First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

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Project ID # STP3

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Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- Percent complete: 20%

Budget

- Requested total: $1.38M
- Cost sharing: 20%
- FY06 $175k (DOE), $44k (cost share)

Barriers

- Access to adequate computing resources
- Efficient and accurate electronic structure algorithms

Partners

- Collaborations with all experimental groups are sought
- Current collaborators:
  - HRL, GE, U. Hawaii, Stanford, UIUC, U. Utah, NIST, JPL, Cal Tech

Objectives

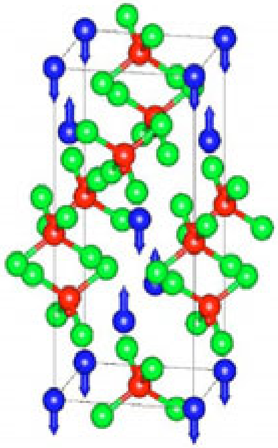
- Compute thermodynamic properties of metal hydride alloys—Heat of reaction, Δ*H*
  - Compute Δ*H* for known reactions to test accuracy of our approach
  - Compute Δ*H* for new reactions to identify promising destabilized compounds
  - This work complements experimental work on identifying destabilized metal hydrides (Focus area A—Destabilized Hydrides)
- Compute interfacial properties of hydrides
  - Metal-hydride interfaces
  - Surface energies of metal hydrides for nanoscopic hydrides
  - Apply principles learned on model systems to more promising novel materials.
  - Complements experimental work on improving kinetics for destabilized hydrides and other materials

Objectives

- Fundamental processes in hydrogenation
  - Study hydrogenation in destabilized hydrides and other systems to assess reversibility
  - Look for common hydrogenation pathways that might be applicable to other materials
  - Assess the role of interfacial transport
  - Some destabilized hydrides are not easily hydrogenated—this work supports experimental efforts to design a practical destabilized hydride system

Approach

- First principles density functional theory (DFT) for periodic systems (plane wave)
- Generalized gradient approximation (GGA) for the exchange-correlation functional
- Finite temperature and entropic properties computed from a phonon density of states approach with the PHONON software package
- Transition state finding methods for reaction and diffusion problems

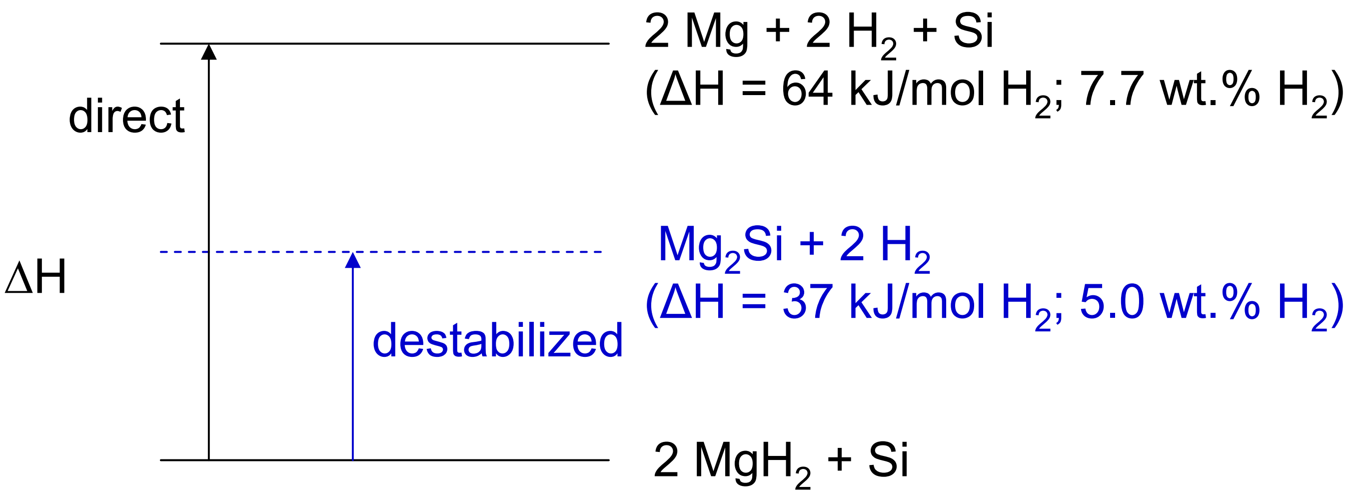


Destabilization of Metal Hydrides

Original concept introduced by Reilly and Wiswall[1] in late 1960's for Ni hydrides

Modification of dehydrogenation thermodynamics using additives
  - Stabilized dehydrogenated state reduces enthalpy of dehydrogenation

Recent application of this concept to light metal hydrides by Vajo et al.[2,3]



$2\,Mg + 2\,H_2 + Si$

(ΔH = 64 kJ/mol H_2; 7.7 wt.% H_2)

direct

$Mg_2Si + 2\,H_2$

(ΔH = 37 kJ/mol H_2; 5.0 wt.% H_2)

ΔH

destabilized

$2\,MgH_2 + Si$

1. J. J. Reilly, R. H. Wiswall, *Inorg. Chem.* **1967**, 6 , 2220
2. J. J. Vajo et al., *J. Phys. Chem. B* **2005**, 109, 3719
3. J. J. Vajo et al., *J. Phys. Chem. B* **2004**, 108, 13977

Technical Accomplishments

A DFT-based Database of Reaction Enthalpies

We have optimized the crystal structures of 52 solid materials listed in Wycoff[1], Pearson[2] and ICSD[3] comprised of Al, B, Ca, Li, Mg, Si, C, N, or H

Using this DFT-based database, we have considered 130 reactions that could not previously be evaluated as potential H_2 storage schemes.

1. R. W. G. Wycoff, *The Structure of Crystals,* The Chemical Catalog Company Inc., New York, 1931.
2. P. Villars, *Pearson's handbook : crystallographic data for intermetallic phases*; Desk ed. ed.; ASM International
3. The Inorganic Crystal Structure Database (ICSD), http://www.fiz-informationsdienste.de/en/DB/icsd/.

Technical Accomplishments

A DFT-based Database of Reaction Enthalpies Crystal Structure Issues:

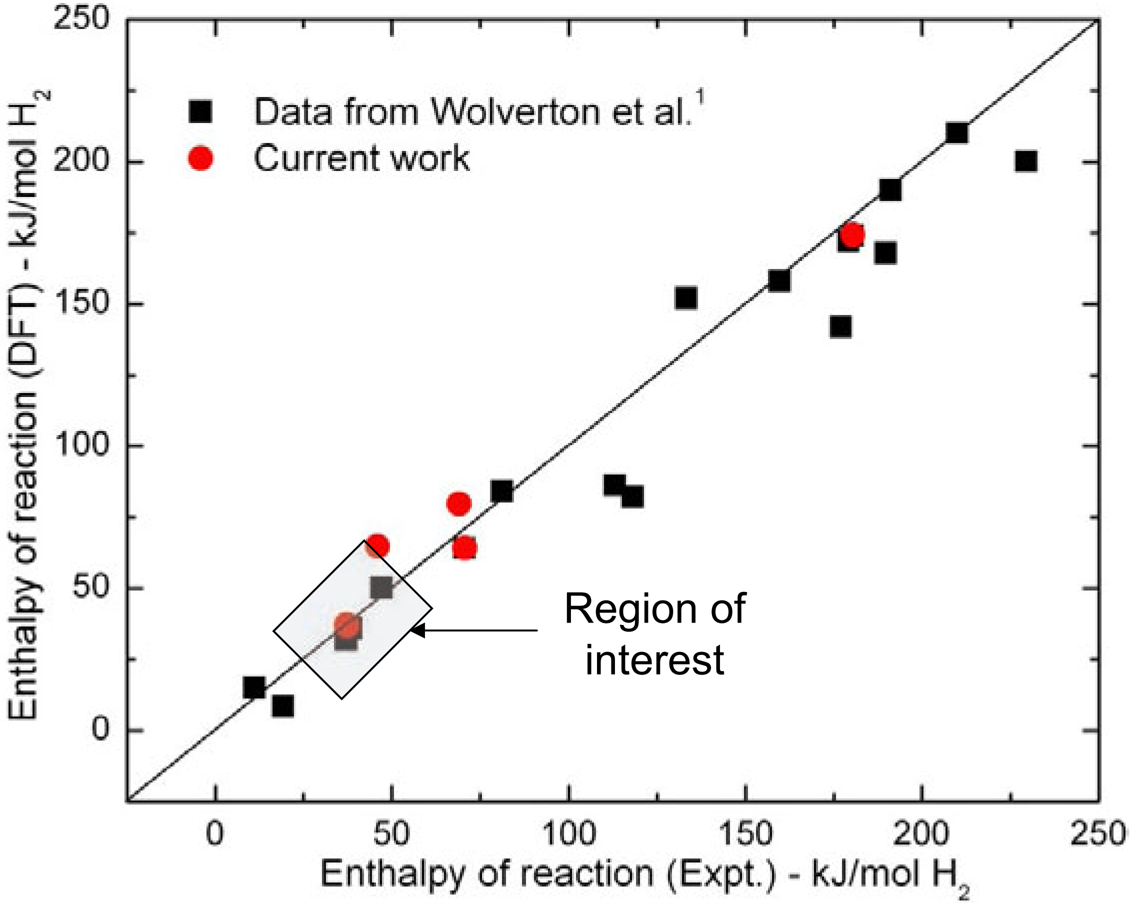
Full crystal structure of $Ca(AlH_4)_2$ is not known experimentally.
We used *ab initio* prediction of Løvvik[1]

Li_5N_3Si has very large unit cell with partial atomic occupancies.
DFT calculations performed with two materials with compositions $Li_{54}N_{32}Si_{10}$ and $Li_{53}N_{32}Si_{11}$ with Si distributed randomly.

1. O. M. Løvvik, *Phys. Rev. B* **2005**, 71, 144111

Accuracy of DFT - based Values of ΔH

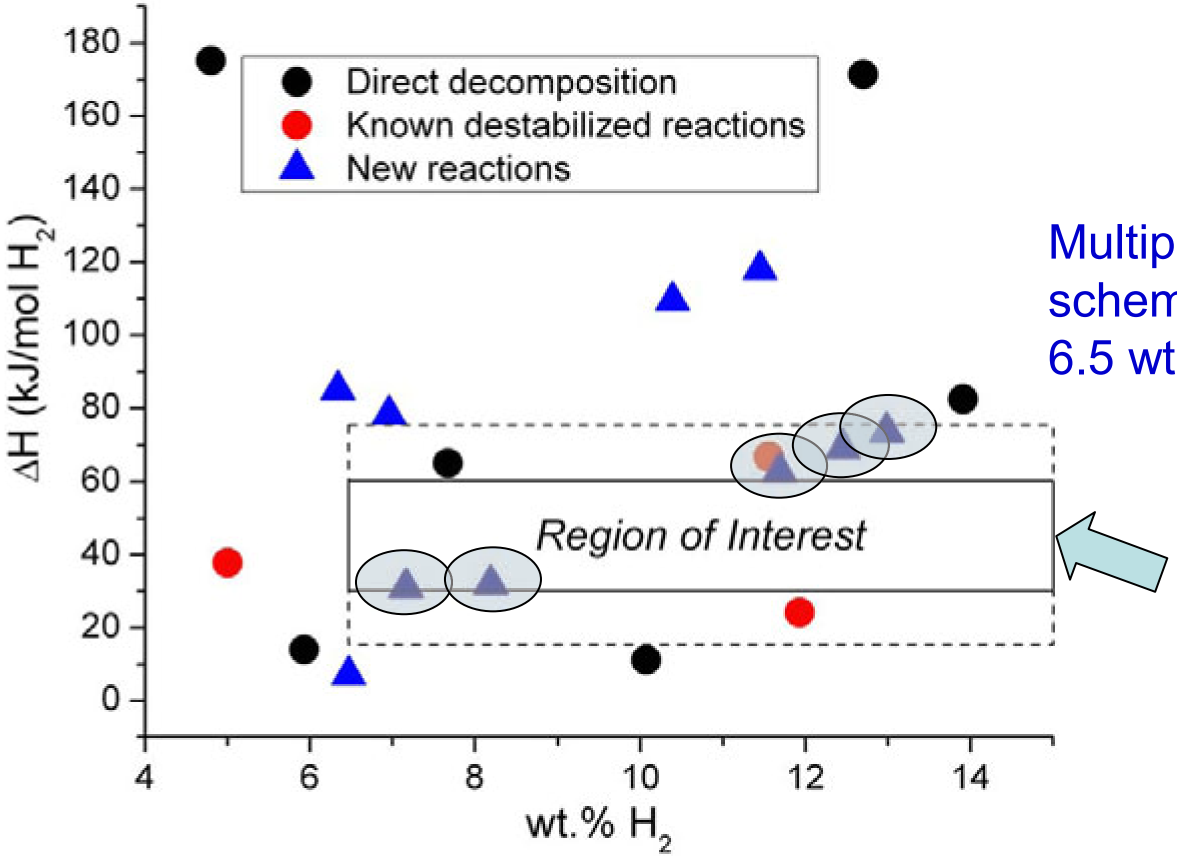
Experimental data available for many high Z metal hydrides (e.g. Sc, Pd, Ni, etc.)



RMS deviation in DFT results is 15 kJ/mol H_2 ;
this is sufficiently accurate for screening purposes

1. Wolverton et al., *Phys. Rev. B* **2004**, 69, 144109

Reactions of Interest

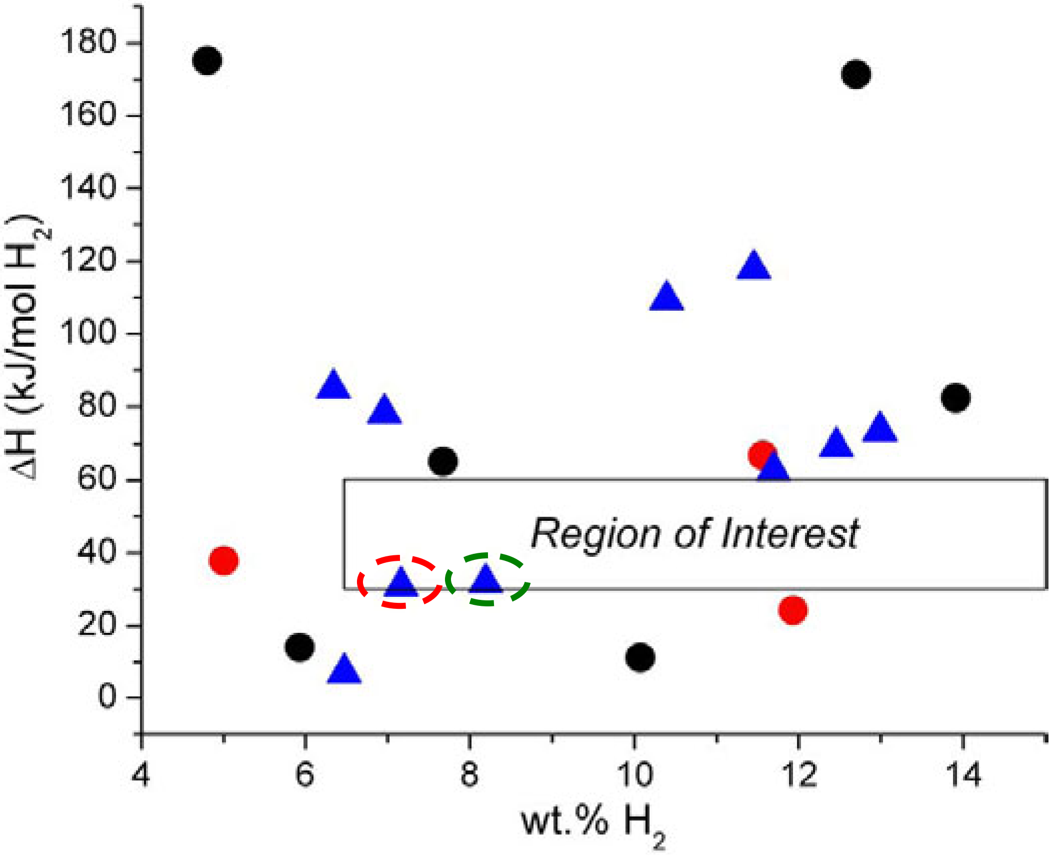


Multiple interesting reaction schemes identified which have > 6.5 wt% H_2

$15 \leq \Delta H \leq 75$

- Five new promising destabilization schemes identified – all have high storage densities and have promising thermodynamics.
- A large number of schemes (not shown) are less promising for either storage density or thermodynamic reasons (or both).

Reactions of Interest (cont.)

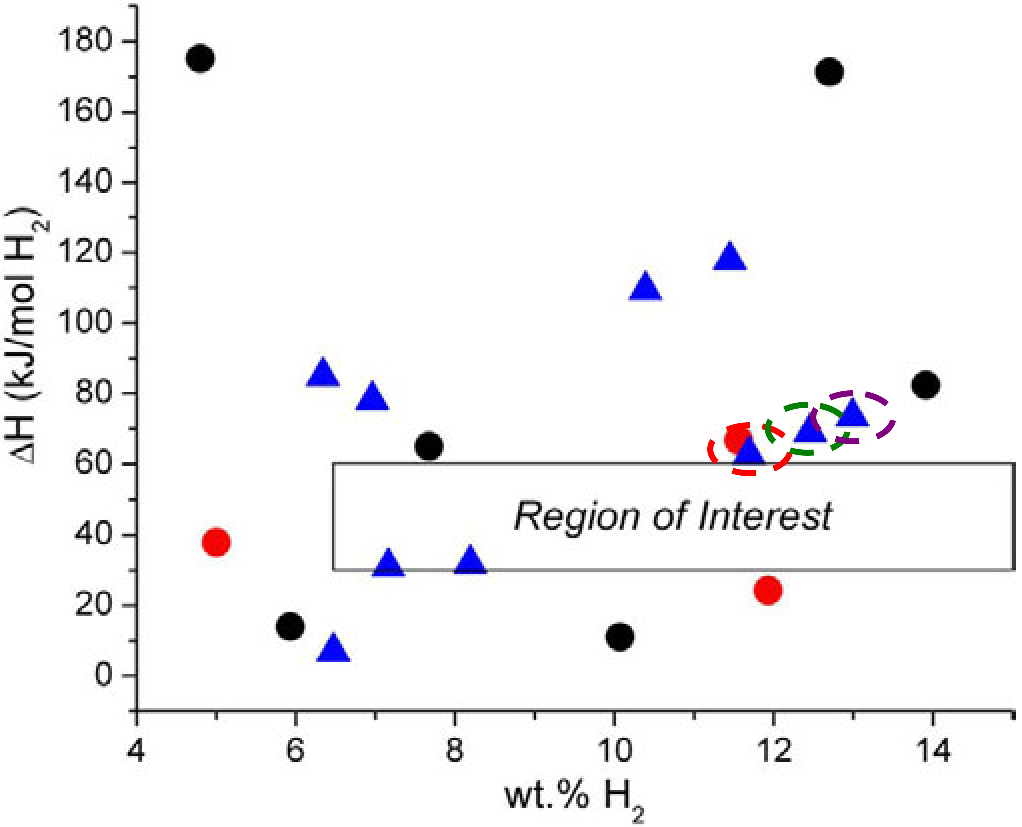


Rxn 1: 3 $LiNH_2$+ 2 LiH + Si → Li_5N_3Si + 4 H_2 ; 7.16 wt.% H_2

Δ H = 24-30 kJ/mol H_2 (variants of Li_5N_3Si stoichiometry)

Rxn 2: $LiNH_2$ + MgH_2 → LiMgN + 2 H_2 ; 8.19 wt.% H_2 ; Δ H = 32 kJ/mol H_2

Reactions of Interest (cont.)



Rxn 3: 6 $LiBH_4$ + CaH_2 → 6 LiH + CaB_6 + 10 H_2 ; 11.7 wt.% H_2 ; ΔH = 62 kJ/mol H_2

Rxn 4: 4 $LiBH_4$ + MgH_2 → 4 LiH + MgB_4 + 7 H_2 ; 12.5 wt.% H_2 ; ΔH = 69 kJ/mol H_2

Rxn 5: 7 $LiBH_4$ + MgH_2 → 7 LiH + MgB_7 + 11.5 H_2 ; 13.0 wt.% H_2 ; ΔH = 75 kJ/mol H_2

Rxn 4 and 5 analogous to Vajo et al.[1] reaction:

2 $LiBH_4$ + MgH_2 → 2 LiH + MgB_2 + 4 H_2

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1. J. J. Vajo et al., *J. Phys. Chem. B* **2005**, 109, 3719

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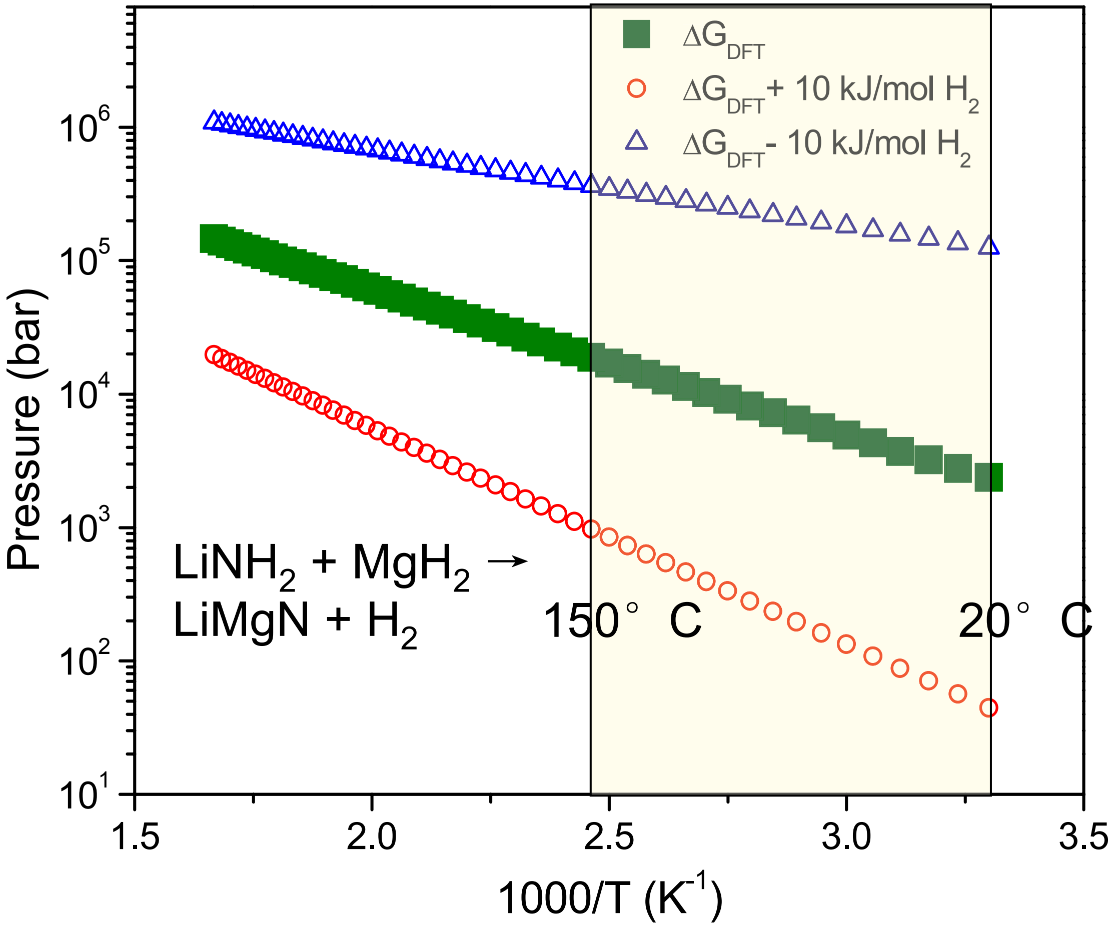
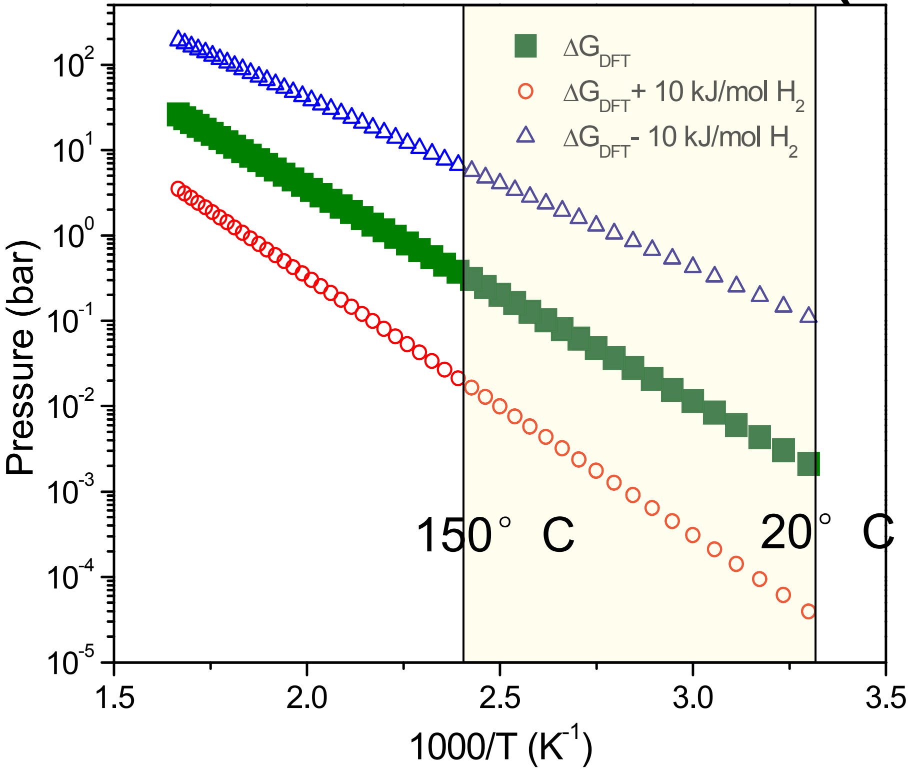
Van’t Hoff Plots for New Reactions



- The equilibrium pressure is very high over the temperature range of interest
- May be a useful material at lower temperatures
- ΔH ~ 20 kJ/mol H_2 over the temperature range

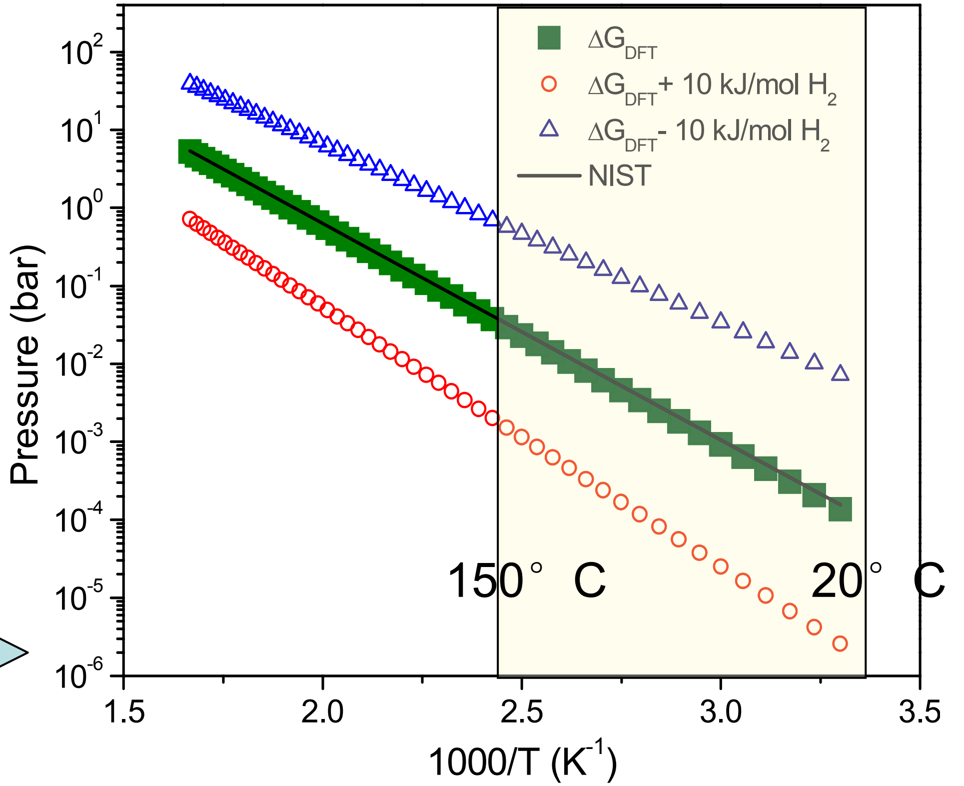
Caveat: Reversibility might be an issue as ΔH is low

Van’t Hoff Plots for New Reactions (cont.)



$6\ LiBH_4 + CaH_2 \rightarrow 6\ LiH + CaB_6 + 10\ H_2$

$4\ LiBH_4 + MgH_2 \rightarrow 4\ LiH + MgB_4 + 7\ H_2$



- Both these reactions have $P_{eq} < 1$ bar at room temperature
- The equilibrium pressure would need to be increased for these reactions to be useful

Computational Study of Dissociation of Hydrogen on Mg_2Si Surface

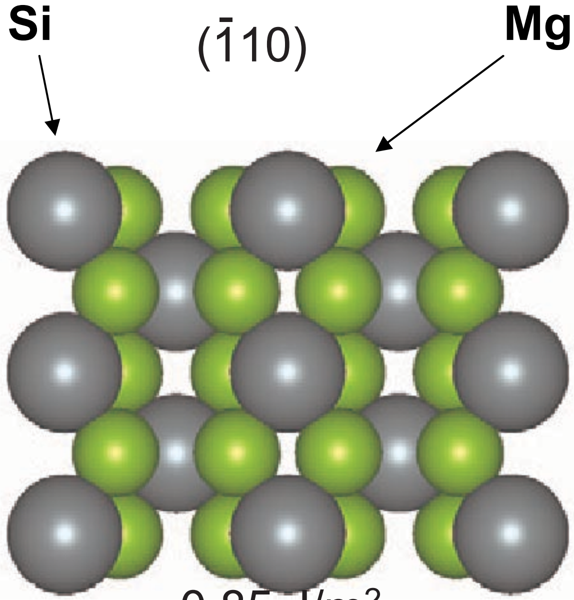
- One possible kinetic barrier to $Mg_2Si + H_2 \rightarrow MgH_2 + Si$ is the dissociation of H_2 on surfaces of Mg_2Si. [Large barriers to H_2 dissociation are known to exist on Mg(0001)[1]]
- This hypothesis can be disproved if facile pathways for H_2 dissociation are identified
- Many other atomic-scale processes must still be considered before a complete description of the overall hydrogenation reaction is available, i.e. oxide overlayer formation

1. T. Vegge, *Phys. Rev. B* **2004**, *70,* 035412

Mg_2Si Surface Energies

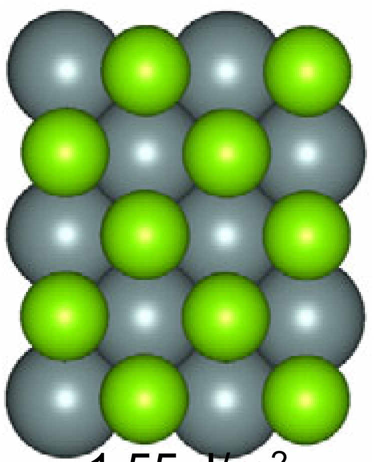
Surface energy is defined as: $E_{\text{surface}} = (E_{\text{total}} - N \times E_{\text{bulk}})/2A$

$(\bar{1}10)$



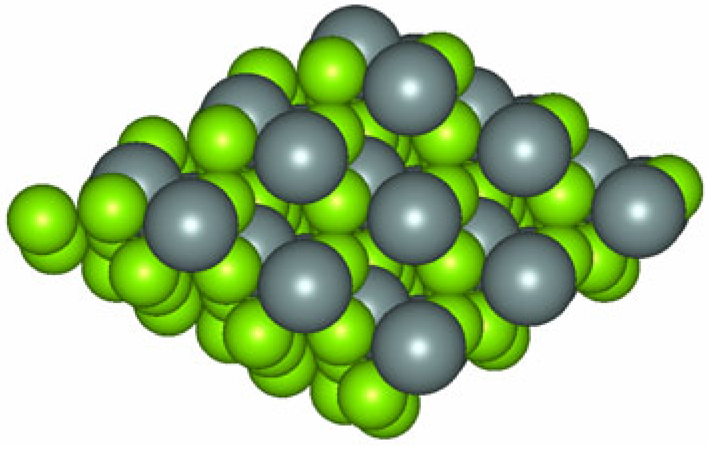
0.85 J/m²

(110)⇔(101)



1.55 J/m²

(111)⇔(100)⇔(010)⇔(001)

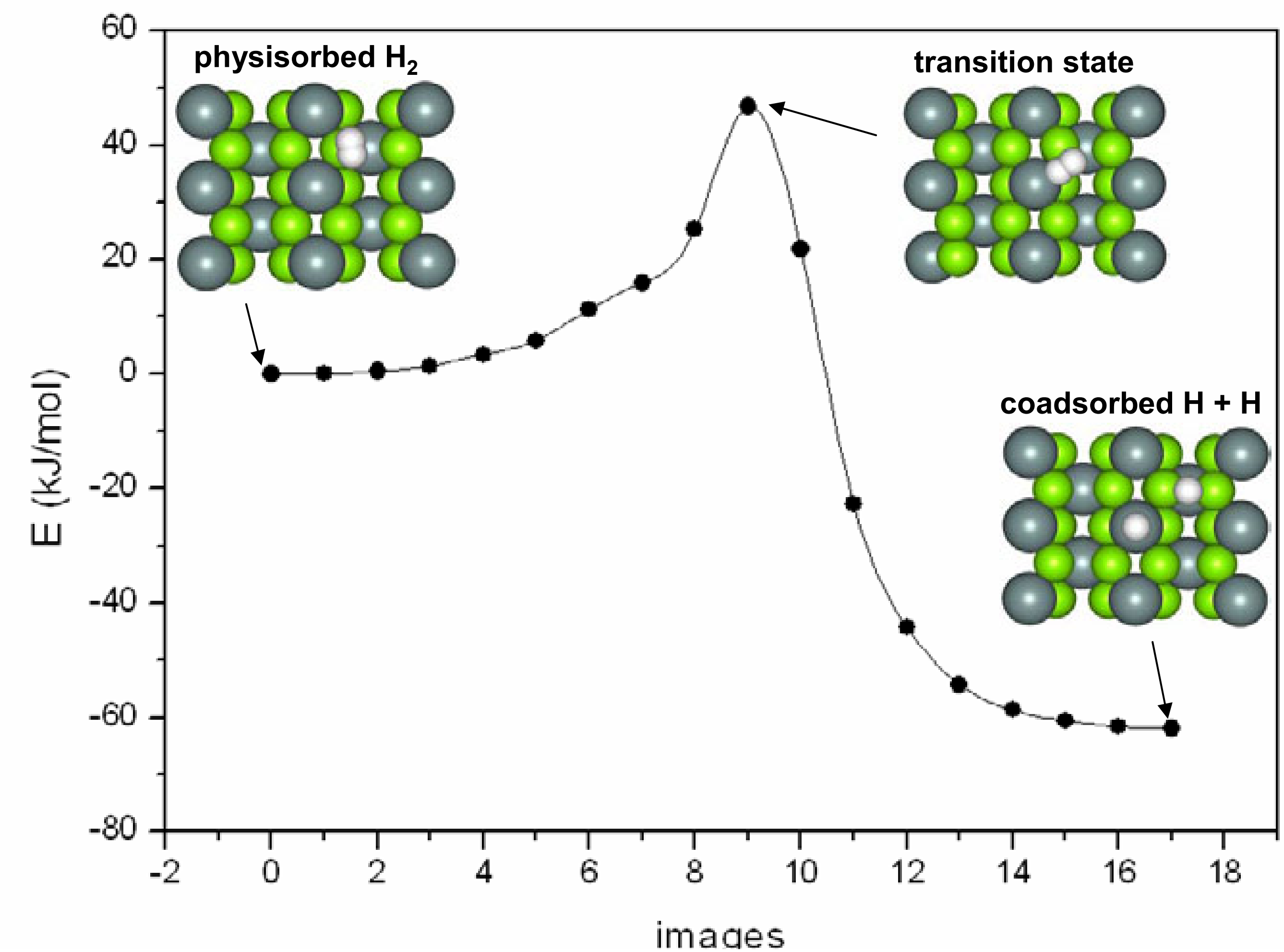


2.60 J/m²

Lower surface energies correspond to more energetically stable surfaces

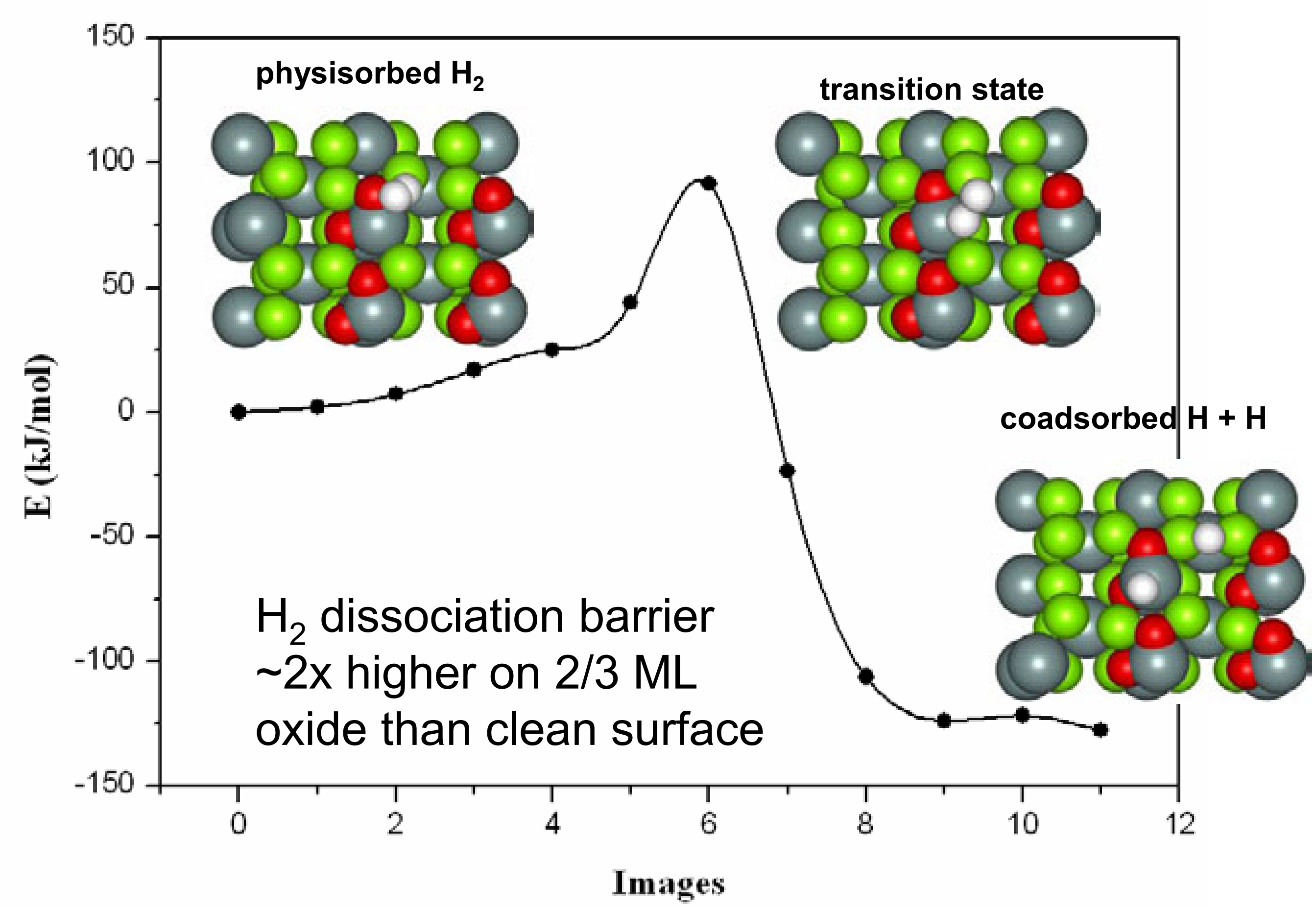
H_2 Dissociation on $Mg_2Si(\bar{1}10)$

Pathway for H_2 dissociation determined using Nudged Elastic Band method



Energy barrier to H_2 dissociation is 47 kJ/mol
(39 kJ/mol after zero point vibrational energy corrections)

H_2 dissociation on 2/3 ML Oxidation Mg_2Si Surface

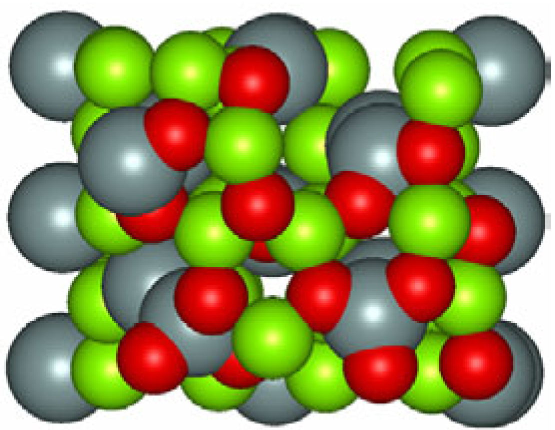


H_2 dissociation barrier ~2x higher on 2/3 ML oxide than clean surface

Energy barrier to H_2 dissociation is 92 kJ/mol (80 kJ/mol after zero point energy corrections)

Mg_2Si Surface Oxide Formation (beyond 7/6 ML)

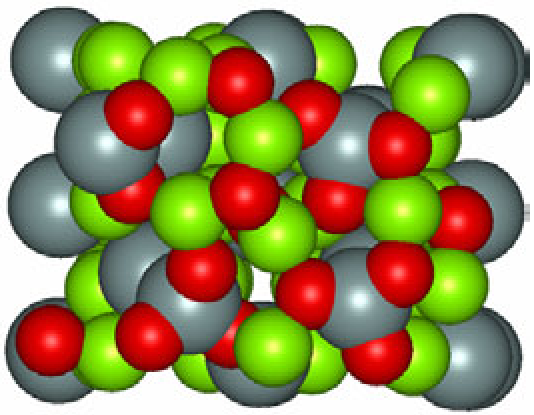
5/4 ML (15 O)



-4.45 eV/Oxygen

+ O

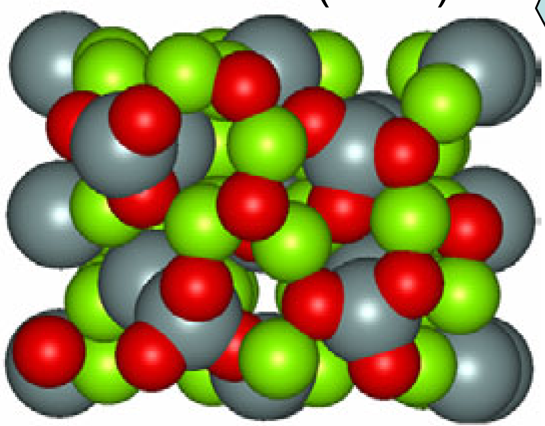
4/3 ML (16 O)



-4.48 eV/Oxygen

+ O

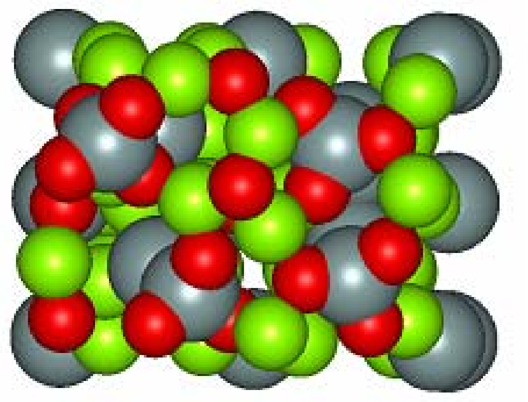
17/12 ML (17 O)



-4.49 eV/Oxygen

+ O

3/2 ML (18 O)



-4.48 eV/Oxygen

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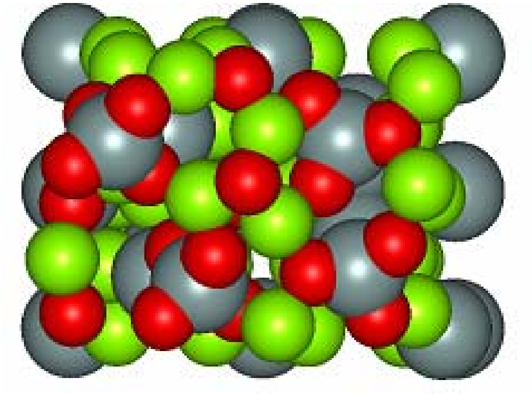
Mg_2Si Surface Oxide Formation (beyond 7/6 ML)

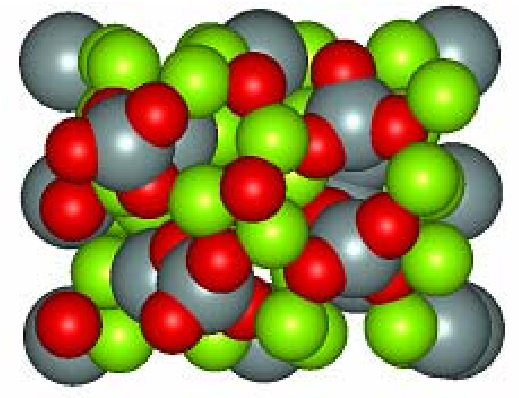
19/12 ML (19 O)



-4.45 eV/Oxygen

+ O

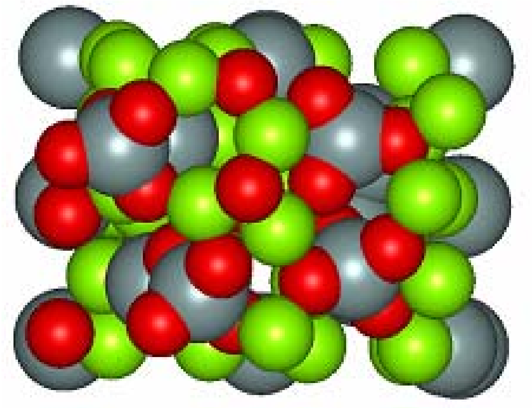
5/3 ML (20 O)



-4.49 eV/Oxygen

+ O

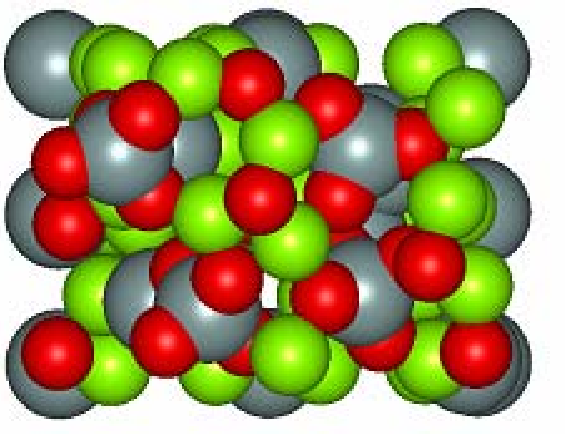
7/4 ML (21 O)



-4.45 eV/Oxygen

+ O

11/6 ML (22 O)



-4.22 eV/Oxygen

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H_2 Dissociation on Oxide Mg_2Si Surface

- The adsorption energy per O atom is roughly constant from 1 ML to 7/4 ML, ~-4.5 eV

Coverage (ML)	1/3	2/3	1	13/12	7/6	5/4	4/3	17/12
$E_{ads/O}$ (eV)	-3.57	-4.01	-4.44	-4.48	-4.45	-4.45	-4.48	-4.49
$E_{ads/H}$ (eV)	----	-0.84	-0.53	-1.21	-0.23	----	----	----
Coverage (ML)	3/2	19/12	5/3	7/4	11/6			
$E_{ads/O}$ (eV)	-4.48	-4.45	-4.49	-4.45	-4.22			

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Future Work

- Continue work on destabilized hydride reversibility
- Investigate new reaction schemes for destabilized hydrides including other light elements
- Continue work on computing P-T diagrams for metal hydrides
- Continue work on interfacial energies
- Contribute data to the UIUC toolbox data base
- Collaborate with Ursula Kattner, NIST by computing thermodynamic properties of Li_5B_4 and other materials

Summary

- We have screened over one hundred destabilization reactions based on reaction enthalpy using DFT calculations
- Five promising reaction schemes have been identified
- Equilibrium pressures have been predicted for three of the reactions from first principles
- Facile dissociation of H_2 should be observed on the clean Mg_2Si surface
- Oxide formation on Mg_2Si is highly exothermic
- Hydrogen dissociation is inhibited on the oxidized Mg_2Si surface
- Our calculations are consistent with the experimental observation that ball milling in a hydrogen atmosphere is required for hydrogenation of Mg_2Si

Publications and Presentations

- Publications:
  - Identification of Destabilized Metal Hydrides for Hydrogen Storage Using First Principles Calculations, by S.V. Alapati, J.K. Johnson, D.S. Sholl, J. Chem. Phys. B, in press
- Presentations:
  - Invited talk at the “Hydrogen Storage with Novel Nanomaterials” workshop, 23-28 October, in Ban Honnef, Germany
  - “Mechanisms of Hydrogen Adsorption in Metal Organic Frameworks”, AIChE Annual Meeting, Cincinnati, Ohio, 31 October to 4 November, 2005.
  - J. Karl Johnson, Sudhakar V. Alapati, Bing Dai, David S. Sholl “Computational Study of Metal Hydride Destabilization” *American Physical Society March Meeting*, Baltimore, MD, 13-17 March, 2006.
  - Bing Dai, Sudhakar V. Alapati, David S. Sholl and J. Karl. Johnson “First Principles Investigation of Adsorption and Dissociation of Hydrogen on the Mg_2Si Surface” *231st American Chemical Society National Meeting*, Atlanta Georgia, 26-30 March 2006.
  - Sudhakar V. Alapati, Bing Dai, J. Karl. Johnson and David S. Sholl, “First Principles Calculations of Destabilized Alloys for Hydrogen Storage Applications” *2006 TMS Annual Meeting*, San Antonio, TX, 12-16 March, 2006.
  - Organized a session on “Nanotechnology related to the hydrogen economy” as part of the Nanotechnology and the Environment symposium, ACS National Meeting, Atlanta, GA, 26-30 2006

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