Supplementary Information

Improved Dehydrogenation Properties of Ca(BH₄)₂-LiNH₂ 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]:

$$\text{CaCl}_2 + 2 \text{NaBH}_4 \rightarrow \text{Ca(BH}_4)_2 + 2 \text{NaCl}$$

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 °C/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.

**NH₃ determination**

NH₃ evolved in sample dehydrogenation was quantitatively measured by a home-made conductivity cell (Thermo Scientific, Orion 3-Star). NH₃ 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 immersed and connected with a conductivity meter (Thermo Scientific, Orion 3-Star). As NH₃ 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 NH₃ into the same acid solution to obtain empirical linear relationship between NH₃ input and conductivity change. NH₃ 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 NH₃ measurement in 100 mL standard volume at ambient pressure and temperature.
Figures and Tables

![Scheme of home-made micro-reactor for TPD measurement](image)

**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) LiNH₂, (ii) Ca(BH₄)₂, (iii) Ca(BH₄)₂-LiNH₂, (iv) Ca(BH₄)₂-2LiNH₂, and (v) Ca(BH₄)₂-3LiNH₂.
Figure S4. XRD patterns of (i) LiNH₂, (ii) Ca(BH₄)₂, (iii) Ca(BH₄)₂-LiNH₂, (iv) Ca(BH₄)₂-2LiNH₂, and (v) Ca(BH₄)₂-3LiNH₂.
Figure S5. TG-DSC results of 2LiNH₂-Ca(BH₄)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:
