

IV.H.12 Atomistic Transport Mechanisms in Aluminum-Based Hydrides

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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 alane amine adducts. The objective is to provide a comprehensive understanding of the role of dopants and complex reaction environments in facilitating the hydrogenation and dehydrogenation of Al-based hydrogen storage materials.

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 pressure. 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., $\text{AlH}_3\text{-NR}_3$), and new methods of separating these adducts at low temperatures.

Abstract

Hydrogen fuel cell vehicles will reduce greenhouse gas emissions faster than any other technology (e.g., batteries) and a system based on solid-state hydrogen storage (e.g.,

metal hydrides) remains the most promising method of achieving high hydrogen storage densities at low pressure. The Al-based kinetically stabilized hydrides (e.g. AlH_3 , LiAlH_4 , $\text{Mg}(\text{AlH}_4)_2$) represent a class of materials that have received little attention due to poor reversibility, but may offer some advantages over the more stable on-board reversible materials, such as high hydrogen density, low reaction enthalpy (<30 kJ/mol) and the ability to supply hydrogen at high pressures >>1 bar and rapid rates at low temperature (<100°C). However, these hydrides cannot easily be formed by direct hydrogenation at low pressure and therefore, their use as hydrogen storage compounds has been limited. This research program is focused on understanding the atomic-scale effects of hydrogen with catalyzed light metals (e.g., Al) and to exploring how complex reaction environments affect and control these fundamental interactions. These results will be used to develop new procedures for the formation of metastable aluminum-based hydrides.

Progress Report

Model systems for Al-based hydrogen storage:

Doping catalytically inactive materials with dispersed atoms of an active species is a promising route toward realizing ultra-dilute binary catalyst systems. Beyond heterogeneous catalysis, strategically placed metal atoms can accelerate a wide range of solid-state reactions, particularly in hydrogen storage processes. We used in situ scanning tunneling microscopy experiments on a Ti:Al(111) model system in a controlled ultrahigh vacuum environment, combined with ab-initio calculations, to analyze the role of atomic Ti catalysts in the hydrogenation of aluminum-based hydrogen storage materials.

Our results show that Ti atoms near the Al surface activate gas phase H_2 , a key step toward hydrogenation. Controlling the placement of Ti we find that the overall reaction – comprising H_2 dissociation and H spillover onto the Al surface – is governed by a pronounced tradeoff between lowering the H_2 dissociation barrier and trapping of the products near the active site. Ti existing as adatoms on the surface or embedded in the Al surface layer efficiently dissociates H_2 , but the products (H) cannot be transferred to the Al surface due to a deep potential well trapping H near the active site. As a result, the Ti catalyst becomes rapidly poisoned, and no significant amounts of atomic H are made available for Al hydrogenation. H spillover can be enabled by burying Ti in subsurface Al layers, an effect which we explored by controlling the placement of Ti with atomic-layer precision. Experiments and calculations show a sharp maximum in the overall activity for Ti in the first subsurface layer. Ti incorporation into deeper subsurface layers causes

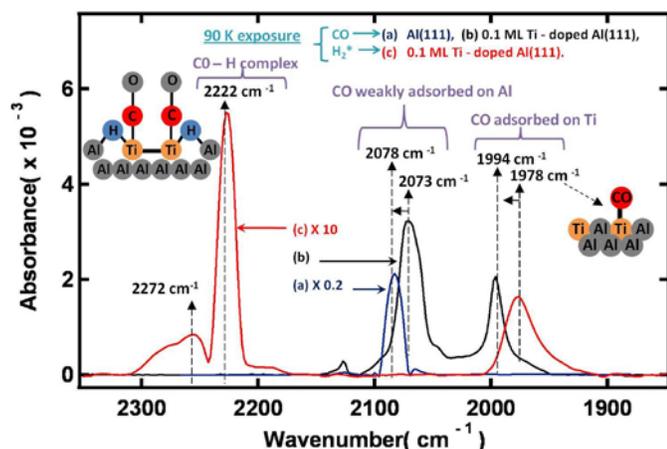


FIGURE 1. Infrared reflection-absorption spectra of CO molecules adsorbed on Al(111) surfaces at 90 K. Pure CO gas (7 L exposure) on (a) clean Al, (b) Al with 0.1 ML Ti and (c) H_2^* on Al with 0.1 ML Ti, where H_2^* is H_2 titrated with CO ($1.2 \times 10^{20} H_2/cm^2$ with $\sim 0.0001\%$ CO). The band at $1,994 cm^{-1}$ is associated with CO adsorbed at Ti sites (spectrum b); a new feature at $2,222 cm^{-1}$ (and $\sim 2,272 cm^{-1}$) is due to CO on Ti complexed with hydrogen.

the H_2 dissociation barrier to rapidly approach the high value ($>1 eV$) for clean Al(111). Our findings demonstrate the importance of controlling the placement of the active species for optimizing the activity in dilute binary systems, and provide important insight into the atomic-scale mechanisms of transition metal catalyzed hydrogenation of Al-based hydrogen storage materials.

Molecular hydrogen activation: Using in situ infrared spectroscopy the first direct experimental evidence for the activation of molecular hydrogen on Ti doped Al(111) was observed. For these experiments CO was used as a probe molecule to investigate the chemical nature of the surface. The changes in the frequency of the CO stretch were shown to be a sensitive probe of the electronic states of surface Ti atoms. Ti arrangement was shown to be a critical parameter for hydrogen activation. Only Ti present in the nearest neighbor or next nearest neighbor configuration was shown to be catalytically active for hydrogen activation with the next nearest sites being more active. The catalytic activity also depends on the Ti concentration/coverage with the highest catalytic activity observed for 0.1 ML Ti coverage. Above 0.1 ML, the additional Ti atoms are inactive. Once dissociated, the hydrogen spills over from these catalytic sites on Al and prevents further CO adsorption on Al. It is interesting to note that CO molecules, selectively adsorbed on catalytically active sites, form a complex with activated hydrogen that is removed at remarkably low temperatures (115 K). These results provide the first direct evidence that Ti-doped Al can carry out the essential first step of molecular hydrogen activation under nearly barrierless conditions, thereby challenging the monopoly of noble metals in hydrogen activation.

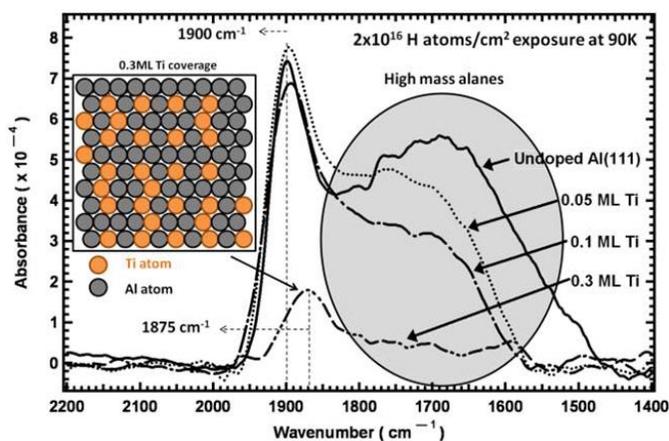


FIGURE 2. Infrared absorbance spectra obtained after saturating four different Al(111) surfaces at 90 K with alanes, using atomic H exposures of $\sim 2 \times 10^{16} H$ atoms/ cm^2 : clean (undoped) Al(111) surfaces; 0.05 ML Ti, 0.1 ML Ti, 0.3 ML Ti. The broad band at $1,600 cm^{-1}$ is associated with bridge hydrogen of high mass alanes formed by oligomerization and the intensity is reduced with increasing Ti.

Effect of Ti on alane mobility and formation: Alanes are critical intermediates in hydrogen storage reactions for mass transport during the formation of complex metal hydrides. The initiation of alane formation occurs through the saturation of steps on the Al surface by H atoms followed by diffusion of small, weakly adsorbed alane clusters on the Al surface, leading to subsequent oligomerization (formation of larger alanes). For Ti doped Al(111) surfaces the diffusion dynamics and oligomerization rates are severely altered as indicated by a marked decrease of higher mass alane concentrations. The mobility of chemisorbed H on Ti-doped Al surfaces at 90 K is substantially lowered by small Ti coverages compared to undoped Al surfaces. Lower mobility leads to a lower diffusion of H to steps, and therefore slows the replenishment of H as AlH_3 , which is eventually released as a mobile, physisorbed species. Titanium also stabilizes Al surface atoms (higher cohesive energy). As a result, fewer Al adatoms (particularly step Al atoms) are available for the formation of AlH_3 , further lowering the rate of alane production.

The location of Ti atoms can also influence alane mobility. When Ti atoms are deposited at 90 K, they remain mostly on the surface, substituting for surface Al atoms. In contrast, when Ti is deposited at 300 K most Ti atoms are thermodynamically expected to go subsurface and therefore there are fewer surface Ti atoms than when deposited at 90 K. Since surface Ti hinders kinetics by trapping H atoms, the Ti deposited at 300 K does not reduce alane formation as much as Ti deposited at 90 K. The incorporation of Ti also lowers the alane desorption temperature primarily due to induced Al-H bond breaking and lower partitioning of thermal energy in translational modes (with Ti doping the diffusing alane clusters are trapped thereby losing

translational modes and thus the rotational modes are populated leading to lower temperatures of desorption).

Surface and solution phase calculation: many alane-amine adducts can be formed at low temperature and pressures from a reaction between H_2 and Ti-doped aluminum suspended in ether solutions of tertiary amines. However, the triethylamine (TEA)-alane cannot be formed by a direct reaction of TEA with AlH_3 formed on the doped aluminum powder. Surface calculations indicate that stabilizing amine molecules can interact with AlH_3 and pull it off the aluminum surface. Since a weak electron donor such as TEA cannot compete with the strong binding energy (27.8 kcal/mol) between AlH_3 and Al(111) surface, the AlH_3 -TEA adduct is not obtained in such an experiment.

Figure 3 shows the optimized structures of different adsorbates on Al(111) surface. A TEA molecule next to AlH_3 does not affect the bonding between AlH_3 and the surface (Figure 3b), which is 2.31 Å and is similar with that of an isolated AlH_3 on Al(111) (Figure 3a). The Al-N distance is 2.43 Å, which is much longer than in the isolated AlH_3 -TEA cluster in gas phase (2.10 Å), indicating weak interaction between AlH_3 and amine. When a dimethylethylamine (DMEA) (Figure 3c) approaches the surface, a strong interaction between Al and N drags AlH_3 away, resulting in a longer distance between Al and the surface. The calculations suggest that removing AlH_3 from the Ti-doped Al(111) surface is the crucial step in alane-amine formation. If it is not removed, the AlH_3 blocks the surface sites and shuts down the surface reaction in which the AlH_3 is formed. The calculations suggest that two properties of the amine are important for promoting alane-amine formation: a strong electron donor with minimal steric hindrance for binding to AlH_3 .

The stabilized alane complexes need to be decomposed to regenerate AlH_3 . An important requirement is that the complex must be sufficiently unstable that the stabilizing molecule is removed before hydrogen is lost from AlH_3 . We have examined five amines [DMEA, $N(CH_3)(C_4H_8)$

(N-methyl-pyrrolidine), DEMA (diethylmethylamine), $N(CH_3)(C_5H_{10})$ (N-methyl-piperidine), TEA] and one ether (Me_2O) which are potential candidates for successful thermal decomposition of alane adducts. Monomer, bis, and dimer complex geometries were all considered. The most stable structures of each complex are shown in Figure 3d. The binding Gibbs free energies were calculated and the overall order of alane adducts stability is $DMEA-AlH_3 > N(CH_3)(C_5H_{10})-AlH_3 > DEMA-AlH_3 > Me_2O-AlH_3 > N(CH_3)(C_4H_8)-AlH_3 > TEA-AlH_3$. This trend is able to provide guidance for thermal decomposition strategies.

Future Work

1. 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).
2. The formation of alane amine and alanate amine complexes will be investigated using in situ infrared and Raman spectroscopy.
3. 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 (TiO₂, Zr, Co, Pd). The nature of the catalyst sites, activity, and arrangements will be investigated.
4. We will explore the effect of solvation on the hydrogenation process and investigate the interaction between the adsorbed surface species and the solute/solvent.

Publications (selected) acknowledging the grant or contract

1. "Site-Dependent Activity of Atomic Ti Catalysts in Al-Based Hydrogen Storage Materials", A. Al-Mahboob, E. Muller, A. Karim, J.T. Muckerman, C.V. Ciobanu, and P. Sutter, *Angewandte Chemie Int. Ed.*, submitted (2012).

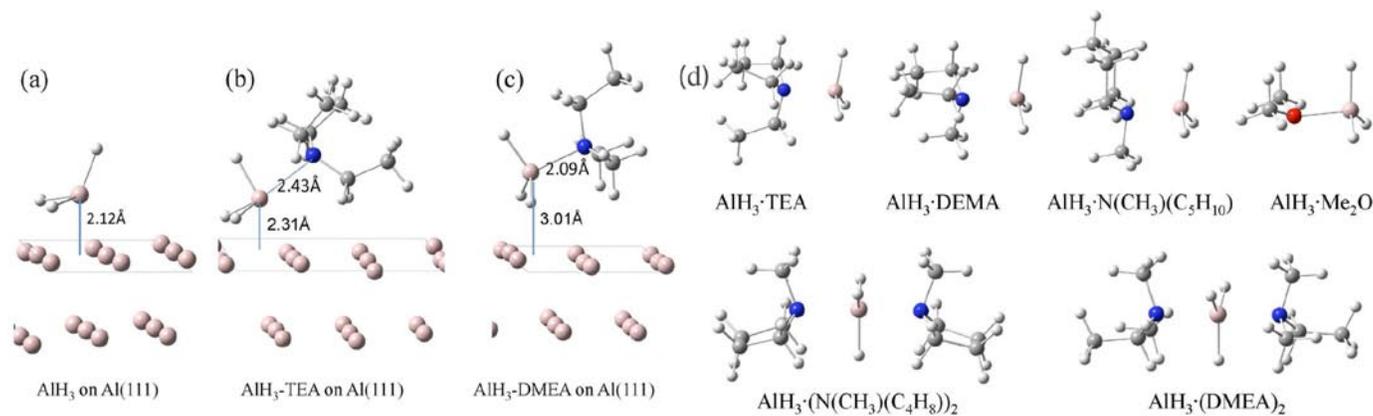


FIGURE 3. Optimized structures of (a) AlH_3 , (b) AlH_3 -TEA, (c) AlH_3 -DMEA on Al(111) surface. (d) Optimized geometries of the most stable configuration of different alane complexes in Et_2O .

2. "Investigation of LiAlH₄-THF formation by direct hydrogenation of catalyzed Al and LiH" D. Lacinca, L. Yang, I. Chopra, J. Muckerman, Y. Chabal, J. Graetz, *Phys. Chem. Chem. Phys.* DOI: 10.1039/c2cp40493a (2012).
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. "Regeneration of Aluminum Hydride using Trimethylamine" D. Lacinca, J. Wegrzyn, J. Reilly, J. Johnson, Y. Celebi and J. Graetz, *J. Phys. Chem. C*, **115** 3789 (2011).