Regenerable hydrogen storage in lithium amidoborane

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Experimental Section

Materials and preparation
The starting materials, ammonia borane (NH₃BH₃, AB, 97 %) and LiH (95 %), were purchased from Sigma-Aldrich and used in as-received form without further purification. Lithium amidoborane (LiNH₂BH₃, 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 N₂-filled glove box equipped with a recirculation system to keep the H₂O and O₂ 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 (FT IR, Nicolet Nexus 470). The solid-state ¹¹B NMR experiments were performed on a Bruker DSX 300 spectrometer operating at 12 kHz, using 4 mm ZrO₂ 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 (H₂), 16 amu (NH₃), 18 amu (H₂O), 27 amu (B₂H₆), 32 amu (O₂) and 80 amu (B₃N₃H₆). 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 °C·min⁻¹.

**Regeneration of LAB from its dehydrogenated products**

The dehydrogenated LAB sample (~150 mg) was suspended in liquid ammonia (30
mL) at -77 °C in a stainless steel reaction vessel with an internal volume of 50 mL.
Hydrazine (N₂H₄, ~200 mg) was added by syringe. The reaction vessel was sealed
and heated to 40 °C. After 3 days the vessel was cooled to -77 °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 °C for 3 days, and to 40 °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 N₂H₄ molecules to 1,3,5-trilithium borazine were calculated by
ABINIT DFT code. These molecules were placed in a 20 × 20 × 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) was employed.
**Fig. S1** FTIR spectra of pristine LAB, dehydrogenated LAB at 250 °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