Atomistic Transport Mechanisms in Reversible Complex Metal Hydrides

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Outline

Atomistic Transport Mechanisms in Reversible Complex Metal Hydrides

1) Introduction: Objectives & Approach
2) Examples of Activities & Findings
4) Future Plans
5) User Facilities at BNL
I. Fundamental questions: doping ⇔ reversible H-storage?

Q1: Role of Ti catalyst in H₂ dissociation?
Q2: Primary carrier(s) of mass transport?
Q3: Fundamental kinetic factors governing reaction rates?

II. Enhancing kinetics in other hydride systems?

Q4: Effects of substitution in mixed metal hydrides?
Re-hydrogenation of bulk alane?
Surface Studies of Re-Hydrogenation Reaction

\[
\text{NaAlH}_4 \leftrightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 \leftrightarrow \text{NaH} + \text{Al} + \frac{3}{2} \text{H}_2
\]

Elementary reaction steps (at surfaces)

1. Ti catalyzed \( \text{H}_2 \) dissociation on depleted material (Al)
2. Formation of mobile species & mass transport.
3. Solid state reaction & ordering.

\{ Relevant to new hydrides (Alane) \}

- Model system for atomic-level surface studies.
- Unprecedented level of interaction with theory.
Research Team

Nanoscale surface imaging
[P. Sutter, BNL]
- Scanning tunneling microscopy
  - atomic scale structure.
- Low-energy electron microscopy
  - surface dynamics & mass transport.

Ab-initio theory & modeling
[J.T. Muckerman, BNL]
- Density functional theory
  - atomic scale structure & energetics.
- Ab-initio molecular dynamics
  - surface dynamics.

Quantitative spectroscopy
[Y.J. Chabal, Rutgers]
- FT-infrared reflection spectroscopy
  - hydrogen containing adsorbates.
  - surface dynamics & mass transport.

Synchrotron & TEM techniques
[J. Graetz, E. Sutter, BNL]
- XRD, EXAFS
  - bulk synthesis, structure, bonding.
- Analytical electron microscopy
  - nanoscale structure & composition.
Activities & Findings

Significant findings to date:

1) Ti-catalyzed $H_2$ dissociation:
   - Local Ti environment similar to TiAl$_3$ with split Al shell at $\sim$2.8 Å (EXAFS).
   - Ti has reduced coordination - near-surface sites.
   - Ti atom pair complexes on Al(001) surfaces that spontaneously dissociate $H_2$ (DFT).
   - Key feature: nodal plane of surface/$H_2$ HOMO midway between Ti atoms.
   - Dissociated H-atoms cannot diffuse to all-Al site on flat Al(001).
   - Spectroscopic STM: Ti resides in near-surface sites & interacts with $H_2$.

2) Formation of mobile species (surface alanes):
   - Bulk materials: stoichiometric mixtures of NaH & AlH$_3$ react to NaAlH$_4$ (w/o Ti!).
   - Atomic-H on Al: clear IR signatures of ad-Al-H, AlH$_3$ & higher oligomers.
   - High Ti concentrations: alane formation inhibited $\rightarrow$ inactivation of Ti dopant.

3) Bulk materials:
   - “Elpasolite” mixed alkali alanates: $K_2LiAlH_6$, $K_2NaAlH_6$ reversible without Ti.
   - No cation mixing on the same site: No tuning of thermodynamics by substitution.
1) Ti-Catalyzed H₂ Dissociation - Predictions

Ti:Al complexes on Al(001): H₂ dissociation
(Density functional theory)

<table>
<thead>
<tr>
<th>Property</th>
<th>Model 3</th>
<th>Model 4</th>
<th>Model 4s</th>
<th>Model 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti Coverage</td>
<td>0.25 ML</td>
<td>0.25 ML</td>
<td>0.25 ML</td>
<td>0.5 ML</td>
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<tr>
<td>Site ΔGᵣ⁺ (eV)</td>
<td>3.13</td>
<td>2.08</td>
<td>1.65</td>
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<td>Eₐ (eV)</td>
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<td>0.00</td>
<td>0.26</td>
<td>1.62</td>
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<tr>
<td>Site ΔGᵣ+Eₐ</td>
<td>4.02</td>
<td>2.08</td>
<td>1.91</td>
<td>2.66</td>
</tr>
</tbody>
</table>

*Reference state: Stable (001) surface of TiAl₃ alloy.

Active sites: nodal symmetry of surface/H₂ HOMO. Other model sites: large activation barriers.

Ti/Al(111) Model System

Ti deposition on Al(111) - STM
Clean Al(111) 0.25 ML Ti/Al(111)

Rough steps
Monolayer islands

Ti distribution?
• In nucleated islands?
• Uniformly embedded?
• At surface?
• In sub-surface layers?

FOV: 80 nm.
Ti/Al(111) deposited at 400 K.
Ti/Al(111) Model System

Ti deposition on Al(111) - STM

$\Theta_{\text{Ti}}^{\text{nom}} = 0.05 \text{ ML}$  $\Theta_{\text{Ti}}^{\text{nom}} = 0.3 \text{ ML}$

Strong spectroscopic contrast, absent on Al(111). **Identification:** STM & DFT.

Randomly dispersed near-surface Ti.
Some clustering/ordering at higher coverage.

• H$_2$ dissociation on these sites?

FOV: 23 nm.
Ti/Al(111) deposited at 400 K.
2) Formation of Mobile Species - Surface Alanes

FT-IR Spectroscopy - atomic H/Al(111)

Hydride/alane related IR modes:

A - Terminal (ν_{H-T} = 1895 cm^{-1}): Ad-Al-H.

- Bridging (ν_{H-B} = 1500 cm^{-1} - 1800 cm^{-1}): higher alanes: Al_2H_6, Al_3H_9, etc.

S - Additional mode at low coverage: Ad-Al-H at step edges?*

Or: signature of small alanes?

Progressive formation of surface alanes.

Sample: Al(111) single crystal.
Atomic-H from W-filament; T = 90 K;
H_2 dose: 10 L to 720 L; about 1% atomic-H
Atomic-H on Al(111)

STM Imaging

- Pronounced *etching* of surface steps.
- Evolution of population of adsorbates: IR $\Rightarrow$ surface alanes.

*<1% atomic H
FOV: 120 nm
T = 300 K
Atomic-H on Al(111)

STM Imaging - Spectroscopic contrast

- Step etching.
- Evolution of surface alanines.

Spectroscopic identification: STM tip functionalization.

a - Clean W-tip.
b - Alane-“functionalized” tip.

FOV: 150 nm.
Sample: Al(111).
Atomic H: ~ 4 ML H, T = 200 K.
Atomic-H on Ti/Al(111)

\( \Theta_{\text{Ti}} = 0.05 \text{ ML} \)

Pronounced alane evolution.

\( \Theta_{\text{Ti}} = 0.25 \text{ ML} \)

No step etching.

No evolution of surface alanes.

But: New electronic signatures

\( 0.05 \text{ Å} \) ‘protrusions’.

High Ti coverages: near-surface Ti strongly binds Al.

\( \Rightarrow \textbf{Saturation effects} \) at high Ti concentrations.

\( \Rightarrow \textbf{Incomplete re-hydrogenation}: \) residual Ti-rich Al grains?

FOV: 20 nm
0.25 ML Ti/Al(111)
~ 4 ML H, T = 200 K.
Future Plans

Near Term Objectives:
1) Identify stable near-surface Ti:Al structures & active complexes for \( \text{H}_2 \) dissociation (Spectroscopic STM, DFT).
2) Quantify \( \text{H}_2 \) dissociation by Ti:Al (STM, IR, DFT).

Future Research - all based on strong interaction experiment-theory
3) Establish kinetics of alane formation (T-dependent STM, IR).
3) Compare & quantify Al and \((\text{AlH}_3)_x\) mass transport (real-time LEEM).
4) NaH/Al: Kinetics of re-hydrogenation to \( \text{Na}_3\text{AlH}_6 \) (LEEM).
5) Test concepts using bulk synthesis and characterization.

Fundamental understanding of Ti-catalyzed reversible hydrogen storage in sodium alanate.

Design rules for new reversible hydride materials.
BNL - Center for Functional Nanomaterials


Now accepting user proposals!
BNL - Center for Functional Nanomaterials

Nano-Patterning
John Warren
Chris Jacobsen, SBU

Theory & Computation
Jim Davenport

Proximal Probes
Peter Sutter

Electron Microscopy
Yimei Zhu

Ultra-fast Optical Sources
Alex Harris

NSLS Ron Pindak

Ultra-fast Optical Sources
Alex Harris

www.cfn.bnl.gov
BNL - National Synchrotron Light Source

X-ray & VUV beamlines - Examples:

- **X-ray absorption spectroscopy:**
  EXAFS, NEXAFS.
- **X-ray diffraction:**
  Powder, time-resolved, high-pressure.
- **X-ray microprobe**
- **IR micro-spectroscopy**
- **Surface microscopy & spectroscopy**
  Photoemission microscopy (PEEM).

[Diagram of X-ray absorption spectroscopy and diffraction]

[www.nsls.bnl.gov]