

Catalytic Effect of Ti for Hydrogen Cycling in NaAlH₄

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Acknowledgment: Yan Wang, Roland Stumpf

Why is NaAlH_4 interesting?

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 NaAlH_4 under moderate conditions by the addition of **catalysts** (compounds containing Ti, Zr, *etc.*)

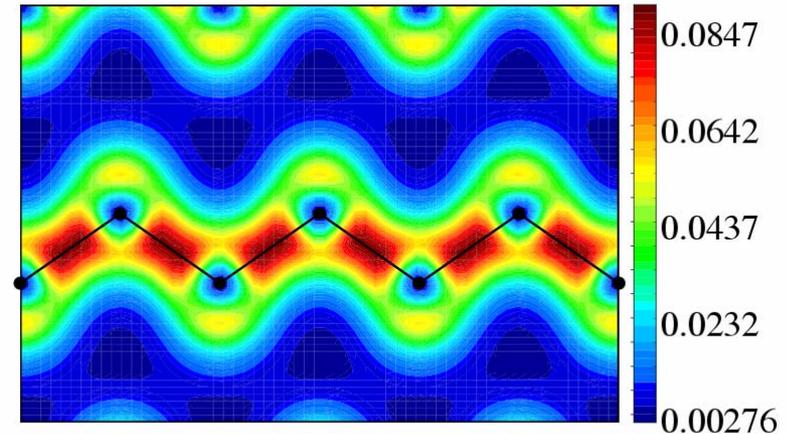
High Hydrogen Contents in Complex Hydrides

Hydride	wt%	Hydride	wt%
$\text{Be}(\text{BH}_4)_2$	20.8	$\text{Mg}(\text{AlH}_4)_2$	9.3
LiBH_4	18.2	$\text{Ca}(\text{AlH}_4)_2$	7.9
$\text{Mg}(\text{BH}_4)_2$	14.9	KBH_4	7.5
$\text{Ca}(\text{BH}_4)_2$	11.6	NaAlH_4	7.5
NaBH_4	10.7	$\text{Ga}(\text{AlH}_4)_3$	7.4
LiAlH_4	10.6	Mg_2FeH_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

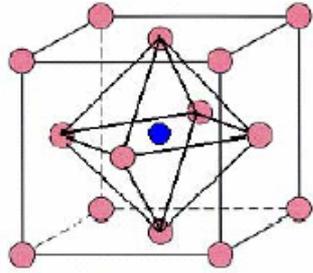
From the total energy as a function of atomic positions, one gets

- 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

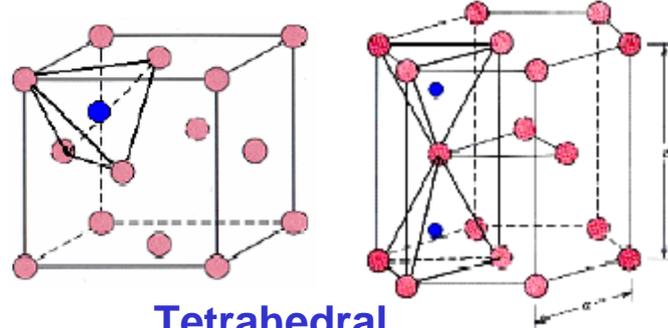
Systems: solids, surfaces, molecules, clusters, nanostructures

Where is hydrogen in metal hydrides?

Transition metals: interstitial sites



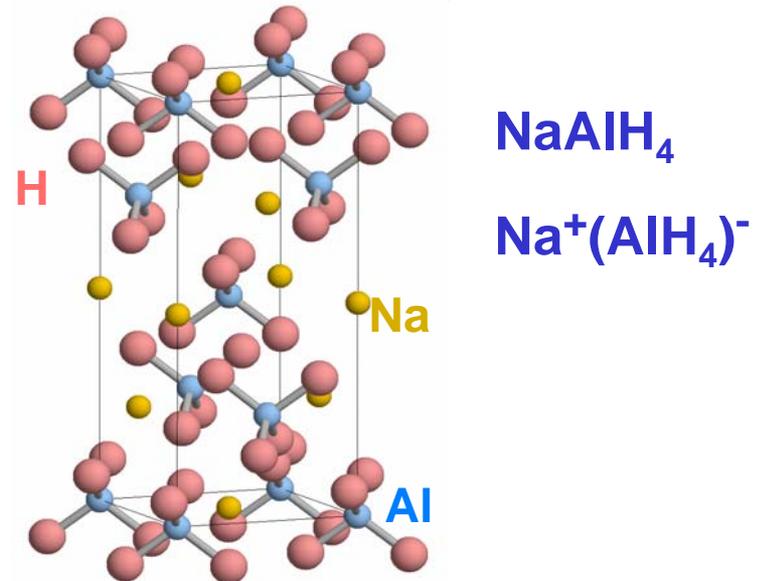
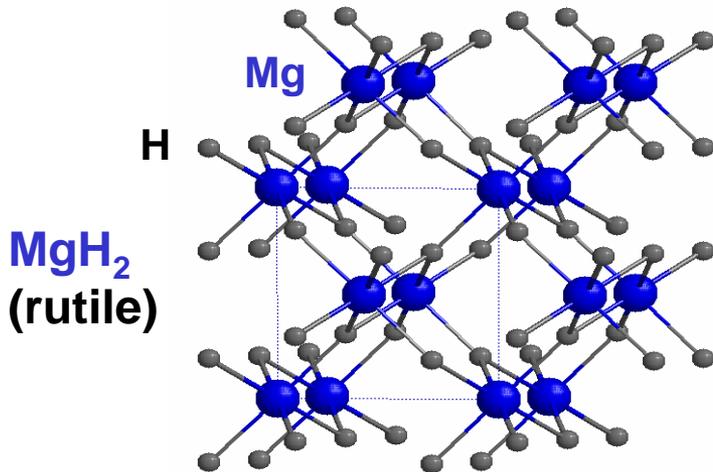
Octahedral



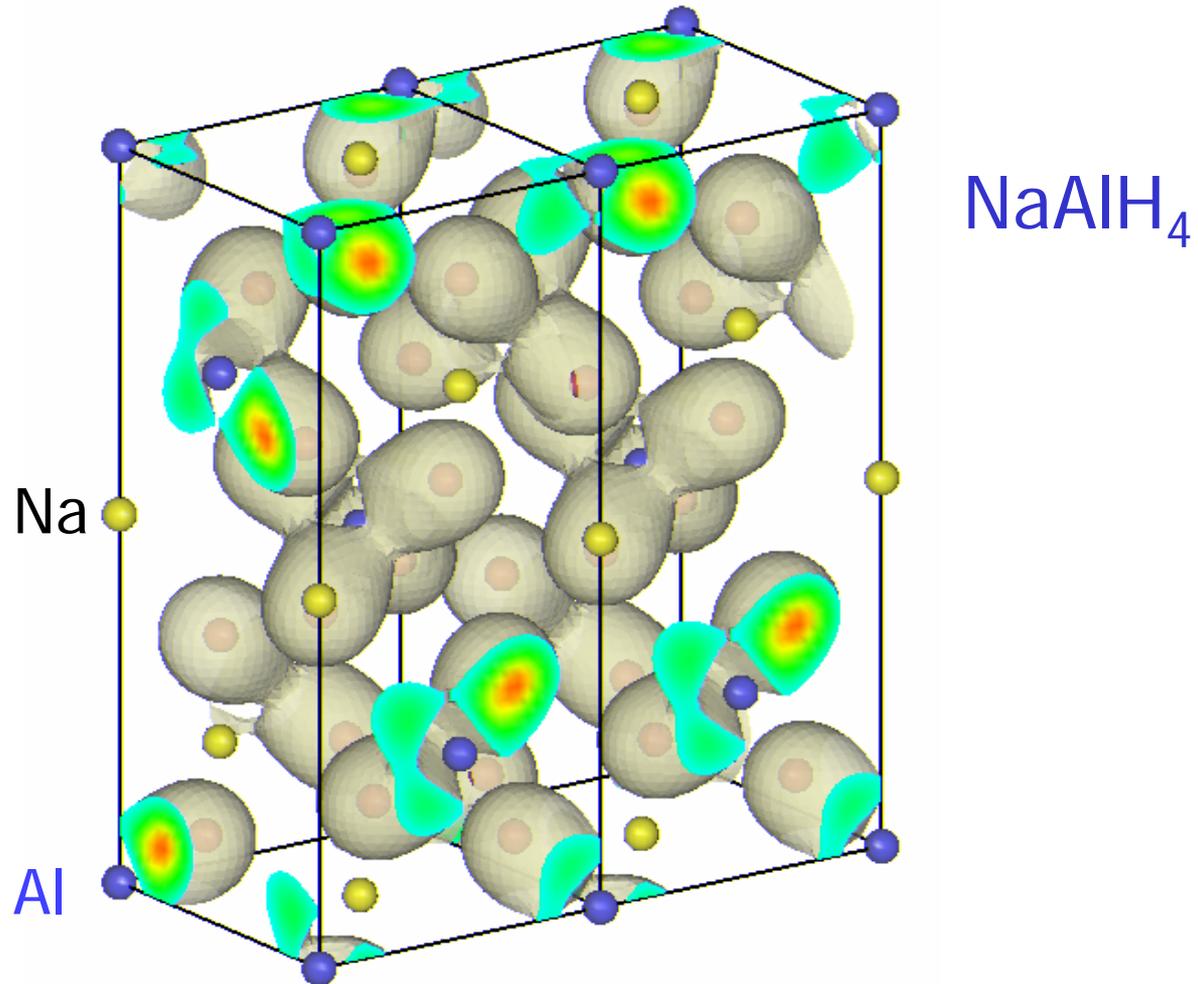
Tetrahedral

Alkalis and alkaline-earths:
new structures

Complex metal hydrides



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



Decomposition and Reformation of NaAlH₄

Improved kinetics with catalysts



1 atm / 33°C 3.71 wt. % H₂

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



1 atm / 126°C 1.85 wt. % H₂

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

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

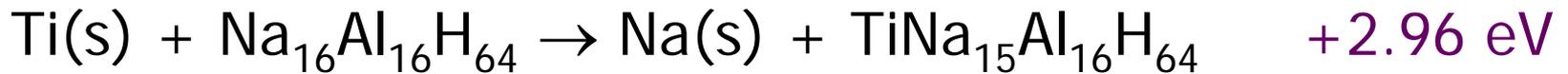
- The catalyst enters the bulk and stimulates phase separation and crystal growth. (Need to check the energetics.)

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:

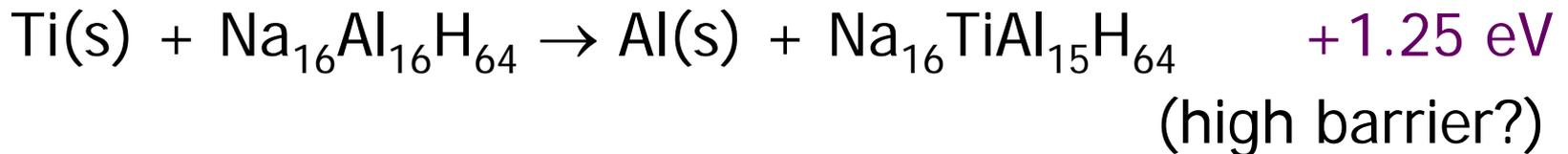
Ti replacing Na:



Ti replacing Na and Na coming out with one H:



Ti replacing Al:

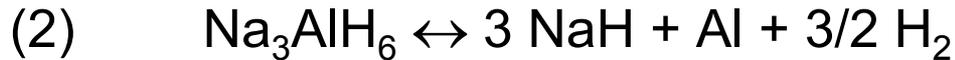


Interstitial Ti:



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 AlH_3 .

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

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 NaAlH₄

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Synthesis of NaAlH₄ from AlH₃ 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).*



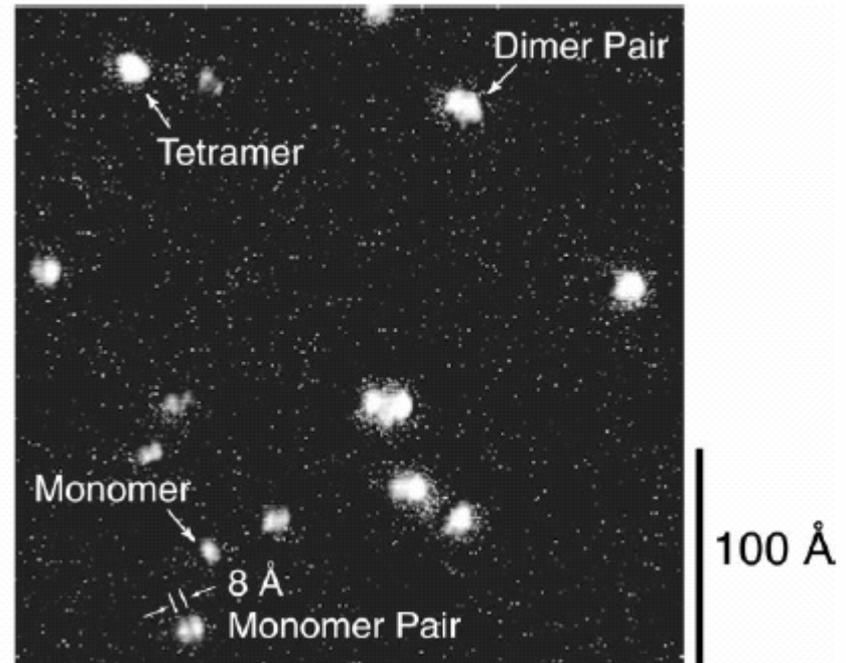
M. Mamula et al., Coll. Czechoslov. Chem. Commun. 32, 884 (1967).

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_3 ? **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 NaAlH₄



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 AlH₃ from solid-state alanates.

Hydrogenation: The catalyst helps the absorption of hydrogen and formation of AlH₃ on Al surfaces.

EXAFS Results of Ti-Activated 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 TiAl_3** . The environment does not change with hydrogenation-dehydrogenation cycles.

The activity of Ti decreases as more crystalline TiAl_3 is formed.

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

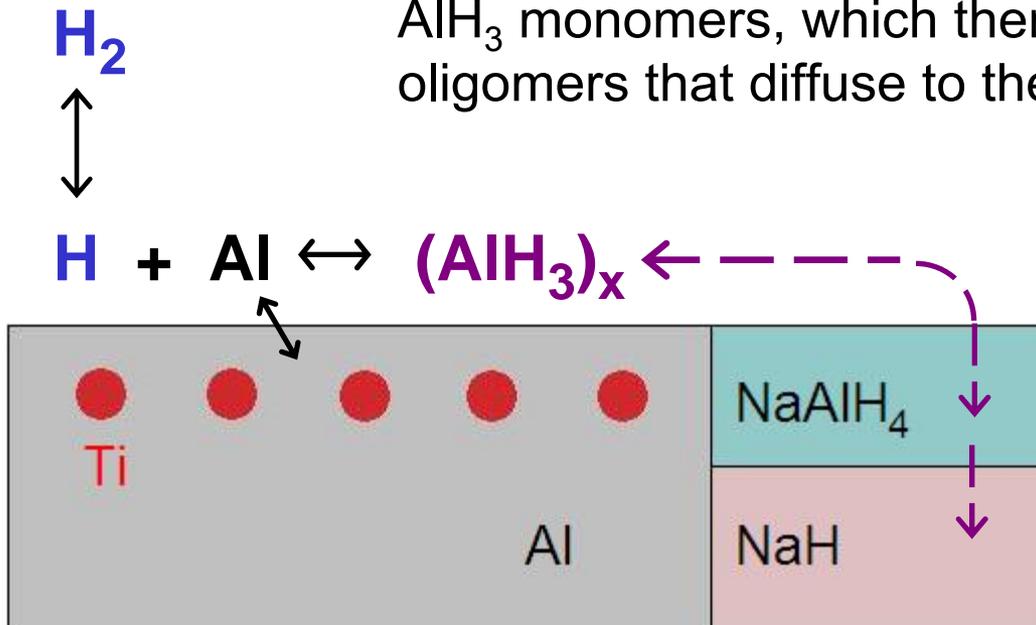
S. Chaudhuri et al., J. Am. Chem. Soc 128, 11404 (2006);

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

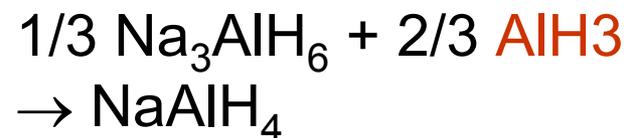
Proposed Mechanism for Catalyst-Assisted Decomposition and Rehydrogenation of NaAlH₄

Dehydrogenation: The catalyst kinetically facilitates the release and decomposition of AlH₃ 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 AlH₃ monomers, which then condense into mobile alane oligomers that diffuse to the NaH region.



Locally,



Consider the hydrogenation process first

Does Ti affect H₂ dissociation on Al surface?

YES (from DFT calculations)

- H₂ dissociation on a clean Al surface:

Not energetically favorable

- H₂ 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

H positions

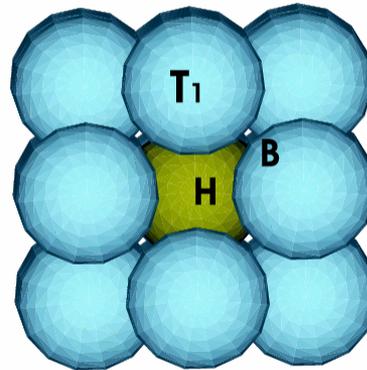
T₁ : on top of Al

B : bridge

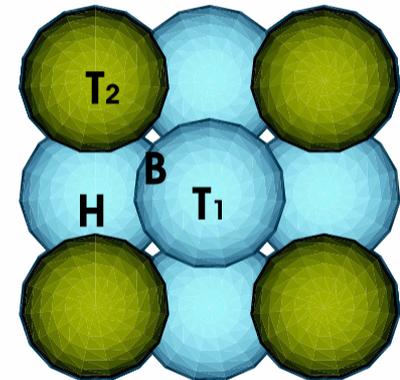
H : hollow

T₂ : on top of Ti

(a)



(b)



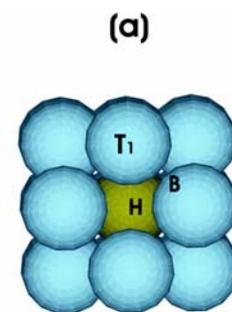
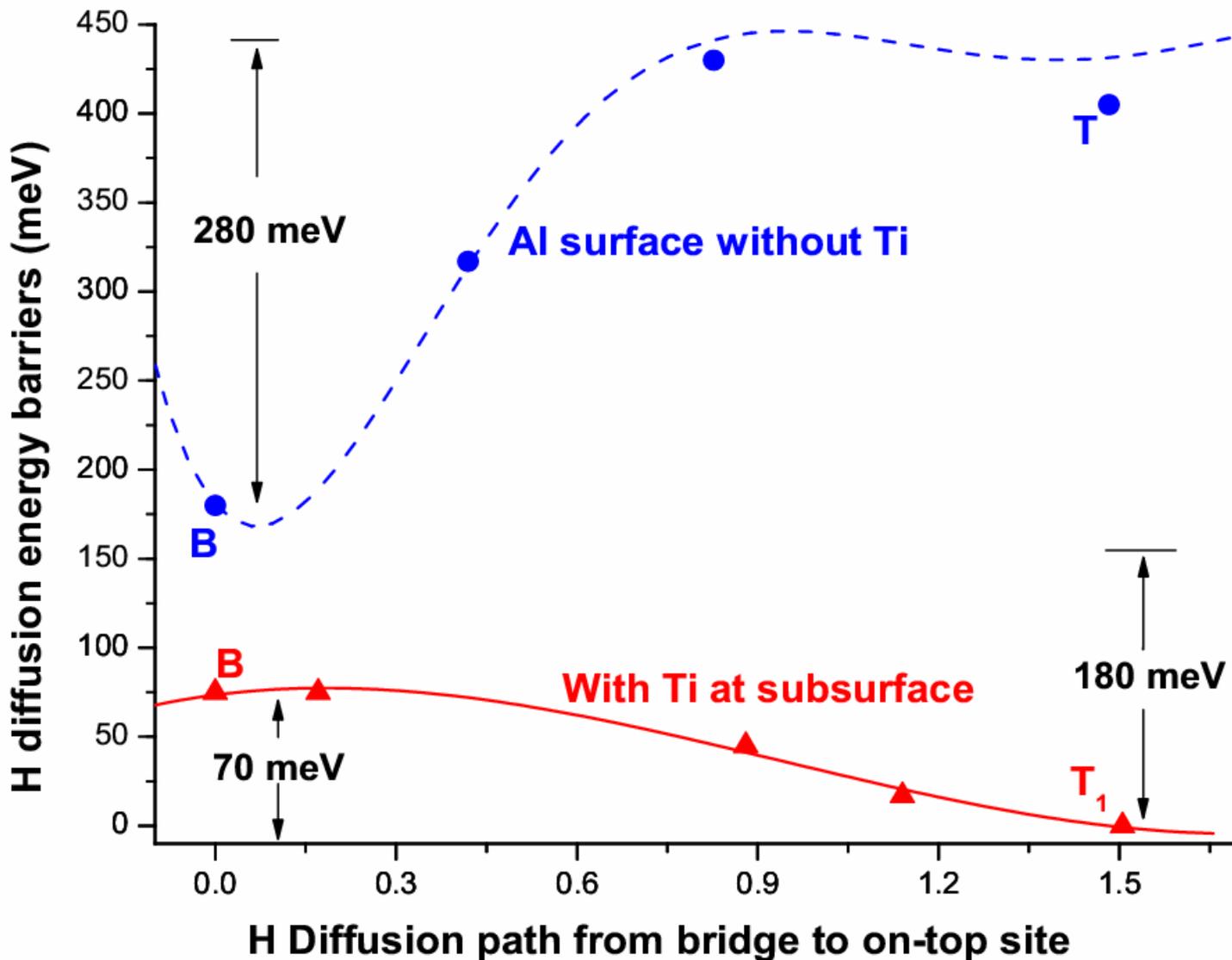
$$E_{\text{ads}}(\text{H}) = E(\text{slab}+\text{H}) - E(\text{slab}) - 1/2 E(\text{H}_2)$$

(eV/surface cell)

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

	(a)	(b)	Al(001)
T ₁	-0.06	1.50	0.35
B	0.01	0.85	0.12
H	0.59	0.71	0.52
T ₂		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 H₂ dissociation energy barrier by ~ 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

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