BES013

Atomistic Transport Mechanisms in Aluminum-Based Hydrides

J. Graetz[1], C. Ni[1], P. Sutter[1], A. Al Mahboob[1], J. T. Muckerman[1], Y. Liu[1], Y. Chabal[2], I.S. Chopra[2]

DOE Annual Merit Review, May 14-18, 2012, Washington D.C.

This presentation does not contain any proprietary, confidential, or otherwise restricted information

DOE - Basic Energy Sciences

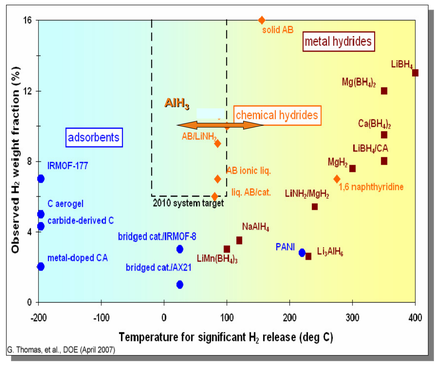
1) BROOKHAVEN NATIONAL LABORATORY

2) UT DALLAS

Program Strategy

Interest in alternative, carbon neutral fuels has grown substantially in recent years, spurred by concerns over climate change and our nation's energy dependency. Reducing our oil dependency and achieving the goal to cut carbon emissions by at least 80% below 1990 levels by 2050 (25% by 2020) will require new forms of transportation, such as fuel cell vehicles. However, hydrogen storage remains a key barrier to the advancement of hydrogen fuel cell technologies for mobile applications. As noted in the Basic Energy Sciences report, *Directing Matter and Energy: Five Challenges for Science and the Imagination [1]*, understanding and controlling materials processes on the atomic scale (and below) is a Grand Challenge. This effort is focused on understanding atomic-scale surface processes relevant to hydrogen storage reactions and using this understanding to develop new hydrogen storage materials with optimized properties, and for identifying new routes to making the storage reactions proceed reversibly.

Our approach is to use of well-defined model systems, probed by complementary atom-resolved imaging and chemically specific spectroscopy in controlled environments. This strategy not only allows us to isolate elementary steps of hydrogen-materials interactions, but it also provides quantitative experimental data on systems that are directly accessible to first-principles theory. The resulting *unprecedented level of interaction between experiment and theory* promises the development of a comprehensive and predictive picture of the mechanisms underlying solid hydrogen storage.



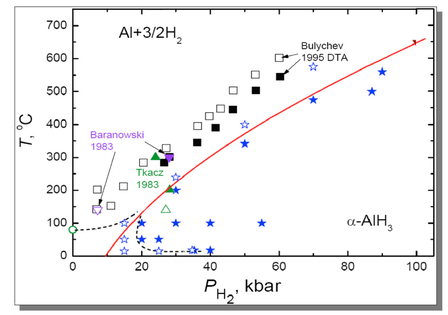
Objectives

Complementary high-resolution microscopy and spectroscopy in close connection with theory will be used to address the following scientific areas: (i) Atomic processes associated with hydrogen uptake and release kinetics; (ii) the role of surface structures and chemistry in affecting hydrogen-materials interactions; (iii) the effect of dopants; the formation of alanes; and (iv) the structure and bonding of alane and alanate amine adducts. The objective of this project is to provide a comprehensive understanding of the role of dopants and of complex reaction environments in facilitating the hydrogenation and dehydrogenation of Al-based hydrogen storage materials, including complex metal hydrides (e.g., $Mg(AlH_4)_2$) and light metal hydrides (e.g., AlH_3).

Technical Barriers

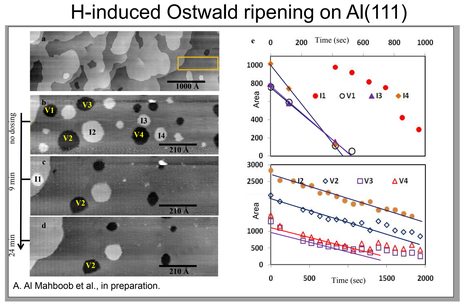
Al-based hydrides (e.g., AlH_3, $LiAlH_4$) exhibit high hydrogen densities and low desorption temperatures, but these materials are often difficult to form by direct hydrogenation at low temperature. The development of new routes for the formation of aluminum-based hydrides requires a better understanding of hydrogen-metal interactions, hydrogenation and the role of catalysts near technologically relevant conditions. In addition, new regeneration routes being proposed to reform aluminum-based hydrides using stabilizing ligands (e.g., ethers, amines) will require new insights into alane chemistry, Al-O and Al-N bonding in alane adducts (e.g., AlH_3-NR_3), and new methods of separating these adducts at low temperatures.

Temperature-pressure phase diagram for Al-H



Pressures > 7 kbar at room temperature required to hydrogenate Al directly from H_2. [2]

H-induced Ostwald ripening on Al(111)

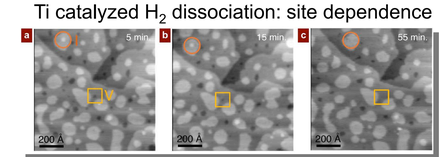


A. Al Mahboob et al., in preparation.

What happens when an Al(111) surface is exposed to atomic hydrogen? Surface modification – Al islands disappear and vacancies are filled.

Mechanism: Upon exposure of atomic H, Al atoms react with H to form mobile alane species. Alanes decomposing at vacancies leads to Al deposition and vacancy filling.

Ti catalyzed H_2 dissociation: site dependence

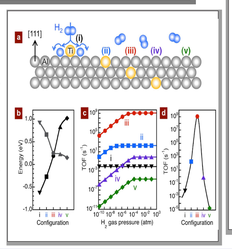


Al Mahboob et al., submitted (2012).

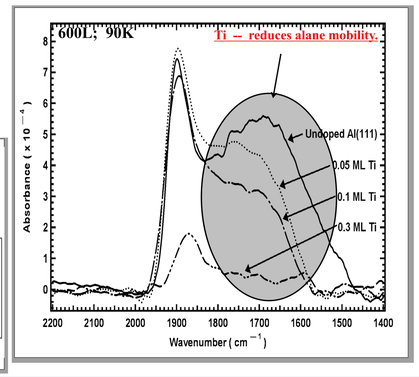
H-induced Ostwald ripening to probe for atomic H generation & spillover on Ti doped Al(111).

Is there a similar effect with **molecular H_2** on a **catalyzed surface**?

- Only observed for Ti in **first subsurface site**.
- Theory shows **strong site dependence**, governed by tradeoff between lowering of H_2 dissociation barrier & increasing spillover energy to all-Al sites.

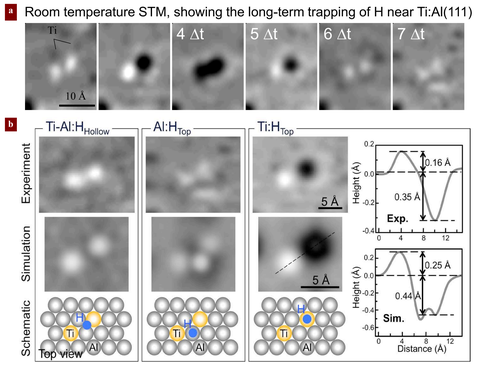


Alane formation & growth on Ti doped - Al(111)



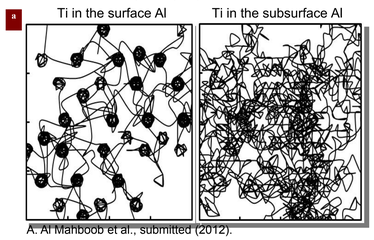
Infrared absorbance spectra obtained after saturating four different Al(111) surfaces at 90K with alanes, using atomic hydrogen exposures of ~ $2x10^{16}$ H atoms/cm^2: (a) clean (undoped) Al (111) surfaces; the other spectra correspond to surfaces doped with Ti: (b) 0.05 ML, (b) 0.1 ML, (c), 0.3 ML (corresponding to 0.045, 0.09 and 0.27 ML of the Al(111) surface). The broad band around 1600 cm^{-1} is associated with bridge hydrogen of high mass alanes formed by AlH_3 oligomerization. With increasing Ti coverage, the absorbance feature at 1600 cm^{-1} is reduced and finally disappears for 0.3 ML Ti coverage. With a high Ti concentration, hydrogen atoms cannot diffuse freely on the surface, thus preventing alane diffusion and large alane formation. The absorbance feature, initially at 1900 cm^{-1} for lower Ti coverages, is now at ~1875 cm^{-1}, and attributed to AlH_3 chemisorbed on Ti sites.[3,4]

Ti substitution in Al(111) surface layer: H trapping



Ti:Al(111): surface & subsurface incorporation (calculations)

Kinetic Monte Carlo simulations of the interaction of surface H with Ti doped Al(111)



A. Al Mahboob et al., submitted (2012).

Surface Ti is effective a separating H_2 and forming alane, but species (alane, Al, H) get trapped around Ti and are much less mobile. Subsurface Ti can also separate H_2 with little barrier, but does not cause trapping – much more effective at forming larger alane oligomers

Regeneration of aluminum-based hydrides

Direct hydrogenation of Al to form crystalline AlH_3 requires extremely high pressures, but we know alane complexes are formed on a Ti catalyzed Al surface when exposed to H_2.

We want to "harvest" alane complexes, trap them as a stable phase that can be isolated and eventually separated to recover the hydride

Two-step approach to regeneration of Al-based hydrides:

Step I (stabilization): Form stabilized alane or alanate adduct by direct hydrogenation of catalyzed Al and stabilizing molecule (e.g. amine (TEDA, TMA), ethers (THF, Et_2O, Me_2O))

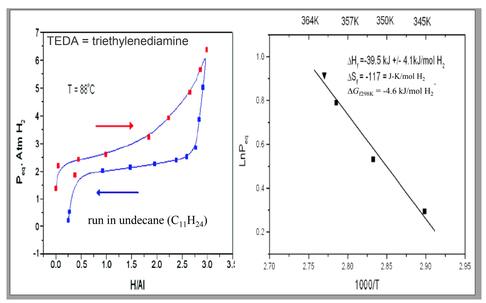
Step II (separation): Remove stabilizing species and recover hydride (alane / alanate)

Metastable hydrides: AlH_3 [5-8], $LiAlH_4$ [9], $Mg(AlH_4)_2$

Stabilizers: ethers (THF), amines (TEDA)

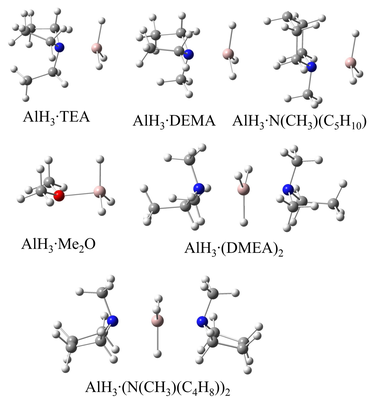
Hydrogenation of Al with Triethylenediamine

Reaction: Al* + TEDA + 3/2H_2 ⟷ AlH_3-TEDA



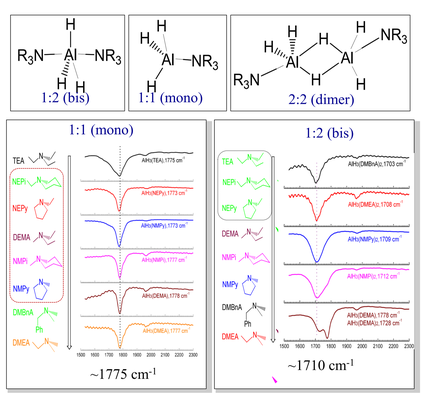
- AlH_3-TEDA is reversible in other solvents (THF, dodecane) [5]
- Reversible capacity ~100% of theoretical (2.1 wt%)

What are the best ligands for alane regeneration?



Amine-Alane Adduct	Binding Free Energy between AlH_3 and Amine (ΔG_S*) at 298.15 K in Et_2O without BSSE Correction		
	monomer	bis	dimer
AlH_3·TEA	-17.14	-11.17	-14.61
AlH_3·N(CH3)(C5H10)	-17.34	-16.11	-14.49
AlH_3·Me2O	-16.43	-15.99	-15.73
AlH_3·DEMA	-20.12	-17.06	-17.57
AlH_3·(N(CH3)(C4H8))	-24.45	-24.63	-21.50
AlH_3·(DMEA)	-25.24	-27.08	-22.54

Screening Candidates by IR Spectroscopy



Alane amine adducts formed by hydrogenation

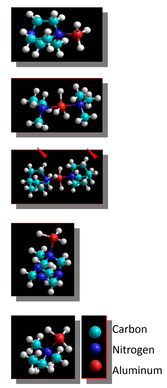
Triethylenediamine alane [5]:
$C_6H_{12}N_2 + Al^* + 3/2H_2 \rightarrow C_6H_{12}N_2$-$AlH_3$
$C_6H_{12}N_2 + AlH_3 \rightarrow C_6H_{12}N_2$-$AlH_3$

Trimethylamine alane [6]:
$2C_3H_9N + Al^* + 3/2H_2 \rightarrow 2C_3H_9N$-$AlH_3$
$2C_3H_9N + AlH_3 \rightarrow 2C_3H_9N$-$AlH_3$

Quinuclidine alane [7]:
$2C_7H_{13}N + Al^* + 3/2H_2 \rightarrow 2C_7H_{13}N$-$AlH_3$
$2C_7H_{13}N + AlH_3 \rightarrow 2C_7H_{13}N$-$AlH_3$

Hexamine alane:
$C_6H_{12}N_4 + Al^* + 3/2H_2 \rightarrow C_6H_{12}N_4$-$AlH_3$
$C_6H_{12}N_4 + AlH_3 \rightarrow C_6H_{12}N_4$-$AlH_3$

Dimethylethylamine alane [8]:
$C_4H_{11}N + Al^* + 3/2H_2 \rightarrow C_4H_{11}N$-$AlH_3$
$C_4H_{11}N + AlH_3 \rightarrow C_4H_{11}N$-$AlH_3$



Can we recover AlH_3 from NR_3-AlH_3?

- No success separating any of the alane amines synthesized by direct hydrogenation - Adducts decompose to Al, H_2 and amine upon heating
- Triethylamine alane can be separated to recover pure α-AlH_3: TEA-AlH_3 $\xrightarrow[3hrs]{70°C}$ AlH_3 + TEA↑

But, TEA-AlH_3 can not be formed by direct hydrogenation – why???

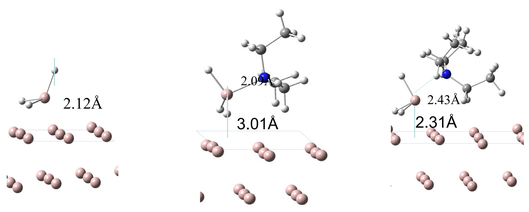
Surface calculations performed to see what happens when a surface AlH_3 species comes into contact with dimethylethylamine (DMEA) and triethylamine (TEA)

1.As AlH_3 binds with DMEA, the distance between Al and Al(111) surface increases from 2.12 Å to 3 Å

2.AlH_3- DMEA cluster on Al(111) has Al-N bond with Al-N distance of 2.09 Å similar to gas phase AlH_3-DMEA

3.Desorption energy of AlH_3-DMEA cluster from Al(111) surface is only 0.002 kcal/mol

It is is interesting to note that this strong Al-N interaction and weakening of the AL-Al bond does not happen with all amines (e.g., triethylamine (TEA)).

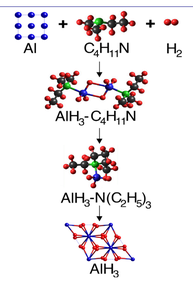


AlH_3 on Al(111) | AlH_3-DMEA on Al(111) | AlH_3-TEA on Al(111)

- We may need to use more than one amine for alane regeneration – one to that forms a strong Al-N bond to extract alane from Al surface and another that has a weaker Al-N bond (TEA-ALH_3) that is easily separated
- This process requires an intermediate transamination (amine exchange) reaction to swap amines:

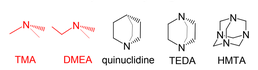
AlH_3-NR_3 + NR_3 → AlH_3-NR_3 + NR_3↑

Full AlH_3 Regeneration Procedure



Step 1: formation of NR_3-AlH_3 by direct hydrogenation

• Six alane adducts formed by direct hydrogenation under mild conditions



Step 2: transamination exchange NR_3 for TEA

• Transamination demonstrated starting with DMEA and TMA

Step 3: separation of TEA-AlH_3

• Separation of TEA-AlH_3 successful with ~80% AlH_3 recovery

Future Work

- Investigate the formation of alane amine and alanate amine adducts by low pressure hydrogenation and identify routes for adduct separation either directly or through transamination (amine exchange).
- Formation of alane amine and alanate amine complexes will be investigated using in situ IR and Raman spectroscopy.
- Spectroscopy experiments will be performed on Al(100) and Al(111) surfaces to study the effect of crystal morphology on alane formation using a variety of different catalysts (TiO_2, Zr, Co, Pd,). The nature of the catalyst sites, activity, and arrangements will be investigated.
- We will explore the effect of solvation on the hydrogenation process and investigate the interaction between the adsorbed surface species and the solute/solvent.

References

[1] "Directing Matter and Energy: Five Challenges for Science and the Imagination" http://www.sc.doe.gov/bes/reports/files/GC_rpt.pdf
Workshop Report "Basic Research Needs for the Hydrogen Economy", Office of Basic Energy Sciences, U.S. Department of Energy, 2nd Printing (2004); http://www.sc.doe.gov/bes/reports/files/NHE_rpt.pdf.

[2] J. Graetz, J.J. Reilly, V.A. Yartys, J.P. Maehlen, B.M. Bulychev, V.E. Antonov, B.P.Tarasov, I.E. Gabis, ***Aluminum hydride as a hydrogen and energy storage material: past, present and future***, JALCOM, ***509***, S517, (2010).

[3] "Effect of Titanium doping of Al(111) Surfaces on Alane Formation, Mobility, and Desorption" S. Chopra, S. Chaudhuri, J.-F. Veyan, J. Graetz, and Y. J. Chabal, *J. Phys. Chem. C*, **115** 16701 (2011).

[4] "Turning aluminium into a noble-metal-like catalyst for low-temperature activation of molecular hydrogen" I.S. Chopra, S. Chaudhuri, J-F. Veyan, and Y.J. Chabal, *Nat. Mat.*, **10** 884 (2011).

[5] J. Graetz, S. Chaudhari, J. Wegrzyn, Y. Celebi, J.R. Johnson, W. Zhou, J.J. Reilly, "The Direct and Reversible Synthesis of AlH_3: Triethylenediamine from Al and H_2" *J. Phys. Chem. C*, **111** 19148 (2007).

[6] D. Lacina, J. Wegrzyn, J. Reilly, J. Johnson, Y. Celebi and J. Graetz, "Regeneration of Aluminum Hydride using Trimethylamine" *J. Phys. Chem. C*, **115** 3789 (2011).

[7] D. Lacina, J. Reilly, J. Johnson, J. Wegrzyn and J. Graetz "The Reversible Synthesis of Bis(Quinuclidine) Alane" *J. Alloys Compd.* **509S** S654 (2011).

[8] D. Lacina, J. Wegrzyn, J. Reilly, Y. Celebi and J. Graetz, "Characterization of Dimethylethylamine-alane and the Regeneration of Aluminum Hydride" *Energy Environ. Sci.*, **3** 1099 (2010).

[9] J. Graetz, J. Wegrzyn and J. J. Reilly, "Regeneration of lithium aluminum hydride (LiAlH4)", *J. Amer. Chem. Soc.* **130** 17790 (2008)