

Atomistic Transport Mechanisms in Aluminum-Based Hydrides

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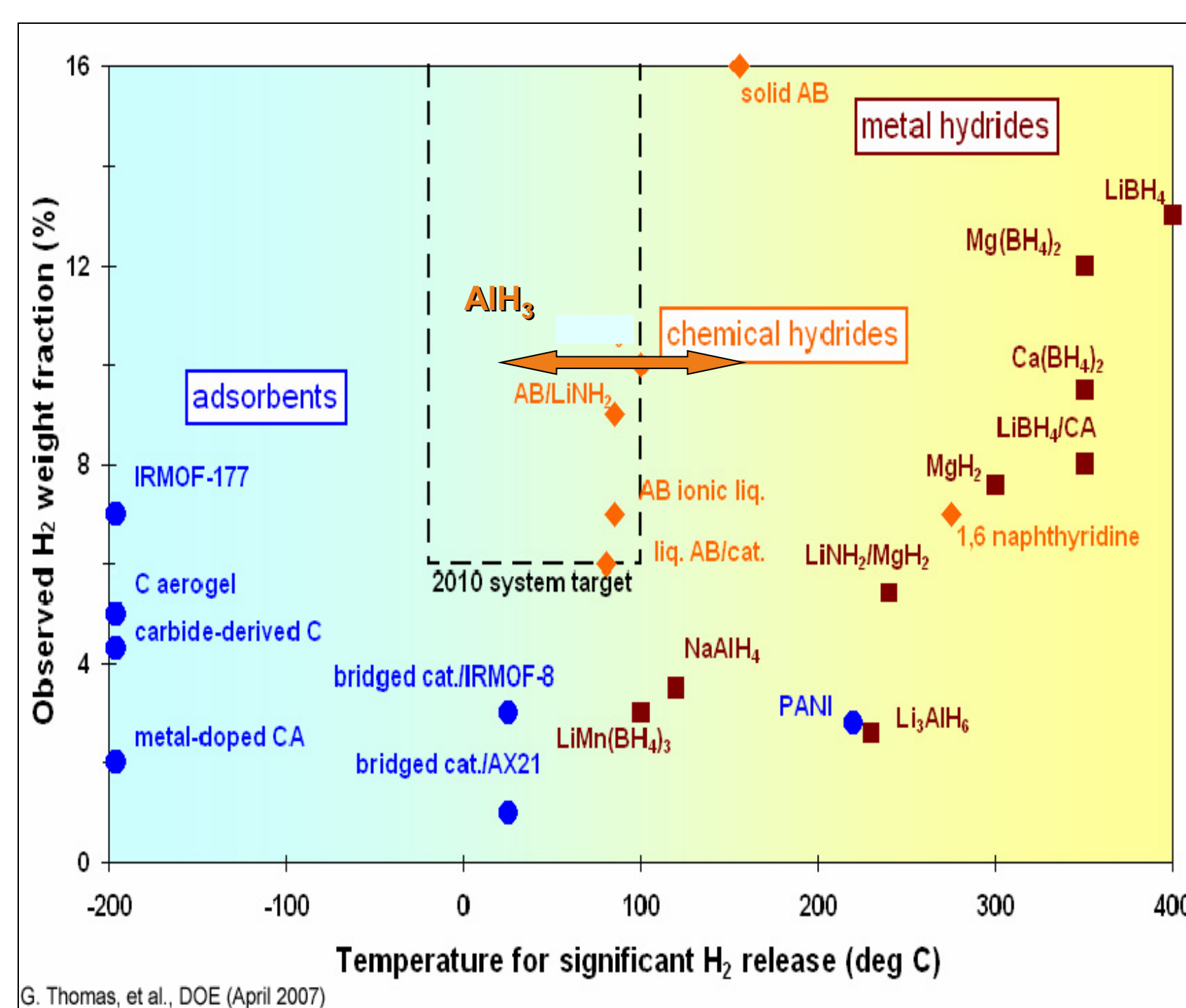
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Program Strategy

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.



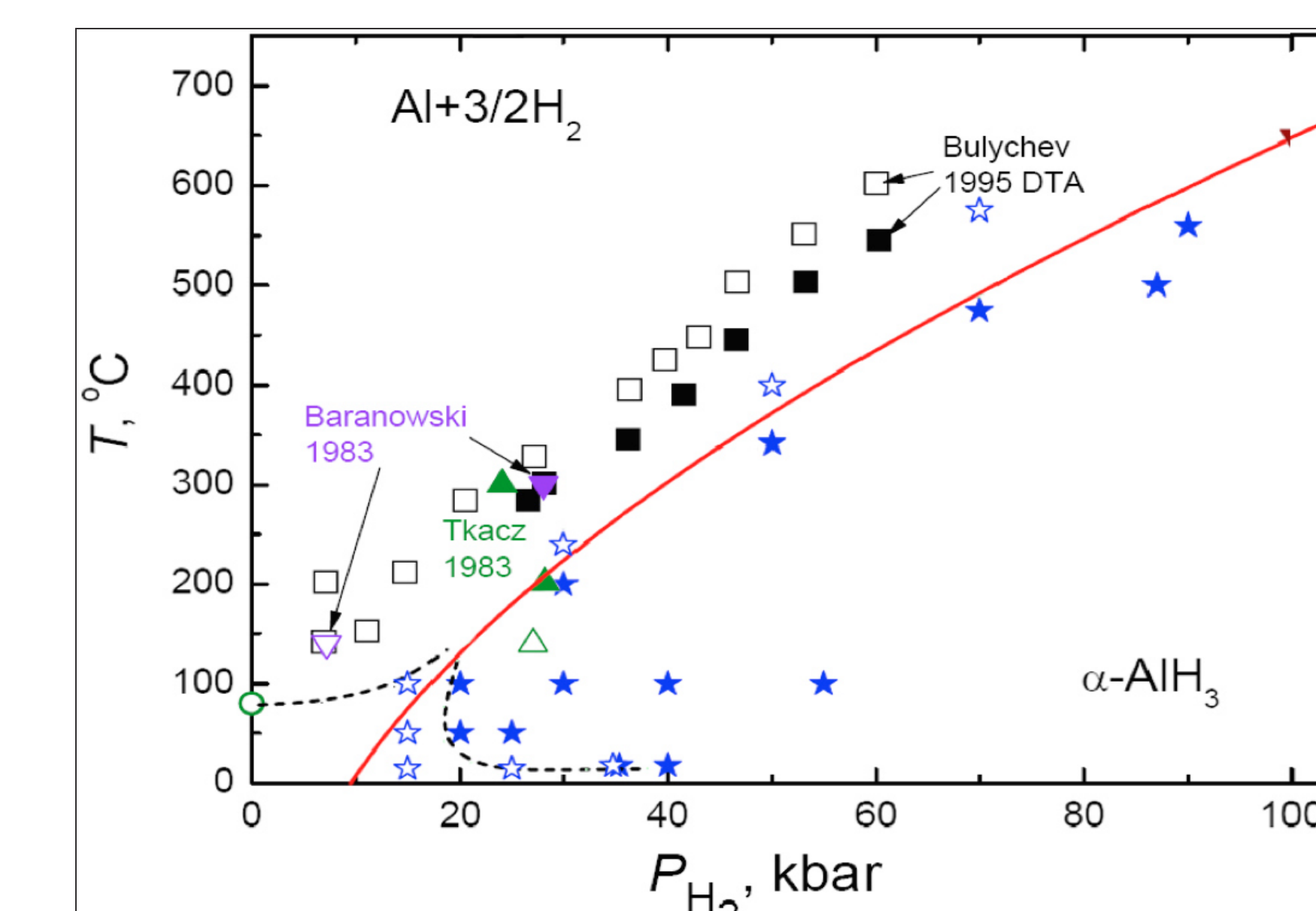
Objectives

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 alane 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(AIH₂)₂) and light metal hydrides (e.g., AIH₃).

Technical Barriers

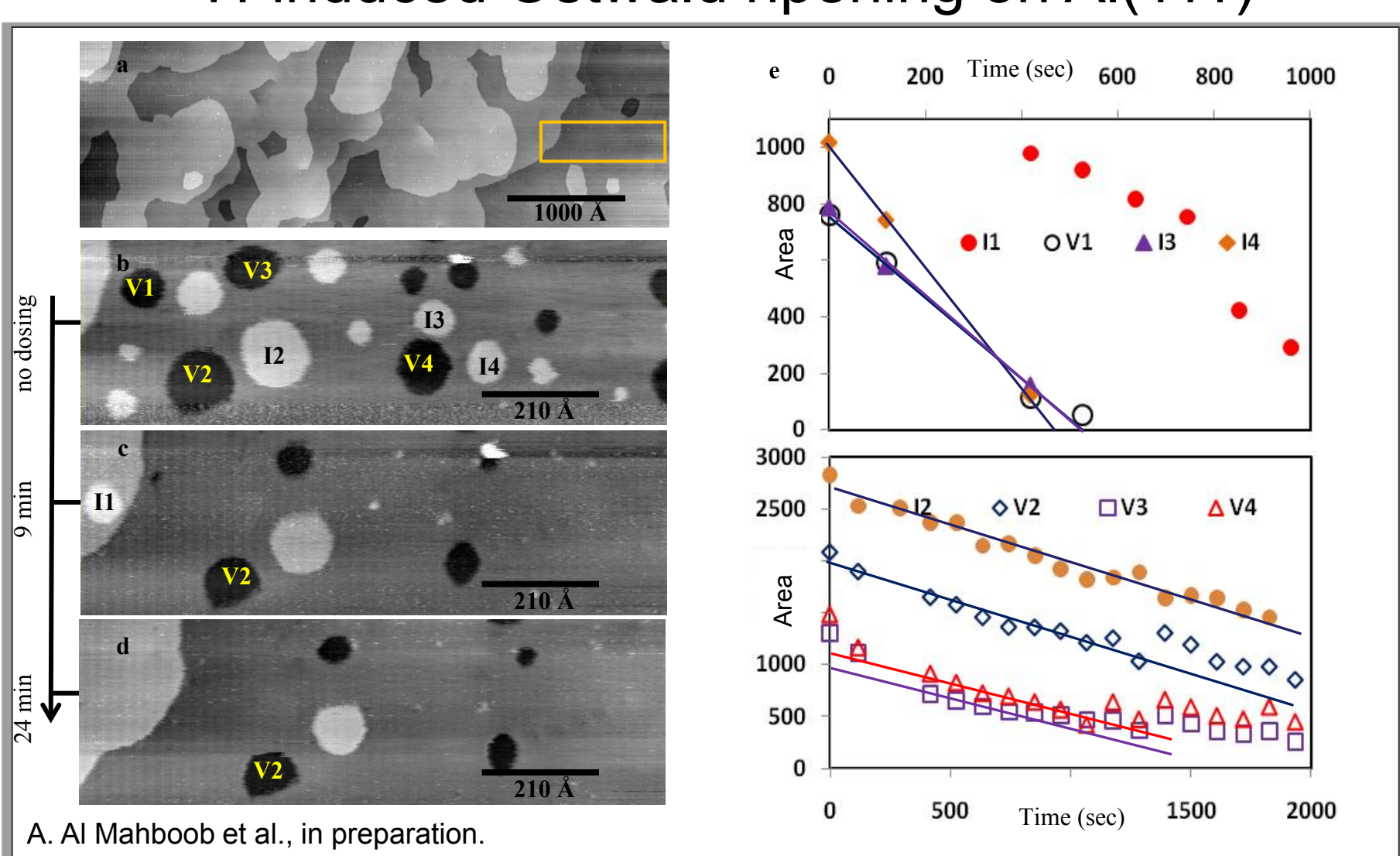
Al-based hydrides (e.g., AIH₃, LiAlH₄) exhibit high hydrogen densities and low desorption temperatures, but these materials are often difficult to form by direct hydrogenation at low temperature. The development of new routes for the formation of aluminum-based hydrides requires a better understanding 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., AIH₃-NR₃), 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 H₂. [2]

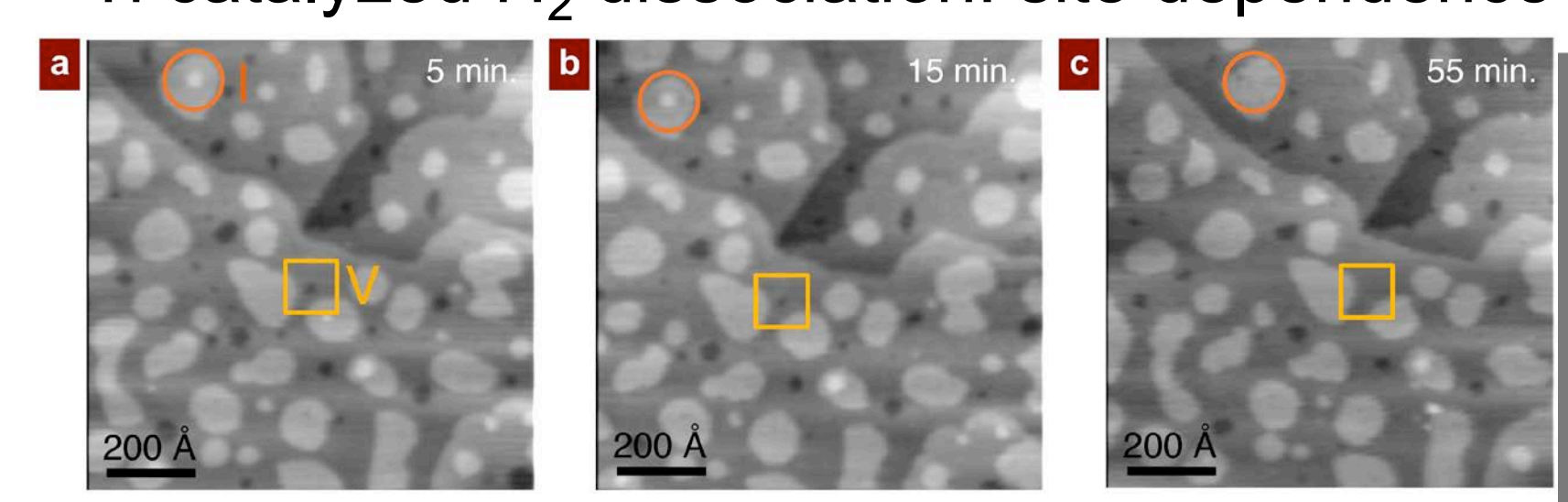
H-induced Ostwald ripening on Al(111)



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 H₂ dissociation: site dependence

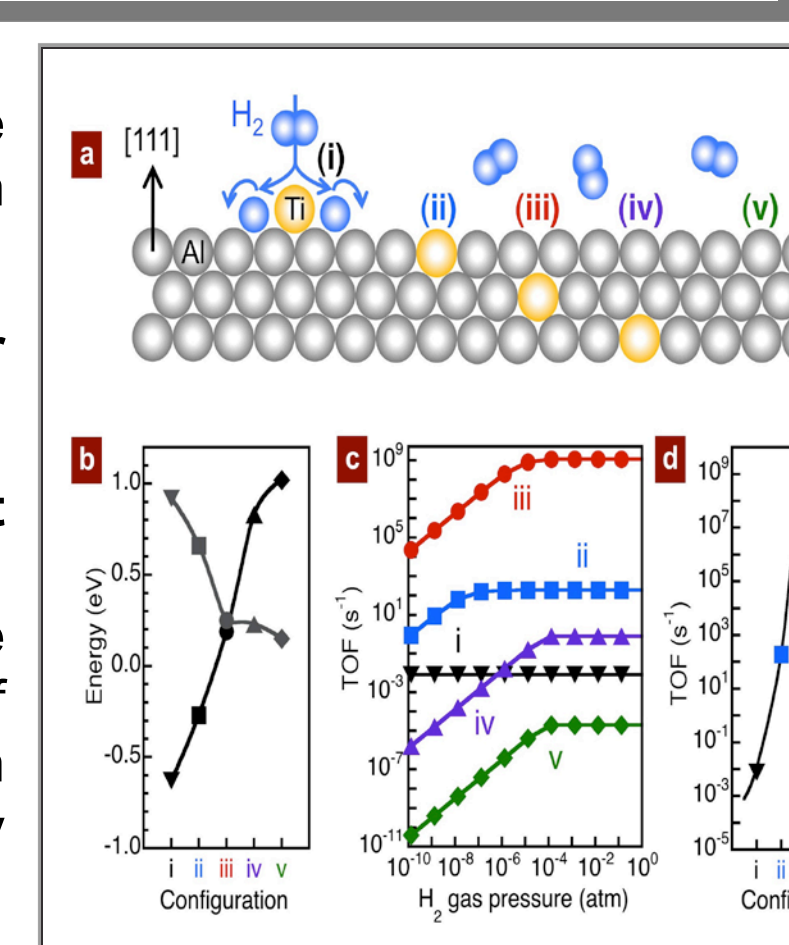


Al Mahboob et al., submitted (2012).

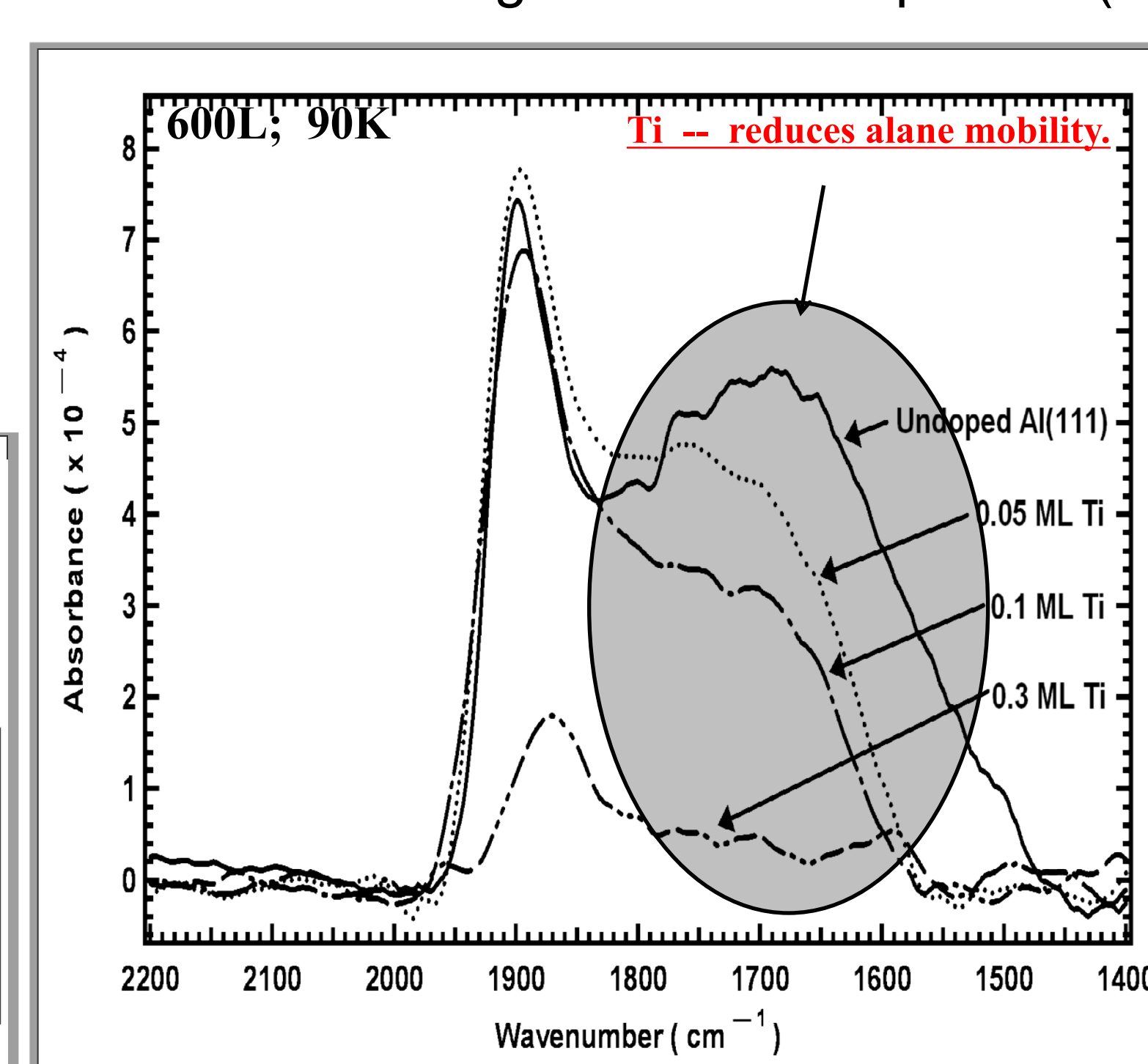
H-induced Ostwald ripening to probe for atomic H generation & spillover on Ti doped Al(111).

Is there a similar effect with molecular H₂ on a catalyzed surface?

- Only observed for Ti in first subsurface site.
- Theory shows strong site dependence, governed by tradeoff between lowering of H₂ dissociation barrier & increasing spillover energy to all-Al sites.

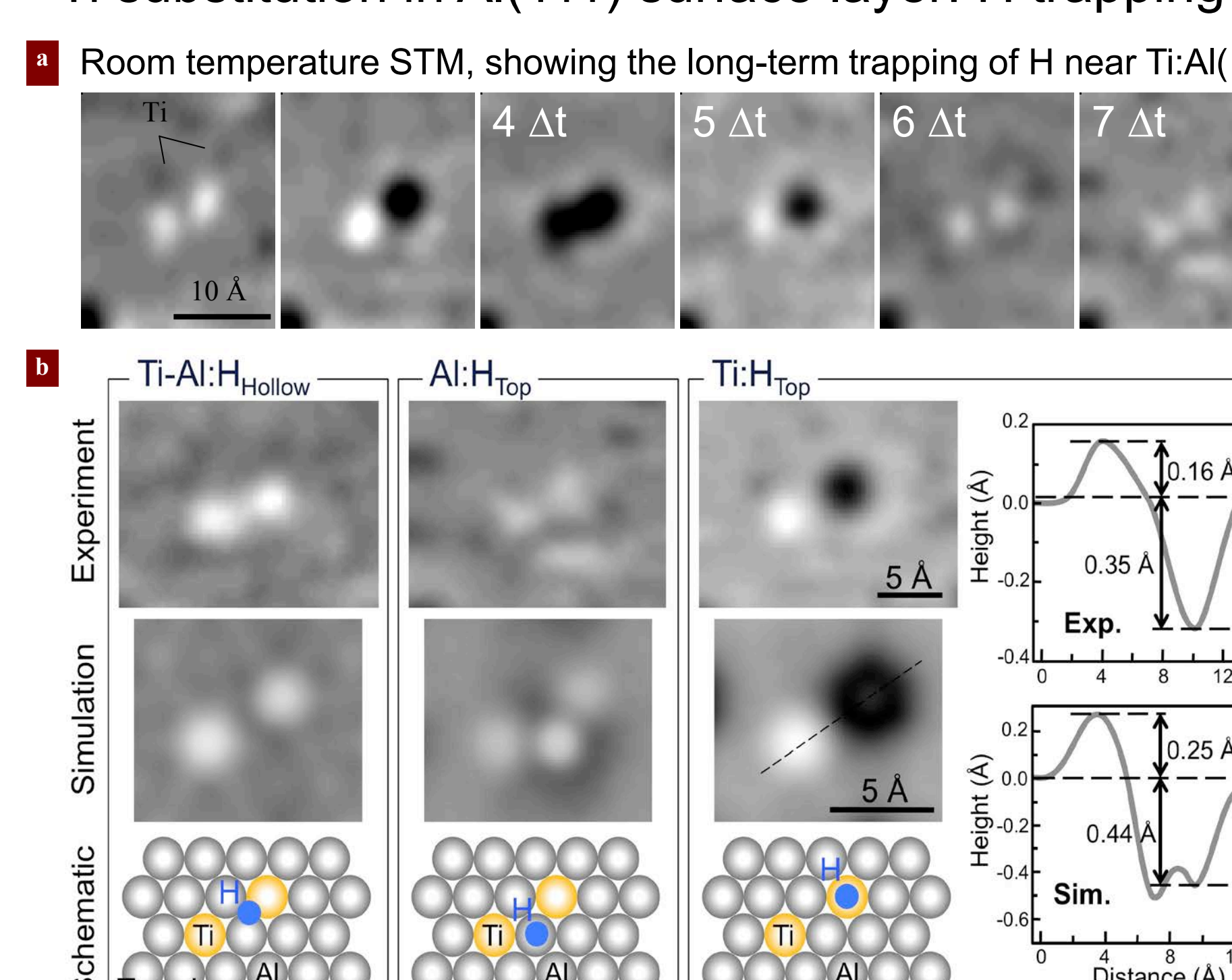


Alane formation & growth on Ti doped - Al(111)



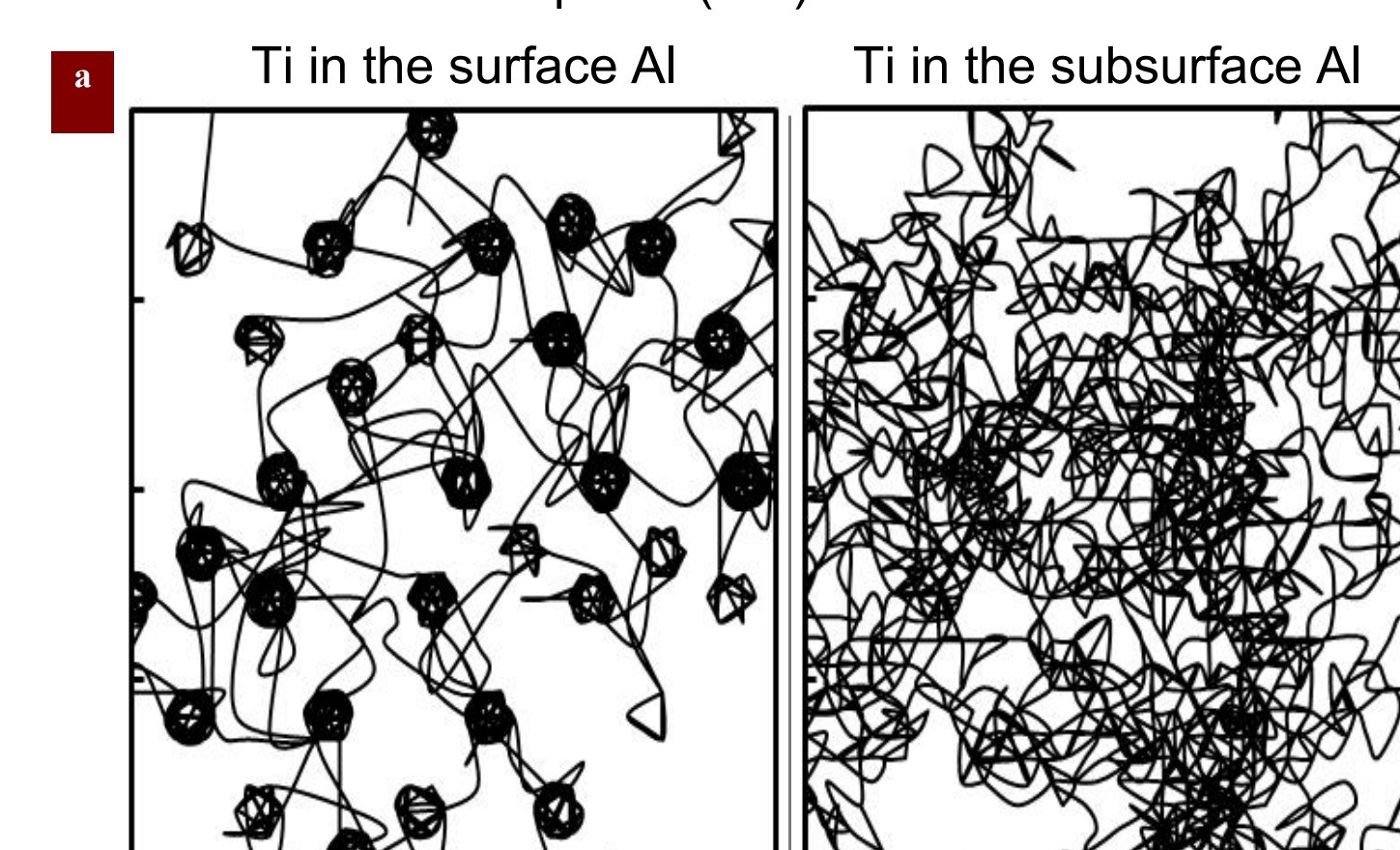
Infrared absorbance spectra obtained after saturating four different Al(111) surfaces at 90K with alanes, using atomic hydrogen exposures of ~2x10¹⁶ H atoms/cm²: (a) clean (undoped) Al (111) surfaces; the other spectra correspond to surfaces doped with Ti: (b) 0.05 ML, (c) 0.1 ML, (d) 0.3 ML (corresponding 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 AIH₃ 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 AIH₃ 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)



Al Mahboob et al., submitted (2012).

Surface Ti is effective at separating H₂ and forming alane, but species (alane, Al, H) get trapped around Ti and are much less mobile. Subsurface Ti can also separate H₂ with little barrier, but does not cause trapping – much more effective at forming larger alane oligomers

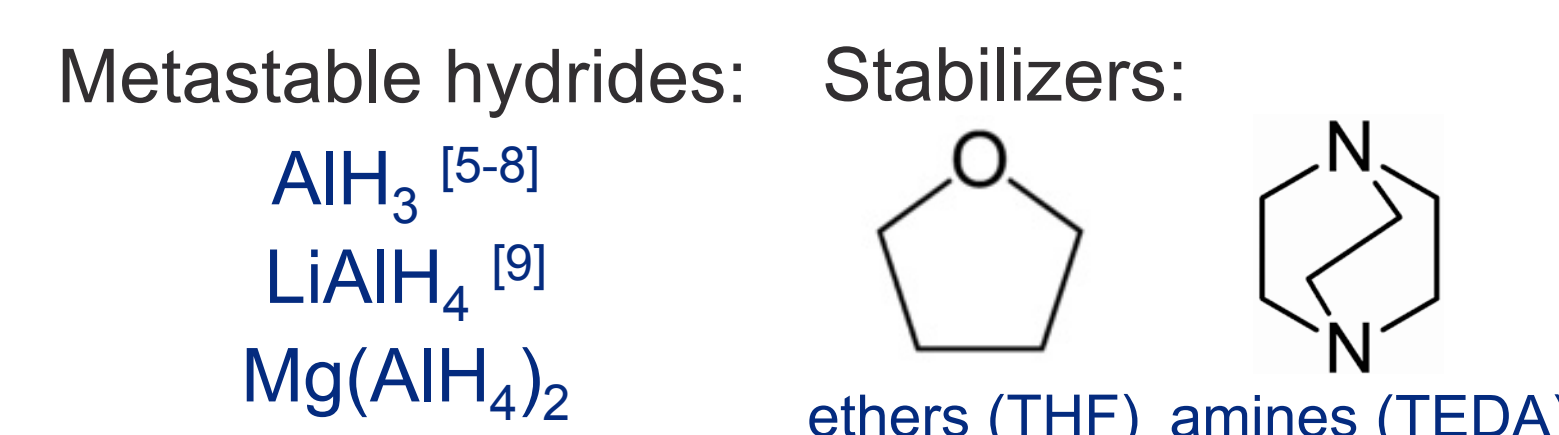
Regeneration of aluminum-based hydrides

Direct hydrogenation of Al to form crystalline AIH₃ requires extremely high pressures, but we know alane complexes are formed on a Ti catalyzed Al surface when exposed to H₂. We want to "harvest" alane complexes, trap them as a stable phase that can be isolated and eventually separated to recover the hydride

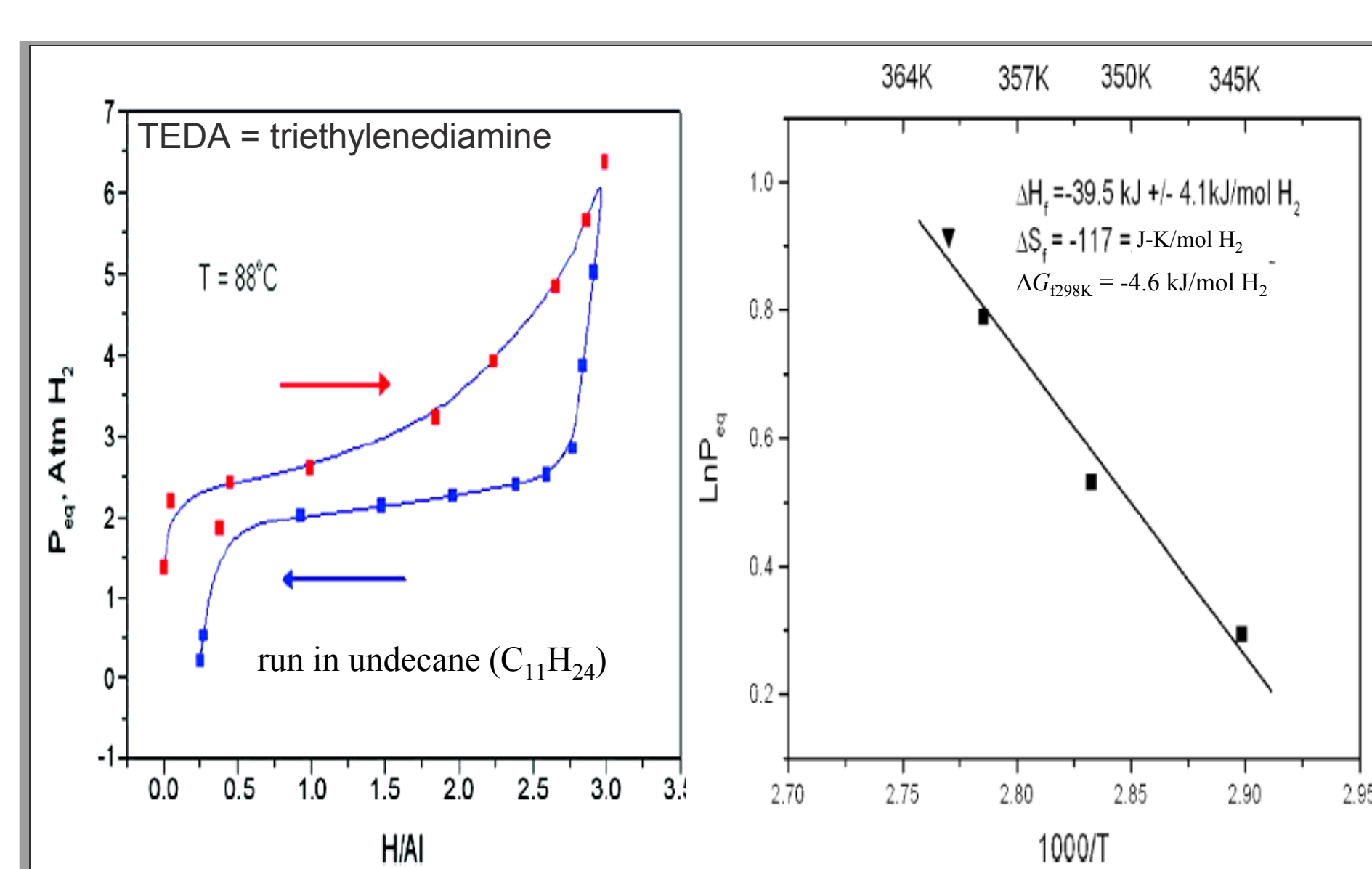
Two-step approach to regeneration of Al-based hydrides:

Step I (stabilization): Form stabilized alane or alane adduct by direct hydrogenation of catalyzed Al and stabilizing molecule (e.g. amine (TEDA, TMA), ethers (THF, Et₂O, Me₂O))

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

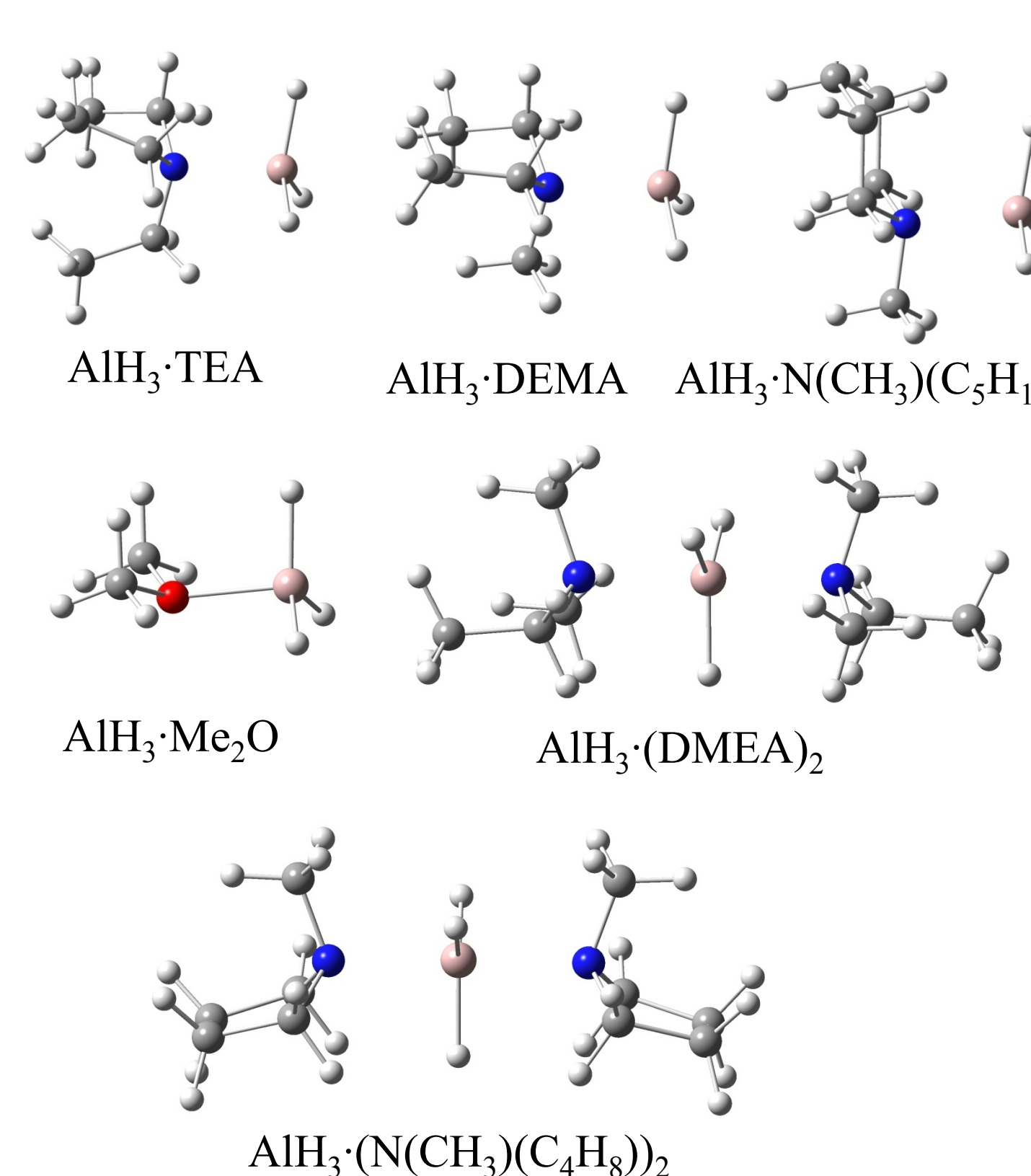


Hydrogenation of Al with Triethylenediamine



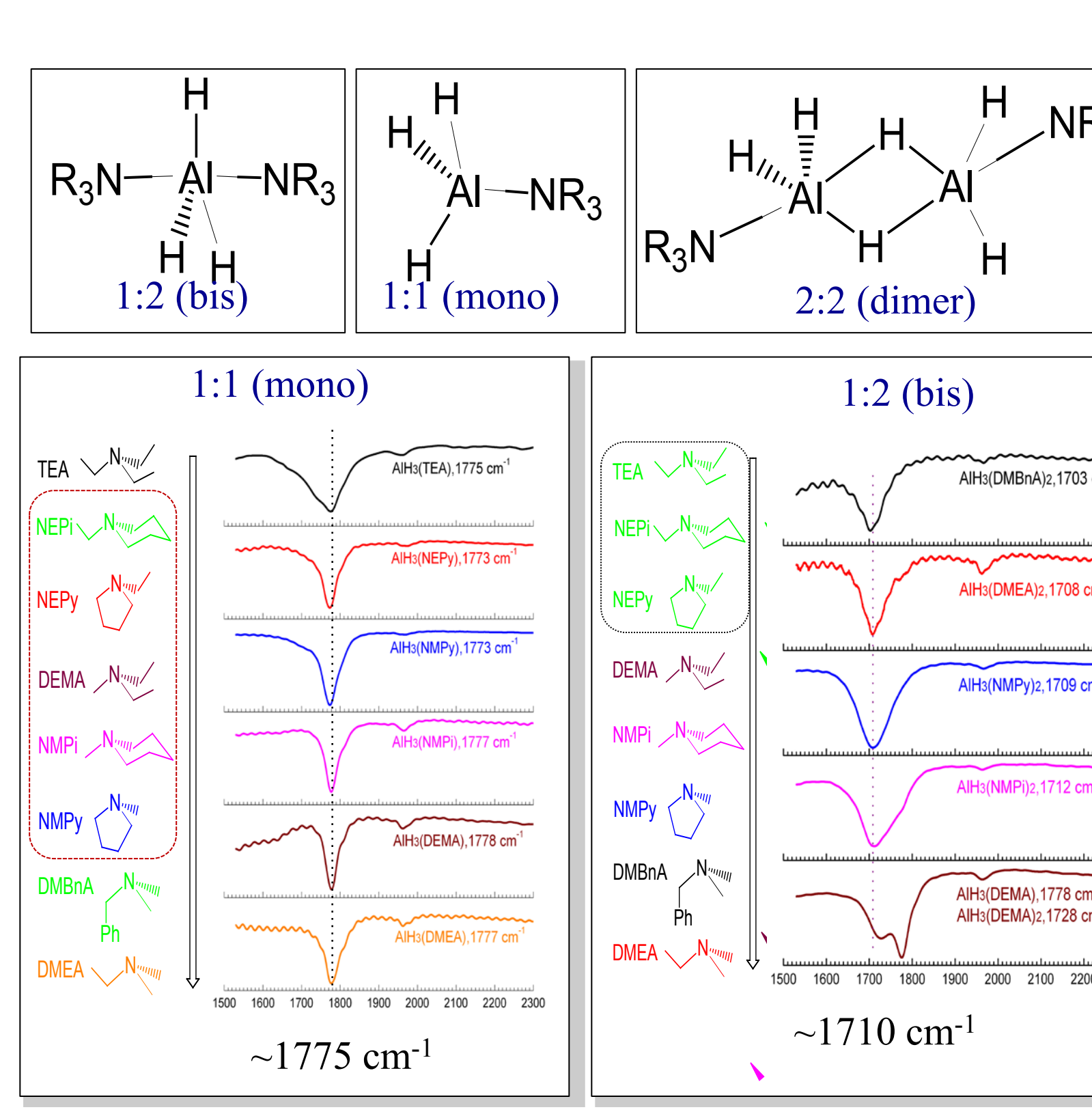
- AIH₃-TEDA is reversible in other solvents (THF, dodecane) [5]
- Reversible capacity ~100% of theoretical (2.1 wt%)

What are the best ligands for alane regeneration?

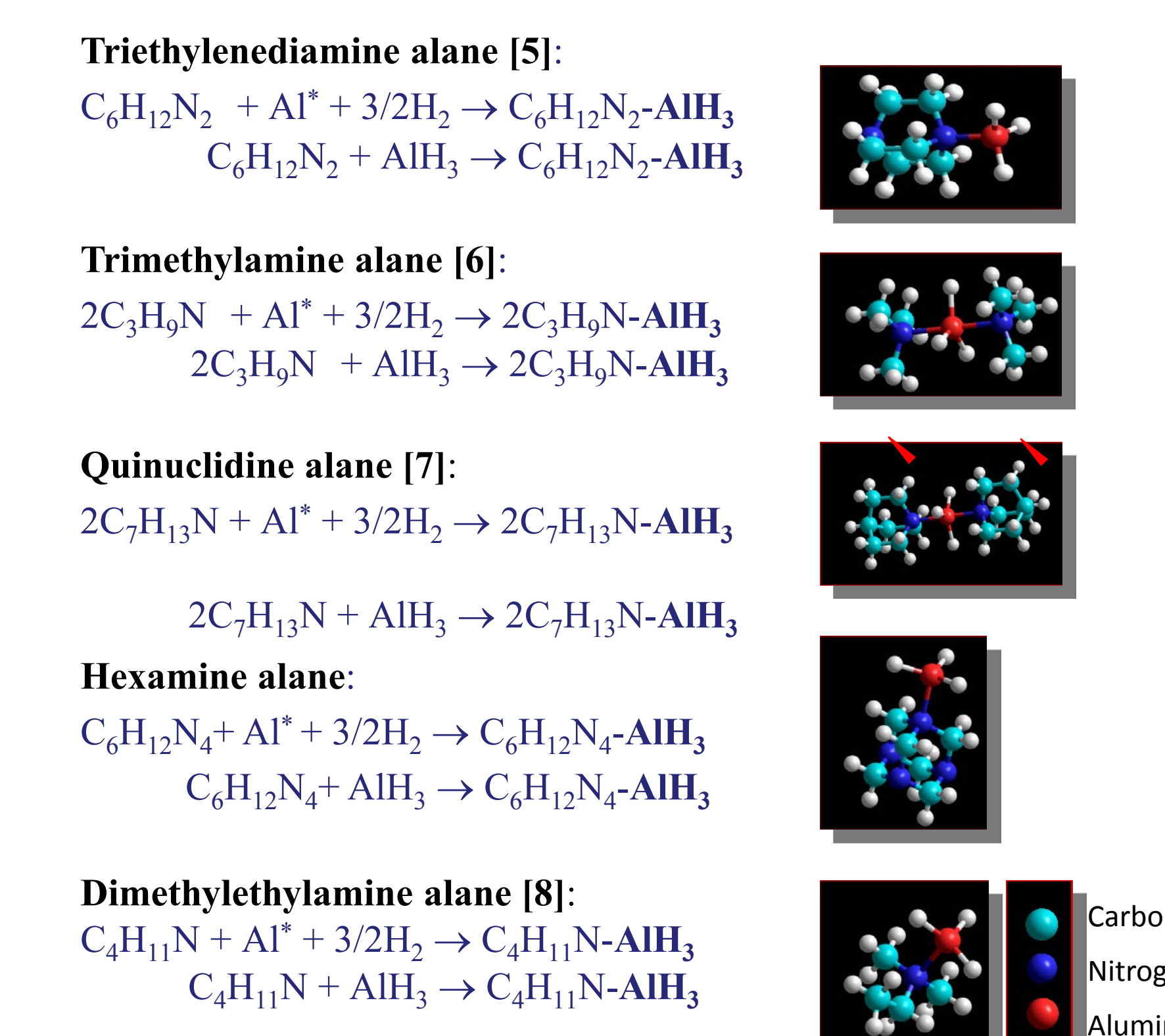


Amine-Alane Adduct	Binding Free Energy between AIH ₃ and Amine (ΔG ₀ [*]) at 298.15 K in Et ₂ O without BSSE Correction		
	monomer	bis	dimer
AIH ₃ -TEA	-17.14	-11.17	-14.61
AIH ₃ -N(CH ₃)(C ₂ H ₅) ₂	-17.34	-16.11	-14.49
AIH ₃ -Me ₂ O	-16.43	-15.99	-15.73
AIH ₃ -DEMA	-20.12	-17.06	-17.57
AIH ₃ -(N(CH ₃)(C ₂ H ₅) ₂)	-24.45	-24.63	-21.50
AIH ₃ -(DMEA)	-25.24	-27.08	-22.54

Screening Candidates by IR Spectroscopy



Alane amine adducts formed by hydrogenation



Can we recover AIH₃ from NR₃-AIH₃?

- No success separating any of the alane amines synthesized by direct hydrogenation - Adducts decompose to Al, H₂ and amine upon heating

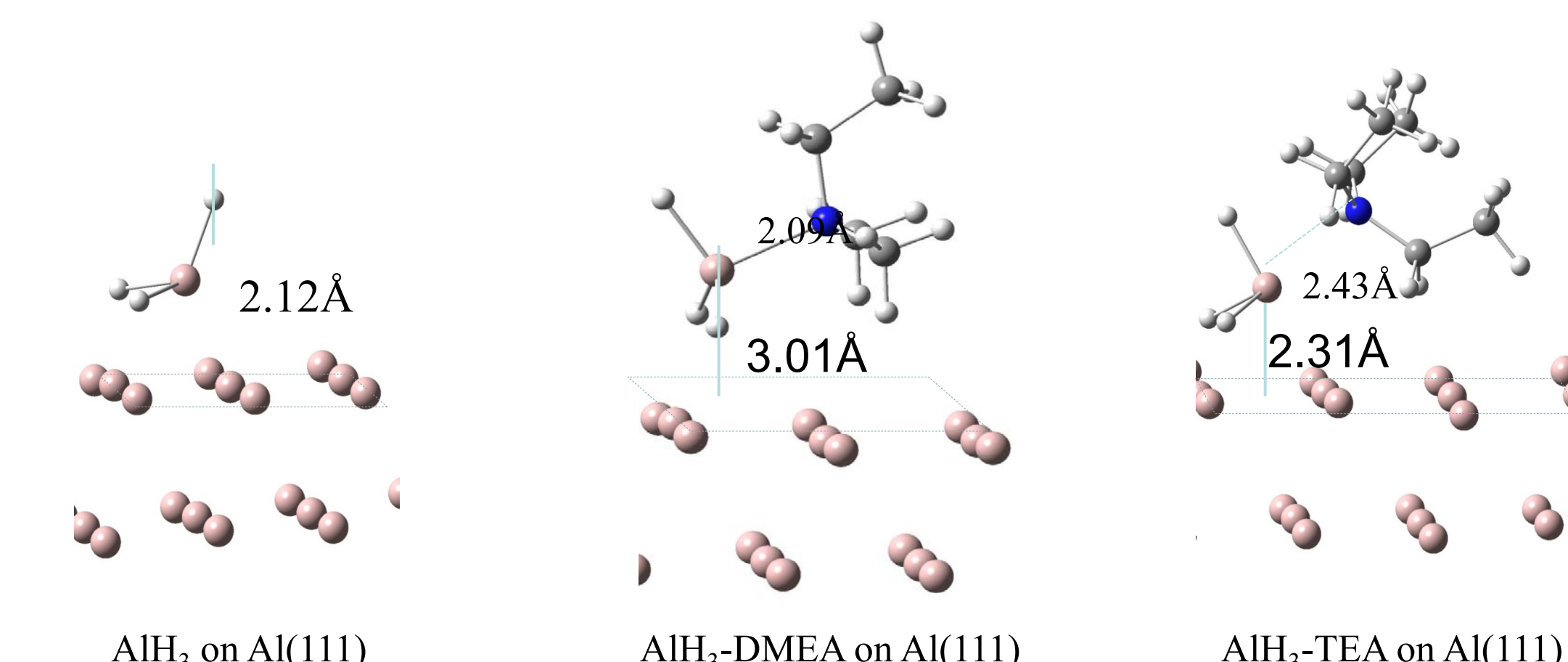
But, TEA-AIH₃ can be separated to recover pure α-AIH₃: TEA-AIH₃ $\xrightarrow[3hrs]{70^\circ C}$ AIH₃ + TEA↑

But, TEA-AIH₃ can not be formed by direct hydrogenation - why???

Surface calculations performed to see what happens when a surface AIH₃ species comes into contact with dimethylethylamine (DMEA) and triethylamine (TEA)

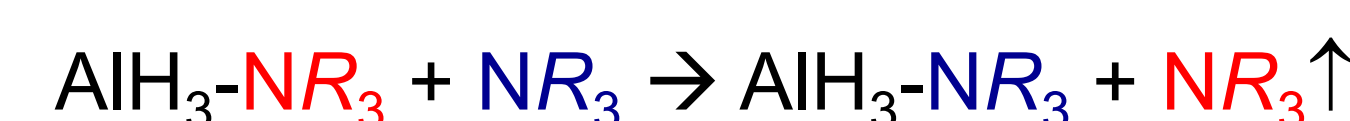
- As AIH₃ binds with DMEA, the distance between Al and Al(111) surface increases from 2.12 Å to 3 Å
- AIH₃-DMEA cluster on Al(111) has Al-N bond with Al-N distance of 2.09 Å similar to gas phase AIH₃-DMEA
- Desorption energy of AIH₃-DMEA cluster from Al(111) surface is only 0.002 kcal/mol

It 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)).



- We may need to use more than one amine for alane regeneration – one that forms a strong Al-N bond to extract alane from Al surface and another that has a weaker Al-N bond (TEA-AIH₃) that is easily separated

This process requires an intermediate transamination (amine exchange) reaction to swap amines:



Full AIH₃ Regeneration Procedure

- Step 1: formation of NR₃-AIH₃ by direct hydrogenation**
Six alane adducts formed by direct hydrogenation under mild conditions
- Step 2: transamination exchange NR₃ for TEA**
Transamination demonstrated starting with DMEA and TMA
- Step 3: separation of TEA-AIH₃**
Separation of TEA-AIH₃ successful with ~80% AIH₃ recovery

Future Work

- Investigate the formation of alane amine and alane amine adducts by low pressure hydrogenation and identify routes for adduct separation either directly or through transamination (amine exchange).
- Formation of alane amine and alane 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 (TiO₂, 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.

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