

Electronic Supporting Information (ESI)

Operando spectroscopic analyses for ammonia absorption process of sodium borohydride

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Experimental Section

Sodium borohydride (NaBH_4 , 99.99 %, Aldrich) was purchased and used for the experiments. All the samples were handled in an argon glovebox purified by a gas recycling purification system (MP-P-60W, Miwa MFG Co., Ltd.) to minimize oxygen and water content. For investigating the NH_3 absorbed state of NaBH_4 , nuclear magnetic resonance (NMR), and Fourier transform infrared spectroscopy (FT-IR) measurements were carried out. Here, NH_3 absorbed NaBH_4 was stable only under the NH_3 pressure thermodynamically, therefore all measurements were performed under NH_3 atmosphere. ^1H and ^{11}B NMR spectra were recorded on a Lambda500 spectrometer (JEOL Co. Ltd.) in a magnetic field of 11.7 T. NaBH_4 was packed into High Pressure Valved NMR Tube (Tokyo Chemical Industry Co., Ltd.) which can be used from vacuum to 0.86 MPa of NH_3 pressure. Chemical shifts were referenced to chloroform at 7.26 ppm for ^1H and saturated boric acid aqueous solution at 19.49 ppm for ^{11}B . Spectra were acquired with the pulse widths of 1.5–2.0 and 1.75–2.0 μs , and relaxation delays of 5 and 6 s for ^1H and ^{11}B , respectively. FT-IR (Spectrum One, Perkin-Elmer) equipped with diffuse reflection cell were used to observe infrared absorption spectra. The sample cell made of stainless and equipped with ZnSe window was hand-made by Hydrolab Inc., and the available pressure range is from vacuum to 0.86 MPa of NH_3 pressure. The samples were measured without dilution. Spectra were recorded at 4 accumulations with 4 cm^{-1} spectral resolution. The NMR tube and sample cell for FT-IR were connected to the Sievert-type experimental system composed of a pressure gauge (Druck, DPI280), NH_3 cylinder (99.999%), rotary pump, and buffer, where the details are explained in the previous paper¹⁵. By using the systems, all the analyses can be conducted with the PCI measurements to know the NH_3 absorption stages. The NMR and FTIR measurements are repeated by the connection and disconnection of the sample tube for NMR and vessel for FT-IR from PCI apparatus, respectively (See Fig. S1).

Figures

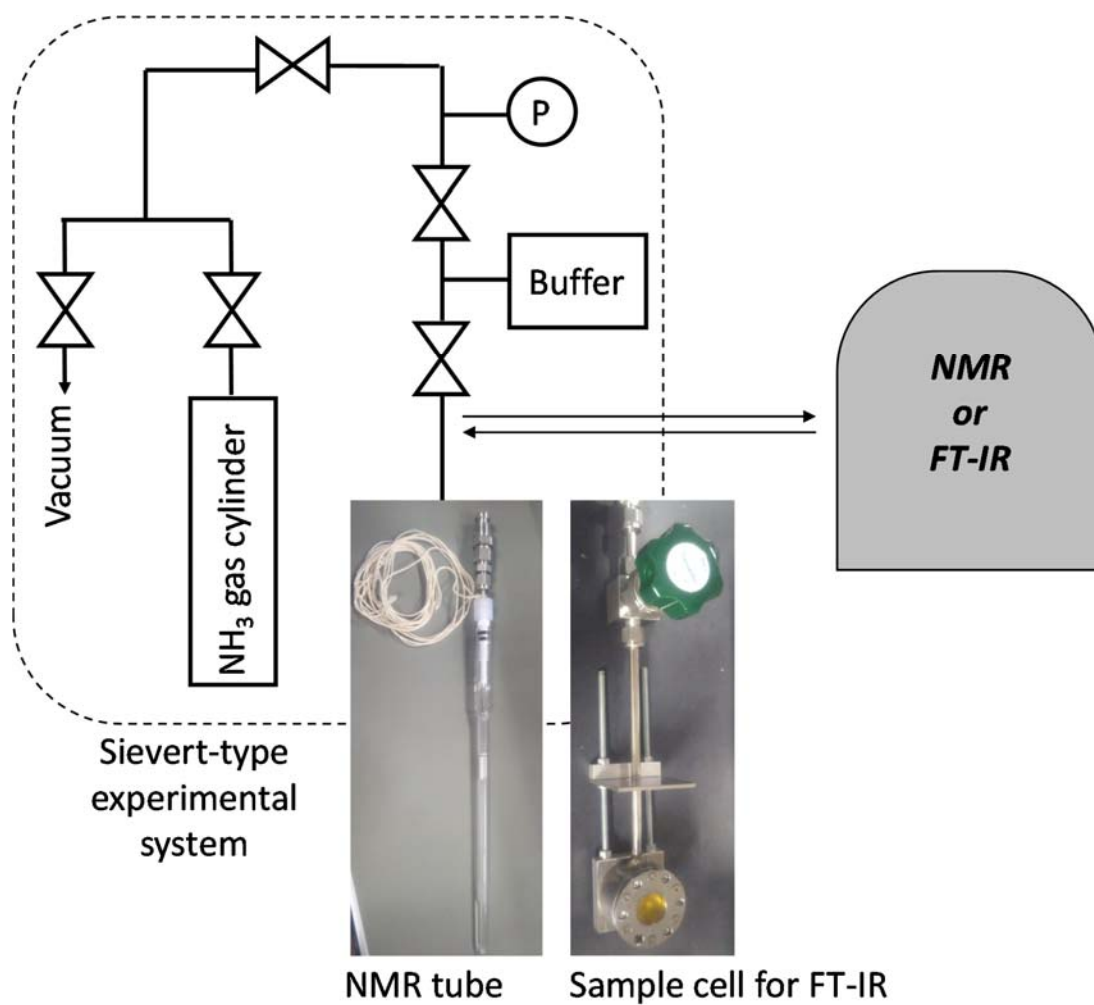


Fig. S1 The schematic illustrations of the operand NMR and FT-IR measurement systems.

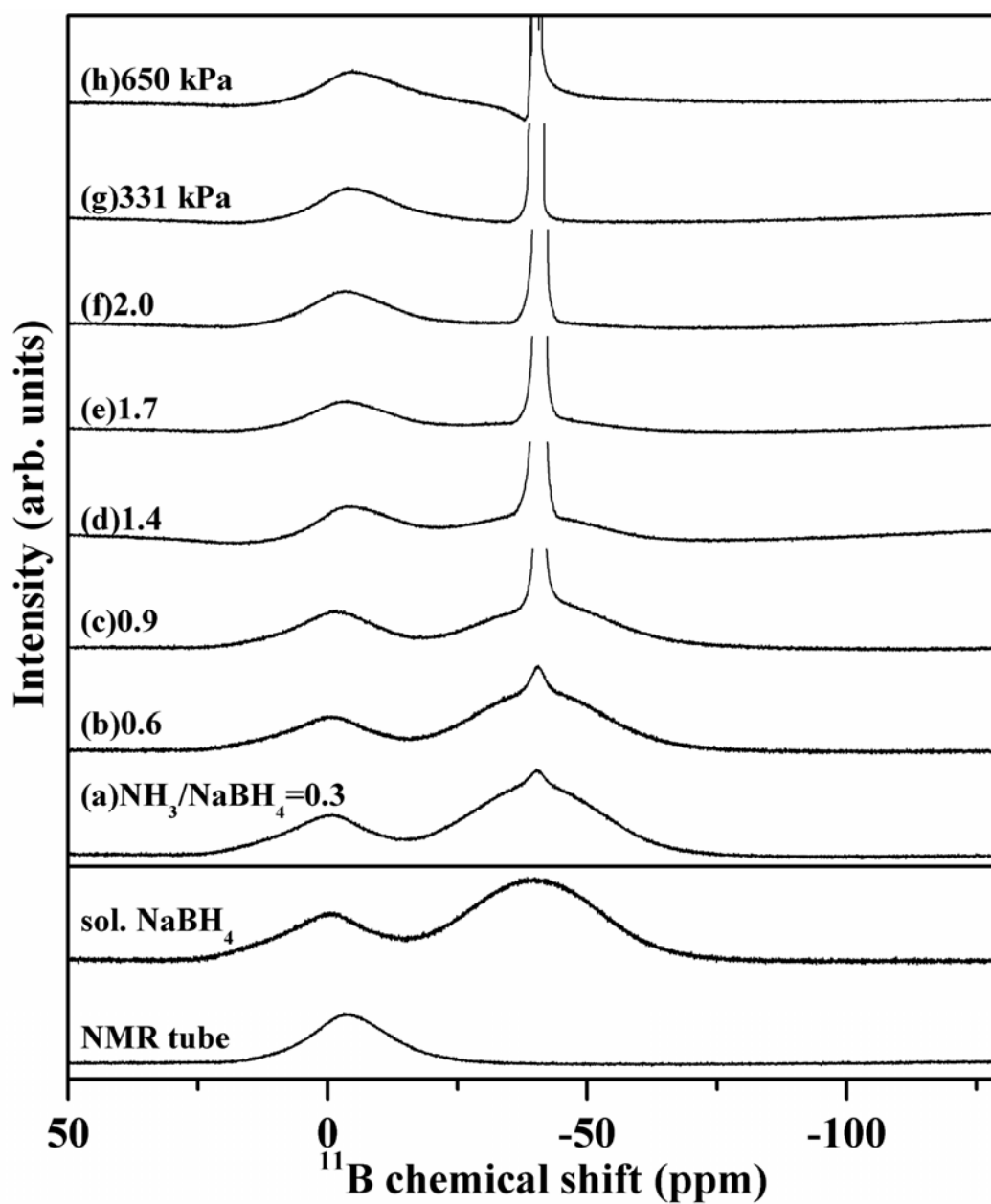


Fig. S2 Operand ^{11}B NMR results for NaBH_4 at the plateau region with $\text{NH}_3/\text{NaBH}_4(\text{mol/mol}) =$ (a) 0.3, (b) 0.6, (c) 0.9, (d) 1.4, (e) 1.7, (f) 2.0, and under (g) 331 kPa, (h) 650 kPa of NH_3 . All the data is same as those of Fig. 1, and scale is normalized by the peak intensity of NMR tube (background).

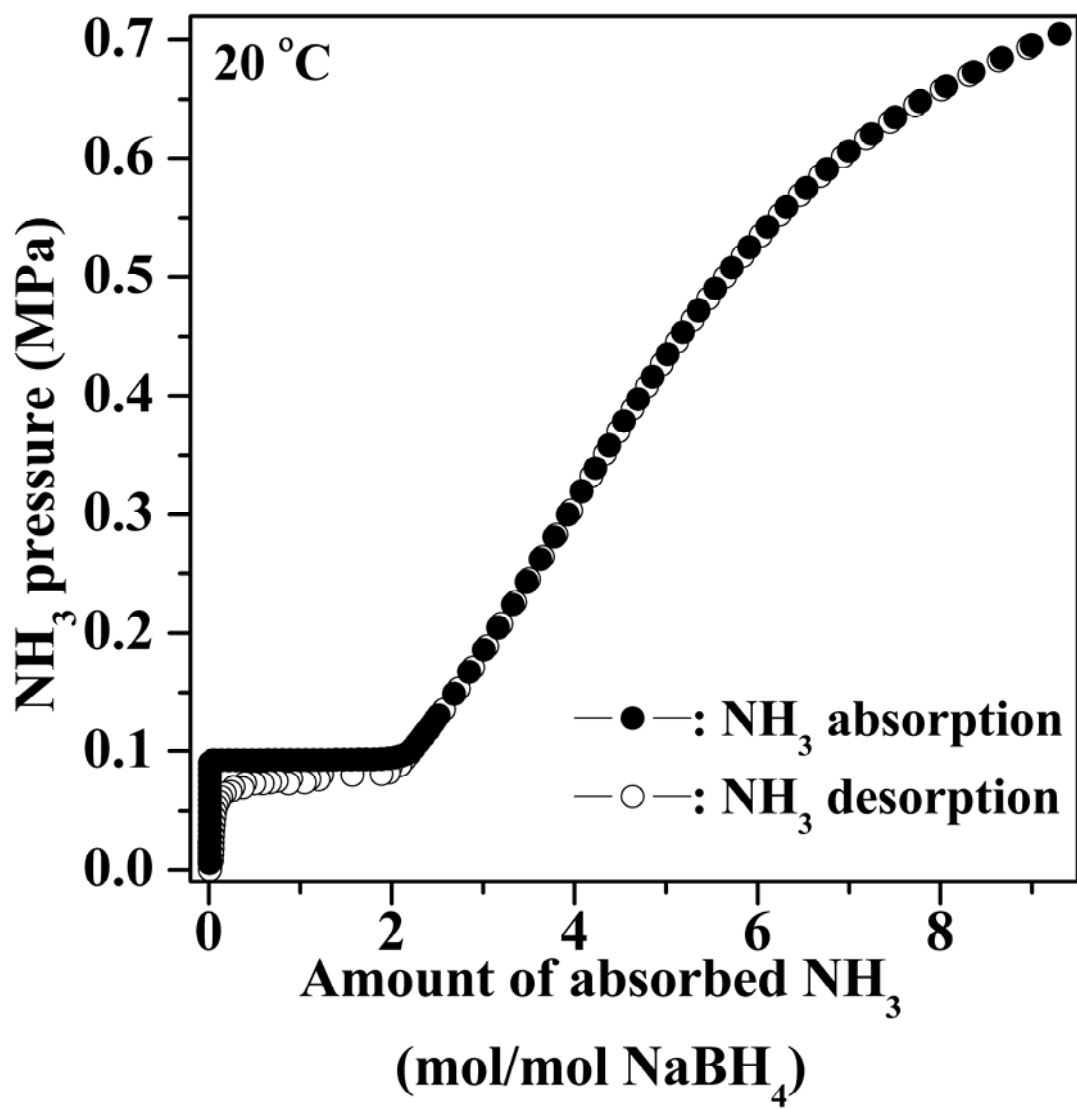


Fig. S3 PC isotherms for NH₃ absorption (●) and desorption (○) of NaBH₄ at 20 °C.

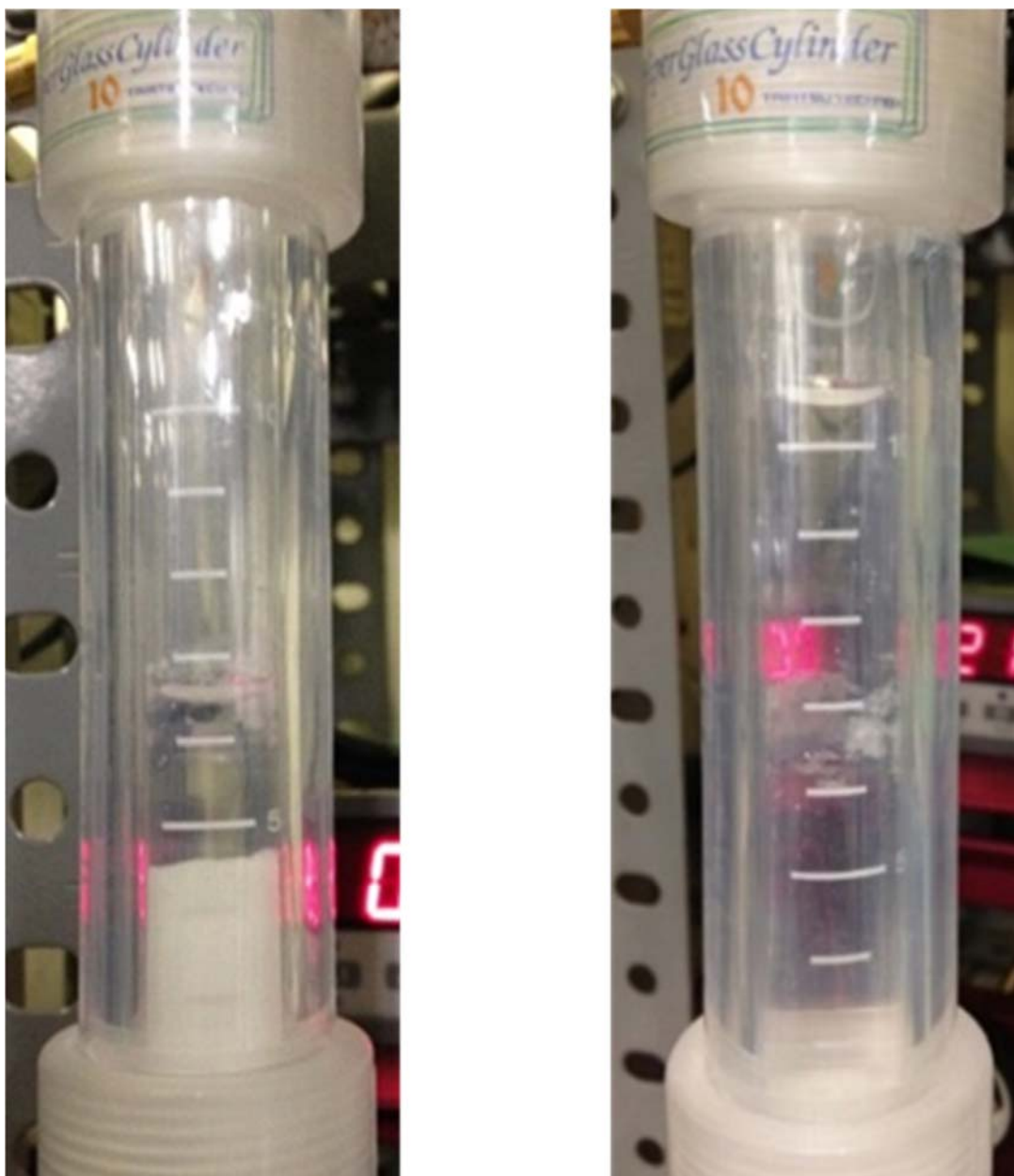


Fig. S4 The images of NaBH_4 under the plateau pressure (left) and the higher pressure than the plateau pressure (right).

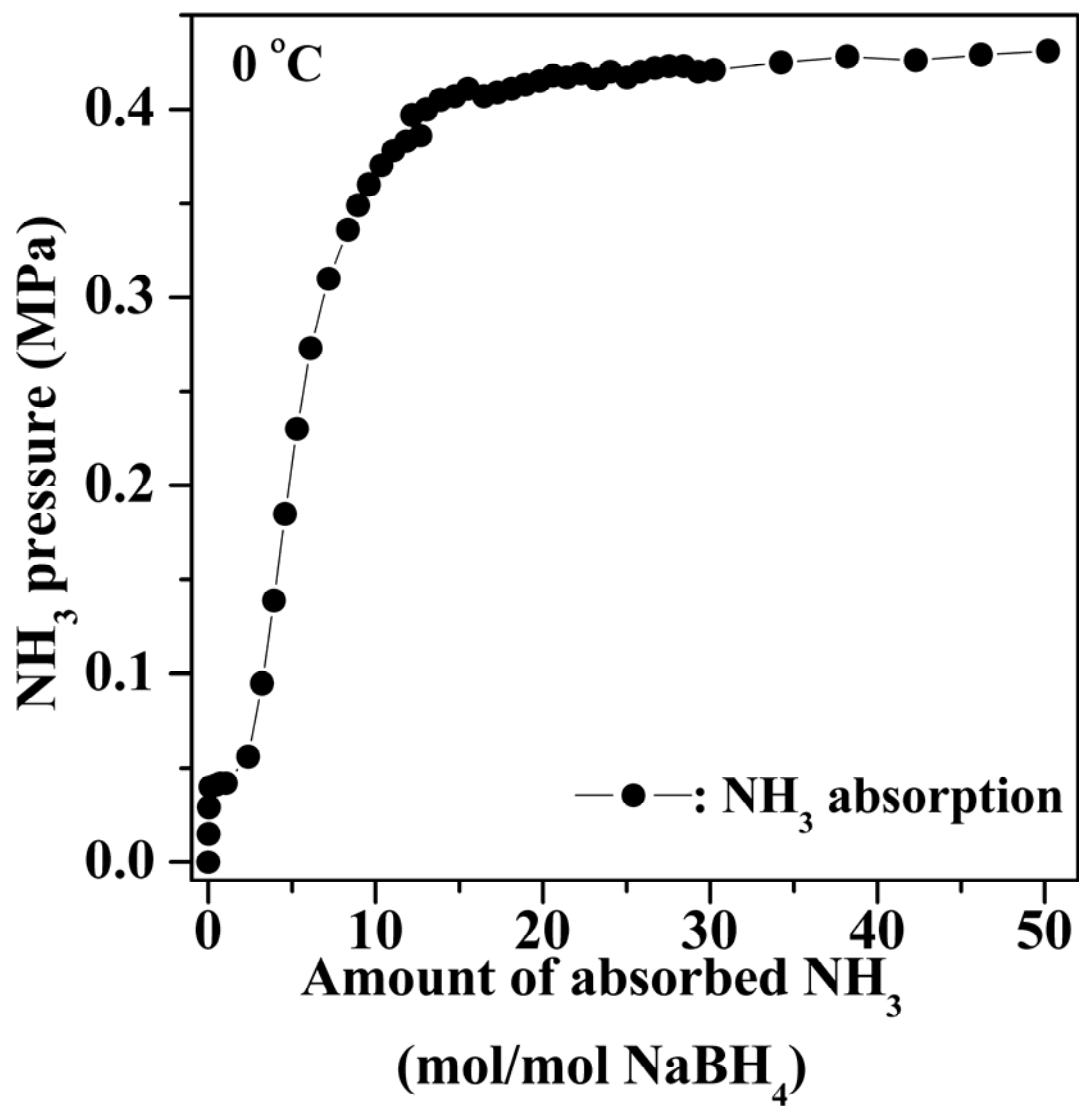


Fig. S5 PC isotherms for NH_3 absorption of NaBH_4 at $0\text{ }^\circ\text{C}$.