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Julie Herberg, Robert Maxwell, Eric Majzoub

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Investigation of Ti-doped $NaAlH_4$ by solid-state NMR

Julie L. Herberg[1], Robert S. Maxwell
Lawrence Livermore National Laboratory
7000 East Avenue, Livermore, CA 94550, U.S.A

Eric H. Majzoub
Sandia National Laboratories
7011 East Avenue, Livermore, CA 94550, U.S.A

ABSTRACT

In recent years, the development of Ti-doped $NaAlH_4$ as a hydrogen storage material has gained attention because of its large weight percentage of hydrogen (~5 %) compared to traditional interstitial hydrides. The addition of transition-metal dopants, in the form of Ti-halides, such as $TiCl_3$, dramatically improves the kinetics of the absorption and desorption of hydrogen from $NaAlH_4$. However, the role that Ti plays in enhancing the absorption and desorption of H_2 is still unknown. In the present study, ^{27}Al, ^{23}Na, and ^{1}H MAS (Magic Angle Spinning) NMR (Nuclear Magnetic Resonance) has been performed to understand the titanium speciation in Ti-doped $NaAlH_4$. All experiments were performed on a sample of crushed single crystals exposed to Ti during growth, a sample of solvent-mixed $4TiCl_3 + 112NaAlH_4$, a reacted sample of solvent-mixed $TiCl_3 + 3NaAlH_4$ with THF, and a reacted sample of ball-milled $TiCl_3 + 3NaAlH_4$. The ^{27}Al MAS NMR has shown differences in compound formation between solvent-mixed $TiCl_3 + 3NaAlH_4$ with THF and the mechnically ball-milled $TiCl_3 + 3NaAlH_4$. ^{27}Al MAS NMR of the mechanically ball-milled mixture of fully-reacted $TiCl_3 + 3NaAlH_4$ showed spectral signatures of $TiAl_3$ while, the solvent-mixed $4TiCl_3 + 112NaAlH_4$, which is totally reacted, does not show the presences of $TiAl_3$, but shows the existence of Al_2O_3.

INTRODUCTION

The decomposition of sodium aluminum tetrahydride ($NaAlH_4$) occurs in the following steps:

$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2 \uparrow$$
$$2Na_3AlH_6 \rightarrow 6NaH + 2Al + 3H_2 \uparrow$$
$$2NaH \rightarrow 2Na + H_2 \uparrow$$

Bogdanovic et al. showed that the $NaAlH_4$ decomposition can be kinetically enhanced and reversible with the addition of Ti-dopants [1, 2]. Even though the addition of the Ti-dopants enhances the rate of reaction by decreasing the activation energy of the absorption and desorption cycles, the change in composition formation with the addition of titanium that occurs in this material is still unknown. X-ray diffraction studies of Sun et al. [3] have suggested that Ti may be substituting into bulk $NaAlH_4$ as Ti^{3+}. Ozolins et al. [4] have shown that there does not exist any large changes in the overall structure of $NaAlH_4$ due to the addition of Ti. Desorption kinetics studies by Majzoub et al. [5] have further suggested that the resultant Ti valence state is

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[1] Corresponding author: Tel.: +1-925-422-5900; Fax +1-925-294-3410. *E-mail address:* herberg1@llnl.gov

independent of the precursor Ti-halide used for doping. As pointed out by E.H. Majzoub et al. [5], the compositional changes that occur by Ti-doping the sodium alienates could either occur in the form of bulk substitution in the alanates structure(s) or from lowering the reaction barrier at the surface.

Since NMR can provide detailed understanding of the influences of metal incorporation on structure, composition, formation kinetics, hydrogen speciation, modes of hydrogen interaction, and release and reversibility mechanisms, NMR is an ideal method to examine these sodium alanates materials. Tarasov et al [6, 7] have preformed ^{23}Na and ^{27}Al MAS NMR on $NaAlH_4$ and $NaAlD_4$ materials and have seen dramatic changes in the composition of this material with varying temperatures. Bogdanovic et al. [8] went one step further in exploring the effects that Ti-doping has on the dehydrogenation and rehydrogenation cycles by performing ^{23}Na and ^{27}Al MAS NMR on a variety of Ti-doped $NaAlH_4$ materials at different stages of the cycle. Even though these authors obtained valuable information about the overall composition of this material, they were unable to determine how Ti-doping affects this material. These authors, however, allude to the fact that an increase in the amount of catalyst leads to an increase in a shoulder on the right side of one of the main ^{27}Al NMR spectrum. These authors tentatively assign this peak to an Al-Ti alloy.

The following paper reports on ^{27}Al, ^{23}Na, and ^{1}H MAS NMR and x-ray diffraction to understand the compounds formed by the addition of Ti has on the bulk or on the surface of $NaAlH_4$ material. Experiments were performed on a sample of crushed single crystals exposed to Ti during growth, a sample of solvent-mixed $4TiCl_3 + 112NaAlH_4$, a reacted sample of solvent-mixed $TiCl_3 + 3NaAlH_4$ with THF, and a reacted sample of ball-milled $TiCl_3 + 3NaAlH_4$.

EXPERIMENTAL DETAILS

The sample preparation and x-ray diffraction data of a sample of solvent-mixed $4TiCl_3 + 112NaAlH_4$, a reacted sample of solvent-mixed $TiCl_3 + 3NaAlH_4$ with THF, and a reacted sample of ball-milled $TiCl_3 + 3NaAlH_4$ are discussed elsewhere[9]. MAS NMR measurements were performed on a Bruker Avance 400WB spectrometer that has a magnetic field of 9.4T. This gives a resonance frequency of 104.25MHz for ^{27}Al (spin = 5/2), 105.84MHz for ^{23}Na (spin=3/2), and 400.13MHz for ^{1}H (spin=1/2). The samples were all packed in 4-mm MAS rotors inside an Ar glove box with oxygen levels below 3ppm. Spinning rates of 9kHz and 12kHz were used. The Free Induction Decay (FID) spectra were taken with a single excitation pulse. For both ^{27}Al and ^{23}Na NMR, a short pulse and small flip angle was used (^{27}Al MAS NMR with a 8 degree pulse width of 0.2μs and ^{23}Na MAS NMR with a 8 degree pulse width of 0.2μs). ^{1}H MAS NMR was taken with a 90 degree pulse width of 4.2μs. The ^{27}Al spectra were referenced to aqueous solutions of $Al(NO_3)_3$ and ^{23}Na was referenced to aqueous solutions of $NaNO_3$. ^{1}H was referenced to water, which was set to zero frequency.

RESULTS AND DISCUSSIONS

The Rietveld refinement using powder X-ray diffraction of 4 at. % “Ti-exposed” single crystal has shown that there is no observable shift in the lattice constants due to the exposure of Ti. This would imply that the titanium does not enter the bulk of the $NaAlH_4$ lattice [9]. Therefore, one can conclude that since the titanium does not enter the bulk of $NaAlH_4$, the Ti has

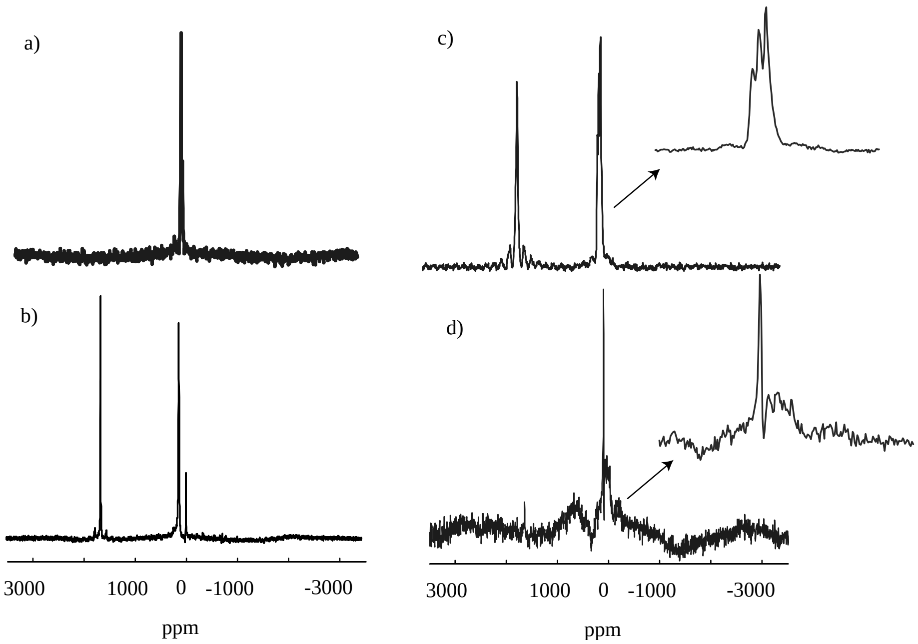

Figure 1: ^{27}Al MAS NMR at 12kHz with a 8 degree pulse width of 0.2μs. The following ^{27}Al MAS NMR represent $NaAlH_4$ Ti-doped in different processes, including a) crushed crystal $NaAlH_4$ with small amounts of Ti, b) $4TiCl_3$ +$112NaAlH_4$, c)$3NaAlH_4$ +$TiCl_3$ that was wet dried with THF, and d) $3NaAlH_4$+$TiCl_3$ that was ball milled. (* indicates spinning sidebands)

to cause compositional changes at the surface of this material. The following NMR data shows some of these compositional changes.

^{27}Al MAS NMR spectra of the four doped $NaAlH_4$ materials are shown in Figure 1. The spectra for a sample of crushed single crystals exposed to Ti during growth (1A) is characterized by a peak at approximately 90ppm due to $NaAlH_4$. The solvent-mixed $4TiCl_3$ + $112NaAlH_4$ material (1B) spectrum is characterized by 3 distinct ^{27}Al NMR resonances: a peak at approximately 1640ppm, assigned to metallic aluminum; a peak at approximately -42.7ppm, assigned to Na_3AlH_6; and a peak at approximately 90ppm, assigned to $NaAlH_4$. These assignments were made based on comparisons to pure materials (data not shown).

As mentioned above, the fully reacted samples of $TiCl_3$ + $3NaAlH_4$ were processed by two methods: wet dried with THF and ball-milled. The 27Al MAS spectra for these materials are shown in Figures 1C and 1D. It is clear that the ^{27}Al NMR that the aluminum speciation dramatically affected by the processing method. The sample that was wet dried with THF (1C) has two distinct peaks: metallic aluminum at 1640ppm and a series of overlapping resonances at 9ppm, 36ppm, and 65ppm, assigned to six, five, and four coordinate aluminum-oxygen species in amorphous Al_2O_3. To confirm that this peak did not represent any AlH_4 species, we performed ^{27}Al {^{1}H} MAS NMR experiments and observed no significant narrowing of the Al2O3 resonances with decoupling. This result indicates that this peak is not due to AlH_4 clusters, which would have large Al-H dipolar couplings due to the short Al-H bonding. And the existence of Al_2O_3 is consistent with Ti-Al nanoclusters where the oxygen in the THF is coordinated with the aluminum [10]. The existence of Al_2O_3 in this sample suggests it may have been exposed to air at some point in the synthesis or processing.

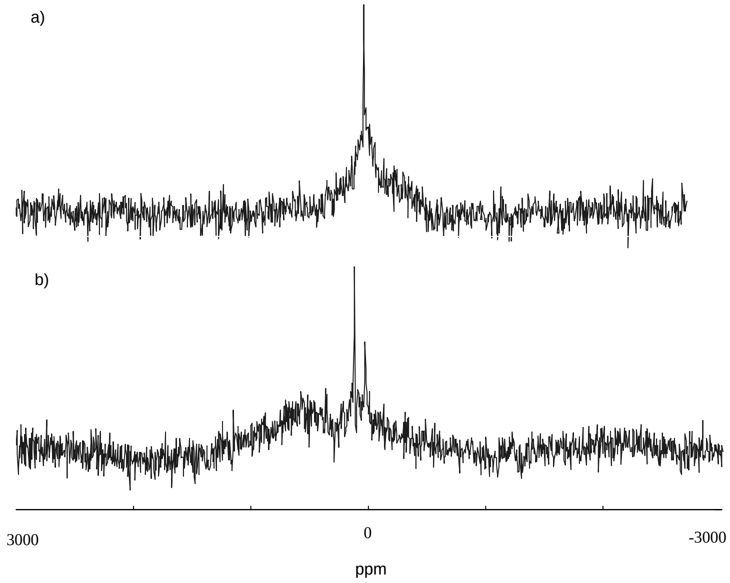

Figure 2: a) the ^{27}Al MAS NMR spectra at 9kHz of TiAl3 and b) the ^{27}Al MAS NMR at 9kHz spectra of reactive sample of $TiCl_3$ + $3NaAlH_4$ that was ball milled.

The ^{27}Al NMR spectra of the ball milled sample of $TiCl_3$ + $3NaAlH_4$ (1D) shows four resonances: two at ~120ppm line widths of 1.9kHz and 3.0kHz, a broad resonance at approximately 664ppm and a metallic aluminum resonance at 1640ppm. The extremely broad line shape of the 664 ppm resonance suggests that there might exist some amorphous or nanoclusters of $TiAl_3$. Figure 2 directly compares the ^{27}Al MAS NMR spectra of pure $TiAl_3$ and of the ball milled $TiCl_3$ + $3NaAlH_4$ sample. It is easy to see that these line shapes are extremely similar and indicate that there exist $TiAl_3$ in the ball-milled $TiCl_3$ + $3NaAlH_4$ sample. The differences in line shape might be a result of the small differences in $TiAl_3$ environments. This observation also agrees with results from X-ray diffraction studies [9], which showed that in a mechanically ball-milled mixture of $3NaAlH_4$ +$TiCl_3$ the formation of $TiAl_3$ was likely[9]. However, the ^{27}Al MAS NMR of $3NaAlH_4$ +$TiCl_3$ that was wet dried with THF showed no presence of $TiAl_3$[9], but did show the presence of Al_2O_3.

^{23}Na MAS NMR spectra are shown in Figure 3. Three of the four samples studied here were characterized by a single resonance at ~10 ppm assigned to $NaAlH_4$. The ball milled $TiCl_3$ + $3NaAlH_4$ sample, however, was characterized by a more complex 23Na MAS spectrum, as can be seen in Figure 3B. For this sample, four resonances were observed: 1) a resonance at 10 ppm due to $NaAlH_4$, 2) a resonance at –10ppm, indicating the presence of $NaAlH_6$, 3) a resonance at approximately 21ppm, indicating the presence of $NaAlH_6$; and at 0ppm, which indicates the presence of NaCl. Figure 3A shows ^{23}Na MAS NMR data from the sample of crushed crystal $NaAlH_4$ with small amounts of Ti. The ^{23}Na MAS NMR indicates that there only exist $NaAlH_4$ in this sample. Figure 3B shows ^{23}Na MAS NMR data from the sample of $4TiCl_3$ +$112NaAlH_4$ ball milled. The ^{23}Na MAS NMR indicates the presence of $NaAlH_4$, Na_3AlH_6, and NaCl. Figure 3C and 3D show ^{23}Na MAS NMR data from the samples of $3NaAlH_4$+$TiCl_3$ that were wet dried with THF and balled milled repectively. This ^{23}Na NMR data indicates that both of these samples are completely reacted and only contain NaCl, since there is no indication that $NaAlH_4$ and Na_3AlH_6 are present The ^{1}H MAS NMR data in figure 4 shows a variety of different line shapes for each of these samples. Since the protons in the sample have strong dipolar coupling and the presence of H_2 in this sample requires different NMR analysis that is beyond the scope of this paper, the full analysis of the ^{1}H MAS NMR will be presented in our upcoming publications. ^{1}H MAS NMR data in figure 4A and 4B is mostly due to hydrogen in the form $NaAlH_4$ and Na_3AlH_6 respectively. Furthermore, it is important to examine the ^{1}H MAS NMR from the samples of $3NaAlH_4+TiCl_3$ that were wet dried with THF and balled milled, which are shown in figure 4C and 4D respectively. The ^{1}H MAS NMR data in figure 4C shows several narrow lines around 0kHz and a broad component at 35kHz. The hydrogen near 0kHz in this sample might be due to the residual THF. The broad component might be due to some form of TiH_2, but this still needs to be investigated. The rather broad ^{1}H MAS NMR line shape in figure 4D could potentially due to some form of Ti hydride nano-particles. However, more ^{1}H NMR studies are needed to determine the different forms of hydrogen in the fully reacted samples of samples of $3NaAlH_4+TiCl_3$.

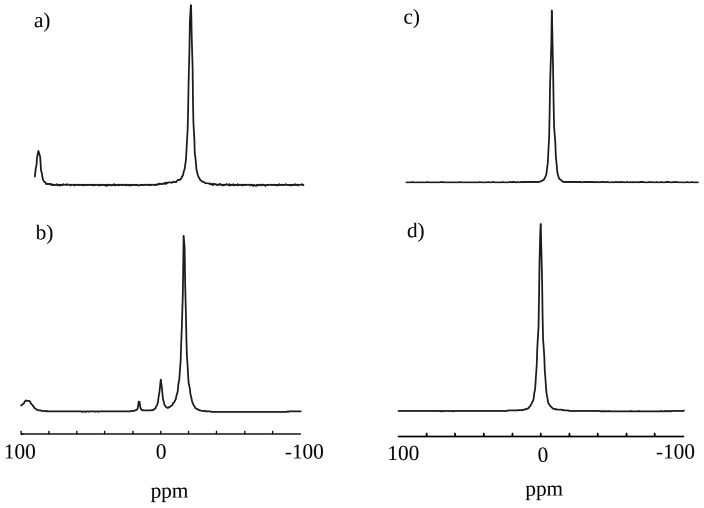

Figure 3: ^{23}Na MAS NMR at 12kHz with a 8 degree pulse width of 0.2μs. The following ^{23}Na in different processes, including a) crushed crystal $NaAlH_4$ with small amounts of Ti, b) $4TiCl_3$ +$112NaAlH_4$ ball milled, c) $3NaAlH_4+TiCl_3$ that was wet dried, and d) $3NaAlH_4+TiCl_3$ that was ball milled.

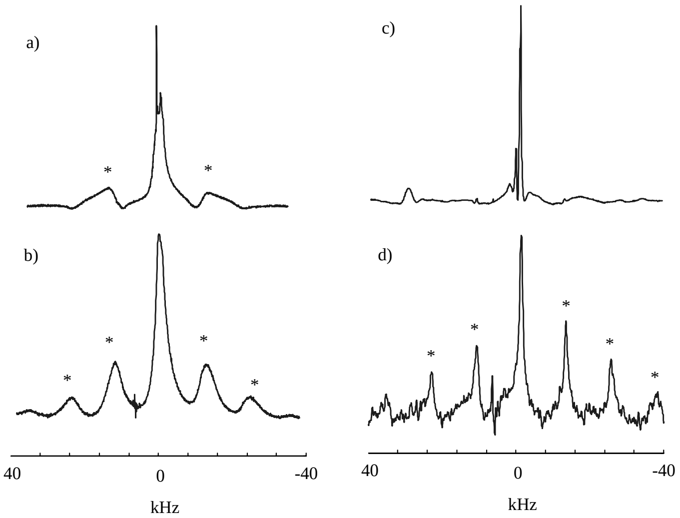

Figure 4: ^{1}H MAS NMR at 12kHz with a 90 degree pulse width of 4.2μs. The following ^{23}Na in different processes, including a) crushed crystal $NaAlH_4$ with small amounts of Ti, b) $4TiCl_3$ +$112NaAlH_4$ Ball Milled, c) $3NaAlH_4+TiCl_3$ that was wet dried, and d) $3NaAlH_4+TiCl_3$ that was ball milled. (* indicates spinning sidebands)

CONCLUSIONS

The ^{27}Al MAS NMR data shows that the $3NaAlH_4$ $+TiCl_3$ ball-milled sample has $TiAl_3$ and a small amount of metallic aluminum present. However, for the sample of $3NaAlH_4$ $+TiCl_3$ that was wet dried with THF shows no $TiAl_3$ present and indicates aluminum in the bulk and potentially Al_2O_3. The ^{1}H MAS NMR data on the sample of $3NaAlH_4+TiCl_3$ that was wet dried with THF shows residual THF in this sample. The ^{1}H MAS NMR data on the sample of $3NaAlH_4+TiCl_3$ that was ball-milled potentially show the presence of Ti hydride nano-particles. The ^{23}Na, ^{27}Al, and ^{1}H MAS NMR data are consistent with the x-ray diffraction data and the picture that the titanium either forms Ti clusters or Ti-Al colloid, which becomes active with ball-milling of the sample. Further NMR studies are being done to determine if there exists Ti nano-particle formation in these samples.

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