



Reversible Hydrogen Storage Materials – Structure, Chemistry, and Electronic Structure

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University of Illinois and Ames Laboratory

9 - 13 May 2011

Project ID # ST035

Overview



Timeline

- Project start date
 - March 2005
- Project end date
 - February 2011
 - **No cost extension granted**
- Percent complete 95%

Budget

Total Budget - \$1,278,396

(DOE Share)

- \$ 318,350 (C/S)

DOE Funds Received - \$1,278,386

Fully funded at this time with \$193,396
obligated in FY11

Barriers

- Issues addressed
 - A: Understanding chemical response to hydrogen
 - B: Understanding system weight and particle packing
 - C: Theory support to address critical issues blocking experimental progress.

Partners

- University of Pittsburg, Georgia Tech and University of Hawaii
- University of Missouri
- Ames Laboratory.

Objectives/Relevance



- Illinois' / Ames Lab main purpose within the MHCoE is
 - Advance the understanding of the microstructural and modeling characteristics of complex hydrides, helping with selection and down-selection.
 - Provide more reliable theoretical methods to assess H-storage materials, including key issues affecting materials under study.
 - Help identify down-selects, via experimental and theoretical characterization.
 - Provide characterization expertise to other critical DoE programs, as suggested by Program Officers.
- Some Illinois / Ames Lab recent impacts
 - Improved 3-D reconstruction/visualization to assess dispersion of particles in scaffold.
 - In MgH_2 , AlH_3 and MOFs, completed understanding dispersion of materials.
 - In MgH_2 , surfaces and NPs have similar H-dissociation energies (no size effects).
 - In MgH_2 , Calculated kinetic barriers with TM catalyst, showed importance of changes to TM moments during H desorption. Developed approximate method to calculated barriers with changing magnetization along pathways.
 - On Al(111), showed AlH_3 formation is vacancy mediated – TM catalyst aids in H_2 dissociation but does not replace the role of vacancies. Explained STM images and the efficacy of ball-milling.
 - Careful, systematic study of surface Alane formation via DFT methods.

Plan & Approach



95 %
complete

- Task 1: Experimental investigation of MHCoe partner materials

- Investigate and model microstructural and chemical changes in hydrogen storage materials.

95 %
complete

- Task 2: Incorporation and development of new models

- Development of new theoretical models to enhance explanation of and to guide experimental effort.



DFT Simulations for Discover and Characterization

Kinetic Barriers for H-Disassociation
on Ti-doped Rutile $\text{MgH}_2(110)$

&

Defect-mediated Alane formation
on Ti-doped $\text{Al}(111)$

Background on (un)doped Rutile MgH₂: Thermodynamics and Kinetics Barriers

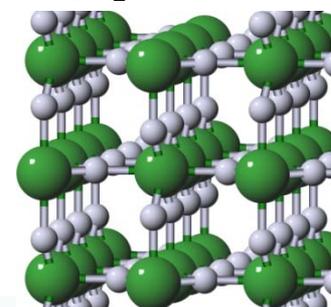


Thermodynamics

Kinetics

7.6 wt%	ΔH (kJ/mol-H ₂)	T _{des} (°C)	E _a (kJ/mol)
Expt.	68	300	160 ~ 250
DFT-PW91	53	180	

MgH₂ Rutile



Background

- **Processes involved are** H₂ surface desorption, H bulk diffusion, phase nucleation (Mg) and interface velocity.

G. Barkhordarian et al. *J. Alloys Compd.* 407, 249 (2006)

- **Barrier for H₂ desorption** is 1.78 eV, for H diffusion 0.7 eV

Theory: A. J. Du et al. *J. Phys. Chem. C* 111, 8360 (2007)

Our Findings

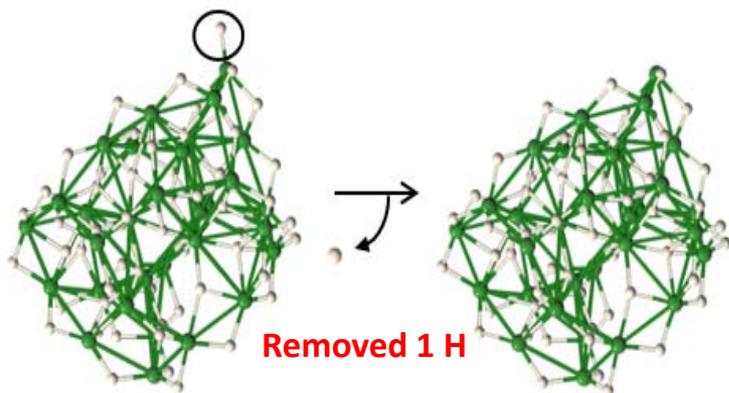
- **Thermodynamics** – DFT results show **NO SIZE Effect** for H-dissociation in Nanoparticles vs. Bulk Surfaces, but **there is a Ti DOPANT Effect**.
- **Step-Edge environments are more favorable dissociation sites.**
- **Kinetics** – **Single surface Ti dopant lowers H₂ desorption barrier by 0.4 eV.**
- **Concerted desorption and diffusion motion of H reduces barrier.**
- *Magnetic degrees of freedom* must be better considered in applying the nudged elastic band (NEB) method to avoid local minima.

Step-Edge H Sites on MgH₂(110) are Most Favored

No Size Effect on Thermodynamics

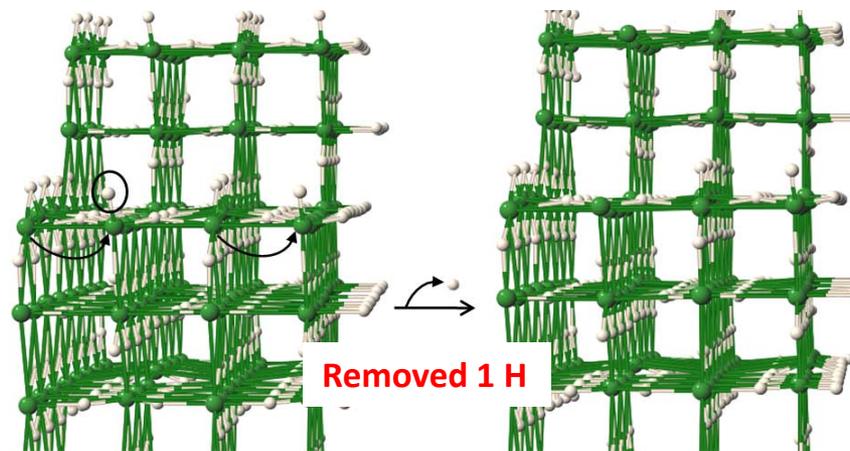


Mg₃₁H₆₂ amorphous nanoparticle
H bonded to 1 Mg atom



NP Dissociation Energy
148 kJ(mol-H₂)⁻¹

Bulk MgH₂(110) Surface with (001) Steps
H bonded to 1 Mg step-edge atom

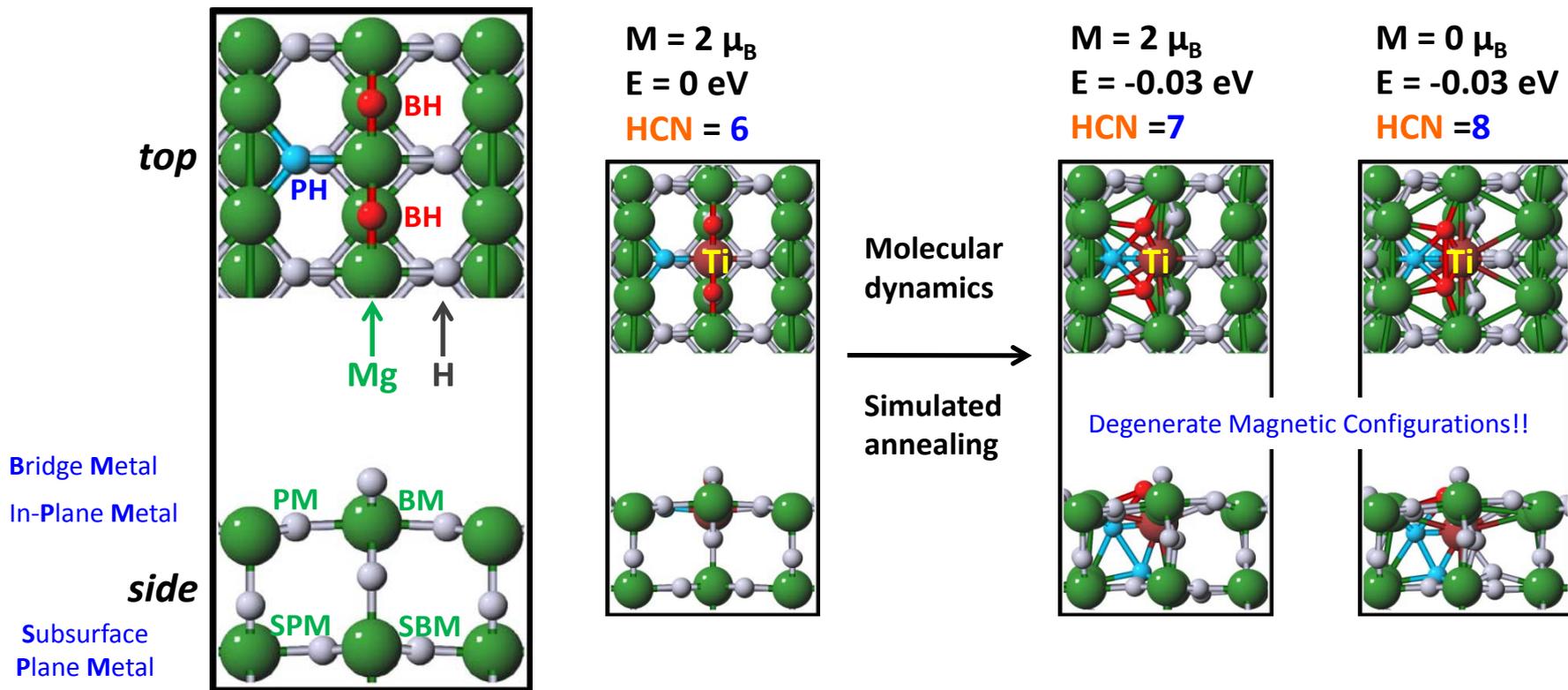


Step-Edge Dissociation Energy
140 kJ(mol-H₂)⁻¹

From DFT desorption energies, we find **NO SIZE EFFECTS** on enthalpies:

- Desorption energies are similar from singly-bonded H in NP and bulk surface step-edge.
- **Surface step edges have the more favorable desorption site for MgH₂(110).**
- Ti-doping in NP or bulk surface site decreases desorption (not shown), as observed.
- Enthalpy of full H removal energy is 54 kJ(mol-H₂)⁻¹, where observed is 68 kJ(mol-H₂)⁻¹.

For Kinetic Barriers need starting configuration for desorption on Bulk MgH₂(110) with(out) Ti Dopant



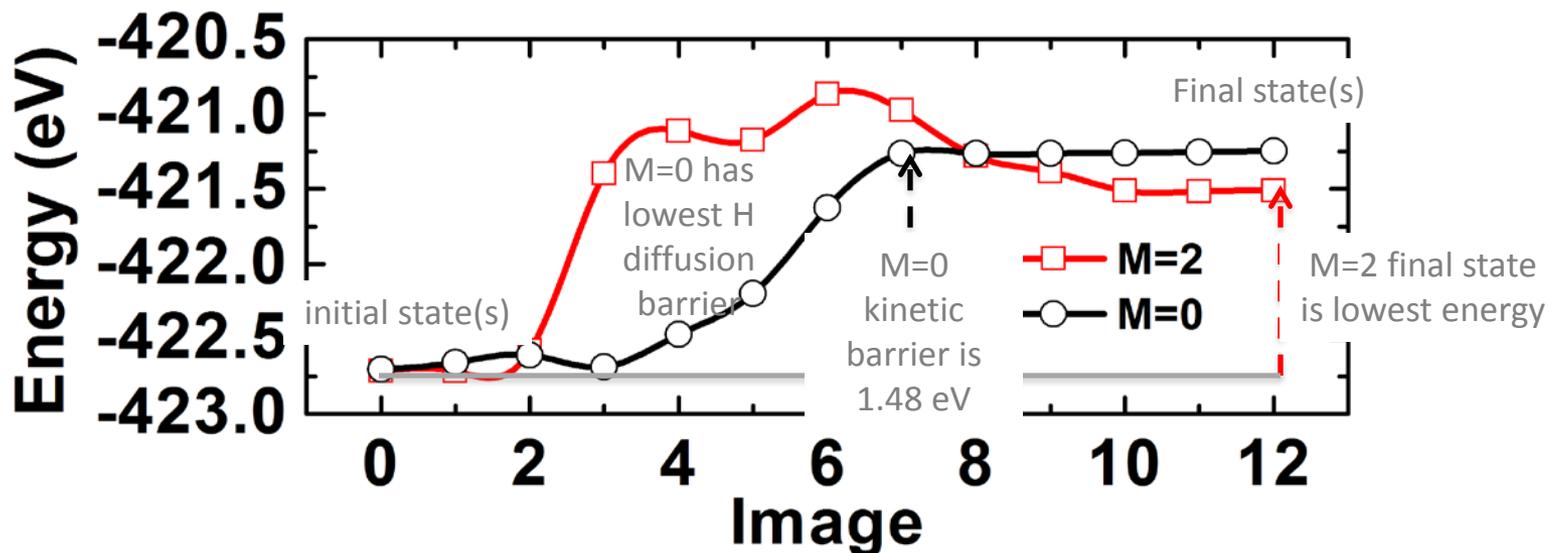
- Two major types of H sites: **bridge H (BH)** and **in-plane H (PH)**.
- Ti prefers surface Mg (**BM**) under two **BHs** and *Ti has competing magnetic states.*
- Reconstruction lowers energy for Ti with higher **H coordination number (HCN)**, two **BHs** in 3-fold hollow site; one **PH** relax inward; bonding to second layer H.

Magnetism along Desorption Pathway in MgH₂(110)



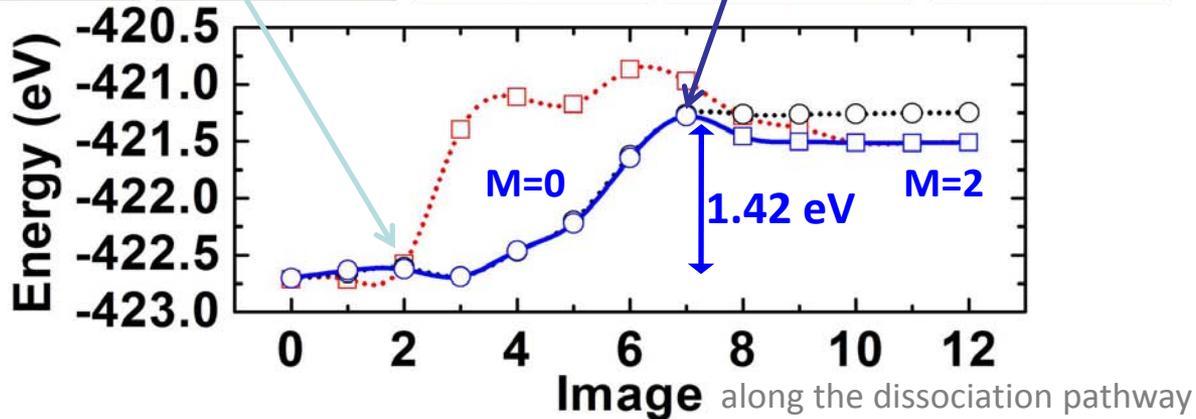
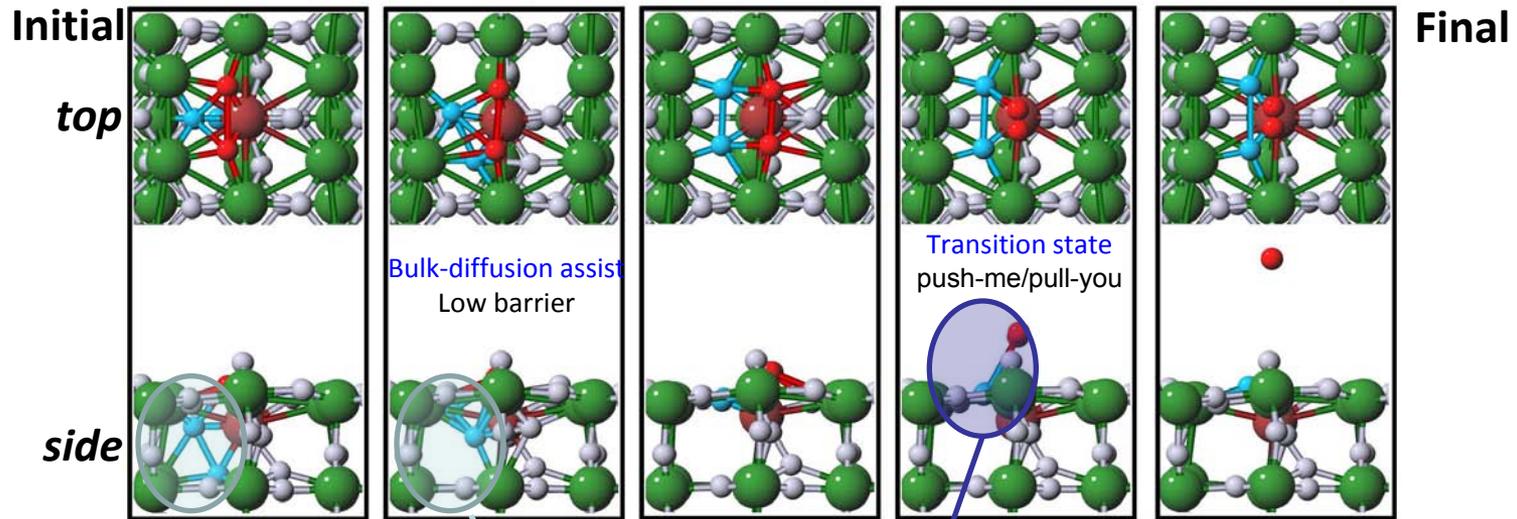
ISSUE: Nudge-Elastic Band (NEB as currently available) does not include coupling to all possible magnetic states (only local minima).

DFT-NEB (VASP) **Desorption Pathway starting with M=0 or 2 μ_B states.**



- **INITIAL (adsorbed) STATE:** Both $M = 0$ and $2 \mu_B$ states are degenerate!
- **FINAL (desorbed) STATE:** $M = 2 \mu_B$ state is lowest energy state!
- **Problem:** Relaxation along *desorption pathway* does not necessarily find the state with correct magnetic state (only finds local minimum).
- **Solution:** Explicit iteration over all possible magnetic states needs to be coded. Intermixing the NEB images from two paths to follow the global min.

Ti-doped MgH₂(110) Desorption Path (M=0 → 2 μ_B)



- Early diffusion of 2nd layer H prefers M = 0 μ_B that has the lowest barrier.
- Desorption of H₂ has a transition from M = 0 to 2 μ_B.
- Final state prefers M = 2 μ_B, with a change in HCN from 8→6.
- NEB code requires extensions to couple allowed magnetic states.

Defect-mediated Alane formation
on Ti-doped Al(111):
Experiment and Theory

Overview of Alane Formation on Al(111)

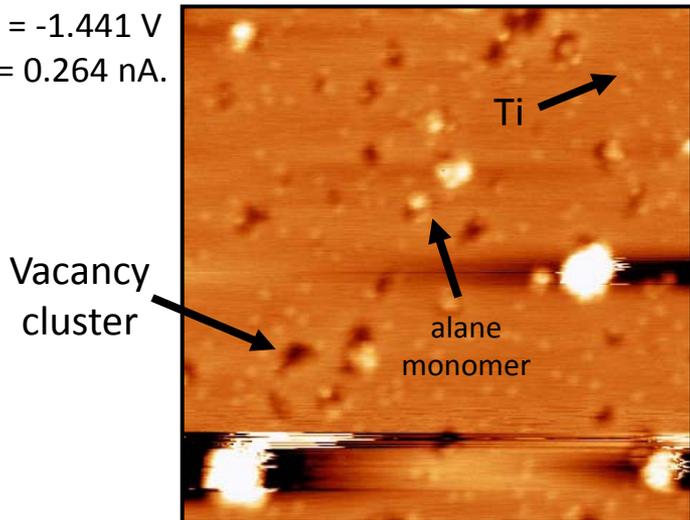


STM Constant-Current Studies

scan size = 24x24 nm²

V = -1.441 V

I = 0.264 nA.



STEM Results (reported FY10)

- Controlled experimental conditions.
- Alane always appears with vacancies.
- Ti preferential near vacancies.
- There remains a challenge of reproducing the initial findings despite extensive efforts.

Other Experimental Studies

- Alane and H can easily diffuse on Al surfaces.
- Ti-doping increases Alane formation.
- Step edges are relevant to Alane formation.

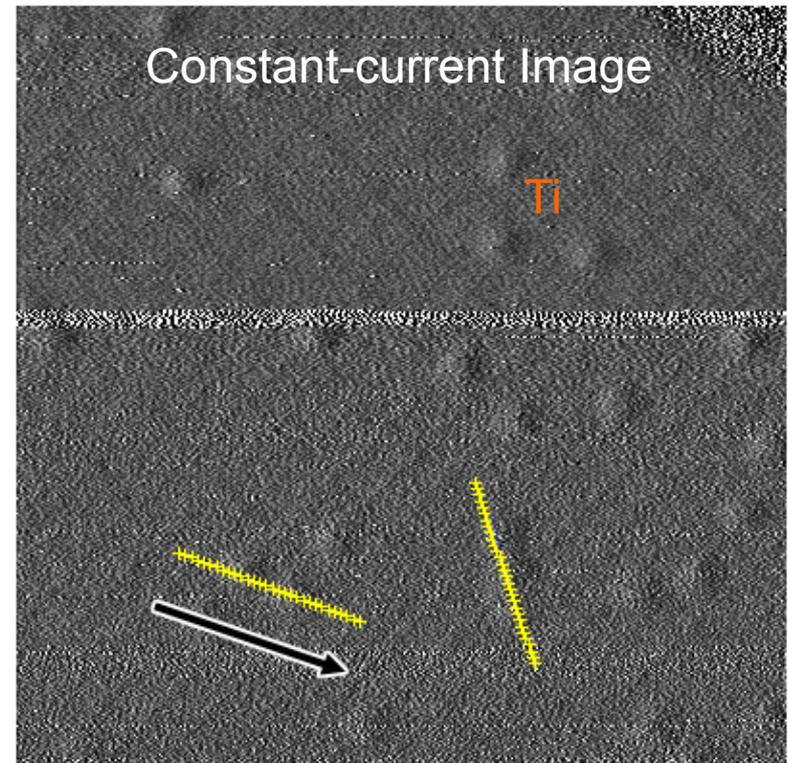
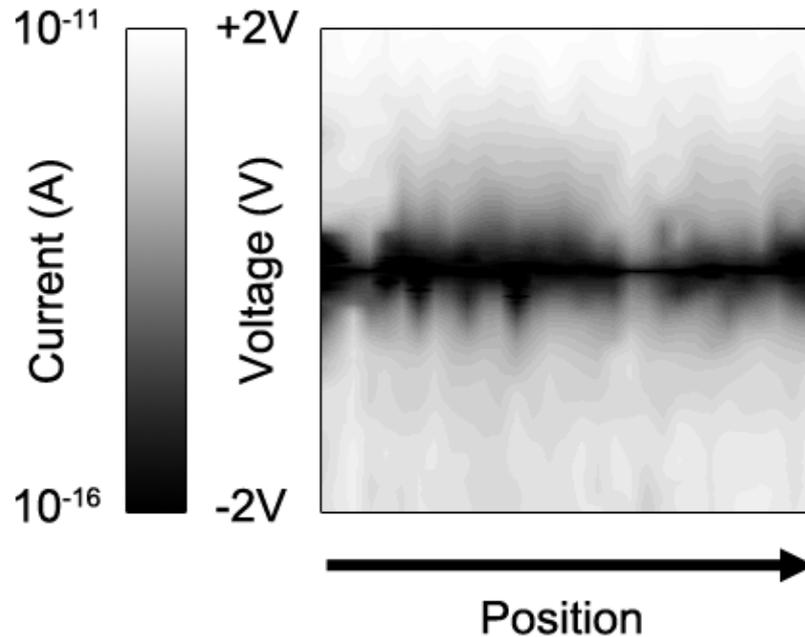
B. Hammer, K. W. Jacobsen, J. K. Norskov, Phys. Rev. Lett. **69**, 1971 (1992)
B. Hammer, M. Scheffler, K. W. Jacobsen, J. K. Norskov, PRL. **73**, 1400 (1994)
V. Zhukov, A. Ferstl, A. Winkler, K. D. Rendulic, Chem. Phys. Lett. (1994)
J. Wang, Y. Du, Y. Kong, et al., Int. J of Hyd. Energy {**35**}, 609-613 (2010).
R. Stumpf, R. Bastasz, J. A. Whaley, W. P. Ellis, Phys. Rev. B **77**, 235413, (2008)

Present DFT studies find that:

- Alane formation is defect-mediated by vacancies.
- Ti stabilized at surface by H, Alane, and vacancies.
- Ti enhances H dissociation, needed for Alane.
- Ti aids but does not replace role of vacancies.
- Multiple defects form Al_nH_m without barriers.
- Explains why ball-milling processing is effective.

Effect of Ti on Electronic Structure of Al(111)

Scanning Tunneling Microscope (STM) with more sensitive spectroscopic capabilities prepared to probe atomic-scale effects of Ti on AlH_3 storage system.



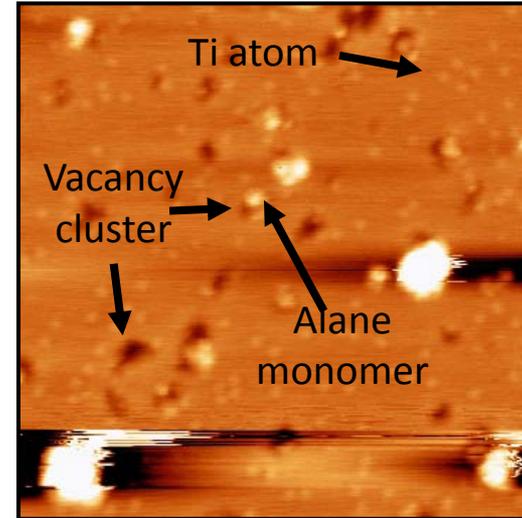
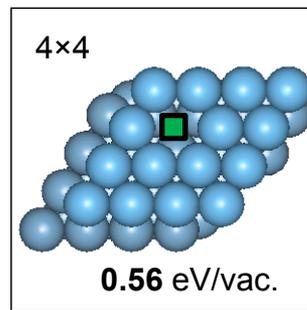
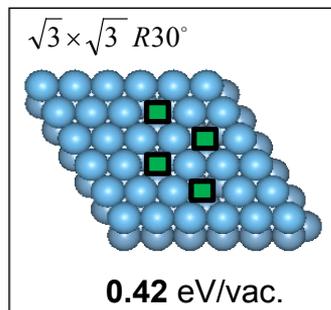
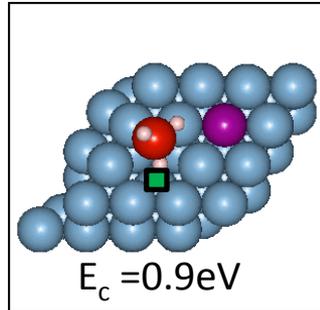
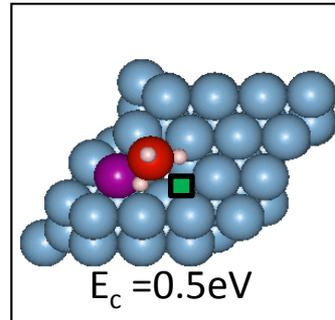
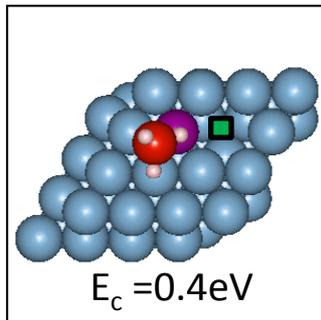
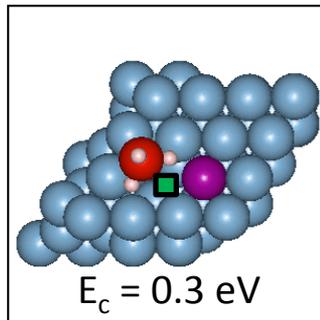
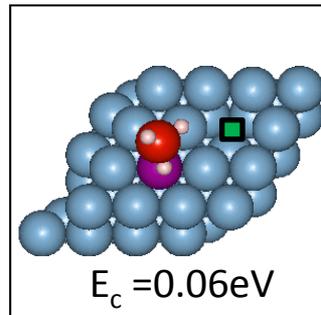
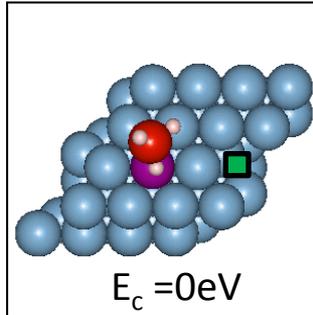
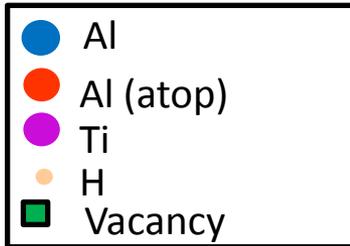
Scan parameters: scan size = $9.7 \times 9.7 \text{ nm}^2$, $V = +2 \text{ V}$, $I = 50 \text{ pA}$.
Yellow line indicates I-V point spectra measurements.

- Similar surfaces to previous runs produced.
- no energy gap observed, it's a metal.

Alane binding site for single Ti-doped Al(111)

A. Herwadkar, L.-L. Wang, D.D. Johnson (2011), in prep.

Constant-I STM Studies

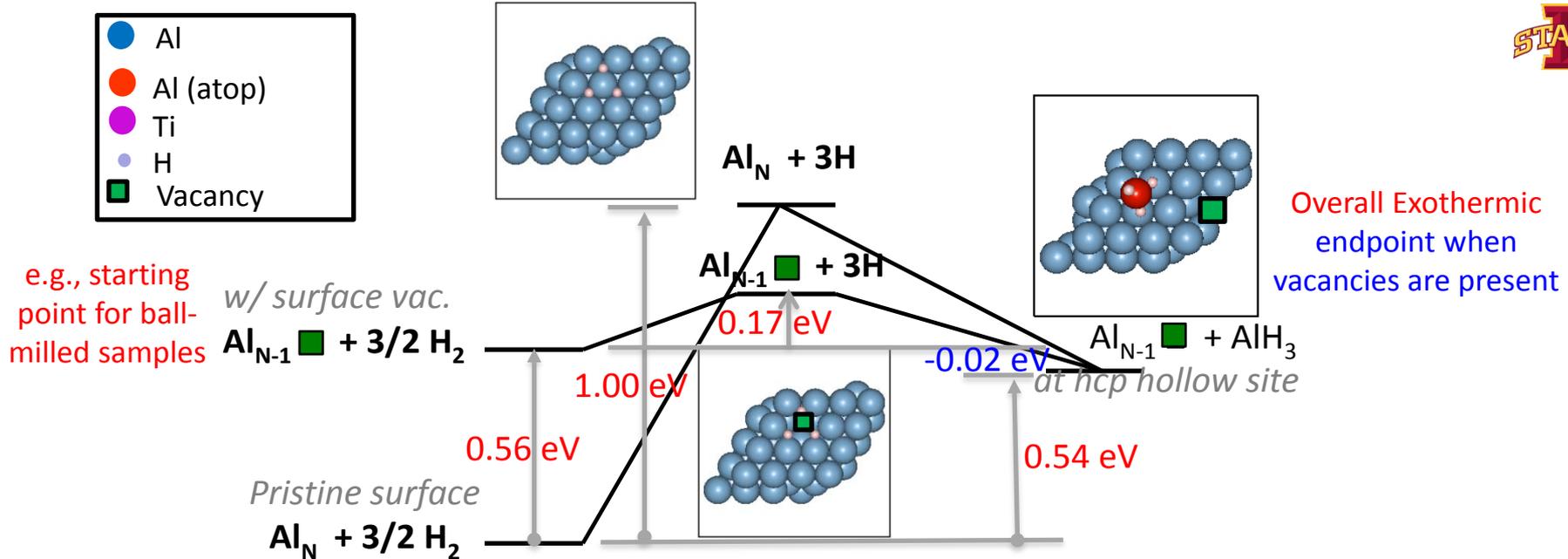


scan size = $24 \times 24\text{ nm}^2$
 $V = -1.441\text{ V}$ $I = 0.264\text{ nA}$.

- Multiple-vacancy defects cost less than single vacancies, and prefer to be clustered.
- After forming, Alane prefers to be near Ti, with vacancy as 2nd or 3rd nearest-neighbor.
- Alane prefers to be away from vacancy cluster, which is consistent to STM results.
- Multi-defects interactions, however, are important (see next).

Alane Formation on Al(111): only Vacancy Effect reactions given pictorially

A. Herwadkar, L.-L. Wang, D.D. Johnson (2011), in prep.



- Albeit vacancies costs 0.56 eV on pristine Al(111), **vacancy facilitates H dissociation.**
- Vacancy results consistent with CVD expts. and STM studies* of alane formation.
- Processing matters: **Ball-milled samples have abundance of vacancies**, hence, **only 0.17 eV need to dissociate H, then Alane forms exothermically by 0.02 eV.**
- Other “intermediate” reaction steps for Al-adatom/vacancy creation may be operative, and controls barrier.
- Need to consider Ti-dopant effect in concert with vacancies.

*Go et al., Surf. Sci. 437, 377 (1999); Ojwang et al., J. Chem. Phys. 132 084509 (2010).

Alane Formation on Al(111): Vacancy + Ti-catalyst Effect

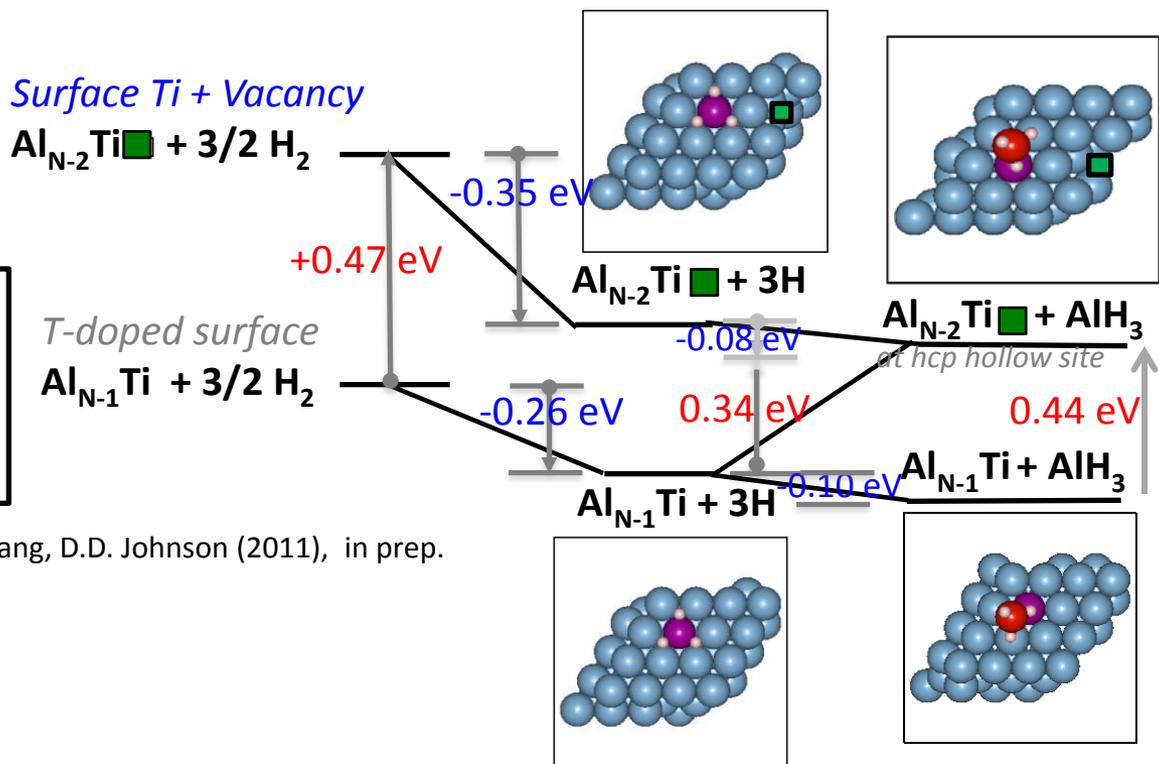
reactions given pictorially



e.g., starting point for ball-milled samples with Ti catalyst

Legend:

- Al
- Al (atop)
- Ti
- H
- Vacancy



Exothermic vacancies and/or Ti catalyst are present.

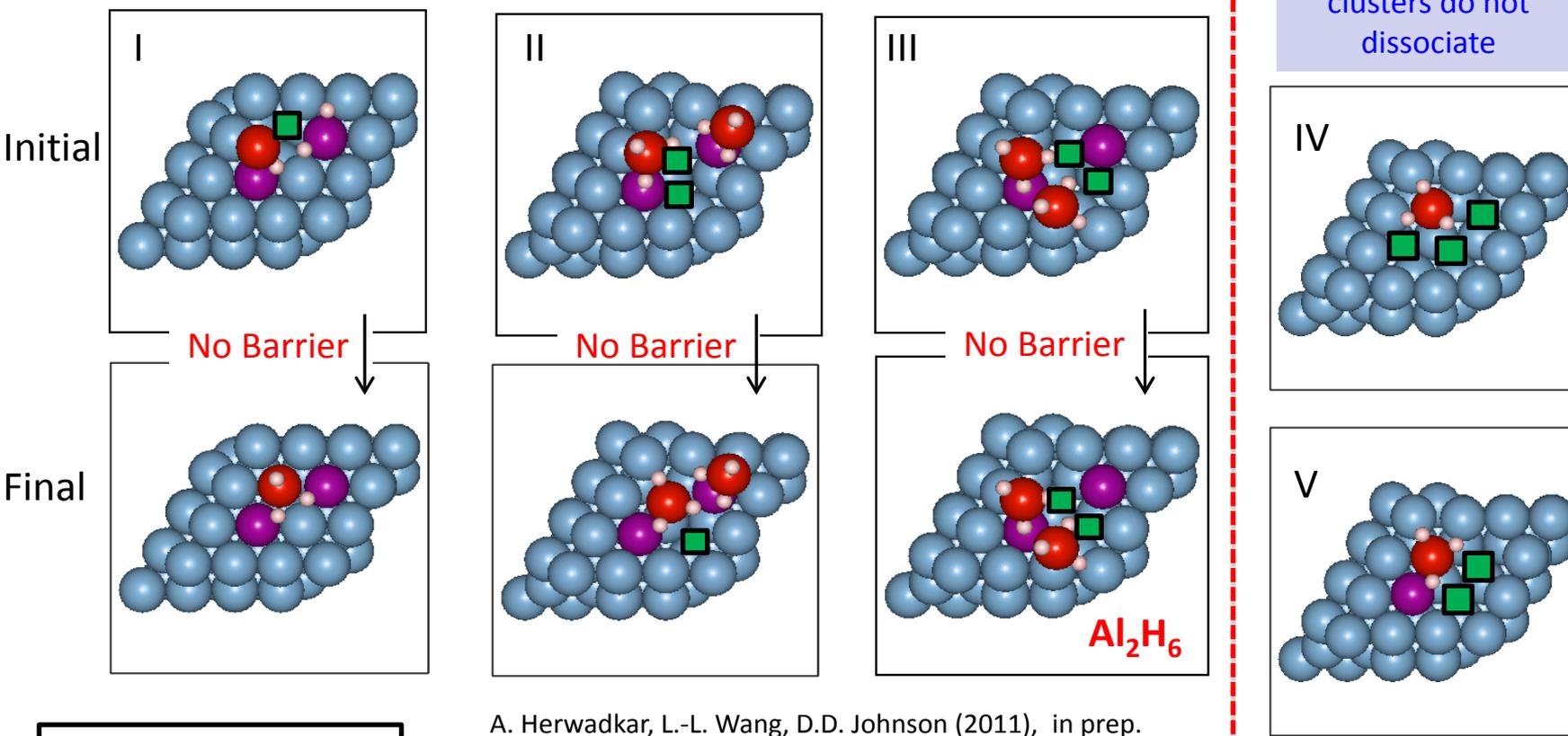
Find NO BARRIER when multiple Ti and vacancies present

*N.B. Last step requires vacancy or Al-atom.

A. Herwadkar, L.-L. Wang, D.D. Johnson (2011), in prep.

- In cases studied, Ti facilitates H dissociation exothermically – with vacancies
- Processing matters: For samples with vacancies present, e.g., ball-milled or STM samples that are not highly annealed, Alane formation is exothermic by -0.43 eV .
- Result show that, while Ti makes H-dissociation exothermic, Alane formation is vacancy-mediated; so Ti do not replace the vacancy effect!
- For completeness, we need to study the kinetic barriers.

Alane Formation with Multiple Ti and Vacancies

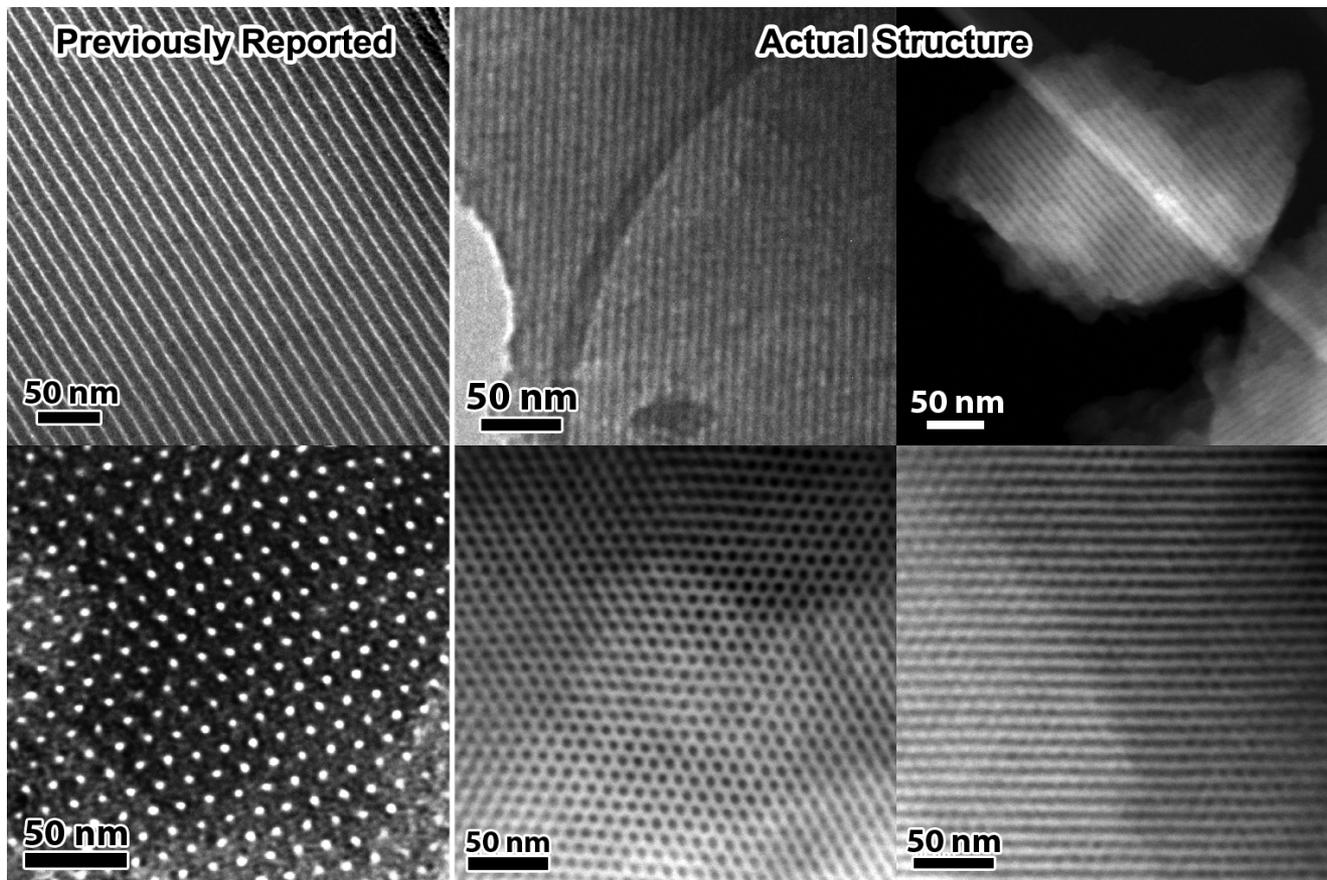


A. Herwadkar, L.-L. Wang, D.D. Johnson (2011), in prep.

- Al
- Al- forming Alane
- Ti
- H
- Vacancy

- Alane forms with low or no barriers when multiple vacancies are present near Ti, which catalyzes the H dissociation.
- Once formed, Alane at vacancy clusters are stable (do not dissociate).
- Al_nH_m clusters form more easily with multiple AlH₃ and Vac. available.

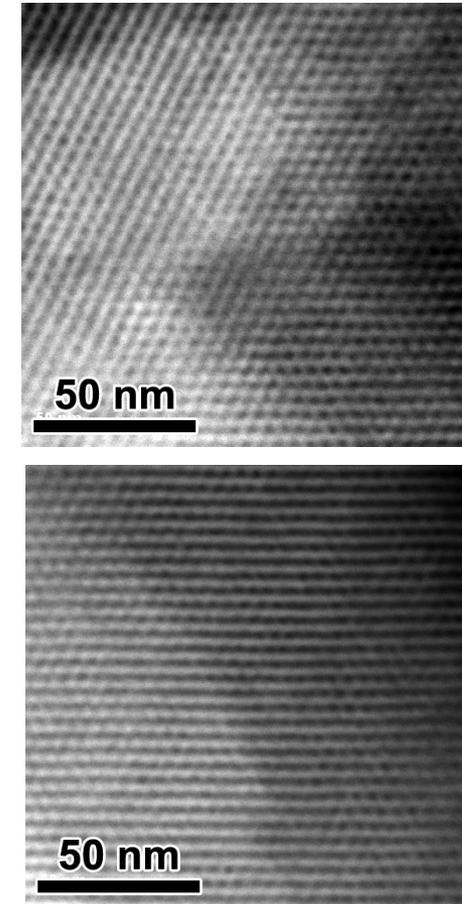
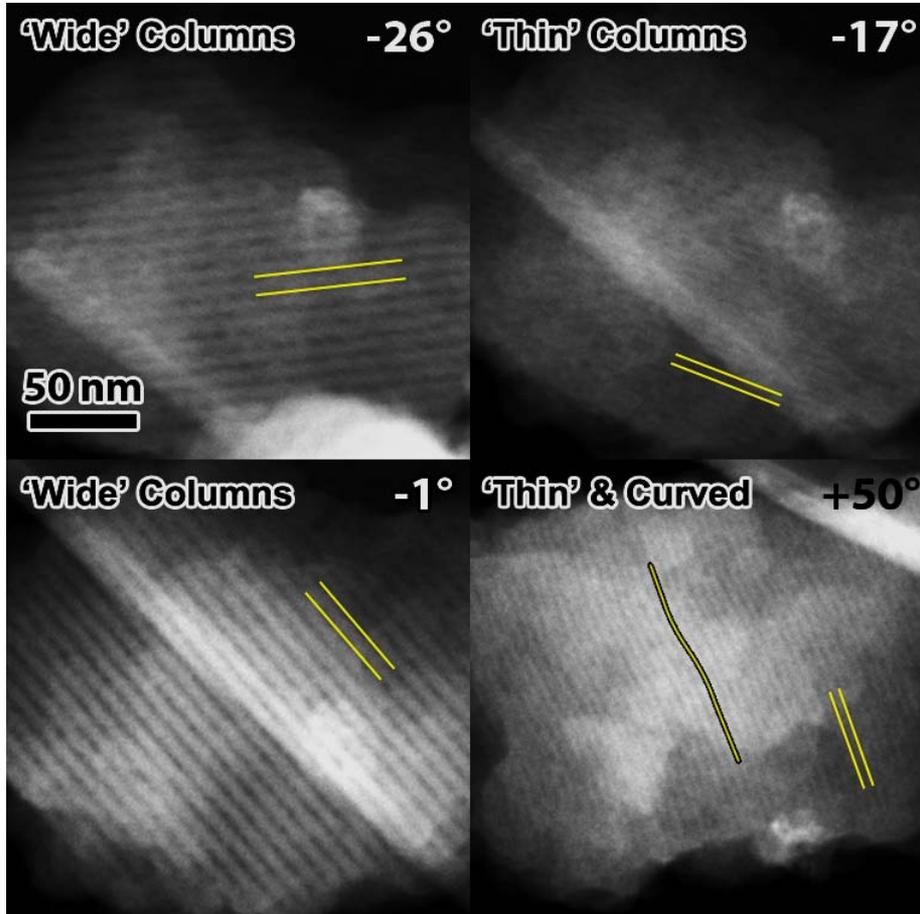
Structure of Nano-porous carbon scaffolds



- Previously reported column structure (size, spacing) was inaccurate.
 - Column wall and pore width are the same. Two sizes of columns observed.
- Collaboration with Prof. E. Majzoub*

Nano-porous carbon scaffolds - Column Orientation and Shape

Sheets/layers of columns are not necessarily oriented the same.



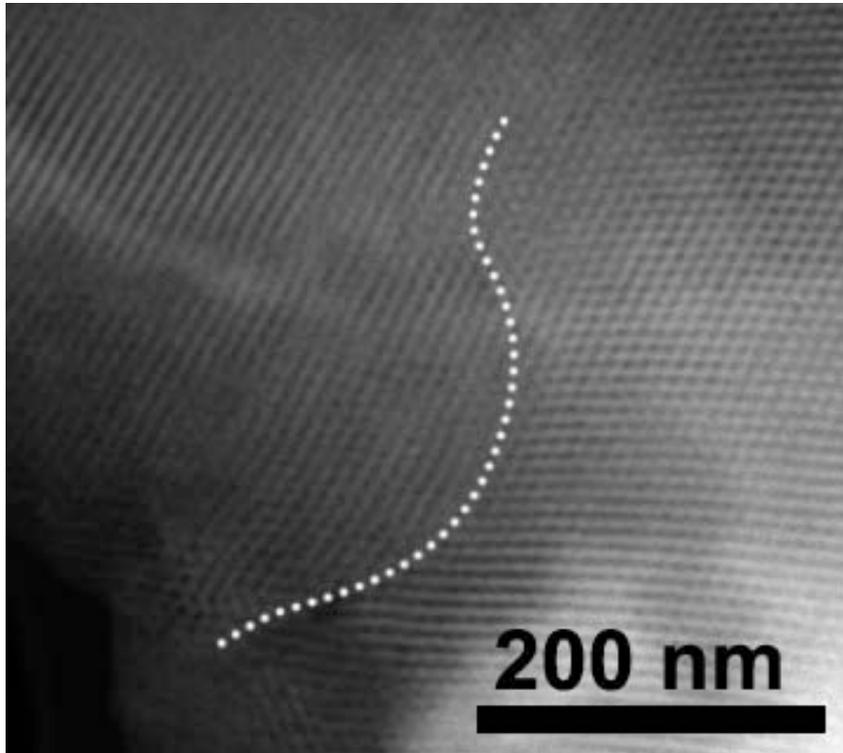
Different orientations, sizes, and curvatures
seen in the same single powder grain.
(Angles listed are x-tilt.)

Hexagonal-offset can lead to
pore-like appearance.

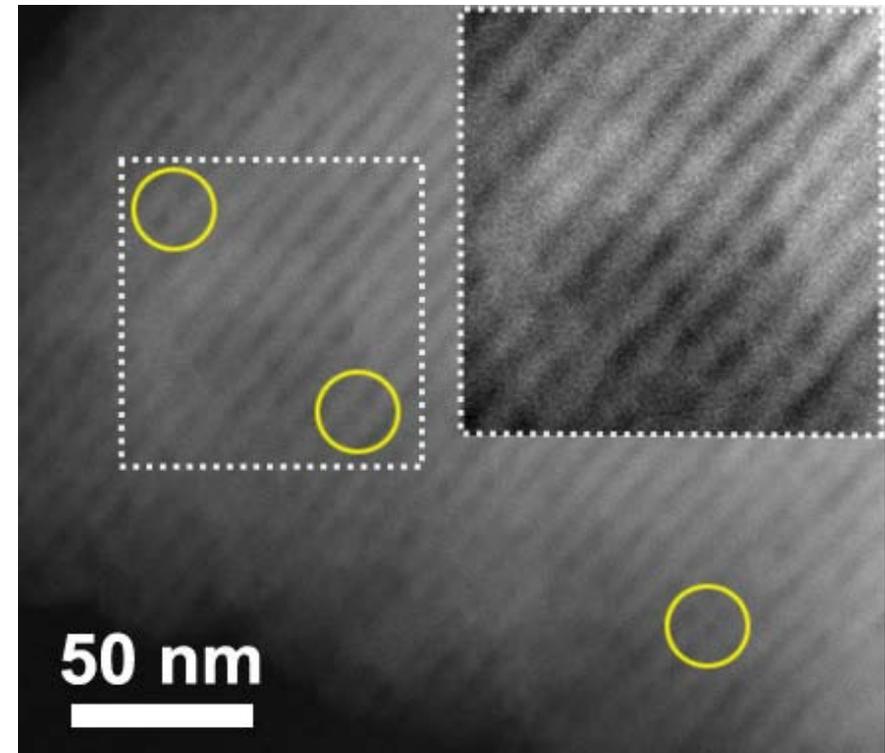


Nano-porous carbon scaffolds - Column Domains and Column Blocking

Some particles exhibit multiple domains of differing column orientation.
Blockage of columns seen – function of oxygen concentration during synthesis?



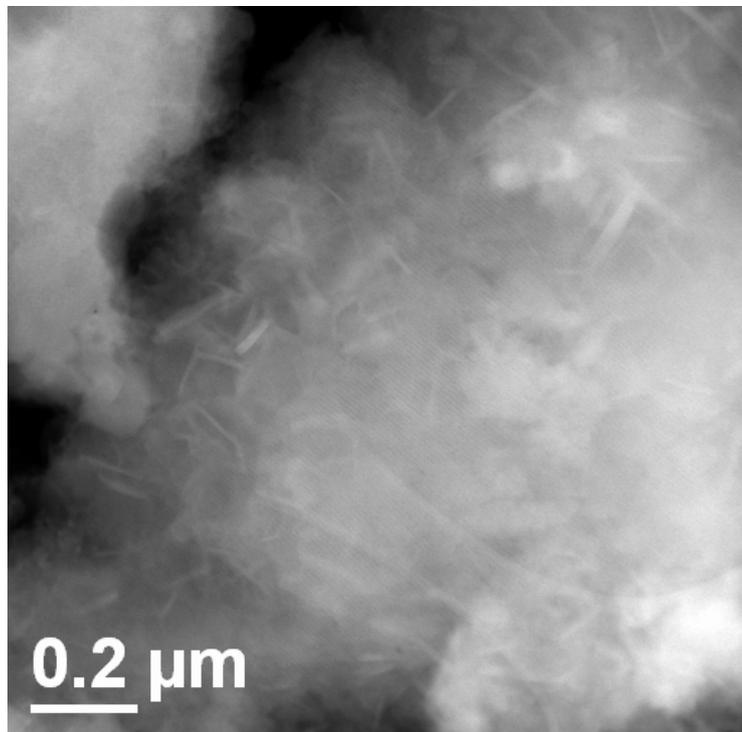
Domains without pores open to the surface would be difficult or impossible to infiltrate fully.



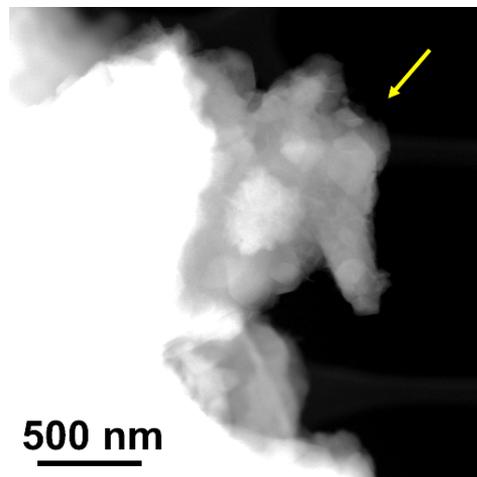
Column blockages could reduce maximum filling capacity of the scaffolds.

Nano-porous carbon scaffolds - Observed Changes with Desorption

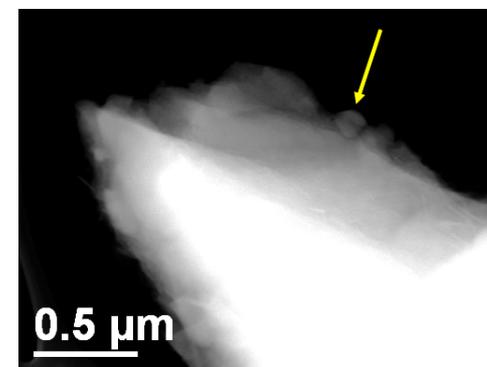
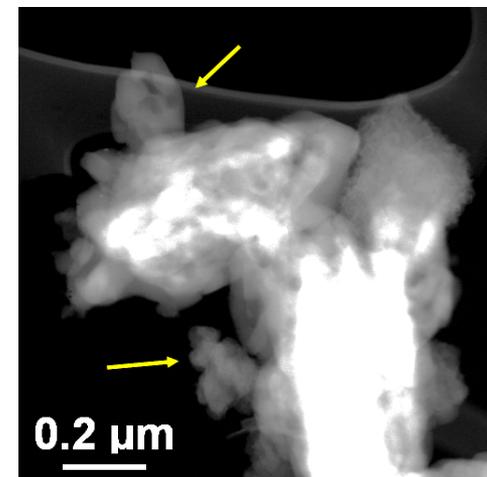
LiBH₄-infiltrated specimens desorbed at 500°C in DSC.
Nodule and “crust” formation observed on particle surface.



Crust



Nodules



- Desorption causes segregation of (B, Li) or some new Li/B compound formation to/at surface.
- Reason for loss of capacity with increasing cycles?

Summary



From our joint theoretical and experimental studies, we find that:

- On Al(111), **surface-vacancy defects mediate Alane formation**; sample preparation, e.g., ball-milling, will impact results via presence of vacancies.
- Vacancy clusters are favorable.
- **Ti catalyst** (on terrace or at steps) **enhances the role of vacancies, but it does not replace them**, as vacancies do also enhance dissociation of H₂.
- Ti enhances H adsorption on Al(111) and acts as dissociation site for H₂.
- **Multiple-defects provide no barrier to formation of Al_nH_m species.**
- **Constant-current STM imaging: Alane always adjacent to Ti and vacancy clusters, supporting the DFT findings.**
- **HR-TEM observations:** Nano-confined structures present a challenge in terms of structure and connectivity of pores and the change in structure and composition with each charge/discharge cycle.

Work has been supported in part by DOE, Office of Basic Energy Science under contract: DEFC36-05GO15064 and DE-FG02-03ER15476 (Chemistry/Catalysis), DE-FG02-03ER46026 (BES/Materials), and Ames Lab DE-AC02-07CH11358 operated by Iowa State University.



Future work

- Complete the papers listed in the publications section
- Repeat the STM study on controlled defected surface.
- Complete Kinetic Barrier study at Step-Edge sites.
- Complete the characterization study with the Majzoub group, addressing questions such as the composition and structure of the material ejected from the scaffold during cycling and determining the degree of filling of the pores.



Technical Back- Up Slides

Computational Method



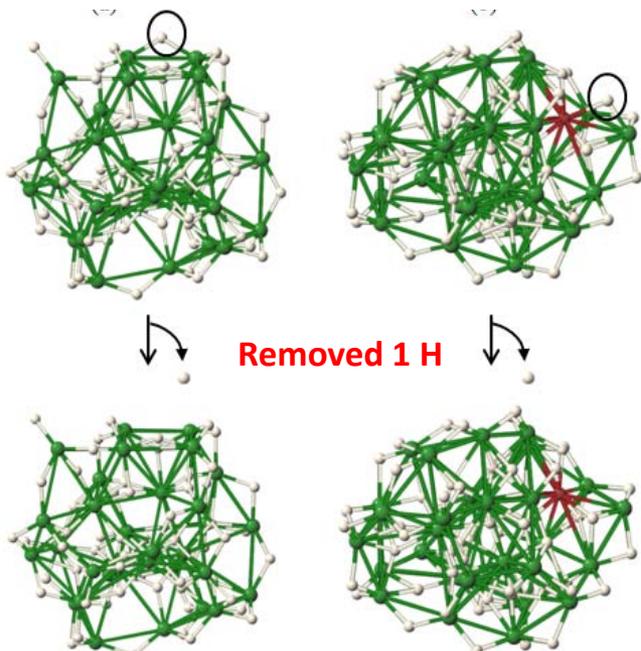
- Simulations are DFT with in local density approximation (LDA) and PW91 as the exchange correlation function as implemented in VASP.
- The clean and adsorbate covered Al(111) are modeled as 5-layer slabs with bottom two layers fixed to mimic bulk during atomic relaxation. Vacuum region is set to thickness of seven Al layers.
- Cells contain 80 atoms with periodic boundary conditions.
- We use a 270 eV kinetic energy cutoff and k-point mesh of 7x7x1, with Gamma-centered grid to sample the Brillouin zone for the Aluminum surface.
- Total energy (Forces) are converged to 1 meV/atom (0.02 eV/Å) vs. size of vacuum and k-point mesh; conjugate gradient is used for ionic relaxation.

Doping Effect but **No Size Effect** on Thermodynamic for H-dissociation on MgH₂(110)

Mg₃₂H₆₄ amorphous nanoparticle

H bonded to 2 Mg atoms

(a) undoped and (b) Ti-doped



Removed 1 H

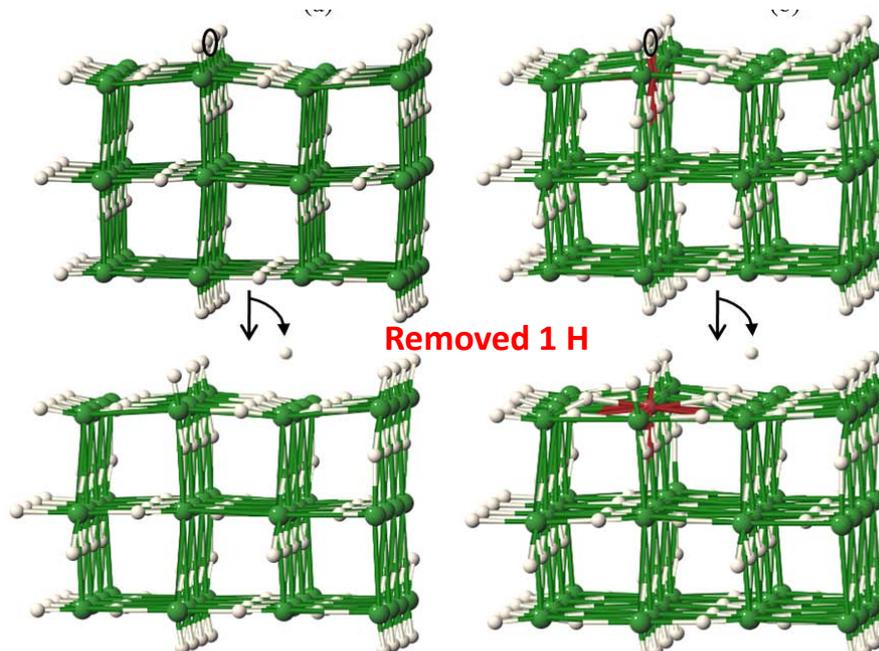
NP Disassociation Energies

252 kJ(mol-H₂)⁻¹ 188 kJ(mol-H₂)⁻¹

MgH₂ (110) Bulk Surface

H bonded to 2 Mg atoms

(a) undoped and (b) Ti-doped



Removed 1 H

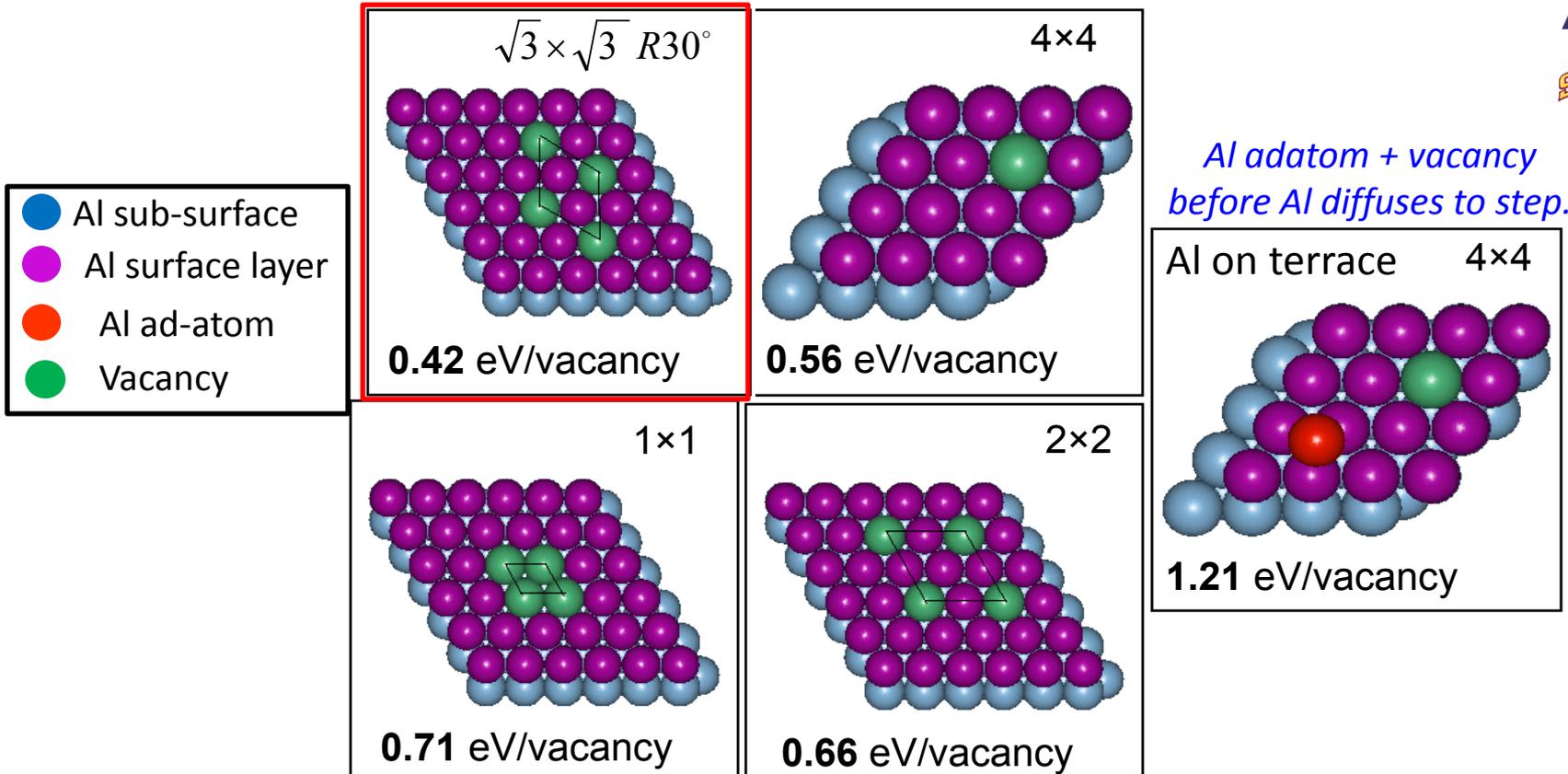
Bulk Disassociation Energies

231 kJ(mol-H₂)⁻¹ 193 kJ(mol-H₂)⁻¹

From single-atom desorption energies from DFT simulations, we find: **NO SIZE EFFECTS**

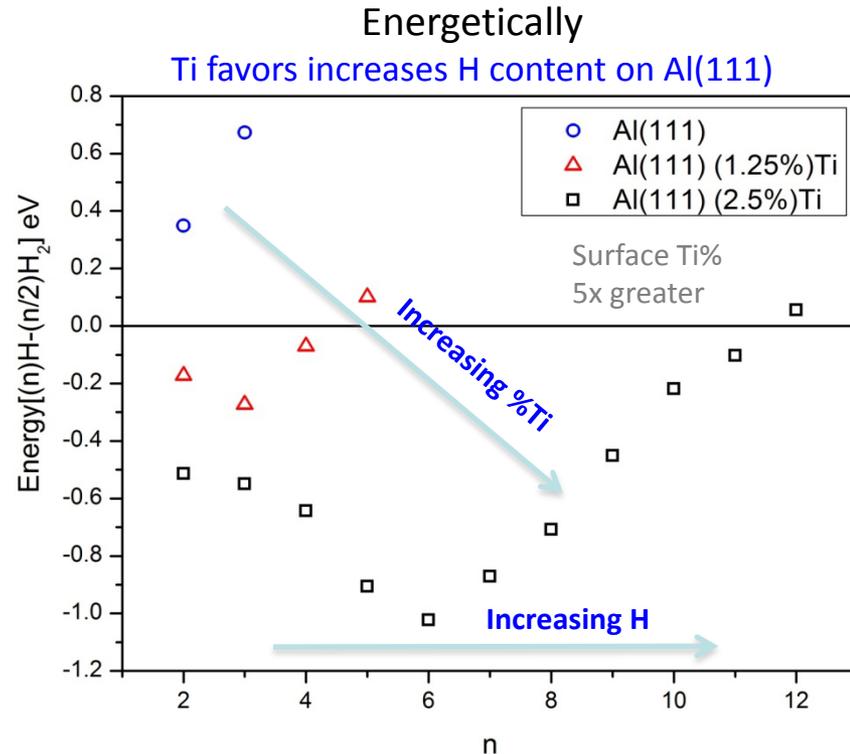
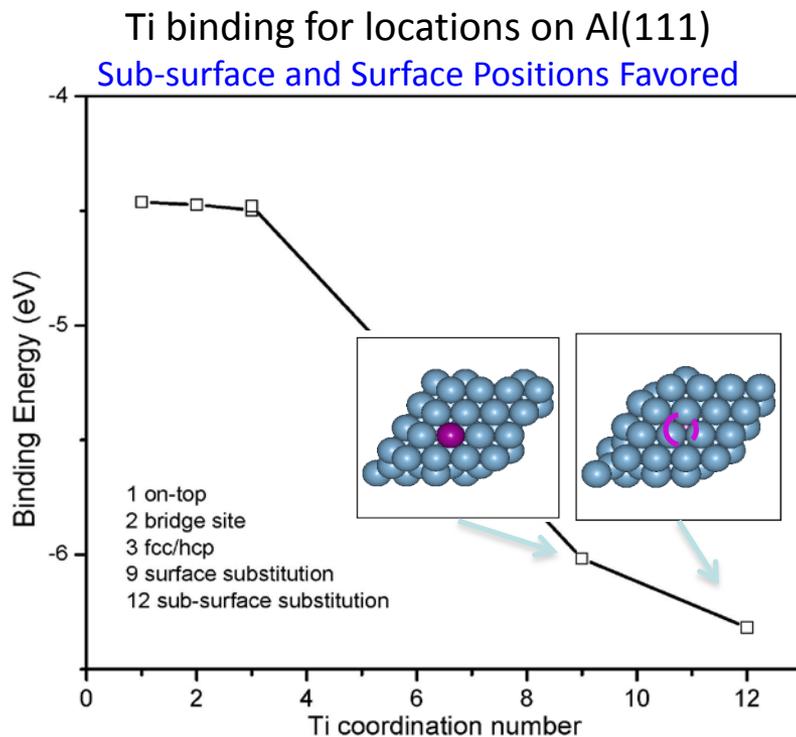
- Thermodynamic desorption energies are similar in Nanoparticle and Bulk Surface.
- Ti-doping in NP or bulk surface site decreases desorption, as observed.

Stability of Vacancy Structure on Al(111): Vacancy Clusters Favored



- Vacancy formation with Al adatom costs ~1.21 eV, and, with Al migration to a step edge, e.g., the surface vacancy cost is 0.56 eV.
- Multiple vacancy configurations are comparable to (or lower than) the single-vacancy case, agreeing with STEM observations of vacancy cluster formation.
- Vacancy with 2nd near-neighbor vacancy is most favored.

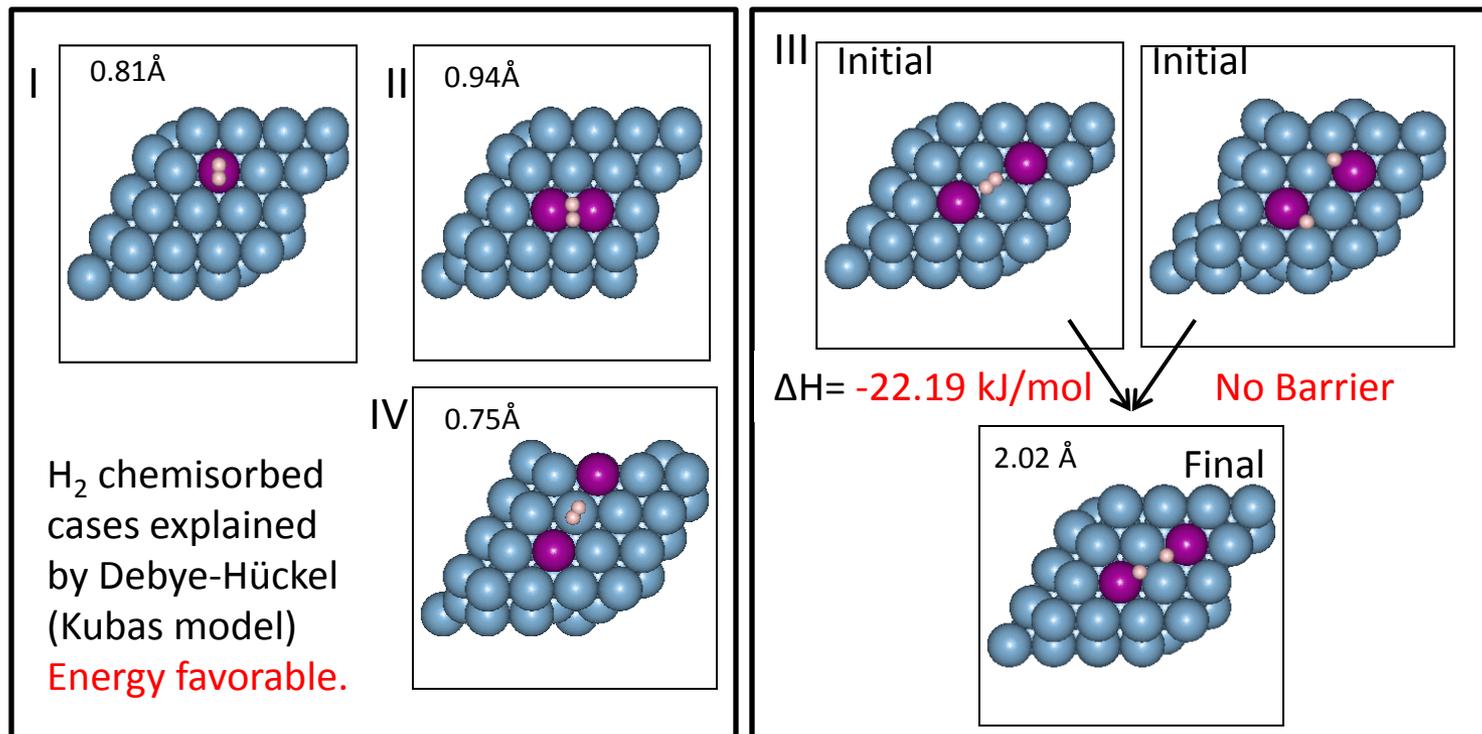
Ti-dopant on Al(111) increases H saturation



DFT simulations confirms some previous results

- Preferring higher coord. #, Ti like sub-surface Al site (lower than surface by 0.28 eV).
- In presence of H or Alane, Al and Ti compete to form hydride.
- **However, DFT simulation also reveal that Ti prefers surface when H, AlH₃, or, especially, vacancies (see below) are at the surface, enhancing H content.**
- Ball-milling increases vacancies improving Ti surface content and dissociation of H.

Ti Catalyst on Al(111): H dissociation



J. Chen, et al., J. Phys. Chem C **113**, 11027-11034,(2009)
G. J. Kubas, J. Organometallic Chem. **635**, (2001)
G. J. Kubas, et al., JACS, **106**,2, (1984)

Similar mechanism (but with correct surfaces): S. Chaudhuri, J.T. Muckerman, J. Phys. Chem. B Lett. **109**, 6952 (2005)

- Ti aids in H₂ dissociation, with a kinetic activation barrier for **most** configurations.
- Ti atoms prefer to be non-nearest neighbors (2nd and 3rd preferred).
- Results confirm previous findings – **but vacancies are very important** (see below).
- **Even for 1 Ti**, the configurations with adsorbed H is downhill in energy.
- **With 2 Ti**, the dissociated configuration has no barrier.
- H diffused around Ti easily, but does have barriers for diffusion away.