Supplementary Information

Improved Dehydrogenation Properties of $Ca(BH_4)_2$-$LiNH_2$ Combined System

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Experimental details:

Materials

Lithium amide ($LiNH_2$) with purity 95% was purchased from Alfa-Aesar and used as received. $Ca(BH_4)_2$ was synthesized by means of the metathesis of $CaCl_2$ and $NaBH_4$ in tetrahydrofuran (THF) solution according to our previous report [S1]:

$$CaCl_2 + 2\ NaBH_4 \rightarrow Ca(BH_4)_2 + 2\ NaCl$$

$Ca(BD_4)_2$ was prepared by the metathesis of $CaCl_2$ and $NaBD_4$ (purchased from Alfa-Aesar) in tetrahydrofuran.

Preparation

The preparation of $Ca(BH_4)_2$-$LiNH_2$ composite samples were conducted on a Retsch PM400 high-energy planetary ball mill for 5 h at a rate of 200 rpm. All the sample handlings were performed in an MBraun glove-box filled with high-purity argon gas. Each batch of composite was about 1 g of $Ca(BH_4)_2$ and $LiNH_2$ mixture in different molar ratios. The ball-to-powder weight ratio was around 100:1 and the ball milling was under inert argon gas. And $Ca(BD_4)_2$-$2LiNH_2$ was prepared under the aforementioned condition. All the sample handlings were performed in an MBraun glove-box filled with high-purity argon gas.

Characterization

Temperature-programmed-desorption (TPD) using purified argon as carrier gas was conducted on a home-made micro-reactor shown in Figure S1 and the tail gas was analyzed by a MS combined system. Detailed operation procedures are described elsewhere [S2].

Volumetric release measurements were performed on a commercial automatic Sieverts type apparatus (PCTPro-2000) and home-made equipment show in Figure S2. Temperature was raised to the preset value at a rate of 2 ºC/min for TPD-MS and volumetric release measurements. Powder X-ray diffraction (XRD) was performed on an X'Pert Pro (PANAnalytical) diffractometer with Cu Kα radiation. N-H and B-H vibrations in all samples were identified by a Renishaw Raman spectrometer using a He/Ne laser with a wavelength of 514 nm.

NH_3 determination

NH_3 evolved in sample dehydrogenation was quantitatively measured by a home-made conductivity cell (Thermo Scientific, Orion 3-Star). [S1] NH_3 evolved in volumetric release process was quantitatively measured by introducing gaseous products into a diluted sulfuric acid (0.6 mmol/L, 100 mL) in which an electrode is immerged and connected with a conductivity meter (Thermo Scientific, Orion 3-Star). As NH_3 is trapped in the acid solution, the proton conductivity of the solution will decrease accordingly. Calibration on the conductivity cell was performed by passing given amount of NH_3 into the same acid solution to obtain empirical linear relationship between NH_3 input and conductivity change. NH_3 concentration in gaseous products can thus be determined from the calibration curve. Noted that the minimum reading for conductivity meter is 0.1 μS/cm, a precision of ~ 10 ppm can be obtained for NH_3 measurement in 100 mL standard volume at ambient pressure and temperature.

Figures and Tables

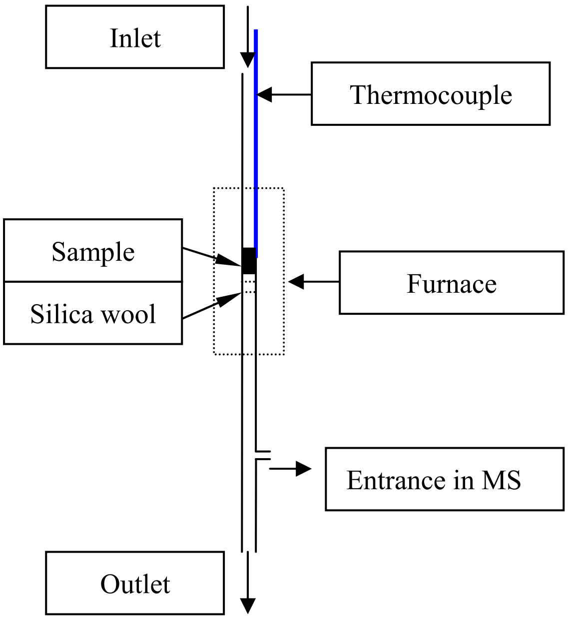

Figure S1. Scheme of home-made micro-reactor for TPD measurement

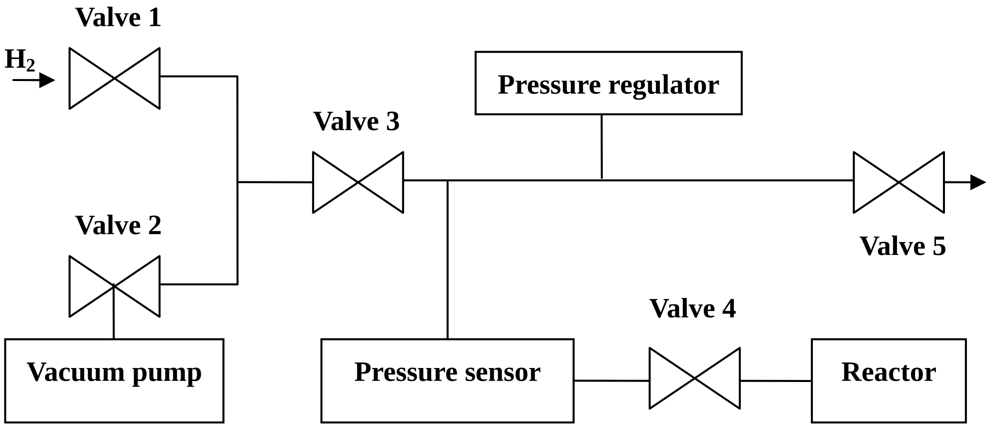

Figure S2. The schematic diagram of a home-made Sieverts PCT apparatus

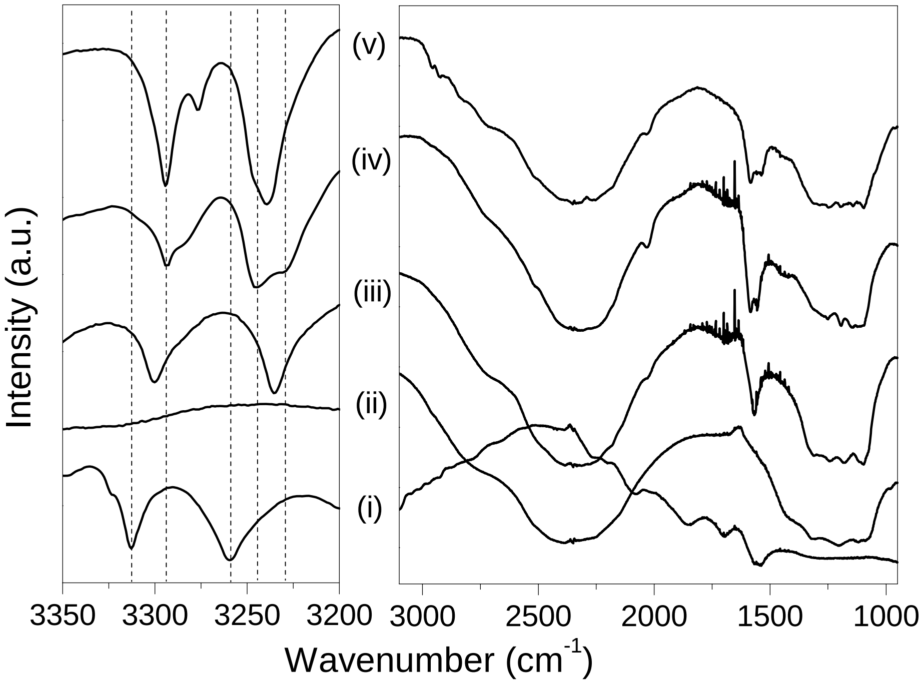

Figure S3. FT-IR of (i) $LiNH_2$, (ii) $Ca(BH_4)_2$, (iii) $Ca(BH_4)_2$-$LiNH_2$, (iv) $Ca(BH_4)_2$-$2LiNH_2$, and (v) $Ca(BH_4)_2$-$3LiNH_2$.

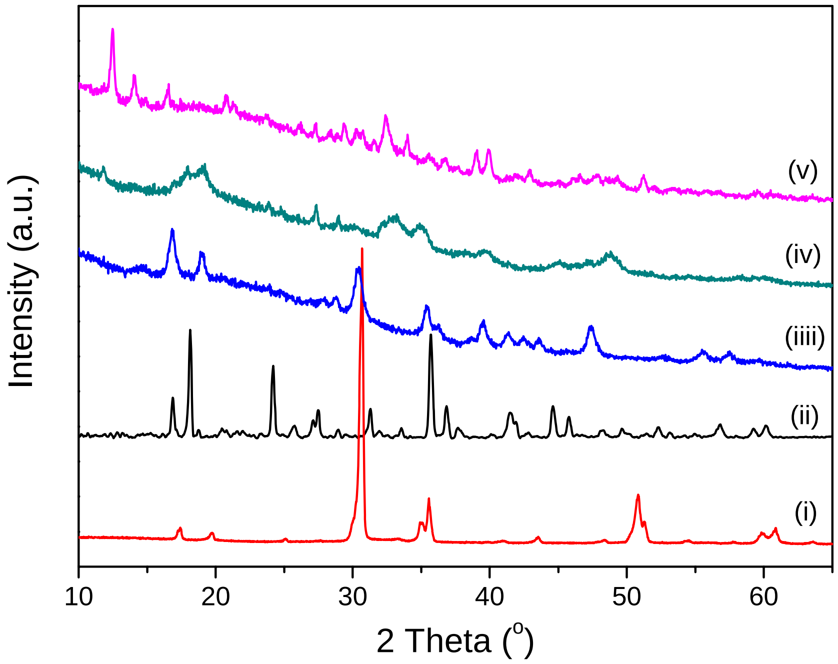

Figure S4. XRD patterns of (i) $LiNH_2$, (ii) $Ca(BH_4)_2$, (iii) $Ca(BH_4)_2$-$LiNH_2$, (iv) $Ca(BH_4)_2$-$2LiNH_2$, and (v) $Ca(BH_4)_2$-$3LiNH_2$.

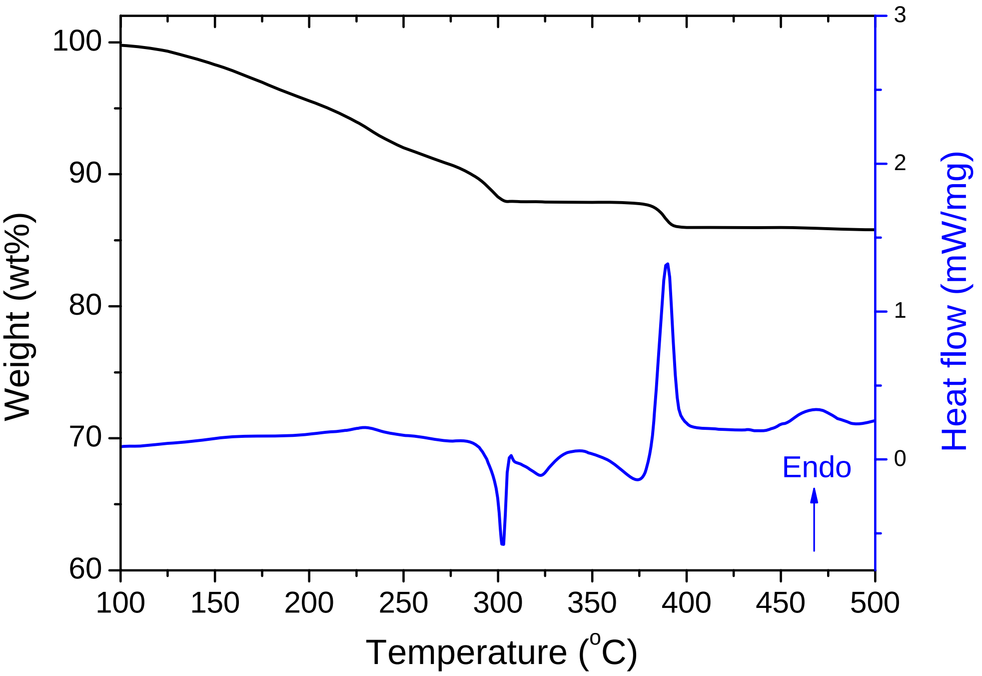

Figure S5. TG-DSC results of $2LiNH_2$-$Ca(BH_4)_2$ with heating rate of 2 °C/min.

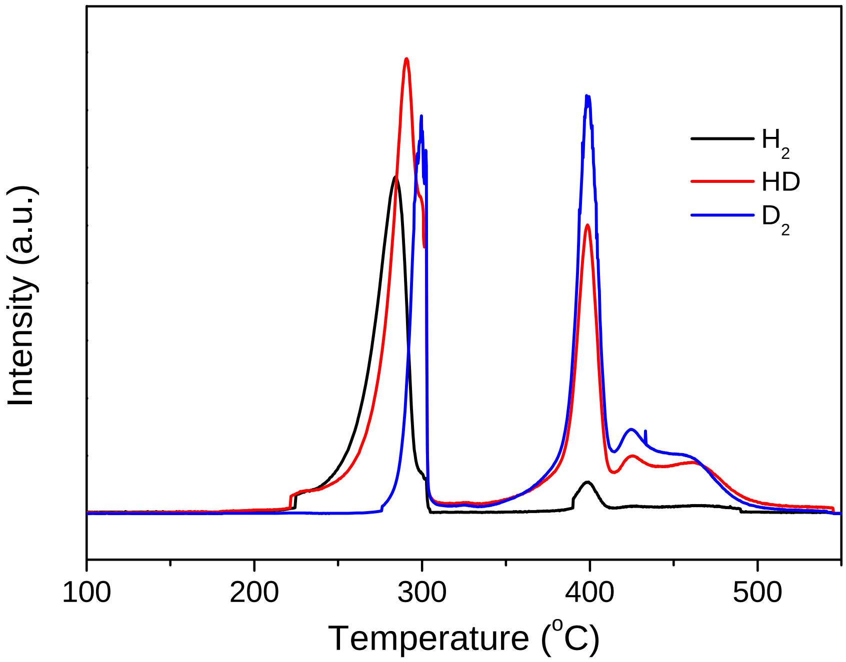

Figure S6. TPD-MS results of $2LiNH_2$-$Ca(BD_4)_2$ with heating rate of 2 °C/min.

Reference:

[S1] H. L. Chu, Z. T. Xiong, G. T. Wu, J. P. Guo, X. L. Zheng, T. He, C. Z. Wu and P. Chen, *Chem. Asian J.*, 2010, **5**, 1594.

[S2] P. Chen, Z. T. Xiong, J. Z. Luo, J. Y. Lin, K. L. Tan, *Nature*, 2002, **420**, 302.