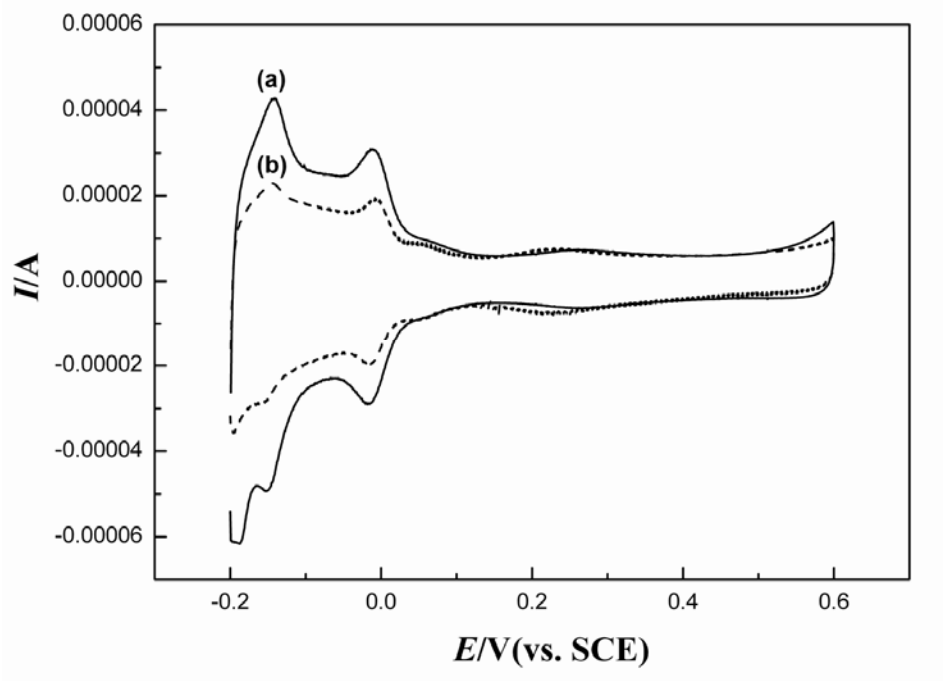

Figure S5 Cyclic voltammograms of (a) as-purchased Pt/C and (b) Pt/C heat-treated at 400 ^oC for 2 h under argon in N_2 saturated 0.5 M H_2SO_4 at 25 ^oC and at a scan rate of 20 mV/s. The Pt loading on the surface of the working electrode is ca. 56 μg/cm^2

Hydrogen adsorption/desorption peaks were used to determine the Pt real surface area of two Pt/C catalysts. **Figure S5** shows the cyclic voltammograms of these two Pt/C catalysts. The real surface areas of Pt nanoparticles (rather than carbon) in these two Pt/C catalysts are 30.7 and 16.9 m^2/g, respectively. These results clearly demonstrate that heat treatment lead to a decrease in the real surface area of Pt nanoparticles. Thus, the enhanced dehydrogenation of the Pt/C doped $LiBH_4$ may be partly relevant to the change in the real surface area of Pt nanoparticles. However, we could not find the direct correlation between the Pt real surface area and the catalytic dehydrogenation of the Pt/C doped $LiBH_4$ sample.

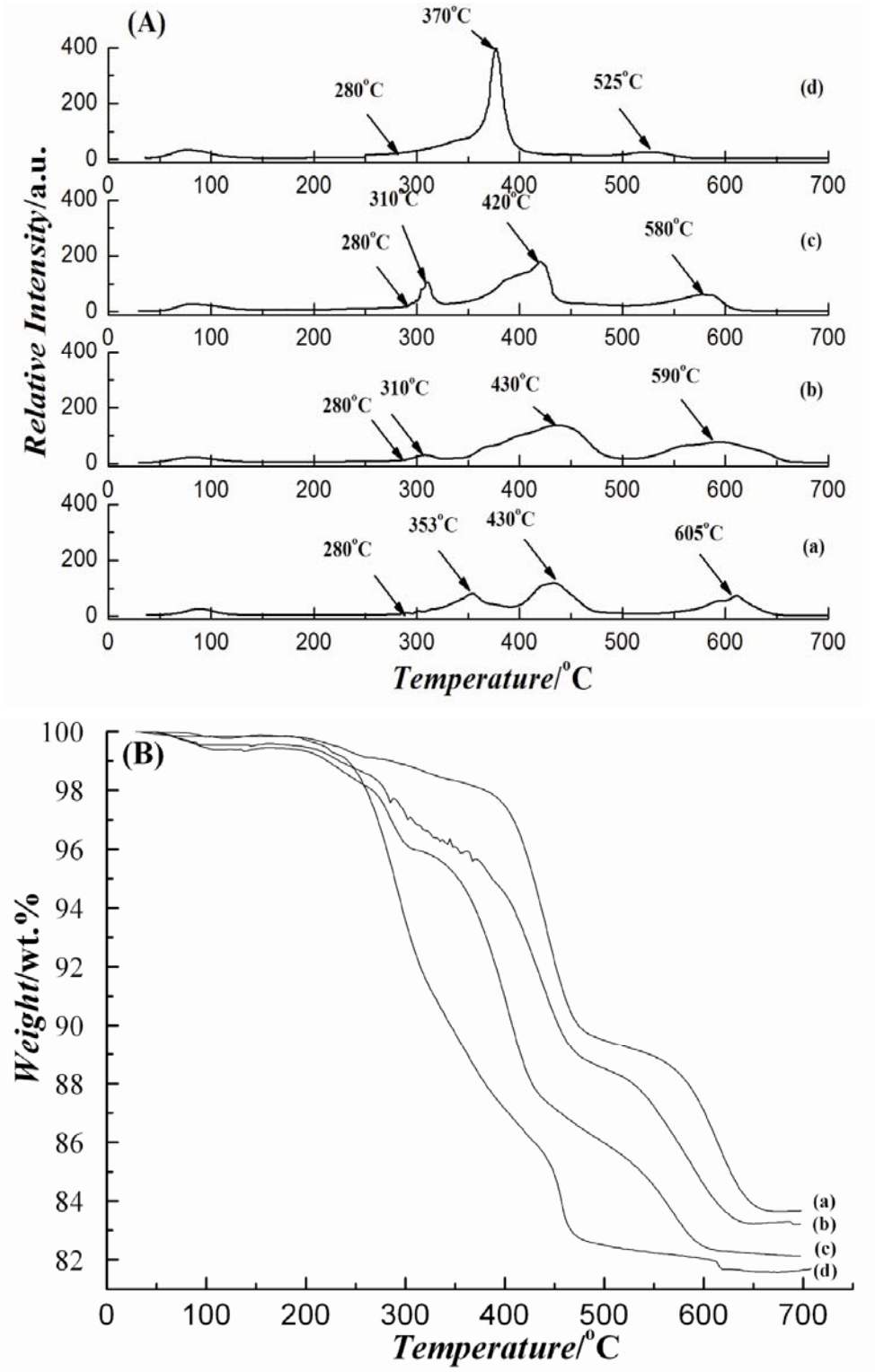

Figure S6. MS (A) and TG (B) profiles of dehydrogenation reactions of the mixture of Pt/C and $LiBH_4$. The mass ratios of Pt/C and $LiBH_4$ are (a) 10:90, (b) 20:80, (c) 33:67 and (d) 50:50, respectively.

Table S4. Hydrogen release properties of the mixtures of Pt/C and $LiBH_4$ of various mass ratios

Sample Name	Catalyst doped amount/ %	Onset dehydrogenation temperature/ ^oC	Main dehydrogenation temperature/ ^oC	Total dehydrogenation capacity/ wt.%
$LiBH_4$	0	420	485; 610	10.7
Pt/C doped $LiBH_4$	10	280	353; 430; 605	16.3
Pt/C doped $LiBH_4$	20	280	310; 430; 590	16.8
Pt/C doped $LiBH_4$	33	280	310; 420; 580	17.9
Pt/C doped $LiBH_4$	50	280	370; 525	18.4

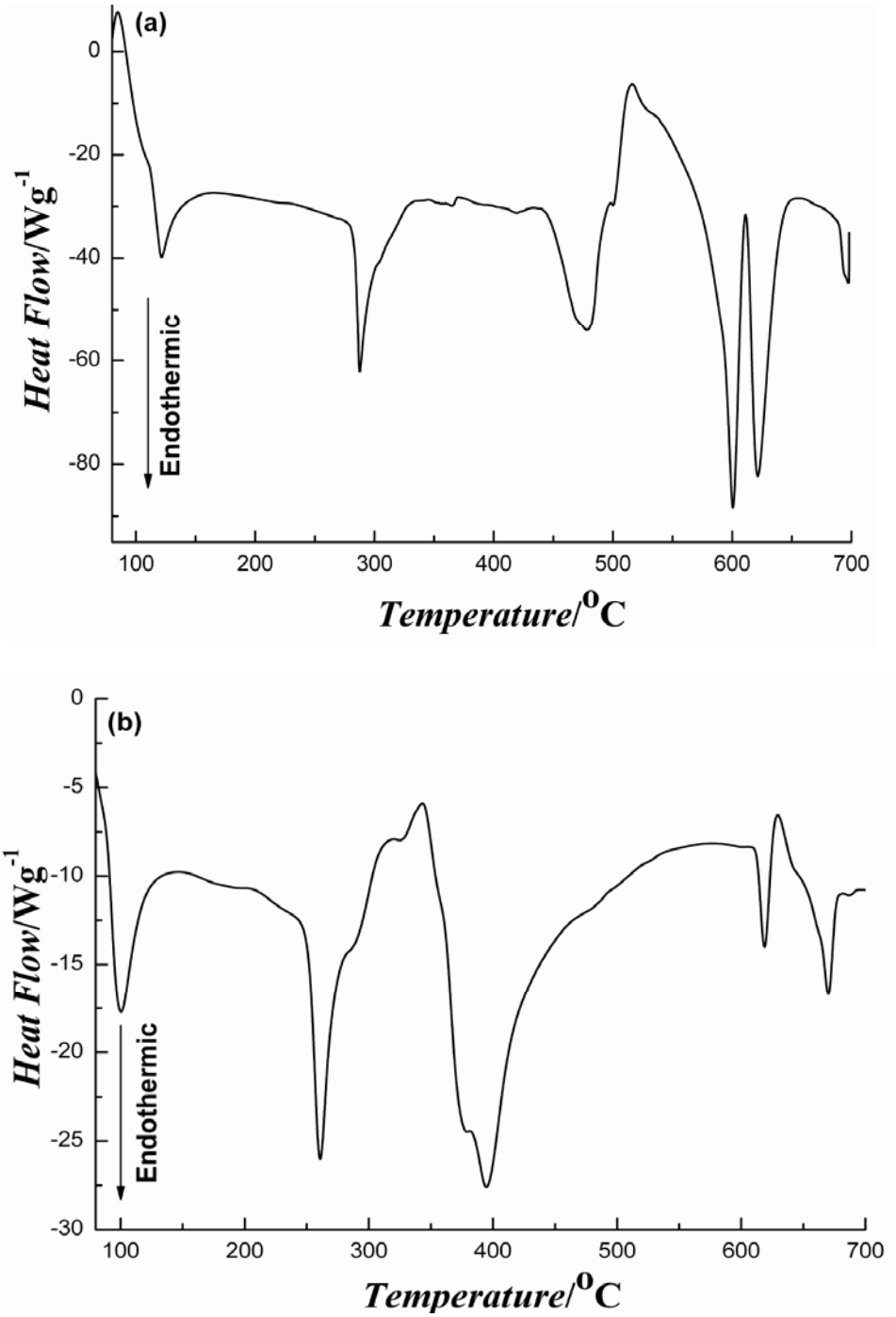

Figure S7. DSC curves of (a) pure $LiBH_4$ and (b) $LiBH_4$ doped with 10 wt. % Pt/C catalyst.

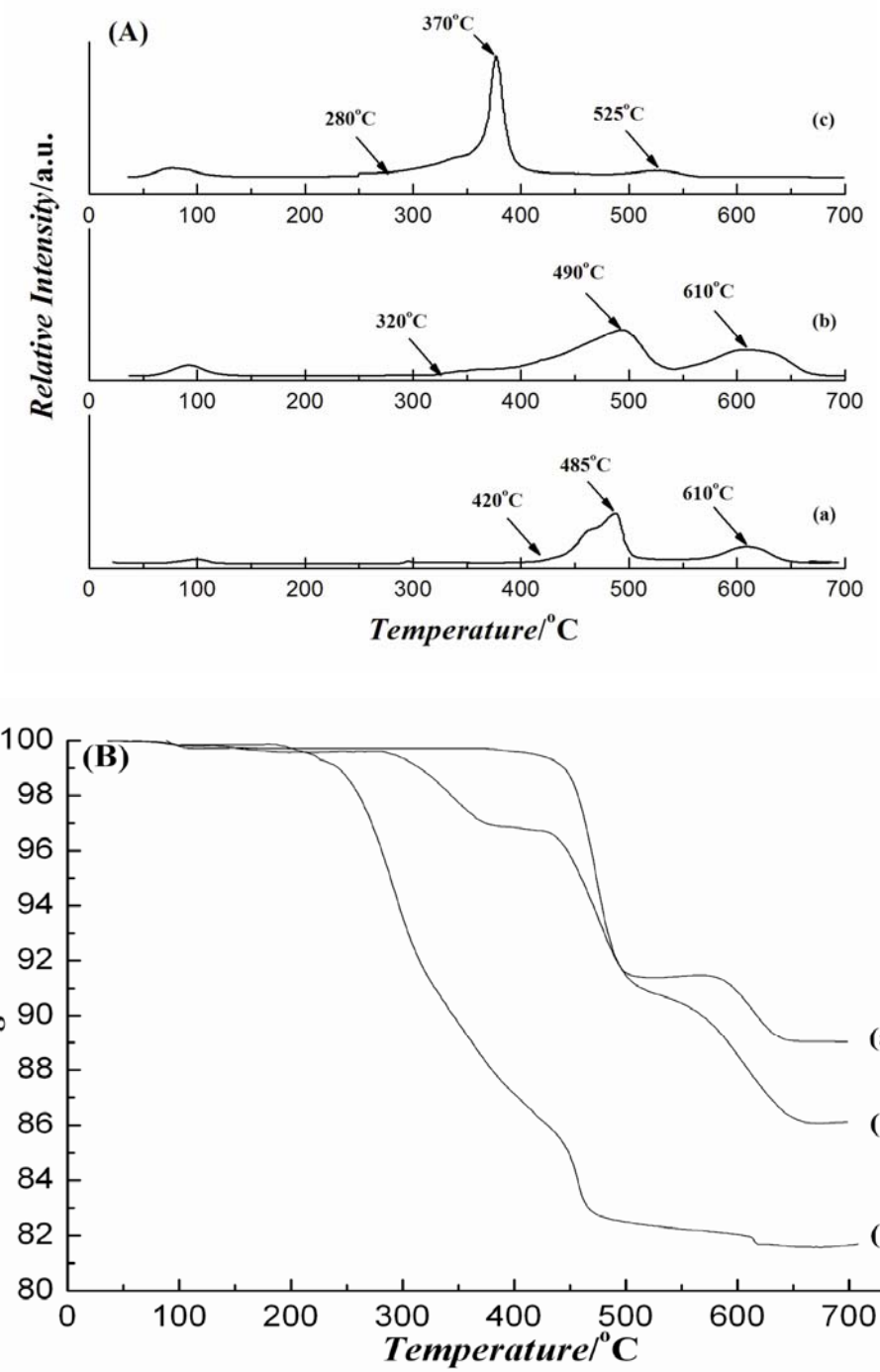

Figure S8. MS (A) and TG (B) profiles of dehydrogenation reactions of (a) pure $LiBH_4$, (b) $LiBH_4$ doped with 20 wt.% carbon and(c) 50 wt.% Pt/C.

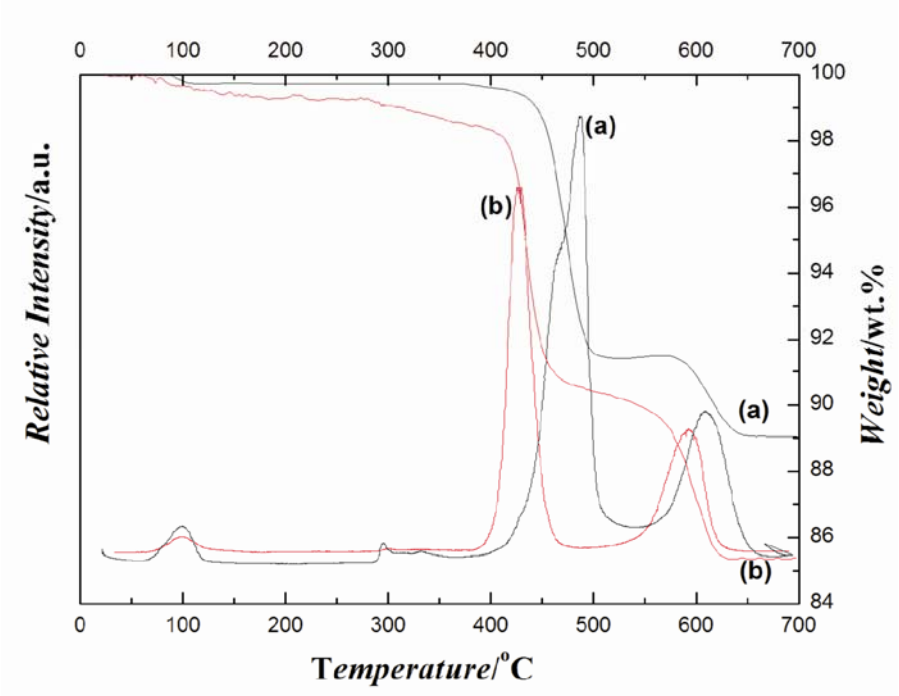

Figure S9. MS and TG profiles of dehydrogenation reactions of (a) pure $LiBH_4$ and (b) 5 wt. % pure Pt nanoparticles doped $LiBH_4$.

Figure S9 exhibits MS and TG results of pure $LiBH_4$ and 5 wt.% pure Pt doped $LiBH_4$. The onset of hydrogen desorption for the 5 wt.% pure Pt nanoparticles doped $LiBH_4$ starts at ca. 390 °C, which is lower than pure $LiBH_4$. Two main desorption peaks located at 425 and 590 °C are observed, with a greatly increased weight loss of 14.7 wt. %.

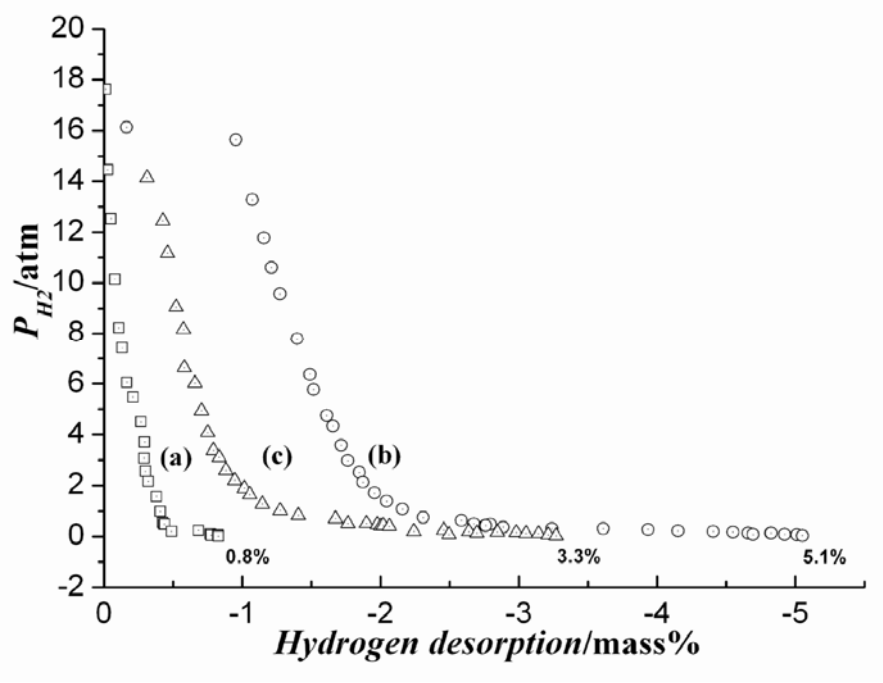

Figure S10. Dehydrogenation curves of pure $LiBH_4$ (a) and $LiBH_4$ doped with 10 wt. % Pt/C catalyst with Pt particle sizes of 4.7 (b) and 16.0 nm (c). The dehydrogenation temperature was set at 350 ^oC.

Figure S10 represents the dehydrogenation curves of pure $LiBH_4$ and $LiBH_4$ doped by 10 wt.% catalysts with two different particle sizes of ca. 4.7 and 16.0 nm. The desorbed hydrogen quantities for these three samples are ca. 0.8, 5.1 and 3.3. wt. %, respectively, which again accessing that the addition of carbon-supported Pt nanoparticles enhanced the dehydrogenation of $LiBH_4$ and that smaller Pt nanoparticles result in greater enhanced catalytic dehydrogenation of $LiBH_4$ than do larger Pt nanoparticles.

To explain the above results, we further compared the physical properties of the as-purchased and heat-treated Pt/C catalysts. TEM images and their corresponding particle size distribution histograms of the two catalysts (cf. Figure S1) present the mean particle size and the morphology of Pt nanoparticles before and after the heat treatment. XRD patterns (cf. Figure S2) reflect the product phases and mean particle size of these two catalyst. No shape and phase change was observed, but the mean Pt particle size changed from ca. 4.7 to 16.0 nm. BET results indicate that the specific surface areas of the as-purchased and heat-treated Pt/C catalysts are 100.2 and 86 m^2g^{-1}, respectively. These results prove that

heat treatment lead to an increase in mean particle size and a decrease in active area, which may cause the decrease in catalytic capability of Pt/C nanoparticles for $LiBH_4$ destabilization.

Reference

1 A. V. Talyzin, O. Andersson, B. Sundvist, A. Kurnosov, L. Dubrovinsky, *J. Solid State Chem.*, 2007, **180**, 510