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Operando spectroscopic analyses for ammonia absorption process of sodium borohydride

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Ammonia absorption process of sodium borohydride for ammonia storage has been studied by using operando NMR and FT-IR measurements under various ammonia pressures. As a result, the characteristic variation of chemical states of both materials due to the liquefaction, has been clarified.

Ammonia (NH_3) is expected as a hydrogen carrier because of its high gravimetric and volumetric hydrogen density (17.8 wt%, 108 g/L)[1-3]. Because of its flammable property, the technical research and developments are required to utilize NH_3 as an energy carrier practically. For instance, safety devices to decrease the vapor pressure of liquid NH_3 has been investigated for establishing a NH_3-infrastructure[1, 4, 5]. Recently, we have focused on the NH_3 absorbing materials to control the NH_3 vapor pressure[5-8]. It was observed that some halides and complex hydrides can absorb large amount of NH_3 to form ammine complexes, and the NH_3 partial pressure is able to be lowered down than that of the original vaper pressure, which depends on the thermodynamic stability of ammine complexes[8-11]. The volumetric hydrogen densities of ammine complexes are high and almost comparable to that of liquid NH_3[1, 3]. Thus, the above NH_3 absorbing materials are attractive as hydrogen (or NH_3) storage materials and/or functional materials for establishing the safety devices. Among them, sodium borohydride ($NaBH_4$) possess characteristic features of liquefaction by the NH_3 absorption[8, 12] with promising cycle properties.[13] This liquefaction is understood from the result of the NH_3 pressure-composition isothermal (PCI) measurement that the vapor pressure was linearly increased with the absorbed NH_3. This feature is practically useful, for example, in that the residual amount of NH_3 in cylinder has to be estimated only from the pressure and temperature.

In this work, the NH_3 absorbing process of $NaBH_4$ has been investigated in further details by using operando nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FT-IR) spectroscopy under NH_3 atmosphere. These measurements were performed by using the hand-made apparatus (see Fig. S1). And, thermodynamic analysis based on solution theory for PCI curve was performed to discuss and understand the phase variation and the absorption behaviour of the $NaBH_4$-NH_3 system.

Operando ^{11}B NMR measurements were performed under NH_3 pressure to understand the variation of chemical states during the NH_3 absorption of $NaBH_4$, as shown in Figure 1. The signals of solid $NaBH_4$ and NMR tube are also shown as a reference. The vertical axis of all the profiles are normalized by the highest intensity of the observed signals. A weak ^{11}B signal was observed for the NMR tube because it is made of borosilicate glass. Here, the signal relating to NMR tube is confirmed in all the measurements (see Fig. S2). It is observed that a total of 2] mol NH_3 could be absorbed in $NaBH_4$ to form $Na(NH_3)_2BH_4$ with a plateau at 93 kPa from the result of PCI measurement (see Fig. S3). The broad signal of solid $NaBH_4$ is appeared around -42.4 ppm. This broadening is caused by the limited

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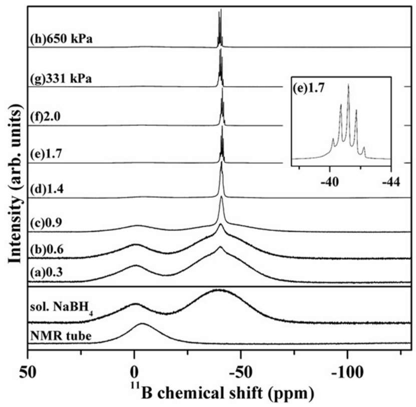

Figure 1 Operand ^{11}B NMR results for $NaBH_4$ at the plateau region with $NH_3/NaBH_4$(mol/mol)=(a) 0.3, (b) 0.6, (c) 0.9, (d) 1.4, (e) 1.7, (f) 2.0, and under (g) 331 kPa, (h) 650 kPa of NH_3. The inset figure is the enlarged profile of (e).

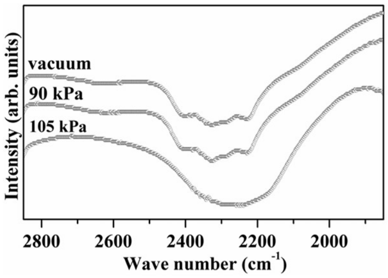

Figure 2 Operand FT-IR results for $NaBH_4$ under vacuum, 90 kPa, and 105 kPa of NH_3.

molecular motion in solid state due to interactions such as dipolar and quadrupole interactions. With the increase in the amount of absorbed NH_3, the signal intensity relating to the solid $NaBH_4$ is decreased with the appearance of a new sharp signal at -40.4 ppm, which is found to be grown gradually. These phenomena are caused by the disappearance of the specific interactions of solids, in other words, the chemical states are averaged by the fast motion of molecules. The sharp signal is split into 5 peaks, as shown in the inset of Figure 1, due to the spin-spin interactions in the B-H bonds[14]. In the previous reports, the peak splitting in solid state borohydride could not be observed by solid state ^{11}B NMR measurements at room temperature even by using magic angle spinning[15]. It can be suggested that the $Na(NH_3)_2BH_4$ phase generated in the plateau region is in liquid state. Namely, solid $NaBH_4$ and liquid $Na(NH_3)_2BH_4$ coexist at the plateau pressure (see Fig. S3 and Fig. S4). At the higher pressure than the plateau pressure, the phase is totally changed to liquid as evidenced from the presence of the sharp signal only. Moreover, the peaks are slightly shifted to lower magnetic field with the increase in the NH_3 concentration. This phenomenon generally suggests that the electron density at B atom in the BH_4 anion is decreased. As one of the reasons to explain the above shift, it is suggested that the polarization of BH bonds is enhanced by the increase in the distance between the Na cation and the BH_4 anion.

Figure 2 shows the FT-IR results of $NaBH_4$ under vacuum, 90, and 105 kPa of NH_3 pressure. Here, $NaBH_4$ doesn't absorb NH_3 under vacuum and 90 kPa, whereas liquid $Na(NH_3)_2BH_4$ phase is formed under 105 kPa of NH_3. It is difficult to observe the changes in the peaks corresponding to N-H vibration mode before and after NH_3 absorption, because the strong peaks of gaseous NH_3 overlapped in the operando measurements. The several peaks derived from the B-H bonds of solid $NaBH_4$ are observed in the wide range from 2100 to 2500 cm^{-1} under vacuum and 90 kPa. These peaks correspond to the symmetric and asymmetric stretching modes of B-H bonds of solid $NaBH_4$. In addition, on the basis of structural analysis by neutron diffraction, it has been reported that $NaBD_4$ contains two different B-D bonds with different bond lengths[16]. The observed broad peak is formed by the B-H bonds with the various chemical states. On the other hand, the single peak related to B-H stretching is appeared at 2246 cm^{-1} for the sample under 105 kPa of NH_3, suggesting that the B-H bonds in the solid phase of $NaBH_4$ are averaged by liquefaction. These results are consistent with the results of ^{11}B NMR. Furthermore, the absorption peaks are shifted to low frequency after the NH_3 absorption. Here, it is known that, in alkali borohydrides and amides, the FT-IR peaks derived from B-H bonds or N-H bonds shift to low frequency with the decrease in the ionization energy of alkali metal species[17, 18]. Therefore, it can be considered that the peak shift in the $NaBH_4$-NH_3 system is caused by the decrease in ionization energy of Na cation due to the coordination of NH_3 to Na cation. As another possibility, the peak may also shift by the interaction between positively charged hydrogen in $NaBH_4$ and the negatively charged hydrogen in NH_3, which is called dihydrogen bond[19]. Actually, $NaBH_4{\cdot}2H_2O$ is known to have a dihydrogen bond formed between H in $NaBH_4$ and H in H_2O according to the analysis of crystal structure and infrared spectroscopy[20].

Operando ^1H NMR measurements under various NH_3 pressure were carried out to investigate the chemical state of NH_3 and $NaBH_4$ solution, and the results are shown in Figure 3. The profile of pure liquid NH_3 without $NaBH_4$ is also shown as reference. The ^1H signals from the sample tube and solid $NaBH_4$ are hardly observed in Figs.

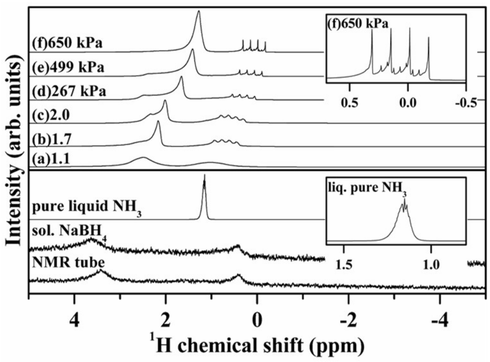

Figure 3 Operand ^1H NMR results for $NaBH_4$ at the plateau region with $NH_3/NaBH_4$(mol/mol)=(a) 1.1, (b) 1.7, (c) 2.0, and under (d) 267 kPa, (e) 499 kPa, (f) 650 kPa of NH_3. The inset figures are the enlarged profile of (f) and pure liquid NH_3.

3(a) - 3(f) because these materials are solid and the interactions such as dipolar and quadrupole interactions are large. A series of 4 signals with high intensity and 7 signals with low intensity are observed in the range from -0.2 to 0.3 ppm, as shown in the inset of Figure 3(f). Actually, $NaBH_4$ is dissociated to Na cation and BH_4 anion, and all the ^1H nuclei in the BH_4 anion are equivalent in the liquid state. Here, the nuclear spins of ^{11}B and ^{10}B are 3/2, 1/2, -1/2, -3/2 and 3, 2, 1, 0, -1, -2, -3, respectively, and the natural abundance ratio of them is 80:20. Therefore, signals originated in the ^1H nuclei in $NaBH_4$ split into 4 and 7 peaks corresponding to the spins of ^{11}B and ^{10}B, respectively. The difference in the intensities is caused by the abundance ratio. The ^1H NMR signals corresponding to $NaBH_4$ were observed under the NH_3 atmosphere, suggesting that $NaBH_4$ is liquefied. The large signal around 1 – 1.5 ppm is assigned to liquid state NH_3. The shoulder peaks are thought to be originated from the different states of NH_3, i.e. strongly and weakly coordinated NH_3 to $NaBH_4$, although the details of origin are not understood completely yet. The shoulder peak actually disappeared with the increase in the NH_3 concentration. When it is considered in the same way as spin coupling in BH bonds, the ^1H signal related to NH_3 should be split into 3 peaks because the nuclear spins of ^{14}N is 1, 0, -1. Actually, the peak is split to 3 peaks for the pure liquid NH_3 as shown in the inset of Figure 3. However, the peak splitting is not found in the $NaBH_4$-NH_3 system. Ogg et al. reported the similar phenomena in the $NaNH_2$-NH_3 system [21, 22]. They added $NaNH_2$ into liquid NH_3 and carried out ^1H NMR measurements. In that case, the number of peaks of ^1H NMR signal is 1 due to the influence of $NaNH_2$. With respect to the chemical shift in ^1H NMR, the signals of NH_3 and $NaBH_4$ are shifted to higher magnetic field with the increase in the absorbed NH_3, although only the ratio of solid $NaBH_4$ and liquid $Na(NH_3)_2BH_4$ is changed under the plateau pressure. It indicates that the local environment of H atoms is slightly changed possibly because solid $NaBH_4$ affects liquid $Na(NH_3)_2BH_4$, however, the detail is not understood yet. At the higher pressure than the plateau pressure, the signals of NH_3 and $NaBH_4$ are also shifted, and the similar phenomenon was confirmed in the case of ethanol-chloroform system. Ethanol can be written by the chemical formula of CH_3CH_2OH, and it was known that the hydrogen bonds are formed between OH groups. When chloroform, which is written by $CHCl_3$ and known as nonpolar solvent, was gradually added to ethanol, the signal of the OH groups shifted to the higher magnetic field because the hydrogen bonds between ethanol molecules are disturbed by chloroform[23]. From this perspective, the hydrogen bonds between NH_3 molecules in the $NaBH_4$-NH_3 system are considered as the reason for environmental change of NH_3 because it is reported that NH_3 molecules also form hydrogen bonds[24]. The peak shift of $NaBH_4$ to higher magnetic field with the increase in the NH_3 concentration corresponds to the increase of the electron density of H in BH_4 anion. Here, the electron density of B in BH_4 anion is decreased as discussed above. Namely, the electron density of H in BH_4 anion is increased to keep the electrical balance. This peak shift is possibly occurred by the polarization of the BH bonds and longer distance between the Na cation and BH_4 anion due to the increase in the NH_3 concentration.

The PCI curve is analyzed in terms of ideal and regular solutions. Here, the PCI measurement was performed at 0 °C to analyze up to the higher NH_3 pressure than the plateau pressure (see Fig. S5). In the ideal solution, the heat generated by mixing the two materials in liquid state, i.e. liquid $Na(NH_3)_2BH_4$ and liquid NH_3 in $NaBH_4$-NH_3 system, is negligible. On the other hand, in the regular solution, the heat generated due to the mixing should be considered. The relative pressure P normalized by the plateau pressure, in the case of ideal and regular solution of degree of ionization α=0 or 1 for $NaBH_4$, is expressed as follows[25],

$$\text{ideal:} \quad P = X_{NH3} \quad (\alpha = 0), \qquad (2)$$

$$= X_{NH3}/(2-X_{NH3}) \quad (\alpha = 1), \qquad (3)$$

$$\text{regular:} \quad P = \exp(\Delta H/RT + \ln X_{NH3}) \quad (\alpha = 0), \qquad (4)$$

$$= \exp(\Delta H/RT + \ln(X_{NH3}/(2-X_{NH3}))) \quad (\alpha = 1). \qquad (5)$$

T is the reaction temperature, ΔH is enthalpy change by mixing, R is the gas constant. X_{NH3} is the molar fraction defined as the amount of NH_3 divided by the total amount of $Na(NH_3)_2BH_4$ in a mixture. The X_{NH3}-P curves for $NaBH_4$-NH_3 system of ideal and regular solution are

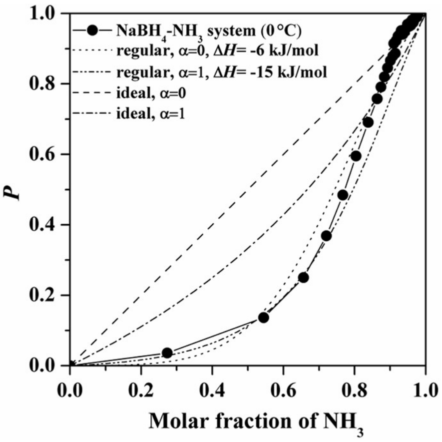

Figure 4 NH_3 absorption curve of $NaBH_4$ and results of analyses by assuming ideal and regular solution at 0 °C. The heat of mixing is -6 and -15 kJ/mol for regular solution of α=0 and 1.

shown in Figure 4. The experimental data are matched with the curve of the regular solution (α=1) in the region from X_{NH3}=0.0 to 0.7 in the case of ΔH=−6 kJ/mol. On the other hand, the curve at high NH_3 concentration region from X_{NH3}=0.9 to 1.0 are well consistent with that of the ideal solution (α=0). From the above, the regular solution (α=1) is changed to the ideal solution (α=0) with the increase in X_{NH3}.

In conclusion, the NH_3 absorption properties have been analysed and discussed based on the results obtained by using operando spectroscopic analyses under NH_3 atmosphere. It is clarified from the operando ^{11}B, ^{1}H NMR, and FT-IR that $Na(NH_3)_xBH_4$, formed by the NH_3 absorption of $NaBH_4$ is in liquid state in all the region of the NH_3 concentration. For $NaBH_4$, it is suggested that the polarization between BH bonds increases with the increase in the NH_3 concentration. In fact, ^{11}B NMR signals and ^{1}H NMR signals, originated in $NaBH_4$ are shifted to the opposite direction. For NH_3, weakness of hydrogen bonds between NH_3 molecules in $NaBH_4$-NH_3 system is found different from pure liquid NH_3. Through the analysis based on solution theory for the $Na(NH_3)_xBH_4$, it is suggested that liquid solution is changed from the regular solution (α=1) to the ideal solution (α=0) with the increase in the molar ratio of NH_3.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

1. C. H. Christensen, R. Z. Sorensen, T. Johannessen, U. J. Quaade, K. Honkala, T. D. Elmoe, R. Kohler and J. K. Norskov, Journal of Materials Chemistry, 2005, **15**, 4106-4108.
2. A. Klerke, C. H. Christensen, J. K. Norskov and T. Vegge, Journal of Materials Chemistry, 2008, **18**, 2304-2310.
3. R. Z. Sørensen, J. S. Hummelshøj, A. Klerke, J. B. Reves, T. Vegge, J. K. Nørskov and C. H. Christensen, Journal of the American Chemical Society, 2008, **130**, 8660-8668.
4. C. Y. Liu and K. Aika, Bulletin of the Chemical Society of Japan, 2004, **77**, 123-131.
5. H. Miyaoka, H. Miyaoka, T. Ichikawa, T. Ichikawa and Y. Kojima, International Journal of Hydrogen Energy, 2018, **43**, 14486-14492.
6. M. H. Sørby, O. M. Løvvik, M. Tsubota, T. Ichikawa, Y. Kojima and B. C. Hauback, *Physical Chemistry Chemical Physics*, 2011, **13**, 7644-7648.
7. T. Aoki, H. Miyaoka, H. Inokawa, T. Ichikawa and Y. Kojima, *The Journal of Physical Chemistry C*, 2015, **119**, 26296-26302.
8. T. Aoki, T. Ichikawa, H. Miyaoka and Y. Kojima, *The Journal of Physical Chemistry C*, 2014, **118**, 18412-18416.
9. C. Y. Liu and K. Aika, *Industrial & Engineering Chemistry Research*, 2004, **43**, 7484-7491.
10. S. R. Johnson, W. I. F. David, D. M. Royse, M. Sommariva, C. Y. Tang, F. P. A. Fabbiani, M. O. Jones and P. P. Edwards, *Chemistry – An Asian Journal*, 2009, **4**, 849-854.
11. Y. Song, F. Wu, X. Zheng, X. Ma, F. Fang and Y. Guo, *Chemical Communications*, 2015, **51**, 1104-1107.
12. H. Miyaoka, K. Nakajima, S. Yamaguchi, T. Aoki, H. Yamamoto, T. Okuda, K. Goshome, T. Ichikawa and Y. Kojima, *The Journal of Physical Chemistry C*, 2015, **119**, 19922-19927.
13. T. Zhang, H. Miyaoka, H. Miyaoka, T. Ichikawa and Y. Kojima, ACS Applied Energy Materials, 2018, 1, 232-242
14. J. Hannauer, U. B. Demirci, C. Geantet, J. M. Herrmann and P. Miele, *Physical Chemistry Chemical Physics*, 2011, **13**, 3809-3818.
15. M. H. W. Verkuijlen, P. Ngene, D. W. de Kort, C. Barré, A. Nale, E. R. H. van Eck, P. J. M. van Bentum, P. E. de Jongh and A. P. M. Kentgens, *The Journal of Physical Chemistry C*, 2012, **116**, 22169-22178.
16. P. Fischer and A. Züttel, *Materials Science Forum*, 2004, **443-444**, 287-290.
17. G. Renaudin, S. Gomes, H. Hagemann, L. Keller and K. Yvon, *Journal of Alloys and Compounds*, 2004, **375**, 98-106.
18. T. Tsumuraya, T. Shishidou, and T. Oguchi, *Journal of Physics: Condensed Matter*, 2009, **21**, 185501.
19. R. Custelcean and J. E. Jackson, *Chemical Reviews*, 2001, **101**, 1963-1980.
20. F. Yaroslav and H. Hans, *European Journal of Inorganic Chemistry*, 2008, **2008**, 3127-3133.
21. R. A. Ogg, *The Journal of Chemical Physics*, 1954, **22**, 560-561.
22. R. A. Ogg, *Discussions of the Faraday Society*, 1954, **17**, 215-220.
23. T. D. Ferris, M. D. Zeidler and T. C. Farrar, *Molecular Physics*, 2000, **98**, 737-744.
24. W. L. Jorgensen and M. Ibrahim, *Journal of the American Chemical Society*, 1980, **102**, 3309-3315.
25. T. Hanai, Membrane and ions, Kagakudojin, Kyoto, 1978, 131-145.