

# Catalytic Effect of Ti for Hydrogen Cycling in $\text{NaAlH}_4$

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Mei-Yin Chou  
School of Physics  
Georgia Institute of Technology  
(DE-FG02-05ER46229)

Acknowledgment: Yan Wang, Roland Stumpf

# Why is $\text{NaAlH}_4$ interesting?

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A viable candidate for hydrogen-storage material:

High theoretical weight-percent hydrogen content of 5.55% and low cost

But (before 1997)

Dehydrogenation occurs at high temperature; rehydrogenation is difficult.

Bogdanovic and Schwickardi, 1997

Hydrogen can be reversibly absorbed and desorbed from  $\text{NaAlH}_4$  under moderate conditions by the addition of **catalysts** (compounds containing Ti, Zr, *etc.*)

# High Hydrogen Contents in Complex Hydrides

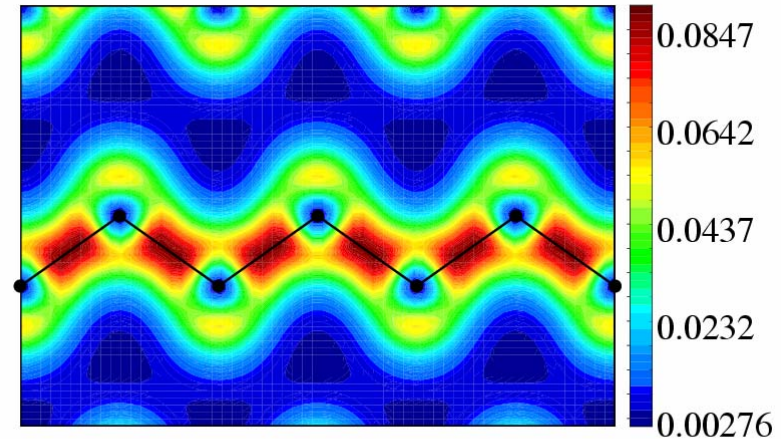
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Hydride	wt%	Hydride	wt%
$\text{Be}(\text{BH}_4)_2$	20.8	$\text{Mg}(\text{AlH}_4)_2$	9.3
$\text{LiBH}_4$	18.2	$\text{Ca}(\text{AlH}_4)_2$	7.9
$\text{Mg}(\text{BH}_4)_2$	14.9	$\text{KBH}_4$	7.5
$\text{Ca}(\text{BH}_4)_2$	11.6	$\text{NaAlH}_4$	7.5
$\text{NaBH}_4$	10.7	$\text{Ga}(\text{AlH}_4)_3$	7.4
$\text{LiAlH}_4$	10.6	$\text{Mg}_2\text{FeH}_6$	5.5

# First-Principles Studies of Materials Properties

State-of-the-Art Simulation Methods:

- **Density Functional Theory**
- **Many-Body Perturbation Theory**
- **Quantum Monte Carlo Methods**



Electron density in Si crystal

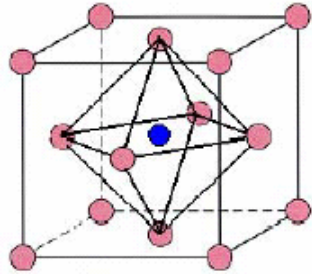
From the total energy as a function of atomic positions, one gets

- phase stability (lowest-energy atomic configurations)
- mechanical/elastic properties
- interatomic forces → phonons, *ab initio* molecular dynamics
- combined with other theories, e.g., calculating transition temperature

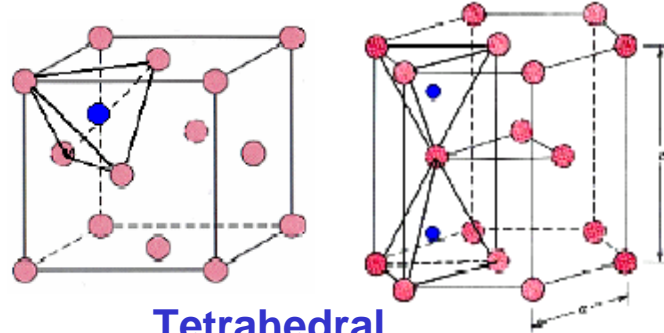
*Systems: solids, surfaces, molecules, clusters, nanostructures*

# Where is hydrogen in metal hydrides?

Transition metals: interstitial sites

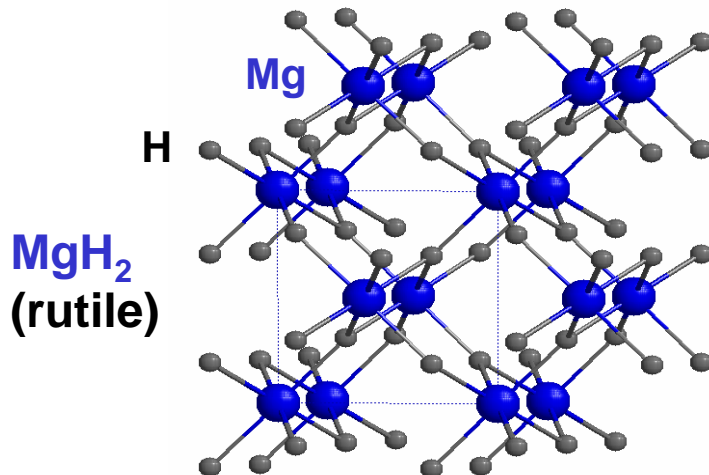


Octahedral



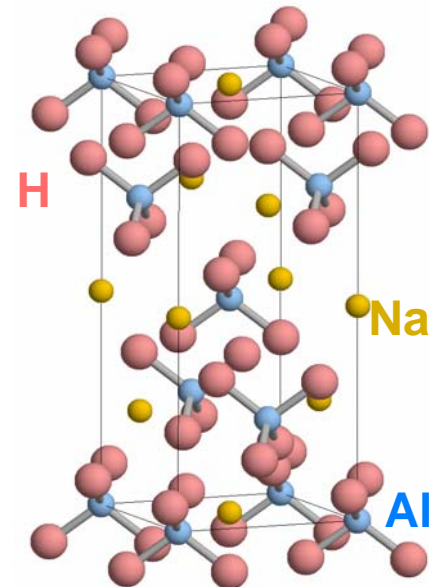
Tetrahedral

Alkalis and alkaline-earths:  
new structures



MgH<sub>2</sub>  
(rutile)

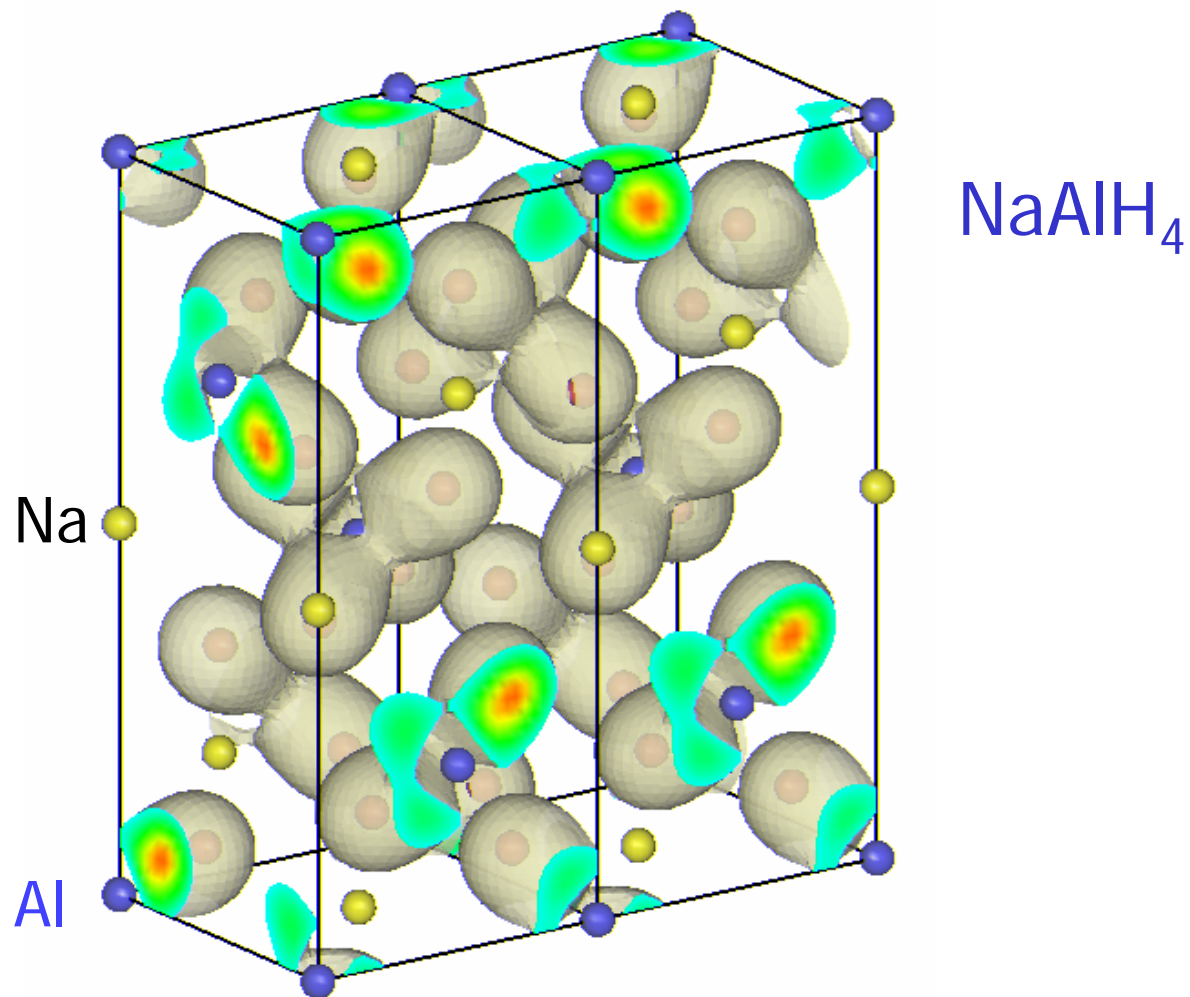
Complex metal hydrides



NaAlH<sub>4</sub>

Na<sup>+</sup>(AlH<sub>4</sub>)<sup>-</sup>

# Density Isosurface ( $0.25 \text{ \AA}^{-3}$ )



# Decomposition and Reformation of $\text{NaAlH}_4$

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## Improved kinetics with catalysts



1 atm / 33°C      3.71 wt. %  $\text{H}_2$

$\Delta H = 37 \text{ KJ/mol}$ ; activation energy = 79.5 KJ/mol



1 atm / 126°C      1.85 wt. %  $\text{H}_2$

$\Delta H = 47 \text{ KJ/mol}$ ; activation energy = 97 KJ/mol

## Possible Roles of the Catalyst (e.g., Ti)

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- The catalyst enters the bulk and stimulates phase separation and crystal growth. (Need to check the energetics.)

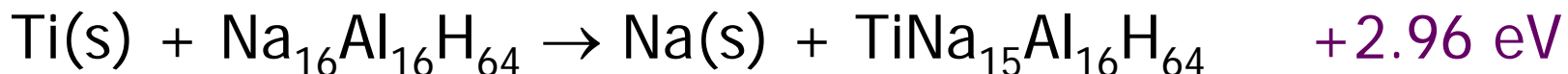
OR

- The catalyst does not enter the bulk, but acts as a hydrogen dissociation-recombination site near the surface. Possibly also helps the nucleation of Al phase. (Need to identify the mobile species.)

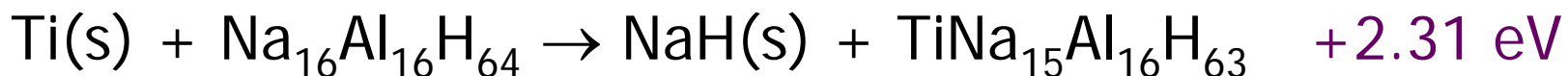


## 2x2x2 supercell calculations of reaction energies:

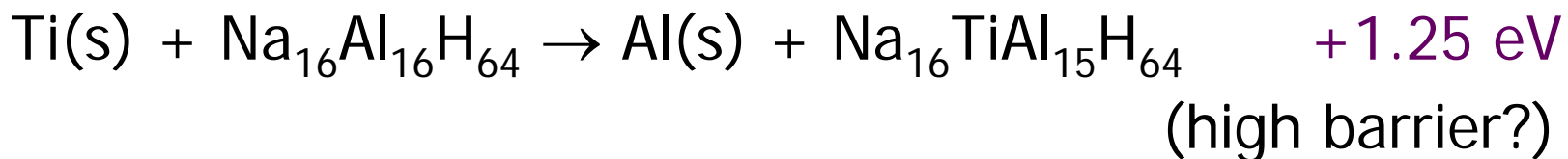
Ti replacing Na:



Ti replacing Na and Na coming out with one H:



Ti replacing Al:

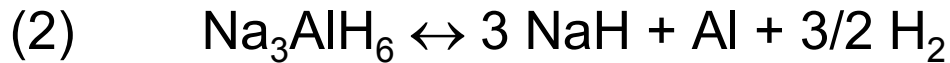
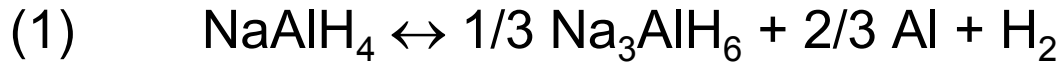


Interstitial Ti:



# Long-range diffusion of Al

*K. J. Gross et al. J. Alloys Compds. 297, 270 (2000).*



With catalysts, Eqs. (1) and (2) are rapid solid-state reactions and one expects to get a homogeneous mixture composed of extremely small grains of each phase. However, the in-situ diffraction experiments showed narrow peaks corresponding to relatively large crystallites ( $> 100 \text{ nm}$ ). Therefore, there must be some long-range mechanism transporting Al over a long distance ( $\sim 1000 \text{ \AA}$ ). We expect a different dehydrogenation mechanism in the alanate than in traditional interstitial metal hydrides (namely, not hydrogen diffusion alone). A possible mobile species containing both Al and H is  $\text{AlH}_3$ .

# Possible Roles of the Catalyst (e.g., Ti)

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Observation: Dehydrogenation process involves long-range diffusion of metal species to generate segregated NaH and Al phases.

- The catalyst enters the bulk and stimulates phase separation and crystal growth. (Need to check the energetics.)

OR

- The catalyst does not enter the bulk, but acts as a hydrogen dissociation-recombination site near the surface. Possibly also helps the nucleation of Al phase. (Need to identify the mobile species.)

# Decomposition and Reformation of $\text{NaAlH}_4$

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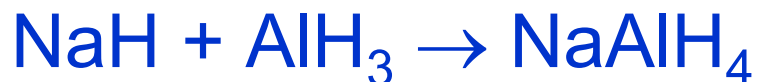
$\Delta H = 37 \text{ KJ/mol}$ ; activation energy = 79.5 KJ/mol



1 atm / 126°C      1.85 wt. %  $\text{H}_2$

$\Delta H = 47 \text{ KJ/mol}$ ; activation energy = 97 KJ/mol

## Synthesis of $\text{NaAlH}_4$ from $\text{AlH}_3$ without a Catalyst



*A. E. Finholt et al., J. Inorg. Nucl. Chem. 1, 317 (1955);  
S. Chaudhuri et al., J. Am. Chem. Soc. 128, 11404 (2006).*



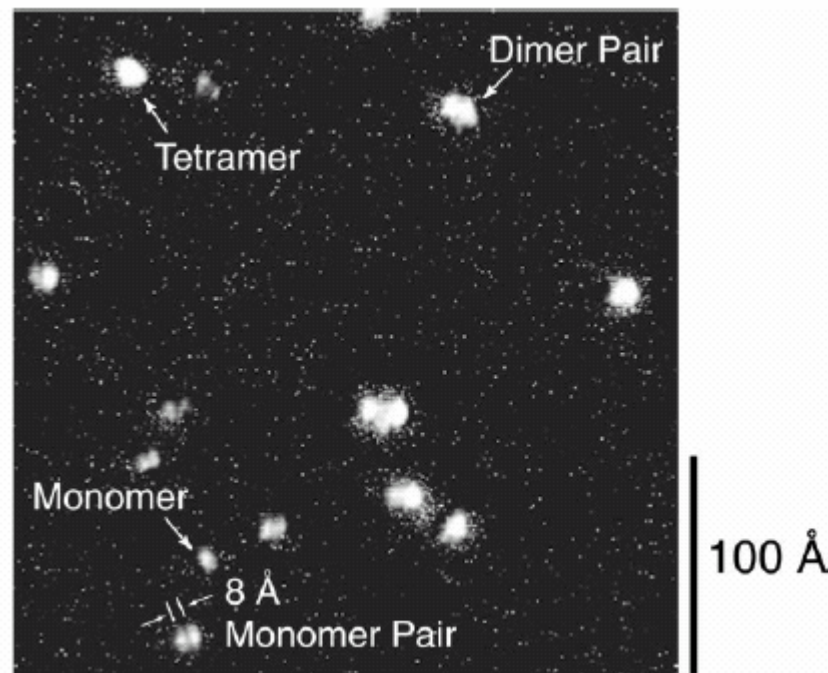
*M. Mamula et al., Coll. Czechoslov. Chem. Commun. 32, 884 (1967).*

# Atomic Hydrogen Interacting with Al Surfaces

*“H adsorption and the formation of alane oligomers on Al(111)”*

*E. P. Go, K. Thuermer, and J. E. Reutt-Robey, Surf. Sci. 437, 377 (1999).*

Complementary scanning tunneling microscopy (STM) and surface infrared (IR) measurements show that H reacts strongly with Al(111), producing a variety of new alane (aluminum hydride) surface species. Alane oligomers, ranging in size from the monomer to 30-mers, form through a sequence of surface etching and condensation reactions.



H extracts aluminium atoms directly from the surface (H etching), forming alane oligomers.

Does Ti affect the decomposition of AlH<sub>3</sub>? YES!!

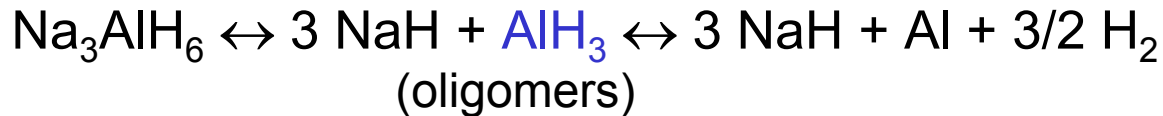
Different decay products of alanes at room temperature:

E. Wiberg and R. Uson, Zeitschrift Naturforschung 6b, 392 (1951).

*“The decay of the metastable aluminium hydride at room temperature happens under the catalytic influence of the finely distributed titanium.”*



## Proposed Mechanism for Catalyst-Assisted Decomposition and Rehydrogenation of $\text{NaAlH}_4$



The catalyst does not enter the bulk (energetically unfavorable), but acts as a hydrogen dissociation-recombination site near the surface.

**Dehydrogenation:** The catalyst kinetically facilitates the release and decomposition of  $\text{AlH}_3$  from solid-state alanates.

**Hydrogenation:** The catalyst helps the absorption of hydrogen and formation of  $\text{AlH}_3$  on Al surfaces.



## EXAFS Results of Ti-Activated $\text{NaAlH}_4$

The Ti atom is located on or near the surface surrounded by metallic Al. There is no long-range order, but **probably with a local tetragonal symmetry similar to that of  $\text{TiAl}_3$** . The environment does not change with hydrogenation-dehydrogenation cycles.

The activity of Ti decreases as more crystalline  $\text{TiAl}_3$  is formed.

*J. Graetz et al., Appl. Phys. Lett. 85, 500 (2004);*

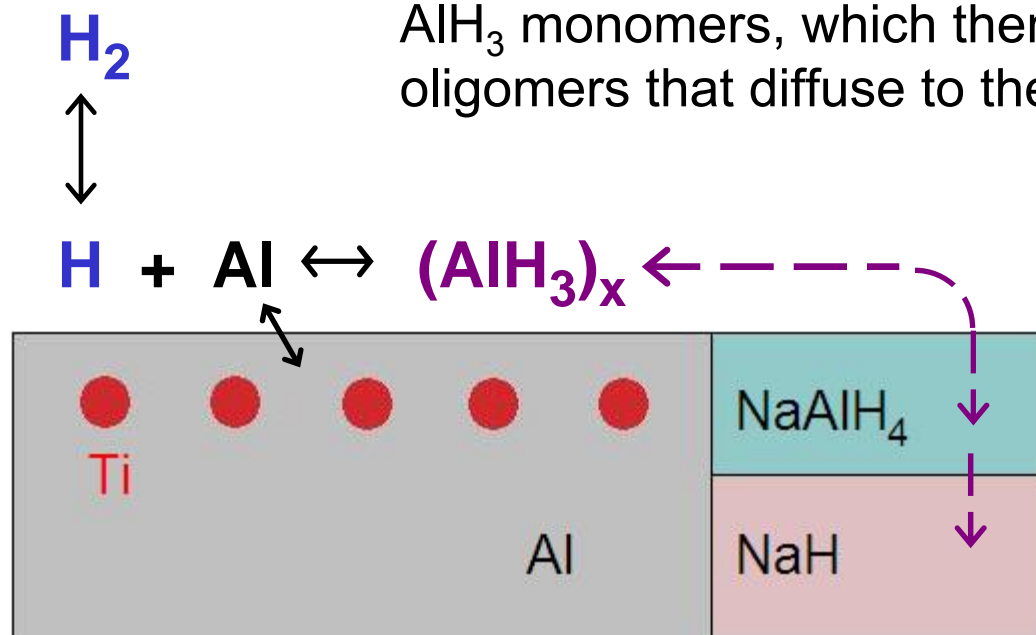
*S. Chaudhuri et al., J. Am. Chem. Soc 128, 11404 (2006);*

*C. P. Balde et al., J. Phys. Chem. C 111, 2797 (2007).*

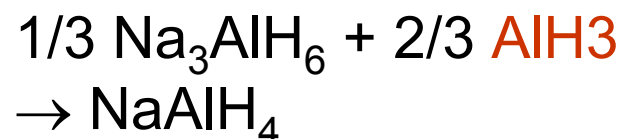
# Proposed Mechanism for Catalyst-Assisted Decomposition and Rehydrogenation of NaAlH<sub>4</sub>

**Dehydrogenation:** The catalyst kinetically facilitates the release and decomposition of AlH<sub>3</sub> from solid-state alanates.

**Hydrogenation:** The subsurface Ti helps the adsorption of hydrogen on the Al surface. Atomic hydrogen extracts Al atoms directly from the surface (H etching) to create mobile AlH<sub>3</sub> monomers, which then condense into mobile alane oligomers that diffuse to the NaH region.



Locally,



Consider the hydrogenation process first

**Does Ti affect  $H_2$  dissociation on Al surface?**

**YES (from DFT calculations)**

- $H_2$  dissociation on a clean Al surface:

Not energetically favorable

- $H_2$  dissociation on a Ti-modified Al surface:

Energy of H(ad) is lowered by a few tenths of eV

# Subsurface Ti enhances H binding on the surface

(a)

(b)

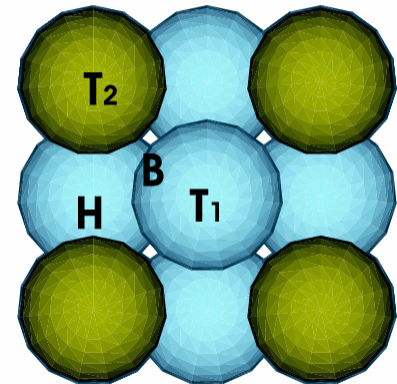
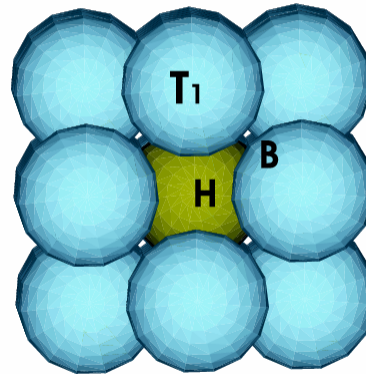
H positions

T<sub>1</sub> : on top of Al

B : bridge

H : hollow

T<sub>2</sub> : on top of Ti



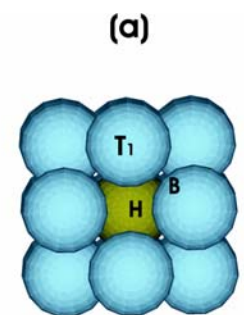
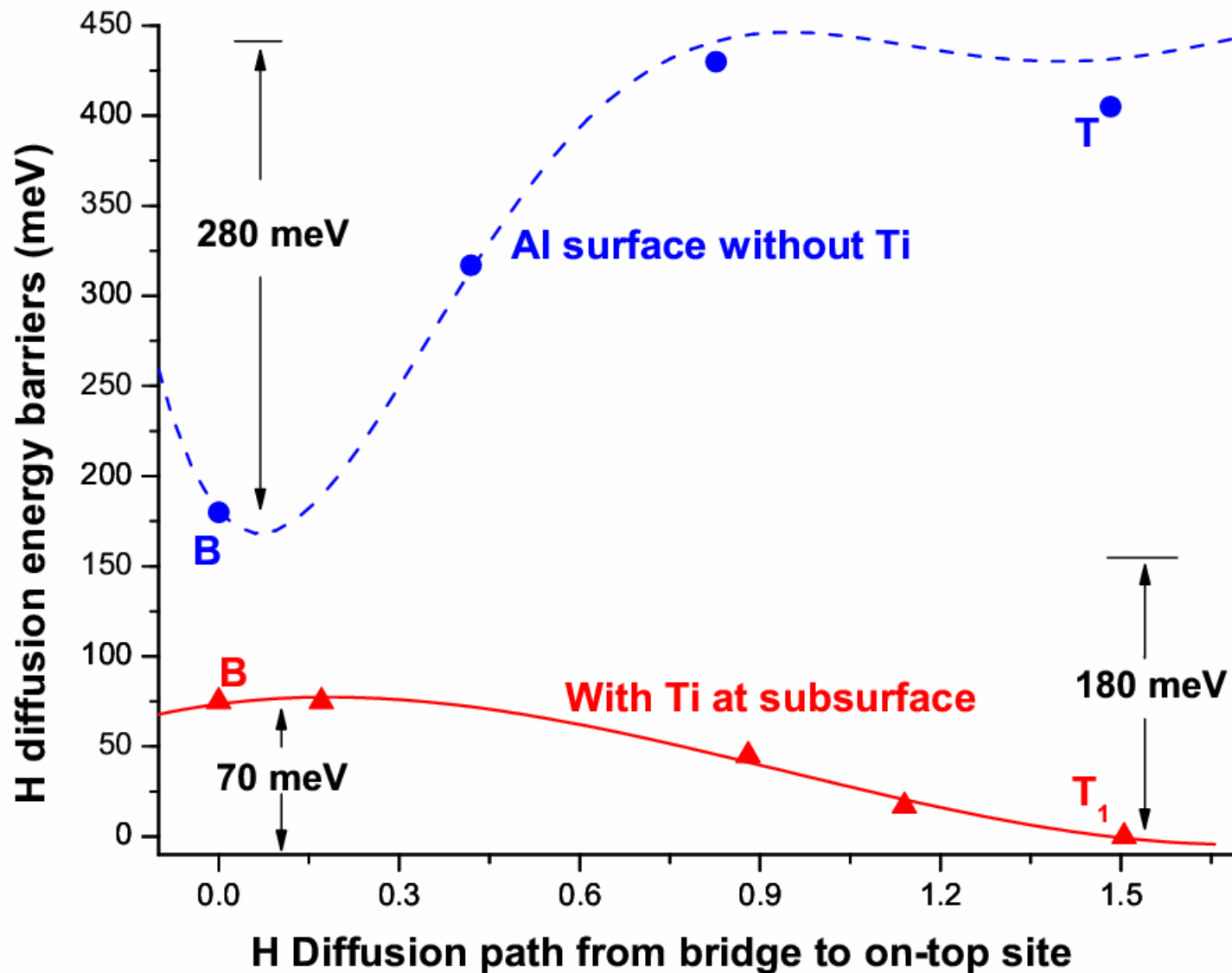
$$E_{\text{ads}}(\text{H}) = E(\text{slab}+\text{H}) - E(\text{slab}) - 1/2 E(\text{H}_2)$$

( eV/surface cell)

Energy of H(ad) is lowered by a few tenths of eV.

	(a)	(b)	Al(001)
T <sub>1</sub>	-0.06	1.50	0.35
B	0.01	0.85	0.12
H	0.59	0.71	0.52
T <sub>2</sub>		1.81	

# Subsurface Ti improves H mobility on the surface



# Effect of Subsurface Ti on Hydrogen Interaction on the Al(100) Surface

## Main Results:

- Ti near the Al surface occupies subsurface sites (no activation center on the surface)
- Subsurface Ti reduces the H<sub>2</sub> dissociation energy barrier by  $\sim 0.6$  eV.
- Subsurface Ti enhances H binding on the surface. (Energy of H(ad) is lowered by a few tenths of eV.)
- Subsurface Ti improves H mobility on the surface.

(STM expt.-- Atomic H extracts Al atoms directly from the surface forming alane oligomers.)

## Future Work

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- Further study of the near-surface alloying effect for other catalysts  
(Is the effect the same as Ti?)