



## Solid-State High-Resolution $^1\text{H}$ -NMR Study for Ammonia Borane of Hydrogen Storage Material

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**Abstract** : In liquids NMR,  $^1\text{H}$  is the most widely observed nucleus, which is not the case in solids NMR. The reason is due to the strong homo-dipolar interactions between the hydrogen atoms which mask the useful chemical shift information. Therefore we must remove the strong homo-dipolar interactions in order to get structural information, which can be investigated by the isotropic chemical shift. There are two ways of obtaining it. One is the ultra-fast MAS of ca. 70 kHz spinning speed, which has become available only recently. The other way is devising a pulse sequence which can remove the strong homo-dipolar interaction. In the latter way, MAS with a moderate spinning rate of a few kHz, is enough to remove the chemical shift anisotropy. In this report, 1D-CRAMPS and 2D MAS-FSLG techniques are utilized and their results will be compared. This kind of high-resolution  $^1\text{H}$  NMR for solids, should become a valuable analytical tool in the understanding and the developing of a new class of hydrogen storage materials. Here ammonium borane  $\text{-NH}_3\text{BH}_3$ , whose hydrogen content is high, is used as a sample.

**Keywords** :  $\text{NH}_3\text{BH}_3$ , Hydrogen storage material, Proton-NMR, High-resolution NMR

### INTRODUCTION

Fuel cell technology is one of the most important candidates for replacing the combustion engine technologies which use various forms of fossil fuel containing carbons. Since it uses the hydrogen as fuel, cars based on fuel cell technologies would not produce

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carbon dioxide which is blamed for causing the green house effect and air-pollution. Also in terms of economical factors, oil prices are highly unstable and could become very expensive in the near future which is something many people believe. Due to such environmental and economical reasons, all advanced countries around the world are investing a tremendous amount of money in establishing the so-called 'hydrogen economy'.

Since petroleum is used most heavily in transportation, one of the most important objectives for the hydrogen economy is to develop a car with an on-board hydrogen storage system. The automobile holds an important status in all facets of our life – cargo, travel, tractor etc. In developing a practical and competitive fuel-cell car to take the place of the current combustion engine automobile, the most challenging task at present is to have a practical fuel system, supplying the hydrogen for a minimum 300 miles driving range without the need to refuel. It must also be safe and cheap compared to the present gasoline fuel system. The production price of a fuel cell engine is still expensive but it is expected to become significantly lower by 2020, which is when the fuel cell car is expected to be mass produced and compete against the gasoline engine car. At present, a practical on-board hydrogen fuel system for the automobile is the key issue for a marketable fuel-cell car. The fuel system is comprised of a hydrogen storage media, hydrogen generation and delivery system to the fuel cell.<sup>1</sup>

Potential hydrogen fuel material should have high hydrogen contents in small volume and total mass. The weight of hydrogen versus total molecular weight for ammonia borane, which we abbreviate as AB for the rest of the paper, is 19 wt.%. US DOE target for hydrogen storage is 6 and 9 wt.% by 2010 and 2015, respectively. The maximum achievable wt.% for the material can vary, depending on how much hydrogen is released in dehydrogenation process. There is a report of achieving 12 wt% using AB with catalytic process.<sup>(2)</sup> During the catalytic process, four equivalent hydrogen atoms are released and its residue is believed to be B-NH<sub>2</sub>, which is denoted as sf-AB from this point.<sup>2</sup> We report high-resolution <sup>1</sup>H-NMR analysis for AB and sf-AB samples hereby. AB is well known and studied extensively,<sup>3-5</sup> however, its NMR study is not well documented as far as authors know. Since the sf-AB is believed to be a new material, its full structural investigations would take lots of efforts in the future. Here we concentrated only on the chemical assignment in terms of <sup>1</sup>H nucleus.<sup>6</sup>

## EXPERIMENTAL

A commercial ammonia borane is purchased from Aldrich and it is purified further to remove impurities in the sample. For a more detailed study, <sup>15</sup>N enriched sample is also synthesized and used for <sup>1</sup>H-NMR analysis. After an application of catalyst, two molecules of hydrogen gas are observed and its residue is analyzed using MAS, CRAMPS, and FSLG(t1)-MAS(t2) 2D-NMR.<sup>7-11</sup>

MAS data taken with 14 kHz spinning rate, did not give the desirable resolution but it is used as reference data. A special combined rotation and multiple pulse spectroscopy (CRAMPS) probe is designed to have a good *rf*-homogeneity and a short ringing time. The chemical shifts were measured relative to a <sup>1</sup>H standard solution of tetramethylsilane (TMS). Details of CRAMPS experiment is explained elsewhere.<sup>11</sup>

For a 2D-NMR technique, FSLG is used for the evolution period to remove the homodipolar interactions between the hydrogen nuclei and the data is obtained during the detection period while the sample is spun at the magic angle. Even though the resolution along the F1 dimension is worse than the CRAMPS result, the overall feature of 2D-spectrum lead us to the better understanding of the catalytic process of dehydrogenation.

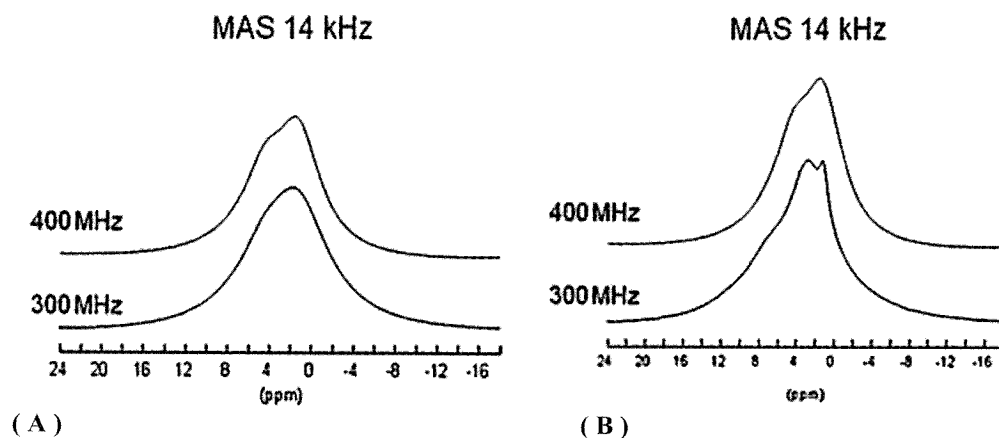
## RESULTS AND DISCUSSION

Fig. 1A and 1B are the MAS spectrum taken for AB and sf-AB. Even though the spinning speed was 14 kHz, the observed spectrum is too broad to get any valuable structural information.

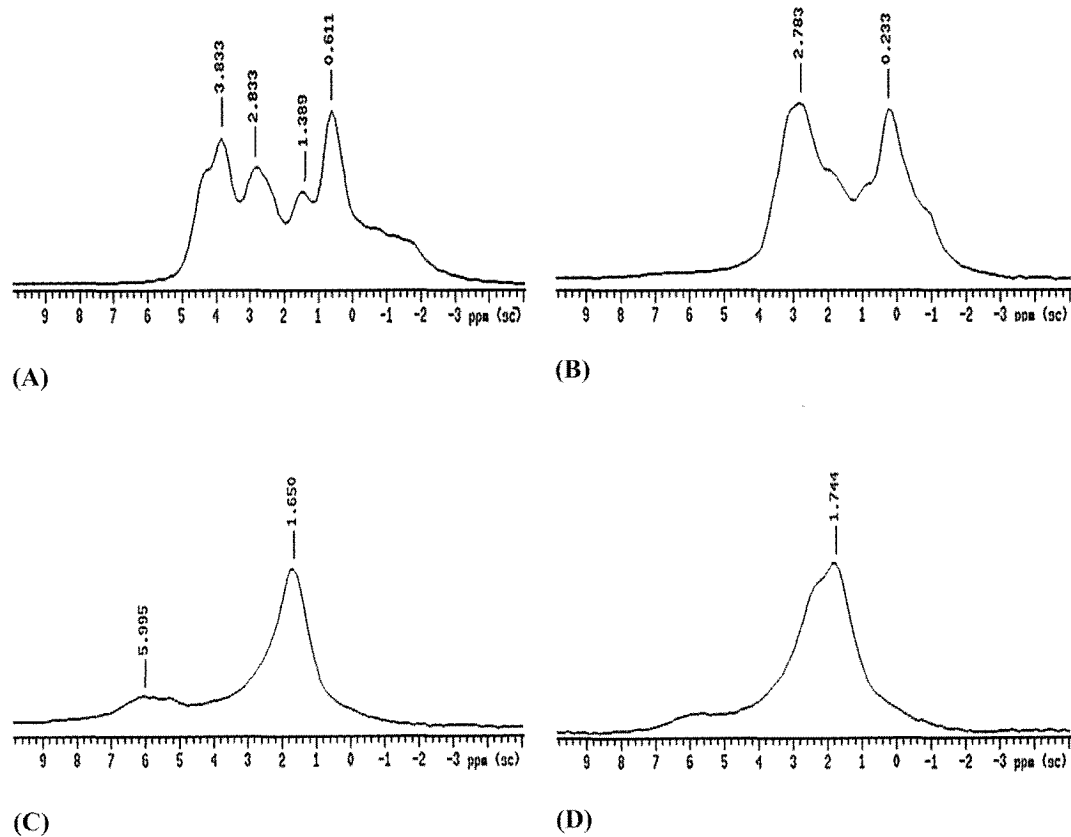
Figures 2A-2D are CRAMPS data showing an excellent resolution for <sup>1</sup>H site assignment. For pure AB, two <sup>1</sup>H peaks are expected and the spent fuel is supposed to give a single peak which is expected from IR spectra.<sup>2</sup> Two additional peaks of Fig. 2A are

attributed from contaminations of the sample. A careful synthesis of  $^{15}\text{N}$ - enriched sample gives the expected 2 peaks as seen in Fig. 2B. For sf-AB, CRAMPS spectrum was identical for both the purified AB and  $^{15}\text{N}$ - enriched AB with the one major peak. It coincides with the prediction of IR spectrum. These results are interpreted as follows. There are two different atomic sites for AB, one site is around the boron atoms while the other around nitrogen atoms. During dehydrogenation, three  $^1\text{H}$  atoms around the boron and one  $^1\text{H}$  atom around nitrogen escaped while two  $^1\text{H}$  remained around the nitrogen atoms. This interpretation is supported also by the results of 2D-NMR spectrum of figures 3A and 3B.

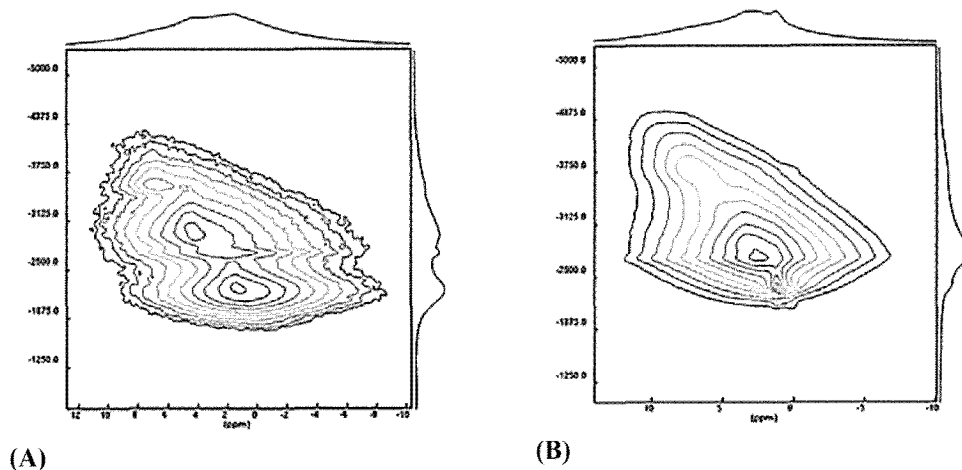
Fig. 3A and 3B are the 2D-NMR spectrum for AB and sf-AB. The evolution period is under FSLG condition while the detection period is under MAS at 14 kHz. The vertical axis is not referenced but shows excellent resolution. The peak assignment is done along MAS axis.



**Figure 1.** (A) MAS data taken at 300/400 MHz for AB (B) MAS data taken at 300/400 MHz for sf-AB, Even with 14 kHz MAS, the spectrum is too broad to analyze.



**Figure 2.** CRAMPS data taken at 200 MHz for AB (A),  $^{15}\text{N}$ -enriched AB (B), and its derivative residue after a catalytic process sf-AB (C, D).



**Figure 3.** 2D-NMR spectrum taken at 300 MHz for (A) AB and (B) sf-AB. (A) There are two major peaks at 1.4 ppm and 4.4 ppm. The 1.4 ppm peak is assigned to hydrogen atoms around boron whereas the 4.4 ppm peak to the one around nitrogen atoms. (B) There is only one major peak around 2.5 ppm, is assigned to hydrogen around the nitrogen atoms.

In summary, we applied various solids NMR technique to understand a structural change during catalytic process of dehydrogenation of the hydrogen storage material. MAS did not give the enough resolution to understand the chemical process. CRAMPS gave the high-resolution  $^1\text{H}$  NMR spectrum. With the help of 2D NMR technique, it is easy to understand the chemical change of the hydrogen during the catalytic process. The high-resolution  $^1\text{H}$  NMR technique on 1- and 2-D NMR seems to be very useful in developing a new class of the hydrogen storage material.

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