Regenerable hydrogen storage in lithium amidoborane

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Experimental Section

Materials and preparation

The starting materials, ammonia borane (NH_3BH_3, AB, 97 %) and LiH (95 %), were purchased from Sigma-Aldrich and used in as-received form without further purification. Lithium amidoborane ($LiNH_2BH_3$, LAB) was synthesized by ball milling stoichiometric ratio of LiH and AB (1:1) by planetary ball milling (QM-1SP2, 350 rpm, ball to powder ratio of 30:1) for 1 h. All the sample handling was performed in an N_2-filled glove box equipped with a recirculation system to keep the H_2O and O_2 levels below 1 ppm.

Characterizations

The crystalline structure of the samples was characterized by using X-ray diffraction (XRD) patterns recorded in a Rigaku D/max-kA diffractometer with Cu Kα radiation (An amorphous tape was used to prevent the oxidation and moisture contamination of samples during XRD measurement). The chemical composition was investigated using Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus 470). The solid-state ^{11}B NMR experiments were performed on a Bruker DSX 300 spectrometer operating at 12 kHz, using 4 mm ZrO_2 rotors filled up in a purified argon atmosphere glove box. A 0.55 μs single-pulse excitation was employed, with repetition times of 1.5 s.

Gas evolution measurements

During the reaction process, gaseous products were analyzed by mass spectrometry (MS). Based on species identified in an initial survey with the Hiden system that sampled all mass channels from 6 to 199 amu, the MS monitored the partial pressures for 2 amu (H_2), 16 amu (NH_3), 18 amu (H_2O), 27 amu (B_2H_6), 32 amu (O_2) and 80 amu ($B_3N_3H_6$). The molecular weight and cracking pattern of each species was taken into account in extracting semi-quantitative information. Typical sample quantities were 5-10 mg, which are sufficient for obtaining accurate results due to the high sensitivity of the employed equipment. Volumetric release for quantitative measurements of hydrogen desorption from samples was carried out with a

homemade Sievert's type apparatus under Ar (1 atm) and under ammonia (3 atm). All gas evolution measurements were using a heating rate of 5 $^{o}C \cdot min^{-1}$.

Regeneration of LAB from its dehydrogenated products

The dehydrogenated LAB sample (~150 mg) was suspended in liquid ammonia (30 mL) at -77 ^{o}C in a stainless steel reaction vessel with an internal volume of 50 mL. Hydrazine (N_2H_4, ~200 mg) was added by syringe. The reaction vessel was sealed and heated to 40 ^{o}C. After 3 days the vessel was cooled to -77 ^{o}C and opened. The ammonia solution was poured into a Schlenk flask and immediately placed under vacuum to remove any trace hydrazine. For a comparison, the reaction conditions were changed to heating the reaction vessel to 30 or 50 ^{o}C for 3 days, and to 40 ^{o}C for 1 or 6 days.

Density functional theory (DFT) calculations

The energies ΔH of possible reactions for yielding intermediates and products for the initial introduction of N_2H_4 molecules to 1,3,5-trilithium borazine were calculated by ABINIT DFT code.[S1, S2] These molecules were placed in a $20 \times 20 \times 20$ Å cubic cell. The electron-ion interactions were described by the ultra-soft pseudopotentials with a cutoff energy of 400 eV. For the exchange-correlation functional, the generalized gradient approximation (GGA) of Perdew Burke Ernzerhof (PBE)[S3] was employed.
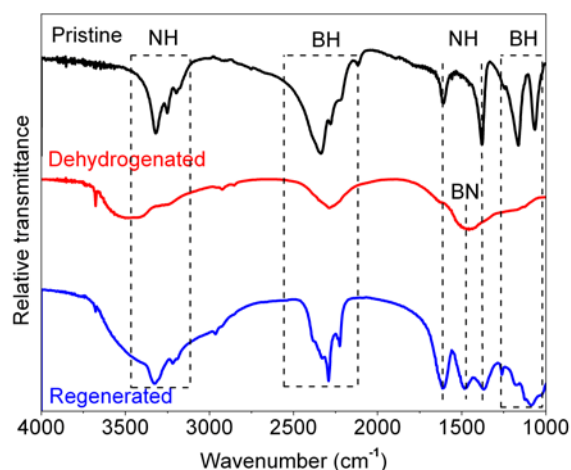
Fig. S1 FTIR spectra of pristine LAB, dehydrogenated LAB at 250 ^{o}C and products obtained from regeneration process.

The FTIR spectrum of LAB shows that the N-H stretching vibrations appear at 3319, 3249, 3199, 3173, 1611 and 1381 cm^{-1}, and the B-H bonds are assigned to the absorptions at 2281, 2230, 2338, 1165 and 1064 cm^{-1}. After dehydrogenation, the depletion of N–H and B–H vibrations is obvious. And after carrying out the hydrogenation reaction on the dehydrogenated LAB, the products exhibit the recurrence of N-H and B-H vibrations, which affords similar results to that performed on an as-prepared LAB. Additionally, in agreement with the ^{11}B NMR result (Fig. 2a), a weak B-N signal can also be detectable.

References

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S3.   J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.