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## PUBLICATION

S. Chaudhuri, J. Graetz A. Ignatov, J. J. Reilly, and J. T. Muckerman, "Understanding the Role of Ti in Reversible Hydrogen Storage as Sodium Alanate: A Combined Experimental and First-Principles Theoretical Approach" *J. Am. Chem. Soc.*, **128**, 11404 (2006).

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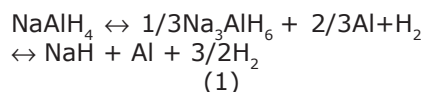
## Hydrogen-Mediated Metal Transport in Complex Metal Hydrides

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*X-ray absorption spectroscopy and density functional theory (DFT) were used to investigate the titanium environment and the role of metal catalysts in sodium alanate. Titanium atoms were found near the surface, coordinated by a shell of aluminum at a distance of 2.82 Å. Combined DFT and molecular dynamics simulations at 450 K reveal a similar local Ti environment. These results suggest that the role of Ti may be linked entirely to active catalytic sites in the metallic Al phase. The formation and migration of transient alane species is proposed as a plausible mechanism for the long-range aluminum transport that occurs during hydrogen cycling.*

The demonstration of reversible hydrogen cycling in Ti-catalyzed sodium aluminum hydride has generated considerable interest in the complex metal hydrides. The reversible (de)hydrogenation occurs through a two-step reaction:



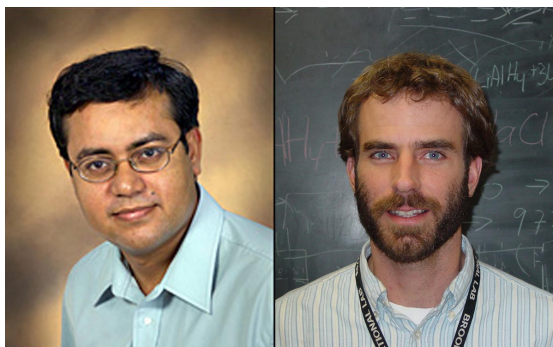
Since this discovery, a number of studies have looked at improving the catalytic effects and understanding the role of additives in H<sub>2</sub> cycling. However, the mechanism by which NaAlH<sub>4</sub> is activated in the presence of a small amount of a transition metal is still not well understood. One of the principle questions is "How do the Al atoms migrate the long distances required during the hydrogenation reaction?" In this study we investigate the atomistic transport mechanisms of the reversible complex metal hydrides using x-ray absorption spectroscopy and first-principles calculations.

structure of the Ti K-edge were used to explore the local titanium environment and valence in catalyzed sodium alanate. An estimate of the oxidation state of the dopant, based upon known standards, revealed a zero-valent titanium atom. Analysis of the near-edge and extended fine structures indicates that the Ti does not enter substitutional or interstitial sites in the NaAlH<sub>4</sub> lattice. Rather, the Ti is located on or near the surface and is coordinated by 10.2±1 Al atoms with an interatomic distance of 2.82±0.01 Å, similar to that of TiAl<sub>3</sub>. The Fourier transformed EXAFS spectra revealed a highly disordered distribution of Ti-Al distances

with no long-range order beyond the second coordination sphere. The similarity of the spectra in the hydrogenated and dehydrogenated samples suggests that the local Ti environment is nearly invariant during hydrogen cycling. A plot of the Ti pair distribution function is shown in **Figure 1**.

Density functional theory was used to calculate the chemical potential of Ti on an Al(001) surface with 0.125 - 0.5 monolayer coverage. Active sites that chemisorb H<sub>2</sub> via spontaneous or only moderately activated pathways were identified. Although Al metal has a low affinity for molecular hydrogen, when

doped with 2-4% Ti the surface characteristics change significantly. The computational model identifies and ranks a host of metastable sites that promote hydrogen chemisorption at low energy costs and act as atomic-level pumps that produce atomic hydrogen. One plausible mechanism for the long-range Al transport is through migration of an aluminum hydride species (alane). Although the proposed alane clusters are



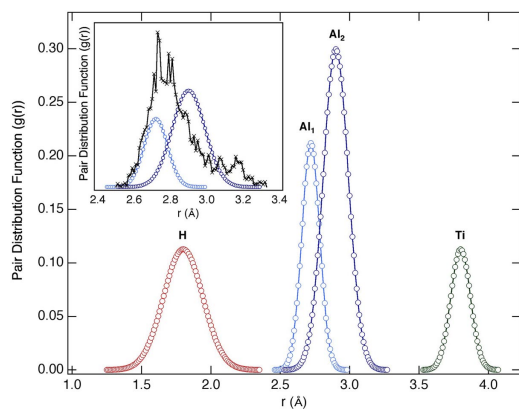
Authors (from left) Santanu Chaudhuri and Jason Graetz

The extended and near-edge

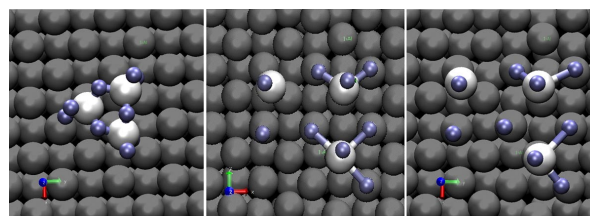
difficult to observe experimentally, the stability and mobility of alanes on Al(001) were studied through temperature-dependent molecular dynamics simulations. The results indicate that larger clusters (e.g.  $\text{Al}_2\text{H}_6$  and  $\text{Al}_3\text{H}_9$ ) quickly break down to  $\text{AlH}_3$  (and  $\text{AlH}_x + \text{H}$ ) on Al(001)

as shown in **Figure 2**. Therefore, the Al transport likely occurs via small clusters (e.g.  $\text{AlH}_3$ ) with high diffusion rates ( $3 \times 10^5$  cm/s for  $\text{AlH}_3$ ) driven by thermal vibrations. This work also demonstrates that the metastable active sites progressively transform into the

more stable, but less active  $\text{TiAl}_3$  alloy with  $\text{H}_2$  cycling. Therefore, maintaining well-dispersed Ti within the Al phase will be essential to mitigating capacity fade during cycling.



**Figure 1.** Pair distribution function determined from EXAFS data on 2 mol % Ti-catalyzed  $\text{NaAlH}_4$  (hydrogenated) and corrected for the phase shift. The inset shows a comparison of predicted and experimental distribution functions for Ti-Al pairs.



**Figure 2.** Dissociation and diffusion of an  $\text{Al}_3\text{H}_9$  cluster on an Al(001) surface showing formation of smaller fragments including a stable  $\text{AlH}_4$  and  $\text{AlH}_3$  cluster.