Dynamics of ammonia borane using neutron scattering

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Abstract

We have used both the backscattering (HFBS) and time-of-flight (DCS) neutron spectrometers to investigate proton dynamics in ammonia borane, a compound of intense interest as a model for 'chemical hydrogen storage' materials. Results indicate that the deposition of ammonia borane on a mesoporous silicate results in longer proton residence times and lower energy barriers for proton motion compared to bulk ammonia borane. The reduced activation energy for proton motions may partly explain the improved thermolysis and lowering the activation barrier for the loss of the first equivalent of H_2. In addition, the phonon density of states for neat ammonia borane compares well with other spectroscopic results, with the intense peak at 22 meV assigned to the librational NH_3 and BH_3 modes, whereas ammonia borane on MCM-41 displays a broad, featureless spectrum indicating a poorly crystalline material. Published by Elsevier B.V.

1. Introduction

Currently there is great scientific and public interest in the challenges facing conversion from a petroleum-based energy economy to one based upon hydrogen as an energy carrier for fuel cell power applications. The future of the hydrogen economy will depend upon significant scientific and engineering advances in hydrogen storage, hydrogen production and hydrogen utilization (fuel cells) [1].

We have been investigating the chemical and physical properties of chemical hydrogen storage materials containing boron and nitrogen as potential solid state hydrogen storage materials for on-board applications. Experimentally, we have focused our efforts on determining the thermochemistry and kinetics of thermally activated release of hydrogen from ammonia borane (NH_3BH_3) confined

within mesoporous silica. We discovered that ammonia borane (AB) confined within the channels of mesoporous silica (SBA-15 or MCM-41) showed a significant rate enhancement for hydrogen release and a change in the enthalpy of reaction for the release of hydrogen [2]. To summarize, the decomposition of bulk AB to yield polyaminoborane (PAB) has an activation barrier, E_a, of $\sim 117 \, \text{kJ mol}^{-1}$ and an enthalpy of reaction, ΔH_{rxn}, of $-21 \, \text{kJ mol}^{-1}$ for loss of hydrogen in the solid state. The decomposition of AB confined in SBA-15 exhibits both a reduced E_a, $\sim 50 \, \text{kJ mol}^{-1}$, and a reduced ΔH_{rxn} of $-1.3 \, \text{kJ mol}^{-1}$ for the loss of hydrogen.

The observed change in thermochemistry and kinetics (ΔH_{rxn} and E_a) reflects a change in the chemical or physical properties of AB when it is confined within the nano-dimensional channels of mesoporous silica. While we have made progress in understanding the mechanism of dehydrogenation in the neat material [3], the fundamental origin of this change in the activation barrier and enthalpy

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upon confining AB to the mesoporous silica scaffold remains to be answered. We have initiated a research program to use quasielastic neutron scattering (QENS), amongst other techniques, to attempt to answer this fundamental question.

2. Experimental details

Isotopically enriched ^{11}B NH_3BH_3 was prepared via a multistep synthetic scheme beginning with the reaction of ^{11}B enriched boric acid with anhydrous methanol. Trimethylborate was extracted and then added dropwise to excess NaH and stirred at $220\,^\circ C$. The resulting $Na^{11}BH_4$ was then purified. Finally, the $Na^{11}BH_4$ was reacted with ammonium carbonate at $40\,^\circ C$, resulting in purified $NH_3^{11}BH_3$ [4] Sample purity was confirmed with ^{11}B NMR, X-ray diffraction and infrared spectroscopy.

Neutron powder diffraction data taken on the BT1 diffractometer at the NCNR were analyzed within a constrained Rietveld model (after Ref. [5]) and gave satisfactory fit despite the high incoherent background. Neutron vibrational spectroscopy performed on the FANS spectrometer (also at NCNR) was entirely consistent with previous spectra obtained on natural boron NH_3BH_3 [6].

Labeled ammonia borane samples were absorbed onto a mesoporous silica substrate by stirring a methanol solution of ammonia borane over the silica substrate. Methanol was removed with a rotary evaporator and the process was repeated three times. The loaded sample was prepared with equal masses of ammonia borane and mesoporous silica.

The Disk Chopper Spectrometer (DCS) [7] and the High Flux Backscattering Spectrometer (HFBS) [8] at the NIST Center for Neutron Research was used to study the bulk and confined ammonia borane. Isotopically enriched ^{11}B samples were loaded into annular aluminum cells and cooled in a closed cycle refrigerator.

On DCS, data were collected at a series of temperatures above the structural phase transition at 225 K to extract activation energies for proton motion on 50 mg of the NH_3BH_3 sample and on a neat NH_3BH_3 loaded MCM-41 material (surface area of $890\,m^2/g$, pore diameter of $19\,\text{Å}$). An instrumental resolution of $\sim0.26\,meV$ is achieved using an incident wavelength of $3.6\,\text{Å}$. On HFBS, data were collected at several temperatures below 225 K to extract information on proton motions at higher resolution $(1.2\,\mu eV)$. By using both spectrometers, we can follow fast proton motions that occur on a picosecond time scale on DCS to slower motions on the nanosecond time scale on HFBS. Data were reduced and fitted using standard software available at the NCNR [9].

3. Results and discussion

The reduced DCS data of the NH_3BH_3 sample can be analyzed in terms of a Gaussian elastic peak, a broad background and a Lorentzian peak arising from quasielastic scattering (an improved fit using 2 Lorentzians could

not be achieved). For this sample, we nominally should include two Lorentzians in the fit, however, a proton NMR study indicates that above 225 K all protons were moving at essentially the same rate and it was hypothesized that the molecule is performing whole-body reorientations [10]. Using incoherent neutron scattering we cannot add to this hypothesis, but it may be possible to address the situation with a completely deuterated sample or by labeling each end of the molecule.

Fig. 1 shows the results of our phenomenological fitting a slice of data taken with DCS at 305 K. Good fits are maintained as a function of both momentum transfer (Q) and temperature. The data can be further reduced to extract an elastic incoherent structure factor (EISF), which is simply the ratio of elastic intensity to that of the elastic plus the quasielastic intensity. A model that fits this EISF, makes physical sense and is consistent with a previous NMR study [10] but not an older one [11] is that of a proton jumping around a three-fold axis. The EISF is dependent on Q and the proton jump distance, R, as $EISF = 1/3(1 + 2\sin(QR)/(QR))$. In this case, we found it is necessary to have an extra Q-independent elastic component that amounts to $\sim10\%$ of the scattering intensity despite removal of the observable Bragg peaks from the data reduction. In addition, this model imposes a Q-independent width on the Lorentzian peak. While it is possible to fit the current data with no constraints, at the lower temperatures there are correlations between parameters that lead to an upturn in the width at higher Q. Fixing the width to a mean width obtained in the mid-Q range, where the Lorentzian intensity is greatest, does not alter the quality of the fits at other Q values significantly. Clearly, there are no 12-fold jumps or free rotations occurring as suggested by Reynhardt and Hoon [11].

The resulting proton jump distance of $1.89(1)\,\text{Å}$ agrees well with the BH_3 distances from the Rietveld refinement
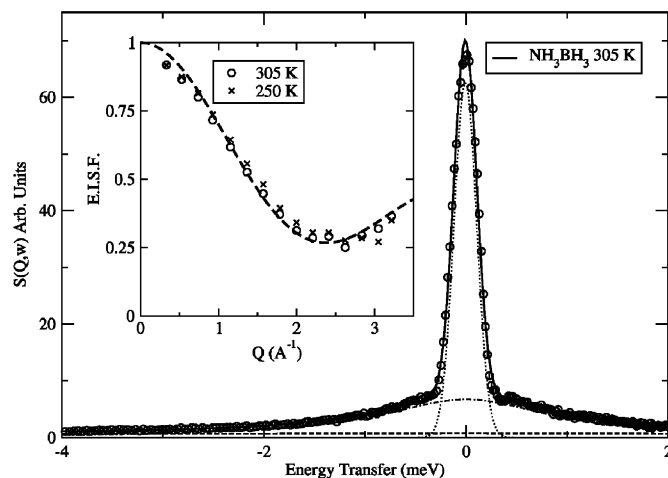

Fig. 1. DCS $S(Q,w)$ data of $NH_3^{11}BH_3$ at 305 K (circles) at $Q = 1.56\,\text{Å}^{-1}$ with the total fit (solid line) and components (elastic: dotted; quasi-elastic Lorentzian: dot-dashed; background: dashed). The inset shows the extracted EISF at 250 and 305 K with a fit to a three-fold jump diffusion model as detailed in the text.

(average distances of 1.87 and 1.63 Å in the BH_3 and NH_3 groups, respectively). However, if all protons are contributing equally to the EISF, this seems to be weighted too much towards the boron side of the molecule. Extracting correlation times from the Lorentzian full widths as a function of temperature allows the extraction of the activation energy for proton rotation, E_a. Arrhenius plots for neat AB yield an E_a of 4.9(5) kJ/mol, slightly lower than the values of 5.9(5) kJ/mol for BD_3 and 7.3(8) kJ/mol for ND_3 by deuterium NMR [10].

We can compare this with data taken between 110 and 180 K on the HFBS spectrometer. Comparison of NMR correlation times with our linewidths indicates that only the NH_3 proton motions are compatible with the time scale of the HFBS measurements. The calculated activation of 7.98 kJ/mol is in good agreement with 8.37 kJ/mol for the reorientation of the NH_3 group [11].

Similar EISFs to the ones shown here can be extracted from the AB loaded MCM-41 data; although we only have two temperatures to compare, there is a greater temperature dependence of the QE intensity and the QE linewidth increases linearly in Q. We suppose that this effect may arise due to preferential association of the polar molecule with the surface, in particular the BH_3 group, and possibly a change in the reorientation mechanism to a more diffusive process. The similar-looking EISFs may also indicate that some bulk-like AB is present in these samples.

The phonon density of states for neat AB compares well with other spectroscopic results; the strong peak at 22 meV assigns to the librational NH_3 and BH_3 modes, whereas ammonia borane on MCM-41 displays a broad, featureless spectrum indicating a poorly crystalline material.

4. Conclusions

We have synthesized and measured QENS spectra of ^{11}B ammonia borane in the low-temperature phase and orientationally disordered tetragonal phase. The source of the disorder in the high-temperature phase can be described as a dynamic three-fold jump diffusion. The activation average for all protons at 4.9(5) kJ mol^{-1} is comparable to that obtained from NMR. We measure 7.98 kJ/mol for the reorientation of the NH_3 group at low temperatures. Preliminary experiments on AB loaded MCM-41 indicate that the activation energy is reduced and may contribute to the beneficial properties of this material. Further work on the ND_3BH_3 and NH_3BD_3 systems will be needed to identify whether the protons associated with N or B interact with the silica scaffold and the nature of that interaction.

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