IV.I.9 Atomistic Transport Mechanisms in Reversible Complex Metal Hydrides

PIs: Peter Sutter[a] (psutter@bnl.gov), James Muckerman[b], Jason Graetz[c]

Collaborators: Yves Chabal[d], Cristian Ciobanu[e], Eli Sutter[a]

[a]Center for Functional Nanomaterials,

[b]Chemistry Department,

[c]Energy Science & Technology Department,
Brookhaven National Laboratory,
Upton, NY 11978,

[d]Materials Science & Engineering Department,
University of Texas at Dallas,
Richardson, TX 75083

[e]Engineering Division, Colorado School of Mines,
Golden, CO 80401

April 24, 2009

Program Scope

The development of materials for efficient hydrogen storage has been recognized as a major obstacle on the way to a hydrogen economy. Most solid-state hydrogen storage materials, for instance, cannot be cycled reversibly between H-rich and depleted phases and exhibit slow reaction kinetics. Dopants and catalysts, nanostructuring, and finely tuned reaction environments could provide improved properties.

This research project aims to establish a scientific basis for such improvements in two interlinked thrusts: (i) development of a comprehensive understanding of the fundamental, atomic-scale mechanisms underlying the facile reversible H storage in titanium-doped sodium aluminum hydride ($NaAlH_4$), one of very few known complex hydrides allowing *reversible hydrogen storage with fast reaction rates*. And ii) Utilization of this basic knowledge for the development of new reversible H-storage materials with high storage capacity and fast reaction kinetics.

We consider the *hydrogenation reaction*, proceeding from a H-depleted phase (NaH and metallic Al) via Na_3AlH_6 to the H-rich $NaAlH_4$, as the basis for understanding reversible H storage, and in particular dopant and catalyst effects. Surface processes are expected to be of central importance. In contrast to previous research on bulk compounds with complex reaction pathways, microstructures, and unknown impurity concentrations, the present program emphasizes the use of *well-defined model systems* and of *state-of-the-art surface experiments* to achieve a quantitative understanding of the important reaction mechanisms. This approach is generating data accessible directly to *density-functional theory (DFT) and atomistic modeling*, and thus allows an unprecedented level of interaction between experiment and theory. Key questions addressed via combined experimental and theoretical efforts include:

- The mechanisms by which a Ti catalyst facilitates H_2 dissociation, a key initial step in the reaction transforming metallic Al to Al-H species and, ultimately, to a complex hydride.
- The fundamental factors determining the formation and diffusion kinetics of alanes, which we have identified as primary carriers of mass transport during hydrogenation.
- The possibility that kinetic bottlenecks in the hydrogenation reaction could be circumvented by tailoring the reaction environment, thus allowing the facile hydrogenation of previously irreversible materials.

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

Recent Progress

1. Role of Ti in Enabling Reversible Hydrogen Storage in Complex Hydrides

Following our theoretical prediction that specific atomic Ti complexes on Al surfaces efficiently dissociate H_2 adsorbing from the gas phase (a crucial first step in the hydrogenation reaction) [4,5], and having studied the formation of such complexes by combined atom-resolved scanning tunneling microscopy (STM) and DFT [9], atomic-resolution microscopy was used to establish how hydrogen interacts with Ti-doped Al surfaces [21]. These recent studies resulted in the following main findings:

- Kinetic barriers slow the dissociation of adsorbing H_2 sufficiently to make it impractical to observe H_2 dissociation near Ti at low H_2 pressures typically accessible to STM. We have thus developed an elevated pressure STM capability extending the operating range to at least 10 torr while maintaining impurity levels near 10^{-10} torr. This new experimental capability is now being used for atomic-resolution studies of hydrogen-metal interactions near practically relevant conditions.
- Combined STM imaging and DFT were used to establish the interaction of atomic H with
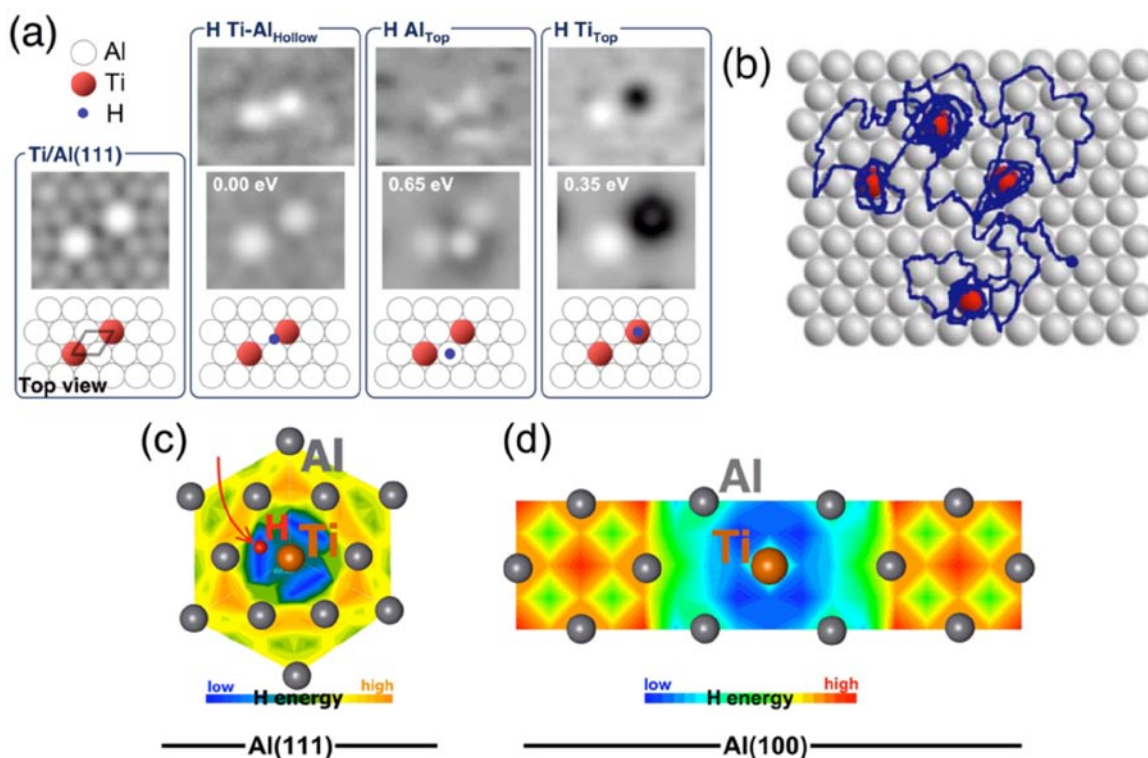
FIGURE 1. (a) Identification of H-binding sites by STM imaging (top) and DFT-based image simulation for second-nearest neighbor Ti-Ti pairs on Al(111), with and without a H-atom in different sites (bottom). (b) Kinetic Monte Carlo simulation of H-atom diffusion near Ti/Al(111) at room temperature, showing the transient trapping of H near Ti atoms. (c), (d) Potential energy surfaces for a H-adatom on Al(111) and Al(100), respectively.

dispersed Ti on Al(111). Individual H atoms near surface Ti dopants were identified by STM, and followed by time-lapse STM over extended time periods (Figure 1a) [21]. Combined with ab-initio calculations and kinetic Monte-Carlo (KMC) simulations, these experiments have identified *specific binding sites for H atoms*, and have demonstrated that H can easily *diffuse onto all-Al surface sites*, thereby regenerating the catalytic Ti complex and allowing further H_2 dissociation.

- In an effort to develop a comprehensive theoretical understanding of H storage processes, we combined DFT with KMC simulations to use atomic-level information in determining the behavior of the system over much larger length and time scales. As a first application, we have elucidated the diffusivity of different species (H, Al, Al_xH_y) on Ti-doped Al(111). Shallow potential wells around embedded Ti atoms transiently trap H and reduce its diffusivity (Figures 1b-d), but not that of the other species. This effect has important consequences on hydrogenation reactions in the presence of Ti dopants. Unexpectedly, Al and alane (Al-H) species diffuse much faster than H; and the rate of mobile alane formation is slowed considerably,

since it involves the rather slow "harvesting" of H by diffusing Al.

- In the second phase of our computational studies, we compared the diffusivities of H and alane species on two different Al surfaces: Al(111) and Al(100). Embedded Ti atoms create potential wells for Hadatoms in both surfaces (Figures 1 c, d), but the well is significantly deeper on Al(100) [0.72 eV] than on Al(111) [0.45 eV]. The diffusivity of alanes is higher on Al(111) than on Al(100), primarily due to differences in surface corrugation. The enhanced diffusion of all species on Al(111) is contrasted by the much lower activity in H_2 dissociation of the (111) surface. While there is a 0.7 eV dissociation barrier on doped Al(111), there is almost zero barrier for H_2 dissociation on Ti-doped Al(100). Specifically designed experiments are now required to determine if H_2 dissociation or surface diffusion is the rate-limiting step, i.e., which Al(hkl) surface allows more efficient alane formation.

- In situ FTIR spectroscopy revealed that Ti-doped Al(100) surfaces show higher concentrations of smaller alanes (AlH_3) than undoped surfaces. Higher Ti doping inhibits the formation of higher-mass alanes, likely due to stronger binding of the
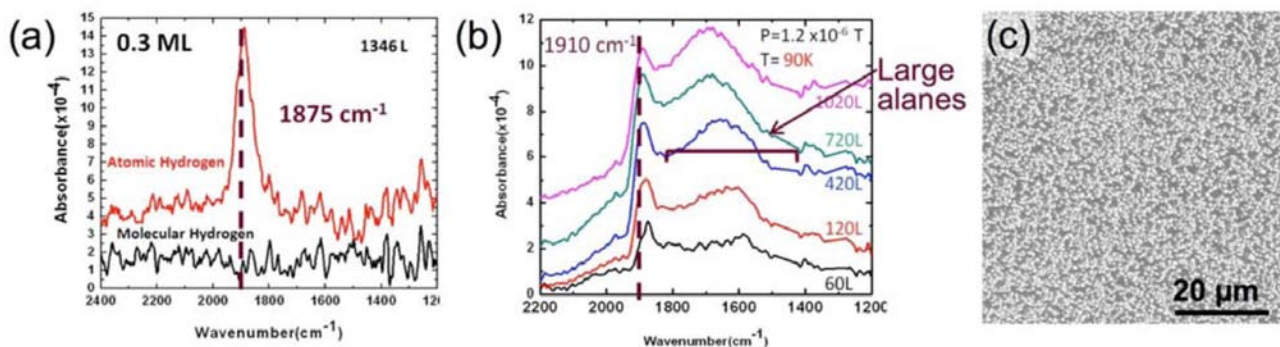
FIGURE 2. FTIR spectroscopy showing different types of alane formation on (a) Ti-doped, (b) undoped Al(100) surfaces. (c) SEM image of Al(100) after several cycles of hydrogenation in H_2, resulting in roughening but no alane formation.

Ti-doped surface and lower alane mobility, already found in our calculations (see above). SEM imaging reveals that Ti-doped Al(100) surfaces roughen dramatically upon repeated H_2 exposure, resulting in a substantial decrease of alane formation.

- The local bonding and atomic environments in the Ni-catalyzed destabilized system $LiBH_4/MgH_2$, and the quaternary borohydride-amide phase $Li_3BN_2H_8$ were studied by X-ray absorption spectroscopy [20]. A qualitative comparison of the Ni K-edge near-edge structure suggests that the Ni, introduced as Ni^{2+}, is reduced to primarily Ni^0 during ball milling. The extended fine structure of the Ni K-edge indicates that Ni is coordinated by about 3 boron atoms with an interatomic distance of ~2.1 Å, and about 11 Ni atoms in a split shell at around 2.5 Å and 2.8 Å. These results, and the lack of long-range order, suggest that the Ni catalyst is present as a disordered nanocluster with a local structure similar to Ni_3B. Calculations by density-functional theory suggest that the lowest kinetic barrier for H_2 chemisorption occurs on the $Ni_3B(100)$ surface.

2. Identification of the Carriers of Long-Range Mass Transport

- STM and IR spectroscopy on Al(111) in UHV, combined with DFT, have established how H atoms interact with the Al surface to form mobile alane species, and how these alanes interact, grow, diffuse, and desorb. Atomic-H first attaches at the step edge, leading to the formation of chemisorbed AlH_3. At higher exposures, these alanes become physisorbed and agglomerate into larger alanes through oligomerization. STM shows a pronounced etching of Al surface steps during exposure to atomic H. Although difficult to interpret, IR spectra analyzed by comparison with DFT-predicted vibrational frequencies have unambiguously demonstrated the *formation of progressively larger alane species* with increasing H-coverage

and temperature, demonstrating the high surface mobility of these species [16].

- We have demonstrated the direct formation of alane from Al and H_2 at low pressure in the presence of a stabilizing molecule, such as an amine, to form an alane adduct. Raman spectroscopy and microscopy have been used to characterize various alane amines in the liquid and solid state.

- The assignment of alanes as a primary carrier of mass transport in the hydrogenation of alanates was confirmed by a series of targeted solid-state-chemistry experiments. Specifically, we were able to show that the hydrogenation proceeds readily *without the need for a catalyst* once alane is available [6]. This finding shows that alane formation is a critical step in the hydrogenation, and that this step is indeed enabled and accelerated by Ti doping.

## 3. Development of New Reversible Hydrogen Storage Materials

Experiments on bulk materials, accompanying our work on model systems in UHV, have focused on AlH_3, a very promising H storage material with 10.1 wt% H-capacity. Little has been known about the crystallographic and thermodynamic properties of AlH_3, and these have now been established:

- The thermodynamic and vibrational properties relevant for hydrogen storage of three different polymorphs, α, β, and γ-AlH_3 have been determined [8,15].

- High-pressure induced structural, chemical, and thermodynamic changes have been determined for α–AlH_3, using combined high-pressure synchrotron X-ray diffraction and ab-initio calculations [7].

- The previously unknown crystal structures of β and γ-AlH3 have been determined. For this purpose, a synthesis route for β-AlH_3 had to be established [10,14].

- The stability and decomposition pathways of the three AlH_3 polymorphs have been determined, showing an actual release of 10 wt% hydrogen at temperatures below 100°C. [11,12].

Our findings for both single crystal model systems and bulk materials suggest rational regeneration routes for AlH_3 and high-capacity alanates, by dissociating H_2 over Al doped with transition metals (Ti), generating molecular alane, which can then be collected and aggregated to a H-rich AlH_3 or alanate phase. Based on free energy arguments *regeneration in solution* holds the most promise. Fundamental research on the interaction of H with doped light metals (e.g., Al:Ti) in complex environments (e.g, liquids), necessary to establish the complex processes involved, have begun in FY 2008:

- We demonstrated a *low energy route to regenerate $LiAlH_4$* (10.6 wt% H) from LiH and Ti-catalyzed A1 [17,19]. The initial hydrogenation in tetrahydrofuran (THF) forms the adduct $LiAlH_4$_4THF. The free energy change in this reversible reaction is small and slightly negative, suggesting an equilibrium H_2 pressure of ~1 bar at 300 K. The adduct $LiAlH_4$_4THF was successfully desolvated at low T to yield crystalline $LiAlH_4$. Regeneration of $LiAlH_4$ from LiH and Al hence is achieved in the two-step process:

$$LiH + Al^* + 3/2\ H_2 \xrightarrow{THF} LiAlH_4 \cdot 4THF \xrightarrow{Vacuum} LiAlH_4 + 4THF\uparrow$$
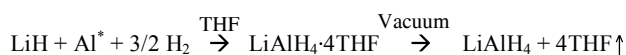
The possibility of using this regeneration process for other metastable hydrides (e.g., $Mg(AlH_4)_2$) is currently being investigated.

Current Research and Future Plans

In ongoing and future work we aim to provide a comprehensive understanding of the role of dopants, nanoscale size effects, as well as complex reaction environments (e.g., fluids) in facilitating the hydrogenation and dehydrogenation of solid-state H-storage materials. A brief summary of these research directions is given below:

1. H_2 Dissociation at Surface Ti Complexes on Al Single Crystals

- Elevated-pressure STM is being used to establish how the hydrogen fuel to be stored (i.e., H_2) interacts with dopant sites on the surface of light metals, e.g., Ti on Al. Working closely with theory and IR spectroscopy important questions regarding the mechanism of H_2 dissociation and the formation of mobile molecular adsorbates (alanes) will be addressed.

- Impurities such as O_2 and H_2O, invariably present in practical storage materials, may fundamentally alter the interaction of hydrogen with light metals. UHV-STM and IR will be used to study their effects, in particular a possible enhancement or decrease in the activity of dopants.

2. Interaction of Hydrogen with Light Metal Nanoparticles

- Nanostructures could significantly enhance the kinetics of hydrogen storage reactions, but experiments at the atomic scale are needed to evaluate this possibility and identify the underlying mechanisms. We are preparing a study on the interaction of H with small metal and alloy nanoparticles in UHV, to understand the effects of nanoparticle size, of dopants at various concentrations, and of impurities, and to observe a possible dynamic reshaping of nanoparticles under H_2 or H exposure.

3. Surface Mass Transport and Initial Hydrogenation Stages

- Our previous work has shown complex H-metal interactions even for seemingly simple systems. A comprehensive model of the hydrogenation process will be invaluable to understand these interactions. By coupling DFT with KMC, we have begun to build a multiscale computational framework for different Al(hkl) surfaces. The energetics of atomic level processes, established by DFT, feed into KMC calculations on the evolution over large length and time scales. Once fully developed, this approach will serve to capture the complex processes involved in hydrogenation reactions and their modification by dopants.

- Experiments on surface mass transport during hydrogenation reactions will be carried out by STM and in situ low-energy electron microscopy. We will probe surface diffusion on Al and Ti doped Al surfaces, with and without H or H_2 exposure, as well as the initial nucleation and growth of hydrogen-rich phases on Al in the presence of NaH and H.

4. Mass Transport Through the Gas Phase

- Our experiments have shown that AlH_3 desorbs at about 370 K from Al surfaces (without Ti doping). Combined DFT and KMC calculations will be used to study temperature programmed desorption of different alane species on Ti-doped Al(khl) surfaces. As we have seen in the case of Al(100), larger alane species can be trapped at Ti sites, an effect that poisons the Ti sites and halts the further dissociation of H_2. Desorption of these species may

help vacating the Ti sites, i.e., would reactivate the Ti catalyst for further H_2 dissociation.

5. Fundamental Mechanisms of Solution-Phase Hydrogenation of Al – Role of Dopants

- AlH_3 has recently been identified as a promising H-storage material with high storage capacity (>10 wt%) and fast dehydrogenation kinetics near ambient temperature. The key bottleneck to the widespread use of AlH_3, as well as of high-capacity complex hydrides that cannot be cycled reversibly in H_2 gas, is the lack of a viable regeneration route following its decomposition to H_2 and Al metal. Regeneration in solution appears promising. Yet it remains unknown how Al and doped Al interact with H_2 in a solvent such as THF. We are using powerful in situ spectroscopy experiments (Raman and infrared) in a microfluidic setup to study the reaction of H_2 on immersed Al (and Al-Ti) surfaces and the resulting formation of H-rich species (alanes and alane adducts) in solution. This work connects strongly with our studies on Ti-catalyzed model systems in UHV, and will establish hydrogen-metal interactions and their modification by dopants in complex environments, such as the liquid-solid interface.

References (2005 – 2009)

1. J. Graetz, Y. Lee, J.J. Reilly, S. Park and T. Vogt, Phys. Rev. B **71**, 184115 (2005).

2. J. Graetz and J.J. Reilly, Adv. Eng. Mat. **7**, 597 (2005).

3. J. Graetz, A.Y. Ignatov, T.A. Tyson, J.J. Reilly and J. Johnson, Mat. Res. Soc. Conf. Proc. **837** (2005).

4. 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 $NaAlH_4$, Mater. Res. Soc. Symp. Proc. **884E**, GG2.1. (2005).

5. S. Chaudhuri and J.T. Muckerman, J. Phys. Chem. B **109**, 6952 (2005).

6. S. Chaudhuri, J. Graetz, A. Ignatov, J.J. Reilly, and J.T. Muckerman, J. Am. Chem. Soc. **128**, 11404 (2006).

7. J. Graetz, S. Chaudhuri, Y. Lee, T. Vogt, J.T. Muckerman, and J.J. Reilly, Phys. Rev. B **74**, 214114 (2006).

8. J. Graetz and J.J. Reilly, J. Alloys Comp. **424**, 262 (2006).

9. E. Muller, E. Sutter, P. Zahl, C.V. Ciobanu, and P. Sutter, Appl. Phys. Lett. **90**, 151917 (2007).

10. H.W. Brinks, C. Brown, C.M. Jensen, J. Graetz, J.J. Reilly, and B.C. Hauback, J. Alloys Comp. **441**, 364 (2007).

11. J. Graetz, J.J. Reilly, J.G. Kulleck, and R.C. Bowman, J. Alloys Comp. **446-447**, 271 (2007).

12. S.-H. Hwang, R.C. Bowman, J. Graetz, J.J. Reilly, W. Langley, and C.M. Jensen, J. Alloys Comp. **446-447**, 290 (2007).

13. S. Chaudhuri and J.T. Muckerman, "Catalytic activity of Ti-doped NaH nanoclusters towards hydrogenation of terminal alkenes," Molecular Simulation **33**, 919 (2007).

14. H.W. Brinks, W. Langley, C.M. Jensen, J. Graetz, J.J. Reilly, and B.C. Hauback, J. Alloys Comp. **433**, 180 (2007).

15. M. Tkacz, T. Palasyuk, J. Graetz, and S. Saxena, J. Raman Spectr. **39**, 922 (2008).

16. S. Chaudhuri, S. Rangan, J.-F. Veyan, J.T. Muckerman, and Y.J. Chabal, J. Am. Chem. Soc. **130**, 10576 (2008).

17. J. Graetz, J. Wegrzyn and J.J. Reilly, "Regeneration of lithium aluminum hydride ($LiAlH_4$)", *J. Amer. Chem.* Soc. **130** 17790 (2008).

18. Allen, P.B., Davenport, J.W., Liu, P., McGuigan, M., Muckerman, J., Hybertsen, M., Karim, A., Shen, X., and Small, Y. Computational energy research at the CFN. SciDAC Review, Winter 2008, **38-47**. BNL-81516-2008-JA.

19. J. Graetz, "New Approaches to Hydrogen Storage" *Chem. Soc. Rev.*, **38** 73 (2009).

20. J. Graetz, S. Chaudhuri, T.T. Salguero, J.J. Vajo, M.S. Meyer, F.E. Pinkerton, "Local bonding and atomic environments in Ni-catalyzed complex hydrides" *Nanotechnology*, in press (2009).

21. E. Muller, T. Davies, A. Karim, P. Zahl, J.T. Muckerman, C.V. Ciobanu, and P. Sutter, in preparation (2009).

Senior Personnel

Peter Sutter, PI (BNL); James Muckerman, Co-PI (BNL); Jason Graetz, Co-PI (BNL); Yves Chabal (UT-Dallas); Cristian Ciobanu (CSM).

Postdocs and Students (2008 – 2009):

Altaf Karim (BNL); David Lacina (BNL); Abdullah Al-Mahboob (BNL, 06-2009); B. Ozturk (BNL, 2008), E. Muller (BNL, 2008), Irinder S. Chopra (UT-Dallas); Teresa Davies (CSM, 2008).