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

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Project ID # ST035

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Overview

Timeline

- Project start date
  - March 2005
- Project end date
  - February 2010
    - Application to extend project has been approved.
- Percent complete 90%

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.

Budget

- Total project funding
  - $1 600 000 committed
  - $1 231 250 funded
- FY09: $100,000
- Funds Remaining: $132,000

Partners

- Project lead: Sandia National Laboratory & MHCoE
- Brookhaven National Laboratory
- Savannah River National Laboratory
- University of Pittsburg, Georgia Tech and University of Hawaii

Objectives/Relevance

- Illinois' 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 MHCoE and other critical DoE programs, as suggested by Program Officers.
- Some Illinois recent impacts
  - Improved 3-D reconstructions and visualization to address the question of the dispersion of particles in scaffold.
  - In MgH_2, AlH_3 and MOFs, complete understanding dispersion of materials.
  - In MgH_2 showed that there is no nanoparticle size effect for dehydrogenation enthalpies, although there is an effect on kinetic barriers with TM catalyst.
  - Determined universal behavior for core-shell preference in binary nanoparticles.
  - Demonstration that the amount of Ti needed to activate the system is less than introduced initially.
  - In $Ca(BH_4)_2$ established the existence of numerous $CaB_{12}H_{12}$ polymorphs in intermediate phase, and the origin for observed amorphous-like behavior.

Plan & Approach

90 % complete

- Task 1: Experimental investigation of MHCoE partner materials
  - Determining microstructural and compositional changes in hydrogen storage materials due to hydrogenation and dehydrogenation cycles.

90 % complete

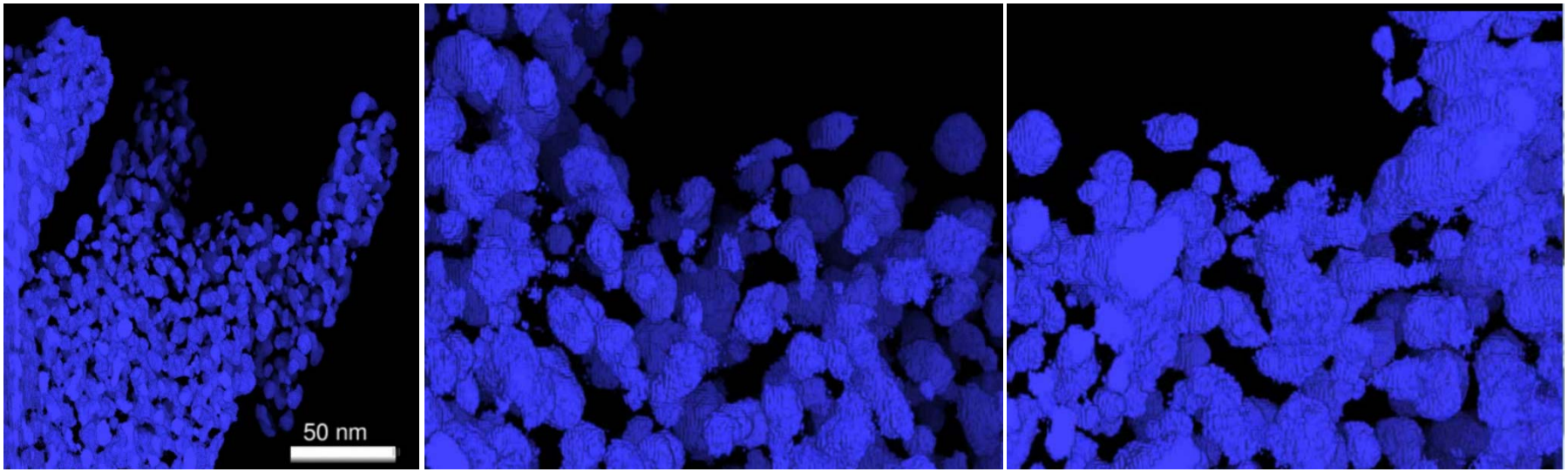
- Task 2: Incorporation and development of new models
  - Predicting and understanding structural, thermodynamic, and kinetic properties of hydrogen-storage materials, including size effects, with direct connection to ongoing experimental measurements, including in MgH_2, Alanes, and Borohydrides

Are particles distributed throughout scaffold structures?

- Electron tomography capability for compositional imaging has been improved significantly, enabling better resolution in the through thickness direction.

Confirming silver particles are distributed inside a MOF. (MOF is removed to show the particles.)

Initial view | expanded | expanded and rotated.



Electron tomography shows the particles distributed throughout the scaffold. The new capability allows full three-dimensional rotation and exploded view capabilities to better visualize and characterize the particles.

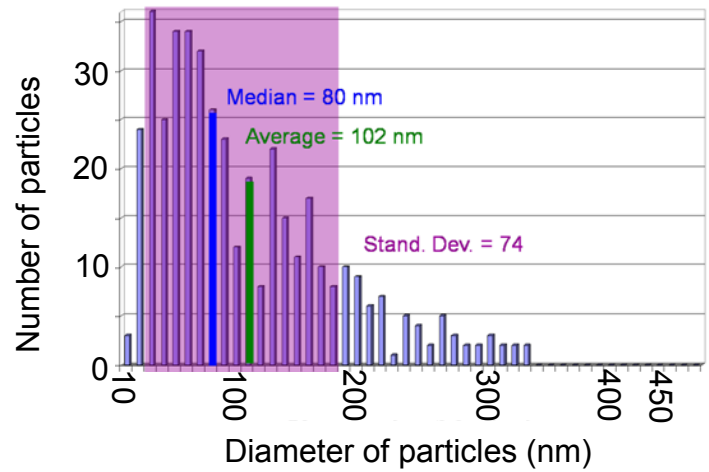
Current effort is exploring the location of MgH_2 in a scaffold – collaboration with the University of Hawaii.

Role of Ti on particle size during cycling

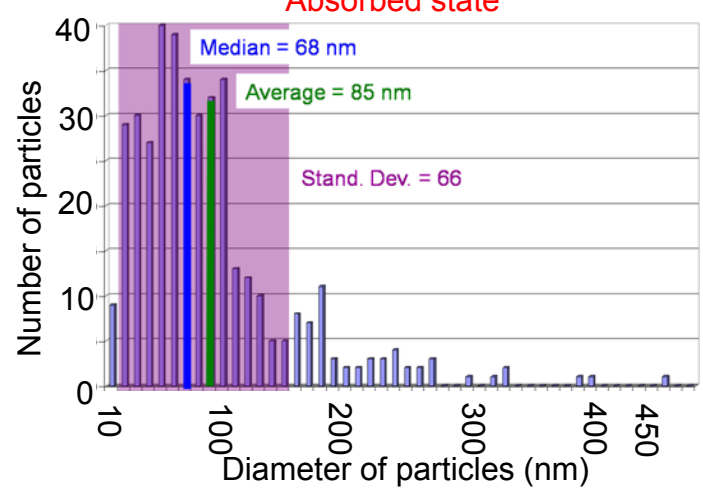
Jensen (U. Hawaii) Robertson (U. Illinois)

condition	Avg Particle Size (nm)	Median Particle Size (nm)	Stand. Dev.
$NaAlH_4$ (Purified)	81	70	48
$NaAlH_4$ Ballmilled	58	48	37
"D1" NaH + Al, doped, 1 cycle	102	80	74
"A2" $NaAlH_4$, doped, 2 cycle	85	68	66
"A5" $NaAlH_4$, doped, 5 cycles	61	55	36
"D5" NaH + Al, doped, 5 cycles	74	54	58
"A10" $NaAlH_4$, doped, 10 cycles	67	52	53
"D10" NaH + Al, doped, 10 cycles	88	61	81

NiH +Al +2mol%$TiCl_3$, cycled once. Desorbed state



$NiAlH_4$ +2mol%$TiCl_3$, cycled twice. Absorbed state



Study shows:

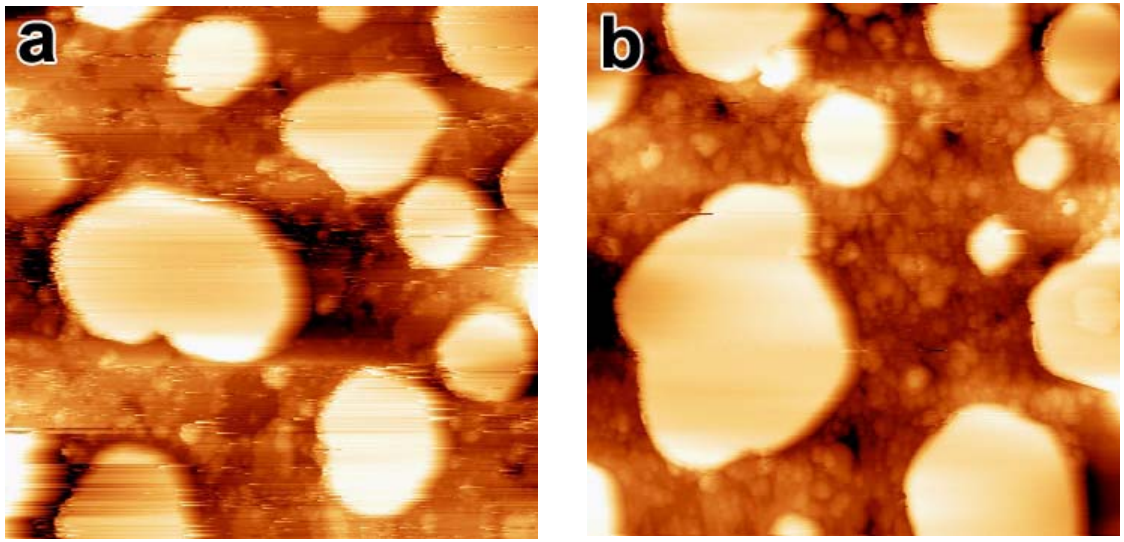
- Ball-milling decreases particle size, thereby enhancing kinetics;
- Sintering occurs during dehydrogenation and desintering occurs during hydrogenation.

And suggests Ti has a dual role:

- in the form of Al_3Ti it suppresses sintering and as Ti it impacts hydrogenation.

Interaction of H_2 with clean Al surface

Dedicated surface study using UHV **Scanning Tunneling Microscopy** to determine atomic-scale effects of Ti on AlH_3 storage system



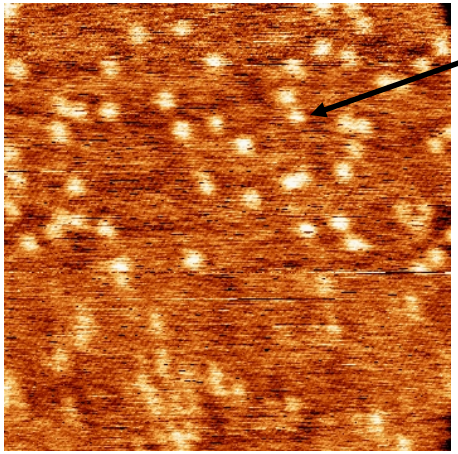
- 20 ML of Al deposited on Si (111) substrate
- Annealed to form atomically flat Al (111) islands, tens of nm wide

Al islands (a) prior to and (b) following exposure to $5x10^{-8}$ mbar of UHP H_2 for 5 hours. Scan parameters: scan size = 100x100 nm^2, V = -1.136 V, (a) I = 0.360 nA, (b) I = 0.456 nA.

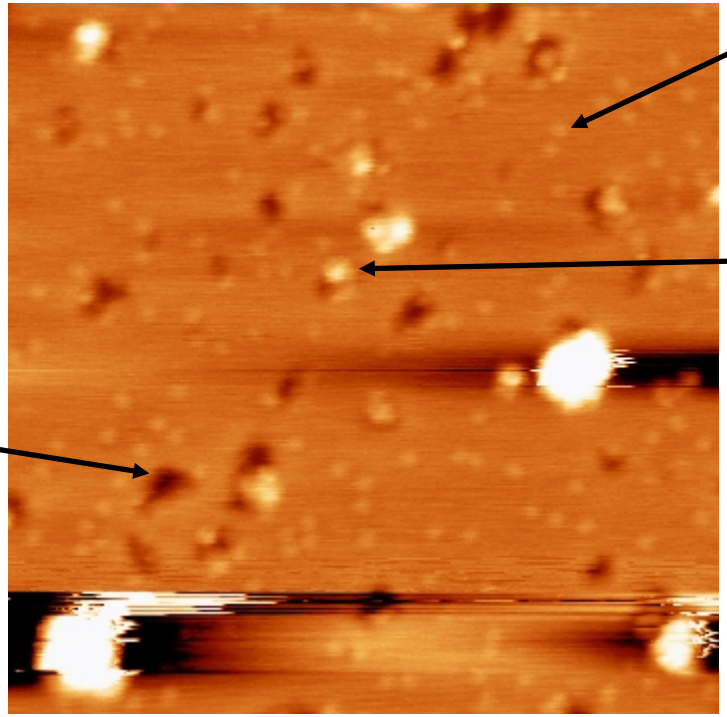
- No change in morphology observed during exposure to H_2 gas
  - This is not surprising, as H_2 has negligible sticking to pure Al

H_2 interaction changes when Ti is present on the surface

Following deposition of 0.02 ML of Ti at 300K and exposure to H_2:

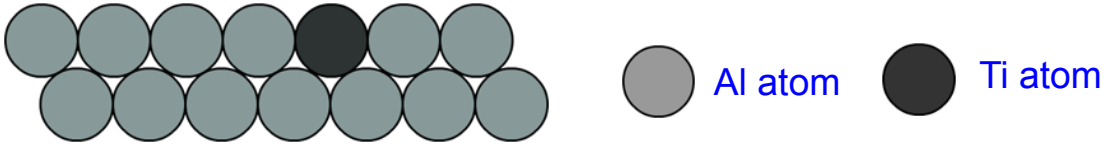


Scan size =15x15 nm^2
V = 1.115 V, I = 0.208 nA.



24x24 nm^2
V = -1.441 V
I = 0.264 nA.

(Above) Al island surface with Ti prior to exposure and (right) during exposure.

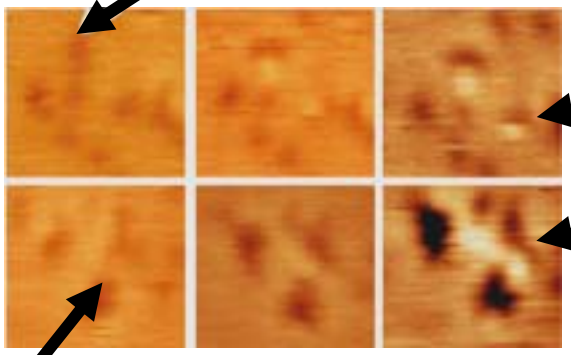


- Ti apparent heights (0.2-0.35 Å) and diameters (6-7.5 Å) correspond with previously observed and calculated values* for first-layer substitutional positions.

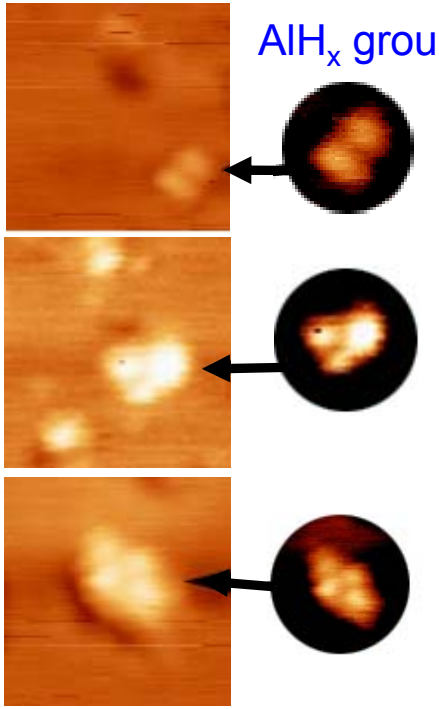
*E. Muller, *et al*. APL **90** (2007)

Time-resolved study of interaction of H_2 with Al(Ti) surface

Time series of vacancy cluster and AlH_x formation:



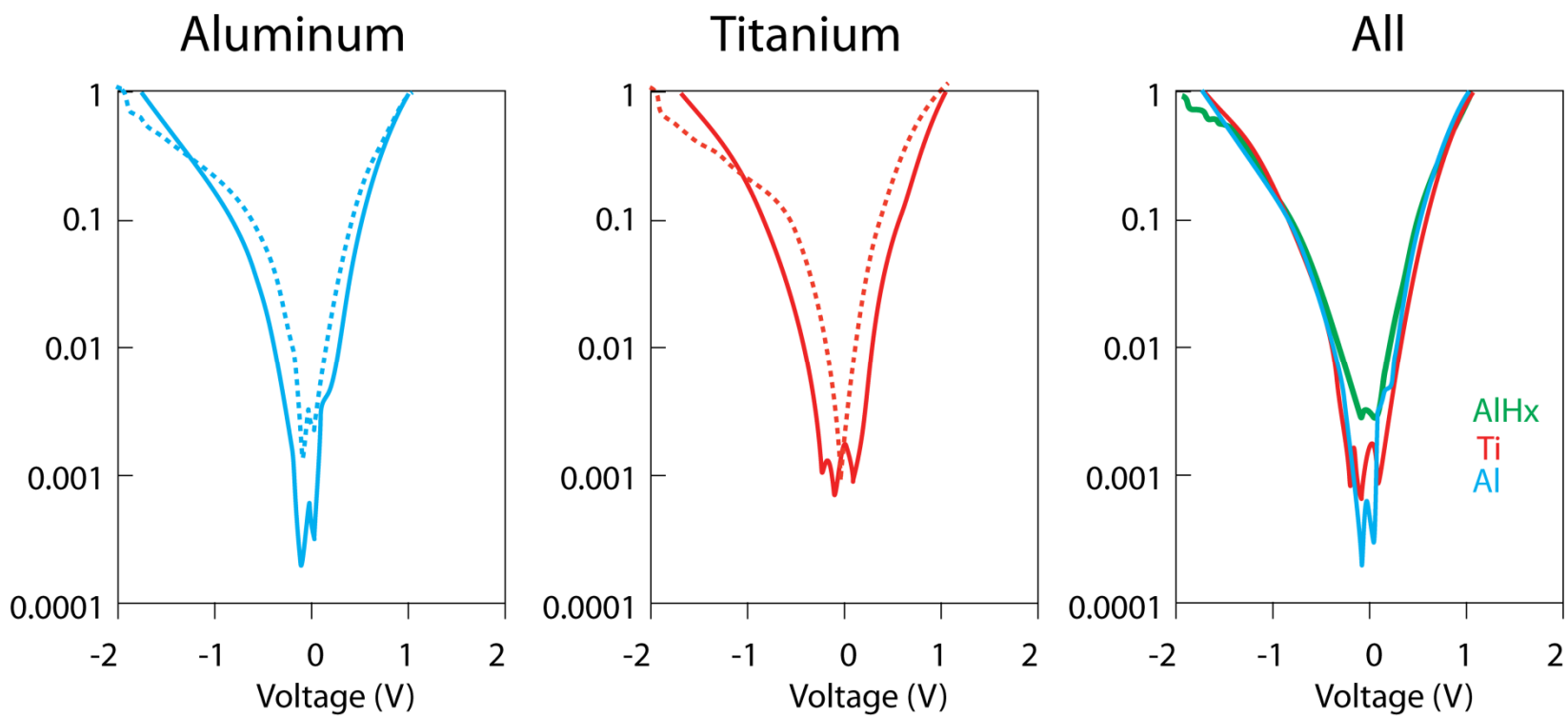
AlH_x grouping:



- No evidence of Ti motion or agglomeration during exposure.
- Formation of vacancy clusters (1.2-1.5 Å deep)
  - Grew in number and width over the course of the exposure.
- Surface AlH_x monomers formed at edges of vacancy clusters.
- Surface AlH_x apparent heights (2-4 Å) and apparent diameters (4-6 Å) are consistent with values observed for surface alane monomers (2.8 Å and ≈ 4 Å, respectively)**.

**P. Eden, *et al*. Surf. Science. 437 (1999)

Changes in the I-V curves on the addition of hydrogen



The I-V curves suggest the formation of a small band-gap on hydrogen charging. This has required use of a different STM with superior spectroscopic capabilities. Experiments and *ab initio* calculations are in progress to verify this result. DFT results are being directly connected to STM results for Al, Ti-doped Al, and AlH_x cases.

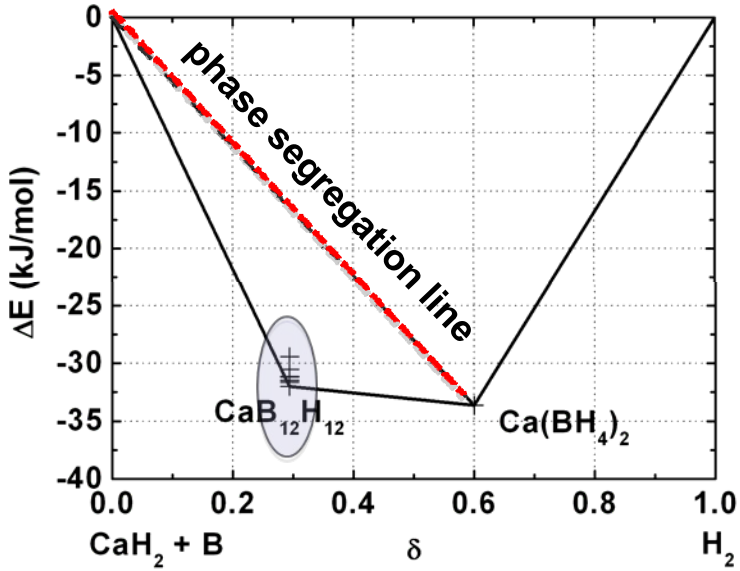
Summary - Characterization

- Characterization tools are available to determine the three-dimensional distribution as well as the size of particles either on surfaces or embedded in scaffolds.
- The role of Ti on clean Al surfaces appears to be to enhance the dissociation of molecular hydrogen to atomic hydrogen.
- In $NaAlH_4$ ball-milling decreases particle size, thereby enhancing kinetics; Al_3Ti has a possible role as a grain refiner; and sintering occurs during dehydrogenation and de-sintering during hydrogenation.

Characterization of $Ca(BH_4)_2$: Reactions and Products

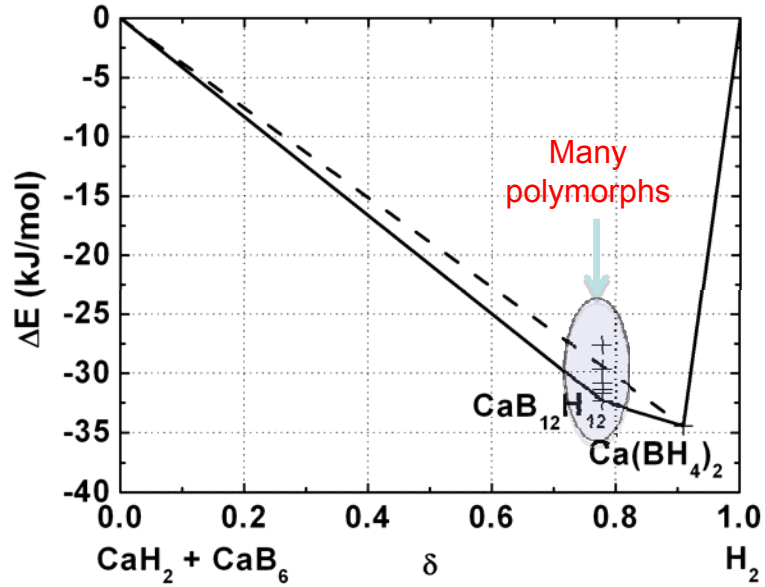
Formation Enthalpy vs H content for two reactions

$$CaH_2 + 2B + 3H_2 \rightleftarrows Ca(BH_4)_2$$



$$\frac{5}{6}CaH_2 + \frac{1}{6}CaB_{12}H_{12} + \frac{13}{6}H_2 \xrightleftharpoons{\text{mod. } P/T} Ca(BH_4)_2$$

$$\frac{2}{3}CaH_2 + \frac{1}{3}CaB_6 + \frac{10}{3}H_2 \xrightleftharpoons[\text{high}T]{\text{high}P} Ca(BH_4)_2$$



yields ΔE~36 kJ/mol-H_2 for all polymorphs.

- Both reactions show $CaB_{12}H_{12}$ is stable, but with many polymorphs (denoted by +).
- Same ground-state as *Ozolins et al.* [*JACS* **2009, *131, 230***] but with many polymorphs.
- Results show that $CaB_{12}H_{12}$ is destabilized at higher T (but the kinetic barrier is high).
- Due to $CaB_{12}H_{12}$ stability, H-release will decline each cycle at lower T (observed) as it arises from remnant CaH_2. Full release only possible at high T.

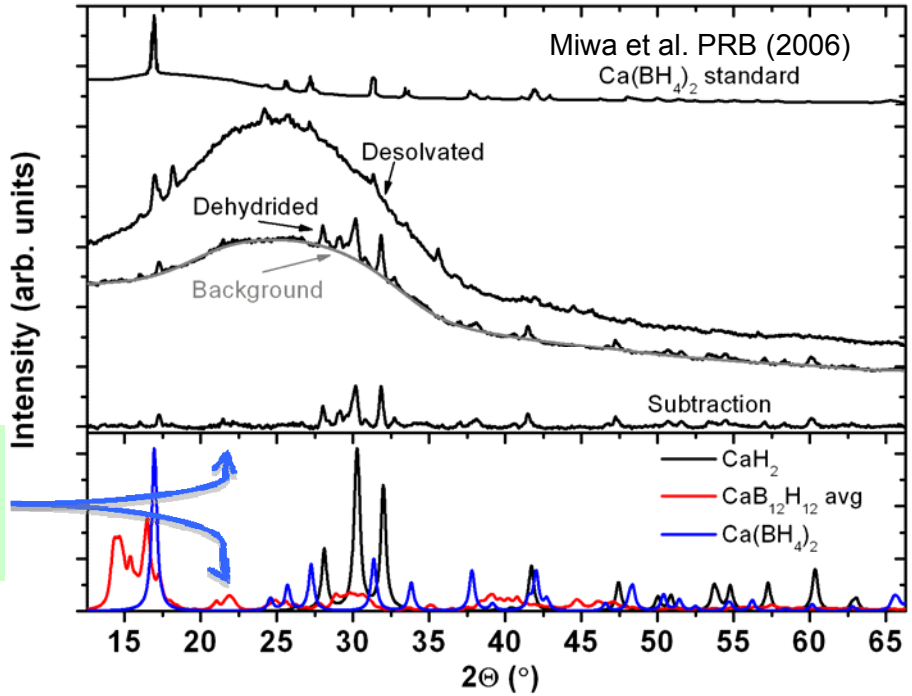
Wang et al., J. Phys. Chem. C 113 (46), 20088-20096 (2009).

Are the $CaB_{12}H_{12}$ polymorphs observed in cycled material?

Experimental (TEM and X-ray Diffraction) scattering indicates amorphous state.

Debye-Waller, finite-size (Sherrer), or volume-fraction effects related to the coexisting phase alter the location of peaks, so we compare locations in 2θ.

E.g., this peak, due to more than one polymorph



Experiment

Theory

- Multiple $CaB_{12}H_{12}$ polymorphs are indicated by matching structure in diffraction.
- Enthalpy and structure characterization suggest dehydrogenation in repeated cycling arises from CaH_2, rather than the very stable $CaB_{12}H_{12}$, limiting low-T $Ca(BH_4)_2$ as reversible H-storage media. Higher T can be reversible (previous slide).

Wang et al., J. Phys. Chem. C 113 (46), 20088-20096 (2009).

Hydrogen Desorption from MgH_2: Nanoparticles and Bulk-Terminated Surface

Two Relevant Energies

1. **Thermodynamics** – enthalpy difference between two states.
2. **Kinetics** – energy barriers between these states.

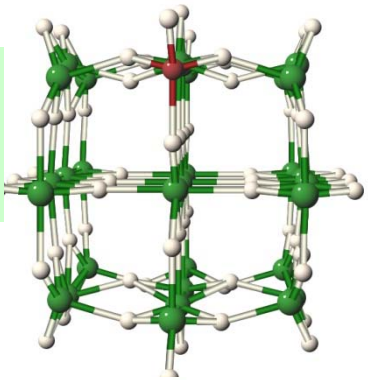
Two Critical Main Questions

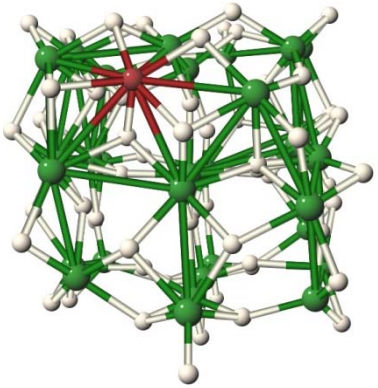
Is there a *size effect* for H-desorption for each case?

For a finite cluster, is the MgH_2 cluster at a global energy minimum?

Both full and single-site calculated desorption are affected by this.

Bulk-terminated
Saturated and Relaxed
$Mg_{30}XH_2$





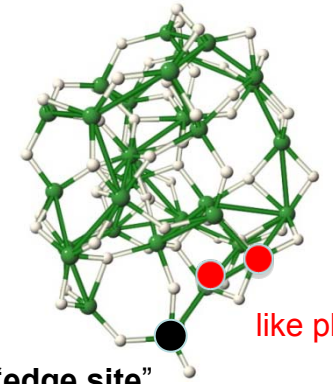
Dehydrogenated
$Mg_{30}XH_2$

LARGE relaxation

Similar to Larsson, et al., *PNAS* 2008, *105*, 8227.

Relaxed, amorphous cluster similar to de Jongh et al., JACS 2005, 127, 16675.

Simulated Annealing
$Mg_{30}XH_2$
With two sites for H
1-metal-atom bonded
2-metal-atom-bonded



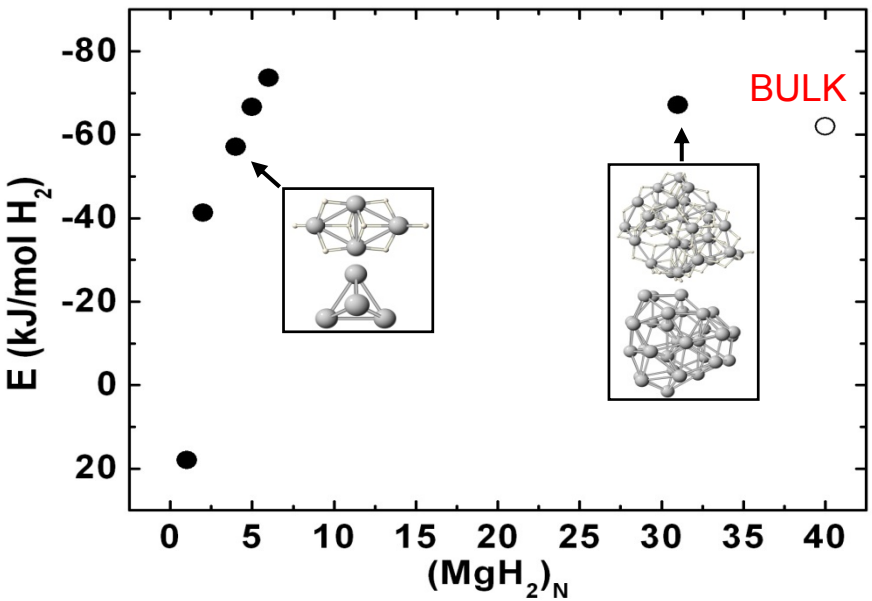
like planar "**surface site**"

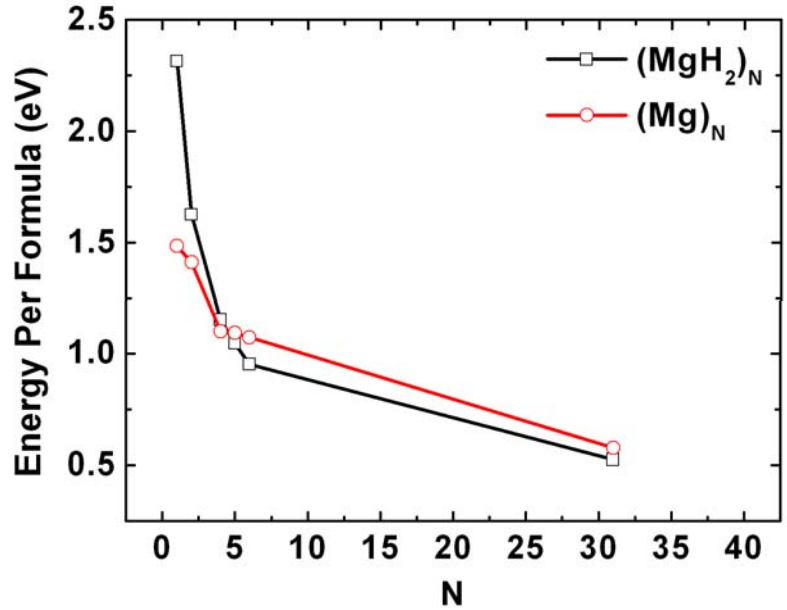
like surface "**edge site**"

✓ **Large relaxation before H removal**, so there is NO exothermic desorption (in contrast to Larsson et al. finding) – *it's local bonding!*

Full Hydrogen Desorption vs. Size of Structurally Optimized Nanoclusters

H Desorption Energy for
Structurally Optimized Clusters

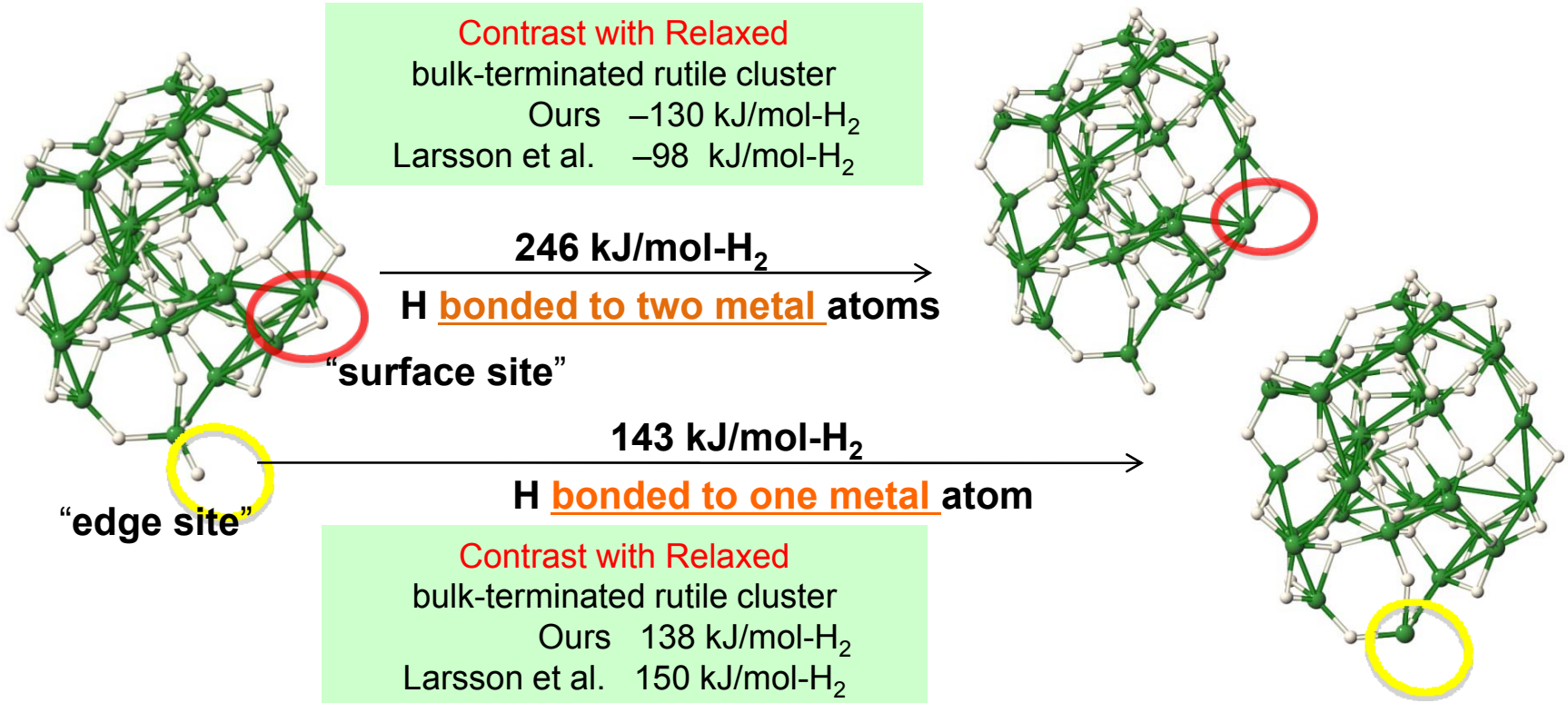




- $(MgH_2)_n$ clusters of < 5 F.U. (≥ 5 F.U.) have a smaller (larger) desorption energy than bulk.
- Similar to recent, higher accuracy, QMC results [Wu et al., JACS 2009, 131, 13918].
- 31 MgH_2 is an amorphous cluster, similar to de Jongh et al. [JACS 2005, 127, 16675] but unlike that of Larsson et al. [PNAS 2008, 105, 8227], which are metastable.

PAW-PW91 Results (Wang and Johnson, 2008, unpublished)

Hydrogen Desorption From Low-Energy $Mg_{31}H_{62}$ Amorphous Cluster



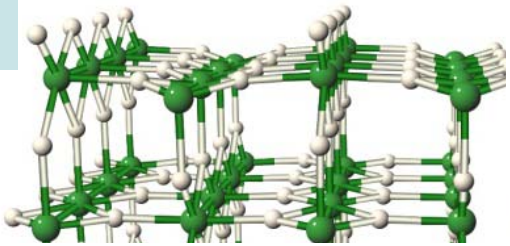
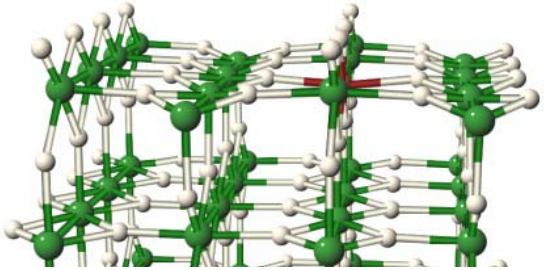
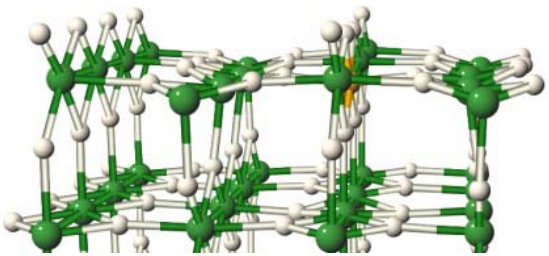
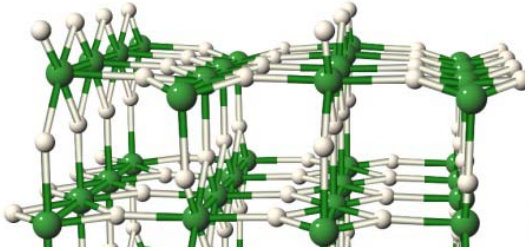
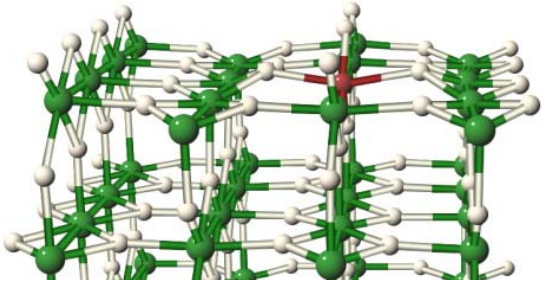
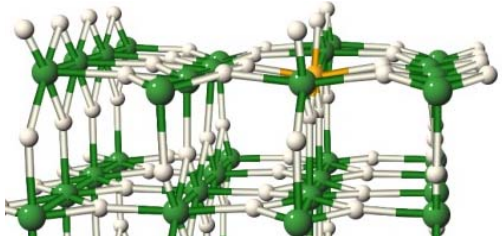
- ✓ We reproduce *spurious exothermic* results of Larsson et al. [PNAS 2008] that used bulk-terminated (locally relaxed) rutile-based clusters.
- ✓ In contrast, there is no exothermic H-desorption, due to large relaxation of bulk-terminated cluster to the amorphous state (found via *simulated annealing*).
- ✓ $\Delta E_{H\text{-desorp}}$: "surface site" 246 kJ/mol-H_2 vs. bulk-surface site 256 kJ/mol-H_2.
- ✓ For fully desorbed $\Delta E_{H\text{-desorp}}$ is 67 kJ/mol-H_2 in cluster vs. 62 kJ/mol-H_2 in bulk.
- ✓ Similar results for Ti and Fe catalyst site (to be published).

Reich, Wang, and Johnson, in preparation (2010).

Desorption From MgH_2 (110) Surface: Is there a size effect or catalyst effect?

Compare bulk-terminated surface with nanocluster results.

- 3 trilayers
- bottom fixed layer
- 4 by 2 supercell
- 15 A vacuum
- Gamma-pt only

	Mg	Ti-doped	Fe-doped
	*256 kJ/mol-H_2	187 kJ/(mol H_2)	264 kJ/(mol H_2)
Fully saturated			
1 bridging H removed from surface site			

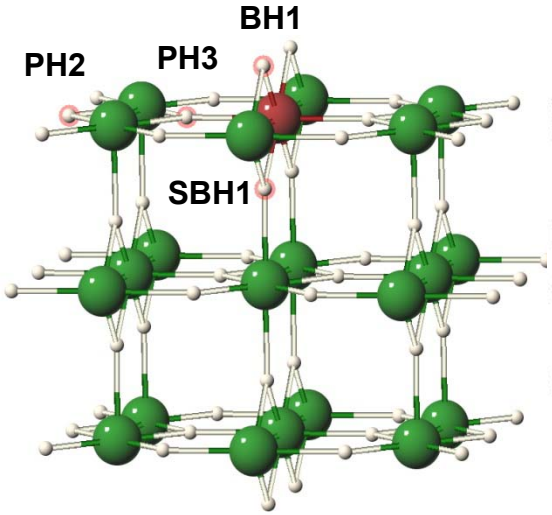
* Same as Du, A. J. et al.,. *J Phys Chem C* 2007, *111*, 8360.

- ✓ $\Delta E_{H\text{-desorp}}$: 256 kJ/mol-H agrees with cluster "surface site" 246 kJ/mol-H_2.
- ✓ Step-edge site should be comparable to "edge site" in cluster (ongoing).
- ✓ Essentially NO thermodynamic size effect for desorption energy.
- ✓ The barrier reduction for H removal – kinetic size effect – is under study.

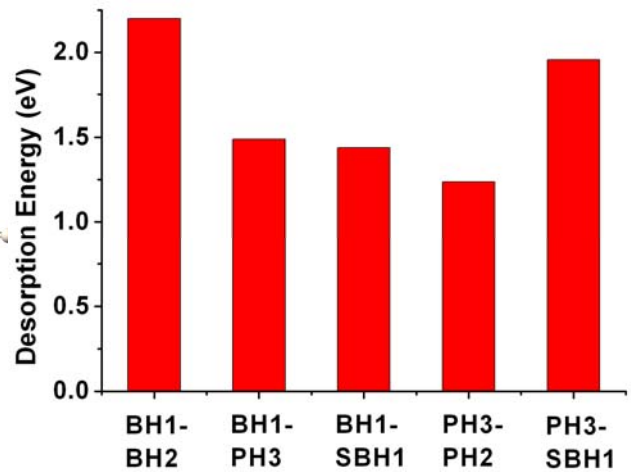
Reich, Wang, and Johnson, in preparation (2010).

Two-H Desorption from $MgH_2(110)$ Surface: VASP Energetics and Kinetic Barriers

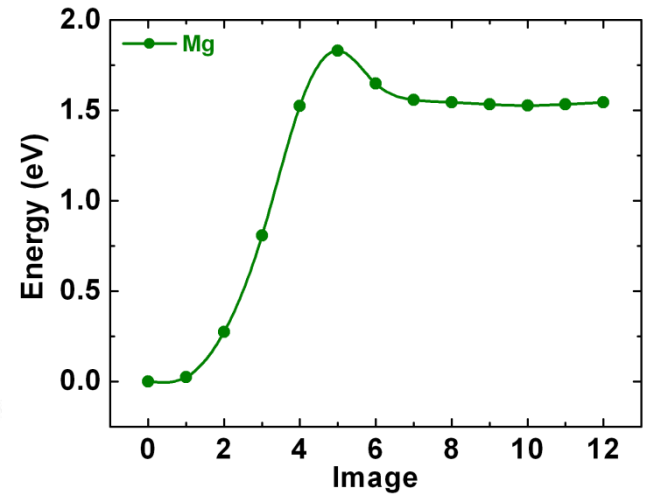
Labels are for H in Bridge (B), Plane (P) and/or Subsurface (S)



2-H Desorption Energy on pure $MgH_2(110)$



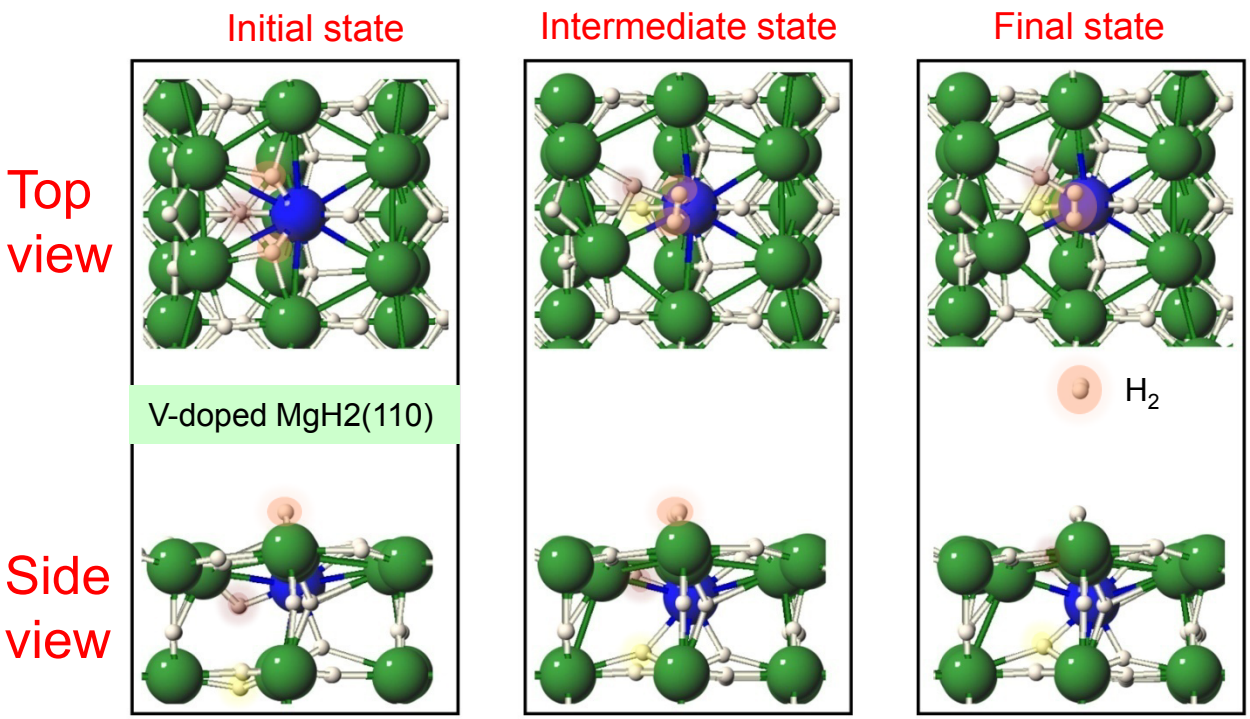
2H (BH1-PH3) Barrier via Nudged-Elastic Band



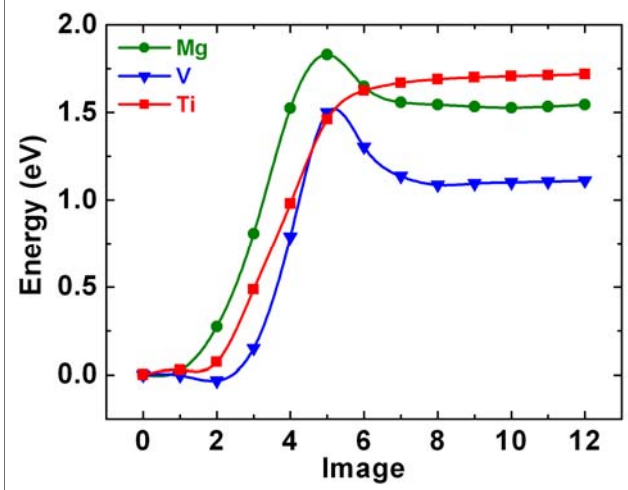
- For 2-H desorption, the lowest-energy structures involve in-plane H, albeit the BH1-PH3 and BH1-SBH1 pairs are close in energy.
- However, see next slide, BH1-PH3 has the lowest-kinetic barrier.
- Large difference between 1-H and 2-H cases, same as Du et al. [J Phys Chem C, 2007].
- Similar to nanoclusters, we need to consider the effect of large structural distortions for initial and final configurations, especially with catalyst (see next).
- Bulk diffusion barrier for H is ~0.2 eV, so rates controlled by desorption energy.

Wang, Reich and Johnson, in preparation (2010).

Two-H Desorption from $MgH_2(110)$ with Catalyst: VASP Energetics and Kinetic Barriers



2 H (BH1-PH3) Barrier via Nudged-Elastic Band



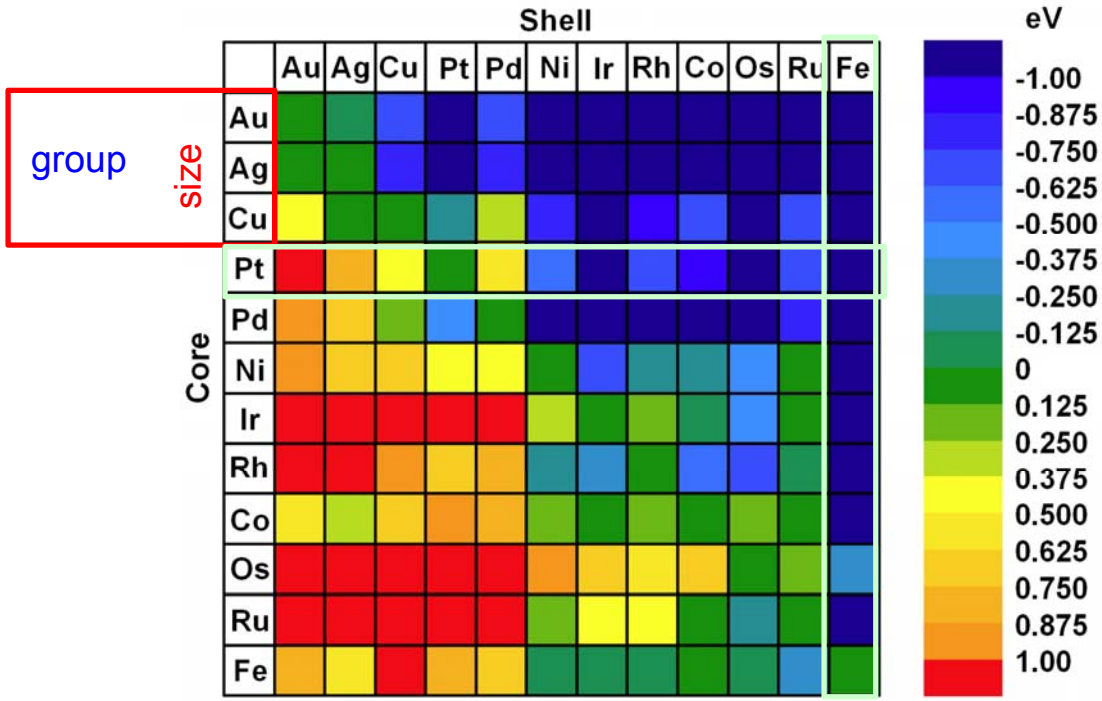
- **For 2-H desorption**, the lowest-energy structures (like NPs) involve dramatic local reconstructions around the catalyst site, with Ti (V) preferring 8 H (7 H) Coord. No.
- **Kinetic barrier results:** For 2-H desorption, there is a ~20% change of barrier due to V (catalyst) site. A "concerted" bulk-to-surface H motion is found.
- Initial Ti site results show no barrier. However, a careful search for true "final" state configuration (involving concerted motions) is underway via *ab initio* MD, as barriers are sensitive to initial-to-final state choices for NEB.

Wang, Reich and Johnson, in preparation (2010).

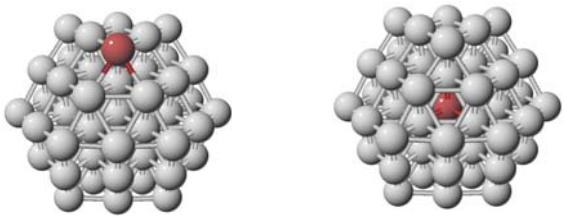
Universal Core-Shell Preference in Binary, Transition-Metal Nanoclusters for Catalysis

•Supported principally by DOE/Catalysis and partially by DOE/MHCoE

Segregation Energy in Nanocluster



Energy Difference between Surface Segregated and Internal "red" atom



A negative (positive) **Segregation Energy** indicates that the surface is the (un)favorable site.

- In contrast to most suggestions, **core-shell preference is determined by only two quantities:** cohesive (or surface) energy and size.
- Molecular adsorption can change the preference (changes surface energy).
- All known experimental results are reproduced with this correlation map.
- Correlation also reproduces surface-alloy segregation preference.
- Universal behavior shown via "tight-binding/Debye-Hückl" model.

Wang and Johnson, J. Amer. Chem. Soc. 131, 14023-14029 (2009).

Summary – electronic structure

- The core-shell behavior in transition-metal nanoparticles is governed by cohesive energy (or surface energy) and size differences, which predicts all observed structure.
- No nanoparticle size effect for dehydrogenation enthalpy exists; there is a reduction in kinetic barrier with catalyst.
- We are able to reproduce quantitatively the experimental observations. Notably errors exist in QC literature that use small clusters to approximate surfaces: So, there are no exothermic reactions in MgH_2 system.

Collaborations

Sandia National Laboratory –Determining if nanoparticles coat the surface or fill the internal structure in a MOF. (Mark Allendorf – non MHCoE collaboration)

University of Hawaii – Determine if MgH_2 particles are distributed inside the scaffold. Also, theory activity with to determining properties of MgH_2 clusters.

Brookhaven National Laboratory – determining the structure and composition of Al-H system. Surface study of Hydrogen interactions on surfaces and the effect of Ti.

Savannah River National Laboratory – characterization of aluminum- based hydrides

U. of Pittsburgh – theoretical characterization of metal-$B_{12}H_{12}$ (de)hydrogenated intermediate phases, including amorphous.

Georgia Tech – theoretical characterization of metal-$B_{12}H_{12}$ (de)hydrogenated intermediate phases, including amorphous.

Proposed Future Work

- Determine if the preliminary results from the surface study are valid, especially the spectroscopy results.
- Determine if atomic hydrogen on clean Al surfaces interacts in the same manner as molecular hydrogen when Ti is present.
- Repeat the study but with the addition of contaminants – carbon and oxygen to determine how they will impact the hydrogen surface interaction.
- Complete *ab initio* calculations of projected density-of-states and Fermi's golden rule to interpret the above STM experimental results.

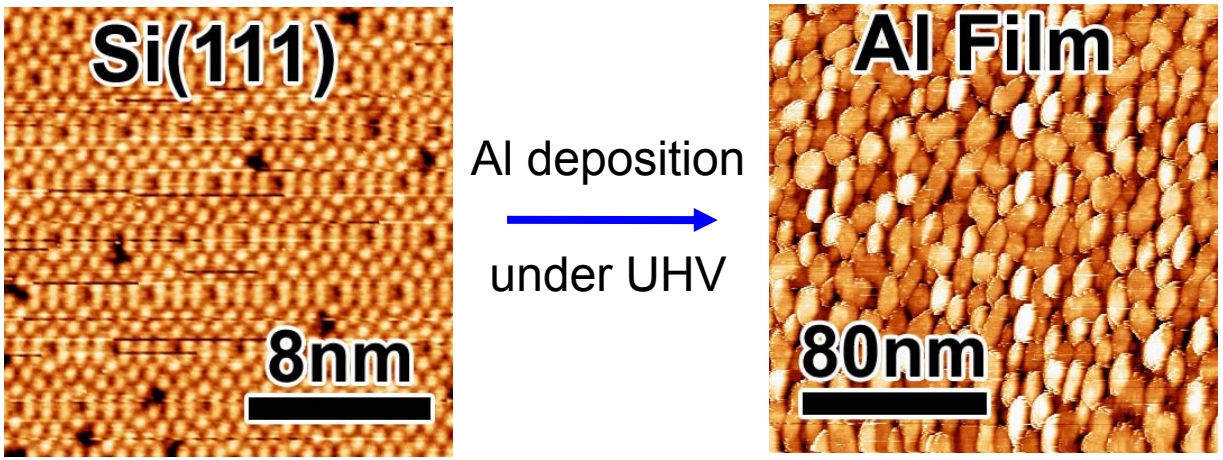
These studies will provide insight as to how to manipulate the surface composition to assist in the regeneration of aluminum hydrogen systems as well as enhancing our understanding of the role of Ti in general.

- Determine if the MgH_2 nanoparticles are distributed throughout the scaffold.
- Complete MgH_2 Kinetic barrier calculations for nanoparticle and bulk-terminated surface (initial results show ~20% reduction vs. size).

Supplemental Slides

How does hydrogen interact with clean surfaces in the presence and absence of a catalyst ?

- Existing work strongly suggests that how hydrogen interacts with pure and contaminated surfaces is crucial to understanding the fundamental processes of hydrogen uptake and release as well as impact of catalyst species. To investigate we have probed the interaction of molecular hydrogen with clean Al surfaces using Scanning Tunneling Microscopy
  - Thin film of Al has been grown epitaxially on Si(111) substrate

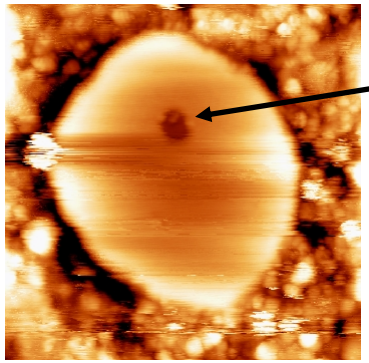


Si(111) with Al epitaxial layer chosen due to know growth conditions and similarity to other hydrogen-storage materials. (See, e.g., Hasan, et al. Vacuum 41 (1990) 1121.)

Contaminants change response of surface to hydrogen exposure !

Al-only surface activity during H_2 exposure:

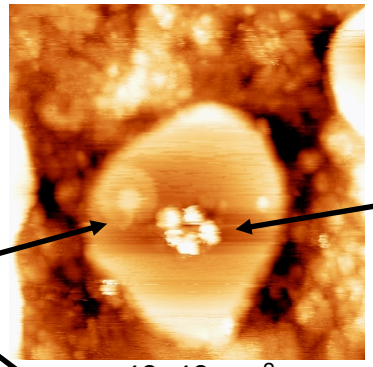
All images at:
V = -1.364 V
I = 0.200 nA.



Vacancy clusters

40x40 nm²

Secondary surface island formation

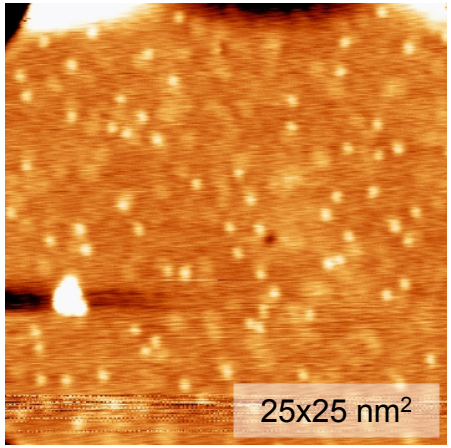


Mobile surface features

48x48 nm²

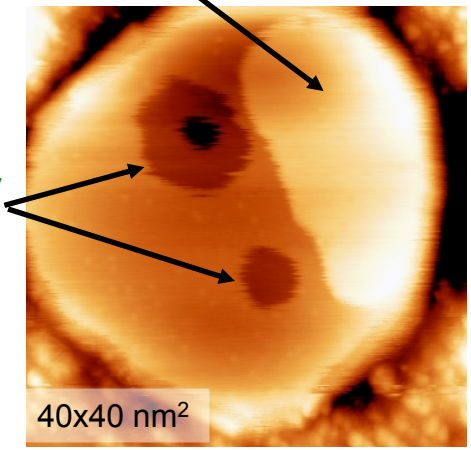
Carbon contamination might be cause of the changes?

Ti-dosed surface differences:

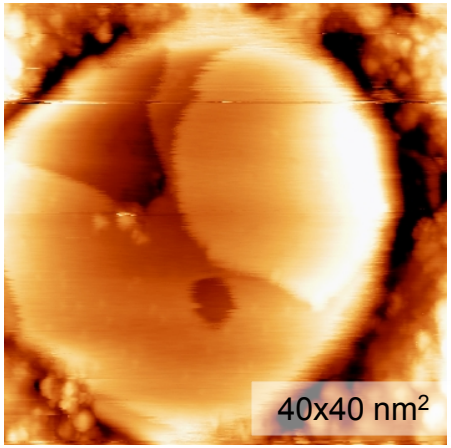


25x25 nm²

Vacancy islands



40x40 nm²



40x40 nm²

Two types of Ti atoms:

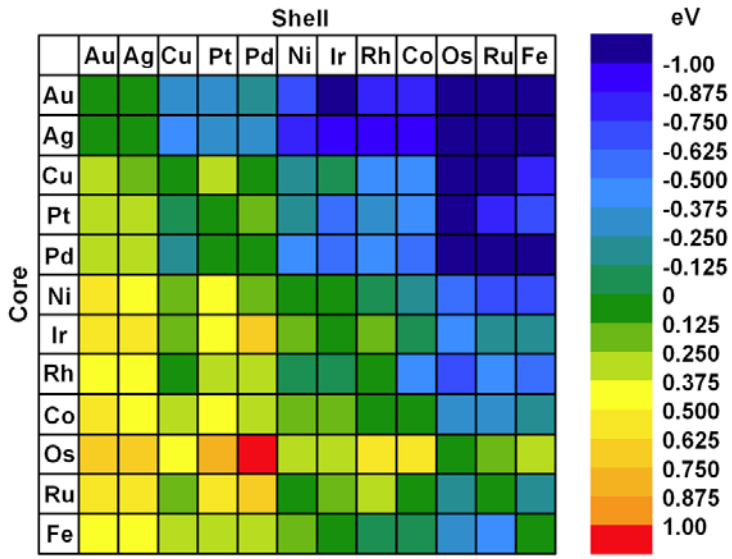
- 0.3-0.4 Å high, 4 Å wide → surface Ti?
- 0.2 Å high, 6 Å wide → subsurface Ti?

- 0.3-0.4 Å high Ti disappear, leaving almost entirely 0.2 Å high Ti.
- Instead of many small vacancy clusters, a few very large ones.
- Formation of large secondary surface islands.
- Fewer, but larger, highly mobile surface features (AlH_x?).

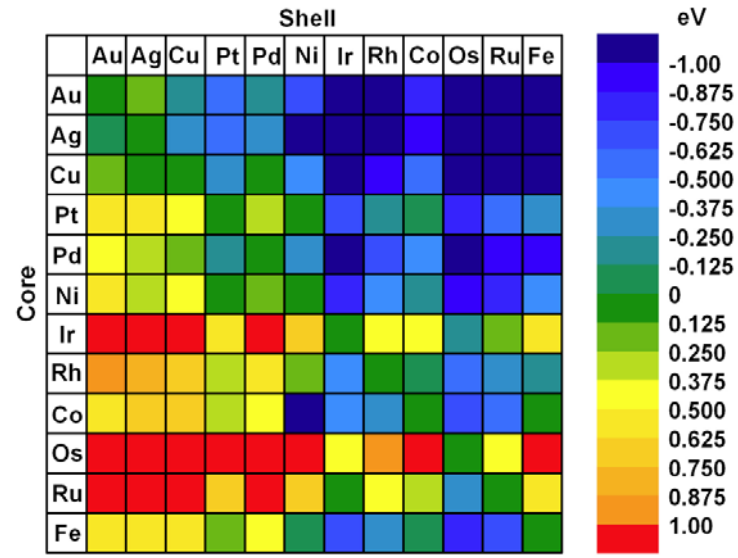
Transition-Metal Surface Alloys for Catalysis: "Design Maps" for Surface Enrichment

We apply same segregation energy arguments to surfaces.

fcc(111) Surface Segregation Energy



fcc(100) Surface Segregation Energy



- Again, we observe "universal" behavior for Core-shell (bulk/surface) preference from NP to bulk surfaces – driven by cohesive/surface energy and size only!
- "Maps" must be amended to include ligand-modified (functionalized) cases, which can alter (even reverse) surface enrichment.
- Correlation reproduces known surface-alloy segregation.
- Observed surface preference can depend on orientation, e.g., Ni-Pt has Ni on(110).

Wang and Johnson, J. Amer. Chem. Soc. 131, 14023-14029 (2009).

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