Molecular Aluminum Hydrides Identified by Inelastic Neutron Scattering during H$_2$ Regeneration of Catalyst-Doped NaAlH$_4$

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Catalyst-doped sodium aluminum hydrides have been intensively studied as solid hydrogen carriers for onboard proton-exchange membrane (PEM) fuel cells. Although the importance of catalyst choice in enhancing kinetics for both hydrogen uptake and release of this hydride material has long been recognized, the nature of the active species and the mechanism of catalytic action are unclear. We have shown by inelastic neutron scattering (INS) spectroscopy that a volatile molecular aluminum hydride is formed during the early stage of H$_2$ regeneration of a depleted, catalyst-doped sodium aluminum hydride. Computational modeling of the INS spectra suggested the formation of AlH$_3$ and oligomers (AlH$_3$)$_n$ (Al$_2$H$_6$, Al$_3$H$_9$, and Al$_4$H$_{12}$ clusters), which are pertinent to the mechanism of hydrogen storage. This paper demonstrates, for the first time, the existence of these volatile species.

Introduction

Hydrogen gas promises to be a major clean fuel if current difficulties of its storage could be overcome. The catalyst-doped sodium aluminum hydrides are candidates for solid carriers of hydrogen for onboard proton-exchange membrane (PEM) fuel cells because of their low operating temperatures and high hydrogen storage capacities.[1] Hydrogen storage materials based on NaAlH$_4$ are distinct from transition-metal hydrides in their structures and their properties. Transition-metal hydrides are formed through the occupation of interstitial sites in the host metal lattices by hydrogen but formation of NaAlH$_4$ involves stepwise reactions leading to alteration of bulk structures (see chemical equations):

$$3NaAlH_4 \rightleftharpoons Na_3AlH_6 + 2Al + 6[H]$$

$$Na_3AlH_6 \rightleftharpoons 3NaH + Al + 3[H]$$

From these chemical equations, one can see that sodium aluminum hydride could be a source of regenerable hydrogen. However, hydrogen release is slow and, more importantly, rehydrogenation after decomposition requires drastic conditions; these facts hampered the use of these materials as effective hydrogen storage carriers. The possibility of developing "regenerable" sodium aluminum hydride was realized by Bogdanović and Schwickardi[1] when investigating potential hydrogen storage materials toward the end of 1997. They discovered that upon doping NaAlH$_4$ with a small quantity (1–2 mol %) of a titanium catalyst, the rates of "dehydriding" and "rehydriding" of NaAlH$_4$ could be enhanced, rendering them reversible under acceptable conditions in the solid state. This breakthrough was followed

by further progress in the development of catalysts for the reversible dehydriding of NaAlH$_4$. The importance of catalysis in this area is recognized but the nature of the active species and the catalytic mechanism are not clear.[2] It remains puzzling how the NaAlH$_4$ phase is rapidly reformed from high-melting Al metal (mp 660 °C) and NaH (decomposes 425 °C) in the hydrogen-depleted, catalyst-doped sodium aluminum hydride[1] in a hydrogen atmosphere at <140 °C. Without a catalyst, the regeneration is difficult (involving H$_2$ activation and a slow diffusion of H atoms through the phase boundary), implying that the role of a catalyst is to bring the phases together. There is a recent suggestion of a highly mobile transient species such as AlH$_3$ formed via the catalyst which is responsible for accelerating the slow solid–solid reactions.[3] However, this suggestion has yet to be confirmed by conventional molecular spectroscopy probably because of the trace level of the mobile transient species and possibly because the structures (such as AlH$_3$) are in a highly symmetric configuration.

We considered that inelastic neutron scattering (INS) could uniquely aid characterization of the catalyst-doped NaAlH$_4$ and so provide insights into the catalysis. The vibrational spectrum obtained with neutrons derives from motions involving displacement of nuclei rather than electrons. Therefore, the intensity of the INS spectrum does not depend on electronic properties, such as the dipole moment or polarizability, and so symmetry-based selection rules are not operable (a particular advantage when we seek to detect symmetric hydrogen-containing species).[4,5] Also, the sensitivity of the INS technique is greatest for hydrogen; other atoms generate a background which may be subtracted. Accordingly, we have applied high-resolution INS spectroscopy supplemented by density functional theory (DFT) calculations to identify the mobile species during the regeneration of the depleted hydride. Prior to this work, there have been two INS studies on Ti doped NaAlH$_4$ with rather low-resolution INS and DFT calculations, which did not provide a convincing understanding of the Ti catalysis.[6]

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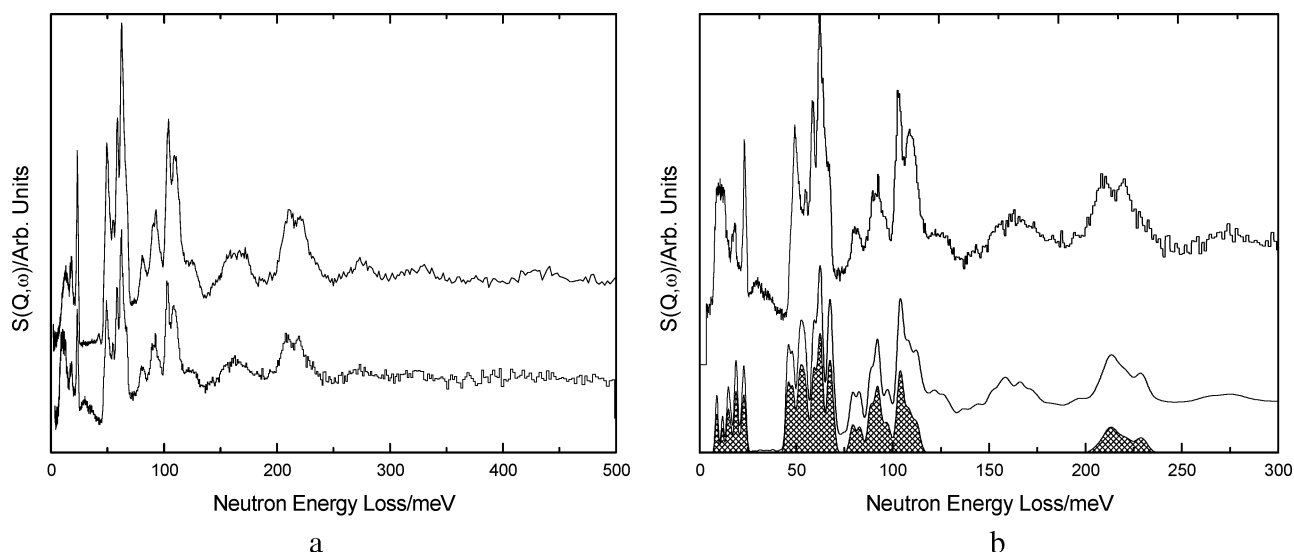
Figure 1. (a) TOSCA INS spectra of Sn/Ti codoped NaAlH$_4$ (bottom line) and pure NaAlH$_4$ (top). (b) INS spectrum of Ti doped NaAlH$_4$ (top line) compared with the aCLIMAX[8] calculated NaAlH$_4$ spectra using DFT calculations (bottom). The shaded area represents the contribution from fundamental vibrations; the total spectrum contains the overtones and combinations.[8]

Experimental Section

The INS spectra were recorded at 20 K with materials in an airtight Al container on the high-resolution time-of-flight spectrometer, TOSCA, at the pulsed neutron spallation source, ISIS, in the United Kingdom. This spectrometer uses an "inverted geometry" configuration and is at present the highest resolution machine of its kind in the world. Spectra were interpreted with the aid of the aCLIMAX program which permits a direct and straightforward comparison of experiment and ab initio theoretical calculations without the need for empirical parametrization.[4]

After the collection of the INS spectra, a series of DFT calculations was performed to identify the origin of the peaks. The calculations included AlH$_3$, Al$_2$H$_6$, Al$_3$H$_9$, and Al$_4$H$_{12}$ clusters. Modeling an AlH$_3$ molecule on a surface was performed using periodic ab initio calculations. Cluster calculations employed the DMol3 package from Materials Studio (Accelrys Inc.) and periodic calculations with CASTEP and DMol3 for the AlH$_3$/Al(111) and solid NaAlH$_4$. Because of the size of the unit cell, only the vibrations at the Gamma point are presented. Calculations for NaH were performed using the Abinit program:[7] we calculated the spectrum from a fine grid in reciprocal space as the dispersion effects were pronounced and there was LO−TO splitting. The calculations with DMol3 used various GGA functionals, the DFT semicore pseudopotentials, and a double-numerical basis set including polarization (DNP). CASTEP calculations used the PBE GGA functional and the default energy cutoffs and the ultrasoft pseudopotentials. The vibrational analysis provided the solution of the eigenvector (displacements) and the eigenvalues (frequencies), and the aCLIMAX program then generated the INS spectra (following the trajectory determined by the geometry of TOSCA). The INS intensities of the spectral features involving hydrogen were taken as proportional to the amplitude of the displacements of the hydrogen atoms.[8,9] The best fit for the calculated spectra was then obtained by allowing a small displacement of the positions of the peaks from their original calculated frequencies using a least-squares fitting routine. The greatest displacement was 5.3%: the average displacement of the peaks' positions was less than 2%. This procedure, based on gas-phase models, provided an empirical assignment of the INS spectra and enabled us to separate internal and external modes and to detect combinations and overtones. Such a fine peak adjustment is acceptable to obtain a vibrational assignment, which is an empirical practice for errors in the potential energy calculations. The main assumption is that the diagonal elements of the dynamical matrix can be modified slightly without affecting the nondiagonal terms. This is usually the case if the changes in the diagonal elements are small, see chapter 4 in ref 8. Nevertheless, this fitting was justified since this provided a better comparison with the results, and it also showed graphically the origin of the spectral intensity. However, it must also be stressed that the calculations were based on models, so that the isolated molecule approximation was assumed; therefore, it is possible to separate the contribution of internal modes from the external modes (this approximation is valid when dealing with molecular systems).[8]

Results and Discussion

Our NaAlH$_4$ materials doped with 2 mol % Ti and 1 mol % Sn/1 mol % Ti (both with good hydrogen storage capacity, see Supporting Information) gave INS spectra similar to the spectrum of pure NaAlH$_4$, see Figure 1a. An ab initio calculation (Figure 1b) indicates that the spectrum corresponds well to pure NaAlH$_4$ (characterized by XRD as the tetragonal system with lattice parameters a, $b = 5.03$ Å, $c = 11.35$ Å). This conclusion is consistent with the INS studies of Ti-doped NaAlH$_4$ from Jensen et al. who noted INS spectra like their undoped samples.[6] Similarly, our INS spectra of hydrogen-depleted Sn/Ti (or Ti) doped NaAlH$_4$ (after complete decomposition, see Figure 2) correspond well to those of pure NaH (in agreement with the DFT calculated spectrum). Our observations and supporting calculations imply that the catalyst doping does not create structural modifications (within the detection limit) in the bulk NaAlH$_4$ structure or final NaH/Al phases (in agreement with XRD data). This result is in contrast to the Ti substitution effect recently reported.[6]

During the early stage of NaH/Al rehriding in both depleted Sn/Ti-doped (Figure 3a) and Ti-doped NaAlH$_4$ (Figure 3b) samples, for which XRD showed predominantly the NaH/Al phases, we observed new peaks in the INS spectra (Figure 3) noticeably at lower energies (<75 meV). These new, sharp peaks do not match those of NaAlH$_4$, NaH α-Al$_3$AlH$_6$, or tin/titanium hydrides where broad peaks, typical of these extended solid-

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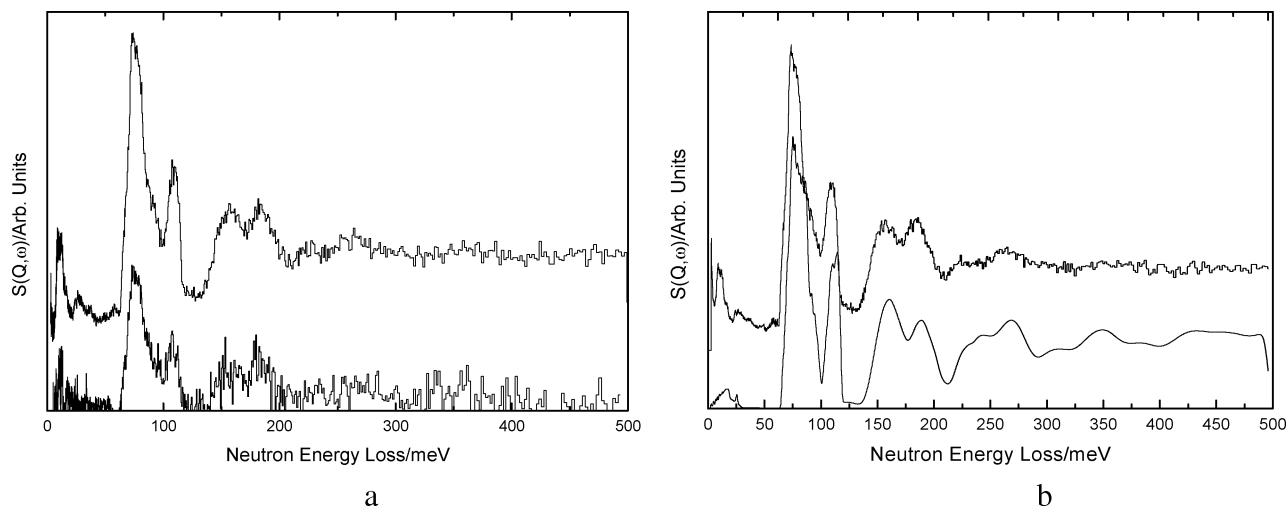*J. Phys. Chem. B, Vol. 110, No. 2, 2006* **713**

Figure 2. (a) TOSCA INS spectra of depleted Sn/Ti codoped $NaAlH_4$ after H_2 desorption (bottom line) and pure NaH (top). (b) INS spectrum of depleted Ti doped $NaAlH_4$ after H_2 desorption (top line) compared with the aCLIMAX calculated NaH spectra (bottom) using DFT calculations.[10]
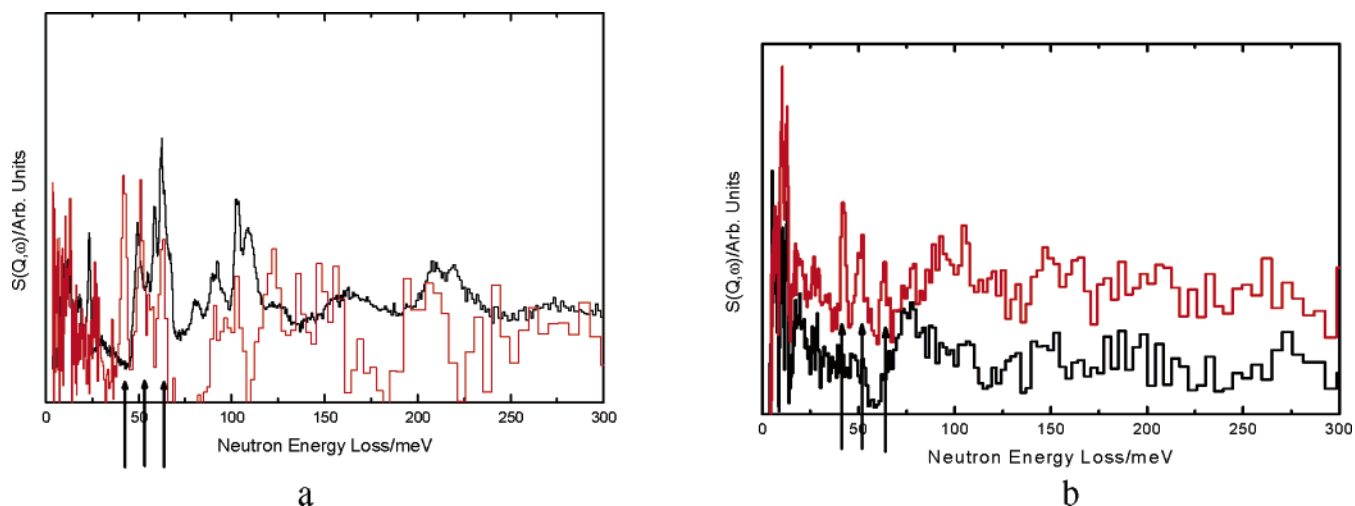

Figure 3. (a) TOSCA INS spectra of depleted Sn/Ti codoped $NaAlH_4$ (red bottom line) after exposing to 140 bar H_2, 130 °C for 0.5 h compared with measured $NaAlH_4$ spectra (top black line). (b) INS spectrum of depleted Ti doped $NaAlH_4$ after exposing to 140 bar H_2, 130 °C for 0.5 h (red top line) compared with the spectra of the total hydrogen-depleted sample of NaH/Al (bottom black line). The red spectra correspond to samples containing different catalysts, and the arrows indicate the position of the new peaks that were used to identify the volatile species.

state dispersed phonon spectra, are seen.[5] The sharp peaks observed below 75 meV are well within the resolution function of TOSCA at these energy transfers. Such sharp peaks arise for molecular species where internal modes are not coupled to those of a lattice. Both materials gave very similar spectra, indicating that both systems were operating in the same way.

The idea that transformations of alkali metal aluminum hydrides proceed through alkali metal hydrides and an aluminum hydride has been around for many years.[11] Recently, it has been speculated that they could be the intermediates for hydrogen uptake and release over catalyzed alkali metal aluminohydrides.[3] We tried two different models to fit the hitherto unknown molecular aluminum hydride peaks: discrete AlH_3 units and derivatives of AlH_3, and low-oligomers of AlH_3 including Al_2H_6, Al_3H_9, and Al_4H_{12}. The frequencies were calculated for an optimized structure with atoms in their minimum energy position giving residual forces close to zero. The justification for an AlH_3 species is that it is the first basic and relatively stable neutral species (decomposing at about 150 °C) which could be produced by disproportionation reactions from both AlH_4^- and AlH_6^{3-}. In addition, Gross et al.[3] have proposed the "zippering" (volatilizing) of AlH_3 in and out of the double-chain AlH_4^+ complex, supported by theoretical modeling accounting for the

reversible conversion of a Na_3AlH_6 intermediate phase to $NaAlH_4$. AlH_3 is still rather chemically unstable, if produced free, and could undergo rapid polymerization to higher hydrides.

Our calculations indicated that basic molecular AlH_3 on an Al(111) surface gave similar spectral line structures as the spectra (Figure 4a and Supporting Information). Fitting is improved following the order of AlH_3 to Al_2H_6, Al_3H_9, and Al_4H_{12}. Notice that a best fit to these peaks corresponds well to the polymeric crownlike Al_4H_{12} cluster (Figures 4 and 5). We therefore conclude that discrete neutral molecular hydrides closely related to the AlH_3 structure are present during hydrogenation of depleted sodium aluminum hydride. We caution that such a close fit to the polymeric crownlike Al_4H_{12} cluster does not necessarily mean that the material contains *only* pure crown-Al_4H_{12} molecules. We cannot be certain whether the species which we have identified are key intermediates or side products in the hydrogenation process. In addition, several smaller but unstable species such as AlH, AlH_2, Al_2H_2, and Al_2H_4 have been detected in matrix isolation experiments[12,13] of Al/H systems, which could also be present in the sample. They might well aggregate depending on the reaction conditions.

Concerning the mechanism for hydrogen storage, we consider that the key problem is that we might expect that the depleted
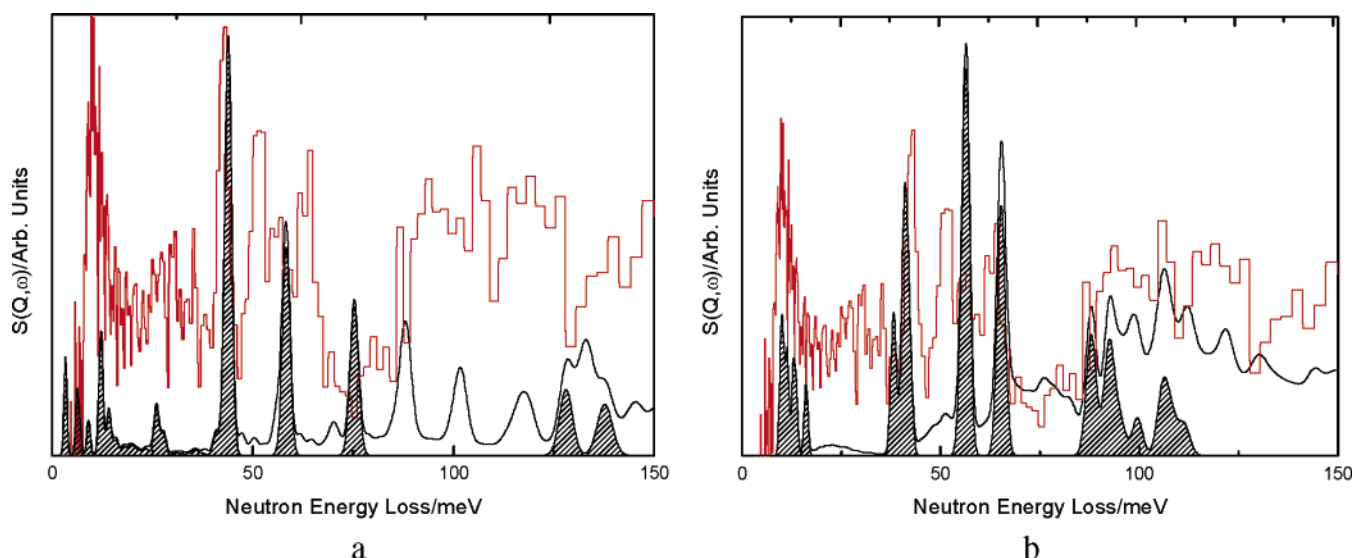
Figure 4. (a) Calculated spectrum for AlH_3 adsorbed on Al metal (bottom line) and experimental data (top). (b) Calculated spectrum for the Al_4H_{12} (crown) molecule. The shaded area represents the contribution from fundamental vibrations, and the total spectrum contains the overtones and combinations.[8]
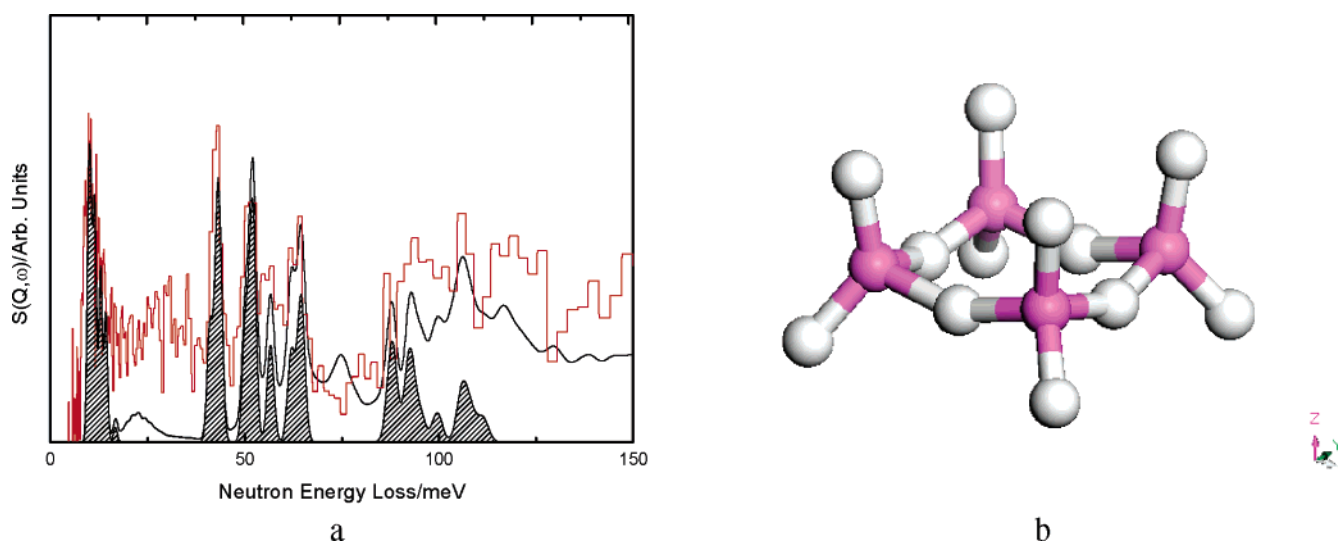

Figure 5. (a) Best-fit model from the intensities shown in Figure 4b, and the fitted peaks show the good agreement in the integrated intensities (see Supporting Information). (b) The best-fit model for the spectrum is obtained with the Al_4H_{12} molecule shown above.

Alanate materials comprising high-melting point bulk phases (NaH/Al) with a strong lattice force should greatly restrict long-range ionic transport to the catalyst (Sn or Ti) at the surface during H_2 regeneration under the reaction conditions (100–130 °C). The aluminum metal surface is also known to be inert toward the activation of dihydrogen at this low temperature.[14] On the other hand, the clear doping effect undoubtedly indicates that the regeneration rate can be much enhanced in the presence of Ti or Sn/Ti (Supporting Information). It has therefore been postulated in the literature that some kind of mobile neutral species may have been involved during the rehydriding processes.[2,3] Our work, reported here, supports the presence of neutral Al−H species.

Conclusion

To summarize, we provide the first direct evidence, on the basis of INS spectroscopy supplemented by computational modeling and theoretical calculations, of the presence of molecular aluminum hydride, possibly in the form of a polymeric molecular mixture, during hydriding of hydrogen-deleted sodium aluminum hydride. As far as we are aware, no other experimental proof for the existence of these species has been collected prior to this study. This is attributed to the fact that the highly symmetrical, hydrogen-containing neutral aluminum hydride species or closely related polymeric molecules at a very low concentration are not easily identified by other spectroscopic methods, but the present specific and hydrogen-sensitive INS technique combined with the ab initio calculations can undoubtedly provide a unique characterization tool for their broad identification. The INS technique is uniquely capable of detecting and characterizing such species. We have been able to provide experimental support for the idea that a volatile aluminum hydride acts as a shuttle in the catalyzed reforming of the $NaAlH_4$ phase from solid NaH under hydrogen storage conditions.

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Supporting Information Available: The evaluation of hydrogen uptake/release of the materials and the fitting of INS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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