Supporting Information

Thermodynamic and Spectroscopic Analysis for Ammonia Absorption Mechanism of Borohydride System

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1. Experiments and Theoretical Calculations

$NaBH_4$ (99.9% purity) and $LiBH_4$ (99.9% purity) were purchased from Sigma-Aldrich Japan. To prevent moisture absorption and oxidation, all samples were handled in a glovebox (Miwa MDB-2BL) under purified argon

Pressure-composition isotherm (PCI) measurements for NH_3 absorption were conducted using BELSORP-HP-nex (pressure range: 10^{-4} Pa to ammonia vapor pressure) and BELSORP-max (pressure range: 10^{-8} Pa to atmospheric pressure) instruments (MicrotracBEL, Japan). In all the PCI results, the *x*-axis in the results is expressed in terms of the amount of NH_3 absorbed per mole of absorbent, with units of mol/mol. The $LiBH_4$ and $NaBH_4$ powder were mixed with 1:1 molar ratio by hand milling using agate mortar and pestle for 5 minutes. To analyze the adsorption reactions of $LiBH_4$ and $NaBH_4$ with NH_3, conventional methods such as powder X-ray diffraction are limited due to the presence of liquid-phase intermediates and NH_3 release during pressure reduction. To address this, *in-situ* spectroscopy was carried out under NH_3 atmosphere conditions. The *in-situ* NMR measurements under ammonia (NH_3) pressure were conducted using a Lambda500 spectrometer (JEOL Co. Ltd.) at a magnetic field strength of 11.7 T. The samples were put into high-pressure valved NMR tubes (Tokyo Chemical Industry Co., Ltd.), which is available for NH_3 in pressure range from vacuum to 0.86 MPa. The chemical shifts were referenced to pure water at 4.21 ppm for ^{1}H, to a saturated boric acid aqueous solution at 19.49 ppm for ^{11}B, and to NaCl 1M solution at 7.21 ppm for ^{23}Na, respectively. *In-situ* Raman spectroscopy was also performed under NH_3 pressure, using indium seals resistant to NH_3. For the Raman measurements, a monochromatic laser (Spectra-Physics Stabilite2017, λ = 488 nm) is focused on the samples, and quasi-backscattered light is collected. The light is directed to a spectrometer (Czerny-Turner grating spectrometer JASCO TSR-600/SH) via a lens and beam splitter, and then it is detected by a CCD (Princeton Instruments LN-1100PB) cooled by liquid nitrogen. Notably, these techniques exhibit complementary spectral behaviors: while NMR signals sharpen upon liquefaction due to increased molecular mobility, Raman peaks tend to broaden as the system transitions from a rigid solid to a disordered liquid. This contrast offers a powerful approach for cross-validating phase evolution across different states.

Geometric optimizations of Li/$NaBH_4(NH_3)_n$ clusters (n = 0–7) were performed using Gaussian 16 (Rev.C02 x86_64 AVX2-enabled CPUs for Linux OS) at the conventional B3LYP/6-31+G(d,p) level to determine the lowest-energy configurations and support the experimental results. The energy calculations were conducted, and energy parameters were obtained through SHERMO post-processing.[25]

2. Supporting PCI Figures

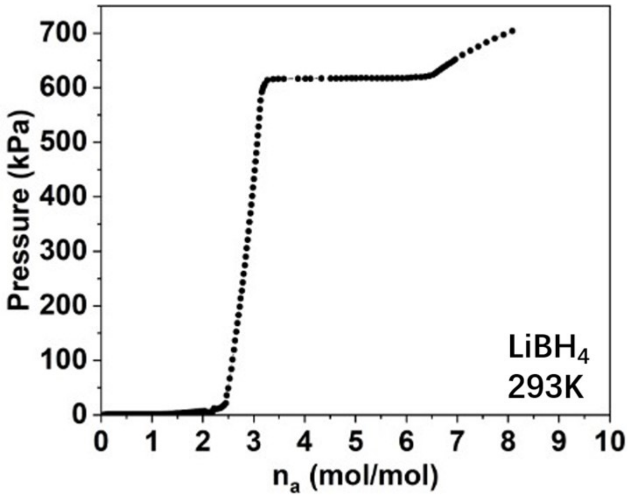

Figure S1. Full range PCI of $LiBH_4$ at 293K.

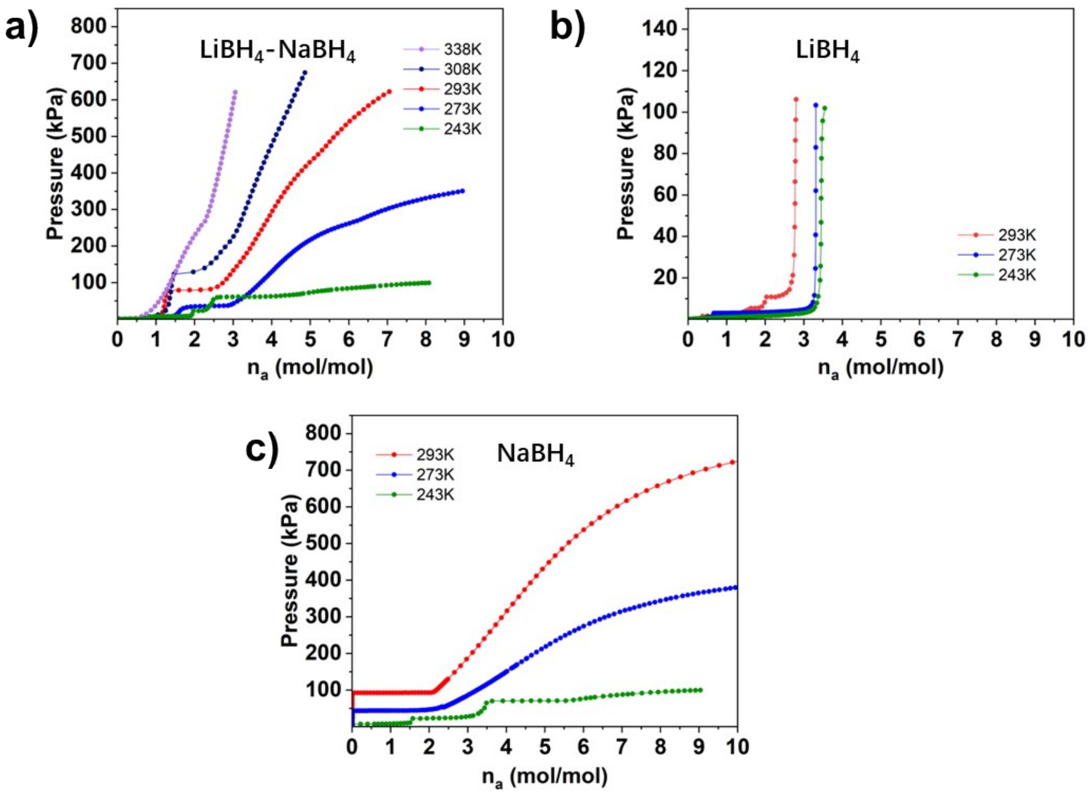

Figure S2. (a) Linear PCI Curves of 1:1 $LiBH_4$-$NaBH_4$ mixture; (b)Linear PCI Curves of 1:1 $LiBH_4$; (c) Linear PCI Curves of 1:1 $NaBH_4$.

3. Thermodynamics Analysis

Based on the plateau pressures (P) and experimental temperatures (T), the enthalpy change (ΔH) and entropy change (ΔS) of the corresponding reactions can be evaluated using the Van 't Hoff equation. Fig S2a and Fig S2b show the Van 't Hoff plots ($\ln(p/p_0)$ vs T^{-1}) for $LiBH_4$ and the $LiBH_4$-$NaBH_4$ mixture, respectively. The slope and intercept of the vertical axis represent the values of ΔH and ΔS, respectively.

$$ln\frac{P}{P_0}=\frac{\Delta H}{RT}-\frac{\Delta S}{R}$$

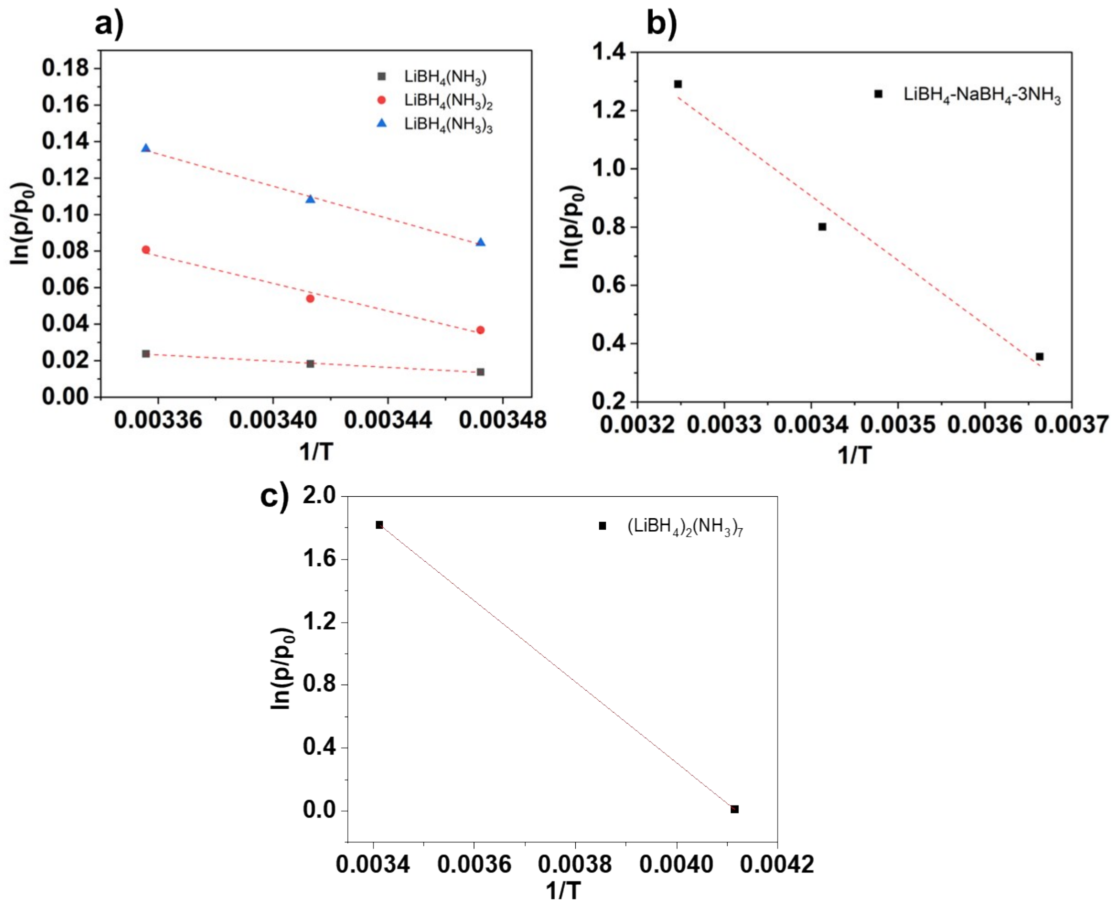

Figure S3. (a)Van’t Hoff plots of $LiBH_4$; (a)Van’t Hoff plots of $LiBH_4$-$NaBH_4$.

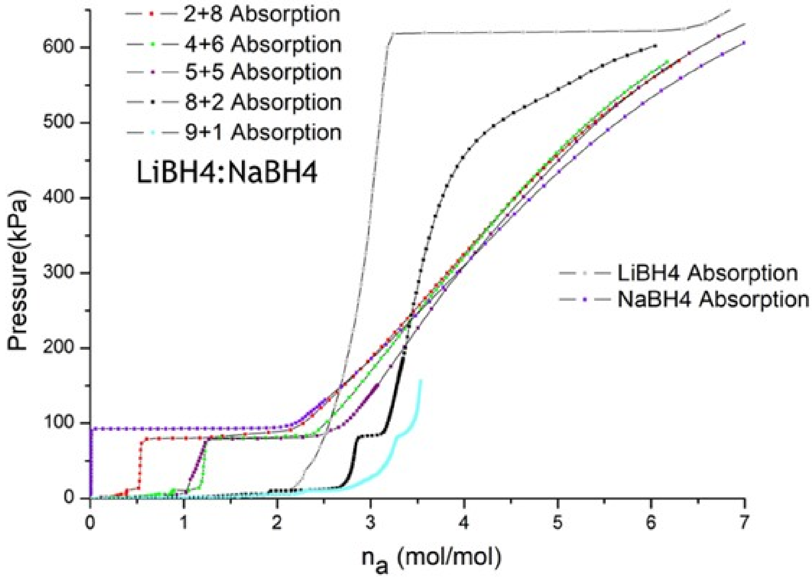

Figure S4. PCI curves of $LiBH_4$–$NaBH_4$ mixtures with different $LiBH_4$:$NaBH_4$ ratios at 293K.

4. Raman Spectroscopy

To validate the analyses of coordination compounds and solutions, in-situ Raman spectroscopy measurements were conducted for $LiBH_4$, $NaBH_4$, and the $LiBH_4$-$NaBH_4$ mixed system. All peaks observed in the results were thoroughly identified as shown in Table S1 and Table S2.[16–24] To avoid confusion, the peak nomenclature follows the conventions established in references.[18,19]

Table S1. Raman Peak Assignments of Pure $LiBH_4$ and Pure $NaBH_4$ at 293 K.

Materials	Vibration Mode	Symmetry	Wavenumber/cm^{-1}	Note
$LiBH_4$	v_4	A_g	1098	B-H bending
	v_4`	A_g	1240	B-H bending
	v_2	B_{3g}	1289	B-H bending
	v_2`	A_g	1320	B-H bending
	$2v_4$	A_g	2156	Overtone of bending vibration v_4
	v_3	A_g	2274	B-H stretching
	v_1	A_g	2298	Tetrahedral B-H symmetric stretching
	v_3`(sh)	A_g	2321	B-H stretching
$NaBH_4$	v_4	F_2	1127	B-H bending
	v_2	A_1	1279	B-H bending
	$2v_4$	E_1	2197	Overtone of bending vibration v_4
	$2v_4$`	A_1	2228	Overtone of bending vibration v_4
	v_1	A_1	2334	Tetrahedral B-H symmetric stretching

	$v_{2+}v_4$(sh)	E	2408	Combination band
	$2v_2$	A_1	2541	Overtone of bending vibration v_2

*sh=shoulder peak

Table S2. Raman Peak Assignments of NH_3 in $LiBH_4$ and $NaBH_4$ after NH_3 Absorption at 293 K.

Materials	Vibration Mode	Symmetry	Wavenumber/cm^{-1}	Note
NH_3 ($LiBH_4$)	$v_{1(sh)}$	A_g	3218	N-H stretching
	v_2	E_g	3293	N-H symmetric stretching
	v_2`	E_g	3380	N-H stretching
NH_3 ($NaBH_4$)	v_1	A_g	3241	N-H stretching
	v_2	E_g	3301	N-H symmetric stretching
	v_2`	E_g	3379	N-H stretching

*sh=shoulder peak