

Atomistic Transport Mechanisms in Reversible Complex Metal Hydrides

PIs: Peter Sutter¹ (psutter@bnl.gov), James Muckerman², Y. Chabal⁴

Collaborators: Jason Graetz³, James Reilly³, James Wegrzyn³, Eli Sutter¹

¹Center for Functional Nanomaterials, ²Chemistry Department, ³Energy Science & Technology Department, Brookhaven National Laboratory, Upton, NY 11978,

⁴Laboratory for Surface Modification, Rutgers University, Piscataway, NJ 08854

Program Scope

This fundamental research program has two major objectives: **i)** the development of a comprehensive, quantitative understanding of the atomic-scale mechanisms underlying the facile reversible hydrogen storage in titanium-doped sodium aluminum hydride (NaAlH₄), the only complex hydride allowing fully reversible hydrogen storage under near-ambient conditions; and **ii)** the utilization of this basic knowledge for a rational search for novel complex hydride storage materials with properties – hydrogen storage capacity, reaction thermodynamics and kinetics during hydrogen uptake and release, etc. – superior to those of NaAlH₄.

Surface processes in the hydrogen storage reaction in NaAlH₄, starting from a depleted phase consisting of NaH and metallic Al, and proceeding via cryolite Na₃AlH₆ to the hydrogen-rich NaAlH₄, are considered as the basis for understanding reversible hydrogen storage in the chosen prototype system. Key questions to be addressed via experiments on carefully designed model systems coupled strongly to theory include:

- The mechanism of hydrogen dissociation on Al surfaces doped with Ti.
- The identification of the predominant carrier of mass transport, and quantitative measurements of its diffusion kinetics
- The detailed reaction mechanisms and their rate-limiting step as NaH and Al react to Na₃AlH₆ and ultimately NaAlH₄ in the presence of hydrogen and of dopants such as Ti.

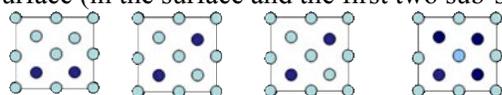
The long-term goal of this project is to develop an atomistic understanding of the interaction of hydrogen with metal and alkali metal surfaces and nanostructures, hence providing a scientific basis for solid-state hydrogen storage in support of the DOE BES hydrogen fuel initiative.

Recent Progress

(a) Interaction of Hydrogen with Al and Ti-doped Al Surfaces

A major initial focus has been to investigate the role of Ti dopants in enabling the facile rehydrogenation of depleted sodium alanate. The depleted material consists of nanoscale particles of NaH and Al metal. As Al poorly activates molecular hydrogen, our working hypothesis is that Ti, localized near the surface of the metallic Al phase, could form active complexes that dissociate H₂ and generate the supply of atomic H or of Al-H molecular species (alanes) necessary to crystallize large grains of the hydrogen-rich NaAlH₄. Predictive theoretical studies are combined with scanning tunneling microscopy (STM) and infrared (IR) spectroscopy experiments on Al single crystal model surfaces, and with x-ray diffraction and fluorescence measurements on the actual storage materials.

In our initial theoretical work, a series of model active sites was constructed by substituting Ti for Al near a Al(001) surface (in the surface and the first two sub-surface layers), at Ti coverages of 0.125 - 0.5



Property	Model 3	Model 4	Model 4s	Model 8
Site ΔG_f	3.13	2.08	1.65	1.04
E_a	0.89	0.00	0.26	1.62
Site $\Delta G_f + E_a$	4.02	2.08	1.91	2.66

Table 1: Free energy of formation relative to TiAl₃ reference (ΔG_f) and activation energy for H₂ dissociation (E_a) of Ti:Al model complexes with 0.25 ML – 0.5 ML Ti coverage.

monolayers (ML). Each of these model sites was characterized by its activation energy for dissociatively chemisorbing H₂, and by its chemical potential with respect to a convenient reference state, taken to be the most stable surface termination of the TiAl₃ alloy. The most effective sites, shown in table 1, are third-nearest neighbor Ti configurations in the surface (Model 4) and in the first

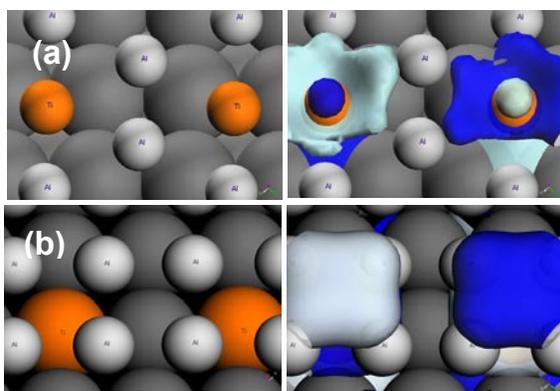


Figure 1: Arrangement of Ti-atoms of Model 4 active sites (left frames): **(a)** surface and **(b)** sub-surface. Right frames show the surface LUMO forming an adduct with the incoming H₂ molecule. Light/dark blue indicates different phases of the molecular orbitals.

sub-surface layer (Model 4s). Hydrogen dissociation is predicted to be spontaneous on the former, and exhibits no barrier in excess of the intrinsic endothermicity in the latter.

All sites with low computed barriers to H₂ dissociation have a common orbital symmetry property that is responsible for their effectiveness: the highest occupied molecular orbital (HOMO) of the incipient doped-surface/H₂ adduct has a nodal plane perpendicular to the Ti-Ti axis and midway between the two Ti atoms (fig. 1). This nodal symmetry arises from the out-of-surface d₂₂ Ti orbitals having opposite phases such that they overlap with the H₂ σ* orbital so that electron density can be transferred from the surface to the antibonding H₂ orbital to weaken the H-H bond. Complexes without this nodal symmetry (e.g., Model 8) have large barriers for dissociative H₂ chemisorption. Additional computational studies

addressed the question of how the hydrogen and aluminum are transported into NaH to ultimately reform hydrogen-rich NaAlH₄. First-principles molecular dynamics (MD) studies show that dissociated H does not readily recombine at Ti:Al active sites, is mobile but cannot migrate to all-Al sites because such a process is both endothermic and activated. The likelihood of H being picked up by Al adatoms breaking off from steps and other mechanisms for alane formation is being explored, as is the chemical behavior and mobility of alanes on Al surfaces.

First experiments on measuring H₂ dissociation on Al:Ti complexes have used STM imaging on extended Al surfaces, progressively complemented by IR spectroscopy. Below the desorption threshold of ~280K, atomic H (but not H₂) interacts strongly with Al by extracting surface atoms to form alane (AlH₃) and its oligomers. Alane evolution can thus be used as a fingerprint for the presence of H on Al, e.g., caused by H₂ dissociation at active Al:Ti complexes. To establish conditions under which H₂ dissociation can be probed in this way, Al(111) and 0.25 ML Ti/Al(111) surfaces were exposed to different amounts of atomic and molecular hydrogen. Dosing of atomic H on clean Al(111) clearly produces a characteristic population of surface alanes (fig. 2 a,b,c.). This is confirmed by IR experiments (fig. 2d) that show H

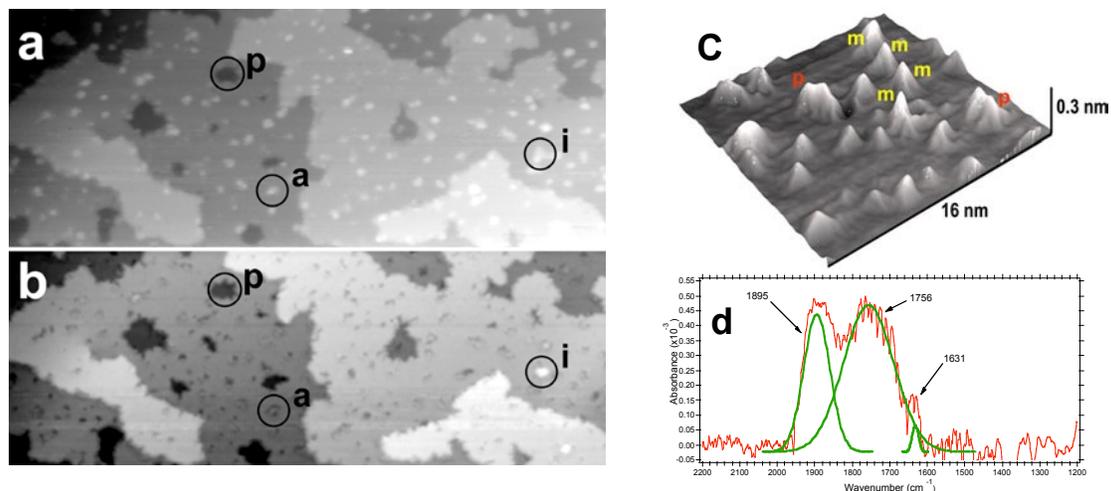


Figure 2: **(a), (b)** STM images (150x60 nm²) of Al(111) after H-dosing at 200 K, with W-tip **(a)**, and alane 'functionalized' W-tip **(b)**. Alane decorated probes can be used to distinguish surface alanes ('a') from topographic features ('i': islands; 'p': surface pits). **(c)** STM image of an alane population obtained by H-dosing of Al(111) at 200 K, with tentative species assignments ('m': monomer; 'p': monomer pair). **(d)** IR spectrum obtained under the same conditions. The vibrational envelope at 1895 cm⁻¹ corresponds to Al-H stretch of terminal H, the broad band centered at 1756 cm⁻¹ to Al-H-Al stretch of bridging H of alane oligomers.

chemisorbed in several configurations (terminal and bridging H) consistent with alane formation. In contrast to pure Al(111), exposure of 0.25 ML Ti/Al(111) to H does not induce any detectable alane. Our STM observations suggest that the Ti atoms are randomly dispersed near the Al surface, which may stabilize the surface layer against H-etching and hydride formation. Thus, samples with high Ti coverage may not be suitable to study H₂ dissociation. A third class of samples, consisting of 0.25 ML Ti/Al(111) capped with 1 ML Al, has shown promise as a model system to detect H₂ dissociation at Ti active sites. Atomic-H dosing onto these samples causes surface etching and alane evolution. First STM experiments, in which such surfaces were exposed to H₂ have shown features similar to surface alanes, i.e., showing the characteristic dual contrast (fig. 2 a,b) found on alane decorated surfaces. These observations suggest that H₂ may indeed have been dissociated on these samples, providing a starting point for a systematic characterization of active Ti:Al complexes. Thorough quantification and comparison with IR spectroscopy and theory are now needed to corroborate this tentative conclusion.

X-ray absorption spectroscopy (XAS) on bulk materials was used to measure the local atomic structure of Ti in doped sodium alane. Our results clearly show that Ti is in a zero-valent state and coordinated by 10 Al atoms at ~ 2.8 Å. The reduced coordination (10 Al atoms, vs. expected 12) and the lack of order beyond the Al first shell suggests that the Ti exists in well dispersed clusters of Ti-Al possibly located on/near the surface, which further justifies the hypotheses underlying our experiments in UHV.

In a key solid-state chemistry experiment guided by theory, finally, we have demonstrated that once alane (AlH₃) is formed, the solid-state reaction of AlH₃ with NaH leads to the formation of NaAlH₄ through the intermediate Na₃AlH₆ phase in the absence of any Ti. Although not excluding other (beneficial) effects of the Ti dopants, this finding suggests that Ti-induced H₂ dissociation and the concomitant formation of surface alanes would be sufficient to enable reversible hydrogen storage in NaAlH₄.

(b) Rational Search for Novel Metal Hydride Hydrogen Storage Materials

Our initial solid-state chemistry effort accompanying the work on model systems has concentrated on the synthesis of novel mixed alkali alanes of the form M_xM'_{1-x}AlH_y (M, M' = Li, Na, K, ...), and investigation of the possibility of tuning the hydrogenation thermodynamics by cation substitution. These studies were complemented by the synthesis and characterization of aluminum hydride (AlH₃) polymorphs, a potential storage material with very high gravimetric hydrogen content. In particular, we have investigated reaction products formed from aluminum hydride and alkali hydrides.

The thermodynamics and structural properties of the hexahydride alanes (M₂M'AlH₆) with elpasolite structure were investigated. Two new alanes were synthesized: K₂LiAlH₆ and K₂NaAlH₆. Both compounds reversibly absorb/desorb hydrogen without a catalyst. Structural analyses using synchrotron x-ray diffraction show that these compounds favor the *Fm-3m* space group with the smaller

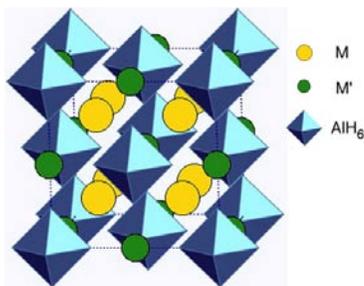


Figure 3: General structural diagram for the mixed alkali alanes (elpasolites) of the form M₂M'AlH₆ showing AlH₆ octahedra, M cations (large) and M' cations (small). Structures of Na₂LiAlH₆, K₂LiAlH₆ and K₂NaAlH₆ were determined by high resolution synchrotron x-ray diffraction.

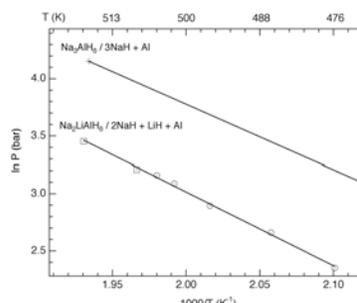


Figure 4: Van't Hoff plot for the reversible dissociation of Ti-doped Na₃AlH₆ (+) and Na₂LiAlH₆ (O-4 mol% TiCl₃ and □-undoped), demonstrating that Li for Na cation substitution results in a significant decrease in equilibrium pressure. In addition, the pressure-temperature data for doped (O) and undoped (□) Na₂LiAlH₆ have identical behavior and therefore no there is no discernable change in thermodynamics with the addition of 4 mol% Ti.

ion (M') occupying an octahedral site and the larger ion (M) in a 12-fold coordinated site (fig. 3). Thermodynamic measurements demonstrated that appropriate cation substitutions could be used to alter the alanate stability (fig. 4).

Future Plans

The next phase of work on well-defined model samples will closely link surface microscopy, IR spectroscopy, and theory to address the following key aspects of reversible hydrogen storage in NaAlH₄: i) Atomic pathway and efficiency of Ti-induced H₂ dissociation on Al (STM & IR); ii) Evolution of surface alanates and their role in mass transport (STM, IR, LEEM); iii) Main factors affecting the hydrogenation kinetics, and role of Ti (STM, LEEM). In addition to STM and IR spectroscopy, low-energy electron microscopy (LEEM) will be used to map surface mass transport in real time, and quantify differences in alane and Al diffusion. Building on our initial experiments on the interaction of H/H₂ with Al surfaces, we will begin to analyze complete steps of the hydrogenation reaction, e.g., use NaH/Al(111) as a model system to study the reaction $6 \text{ NaH} + 2 \text{ Al} + 3 \text{ H}_2 \leftrightarrow 2 \text{ Na}_3\text{AlH}_6$. Theory will be strongly coupled to the STM and IR studies now underway. The objective will be to suggest experimental models to isolate individual steps in the rehydrogenation reaction, and to interpret observed surface structures, dynamic phenomena, and IR signatures. The transfer of what is being learned about the sodium alanate system to other promising hydrogen storage materials to make them reversible will be another focus of the theoretical effort.

Our solid-state chemistry effort will expand the studies on transition metal catalysts to include other catalyzed complex metal hydrides, such as metal-doped LiBH₄/MgH₂. XAS will be used to determine the location and valence of the catalyst immediately after ball milling and at different stages of hydrogen cycling. Doped borohydrides have a number of similarities with the alanates. Studies of doping in these materials will lead to a better understanding of kinetic enhancements and long-range mass transport. In complementary studies, we will synthesize various AlH₃ polymorphs for vibrational spectroscopy. Pure phases of α -AlH₃ and γ -AlH₃ and solvated AlH₃ will be prepared. We will determine AlH₃ structures, and attempt to gain a better understanding of how bulk AlH₃ can be stable at room temperature despite its high equilibrium hydrogen pressure.

Publications to Date

1. J. Graetz and J. J. Reilly, "Decomposition kinetics of the AlH₃ polymorphs", *J. Phys. Chem. B* **109**, 22181 (2005).
2. J. Graetz, Y. Lee, J. J. Reilly, S. Park and T. Vogt, "Structure and thermodynamics of the mixed alkali alanates", *Phys. Rev. B* **71**, 184115 (2005).
3. J. Graetz, A.Y. Ignatov, T.A. Tyson, J.J. Reilly and J. Johnson, "Characterization of the local titanium environment in doped sodium aluminum hydride using X-ray absorption spectroscopy", *Mat. Res. Soc. Conf. Proc.* **837** (2005).
4. S. Chaudhuri and J.T. Muckerman, "First-principles study of Ti-catalyzed hydrogen chemisorption on an Al surface: A critical first step for reversible hydrogen storage in NaAlH₄", *J. Phys. Chem. B* **109**, 6952 (2005).
5. S. Chaudhuri and J.T. Muckerman, "A Density Functional Theory Study of the Catalytic Role of Ti Atoms in Reversible Hydrogen Storage in the Complex Metal Hydride, NaAlH₄", *Materials and Technology for Hydrogen Storage and Generation*, ed. G-A. Nazri, C. Ping, R.C. Young, M. Nazri, and J. Wang, *Mat. Res. Soc. Symp. Proc.* **884E**, Warrendale, PA, 2005; GG2.1.
6. S. Chaudhuri, J. Graetz, A. Ignatov, J.T. 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.*, submitted.
7. S. Chaudhuri and J.T. Muckerman, "Catalytic activity of Ti-doped NaH nanoclusters towards hydrogenation of terminal alkenes", manuscript in preparation for Communication in *Phys. Chem. Chem. Phys.*
8. E. Muller, P. Zahl, E. Sutter, and P. Sutter, "Ripening and Texture Evolution in Al Epitaxy on Si(111)-(7x7)", manuscript in preparation.
9. P. Sutter, E. Muller, S. Chaudhuri, and J.T. Muckerman, "Hydrogen chemisorption on Ti-doped Al(111): implications on reversible hydrogen storage in NaAlH₄", manuscript in preparation.