Atomistic Simulations of Hydrogen Storage in Metal Hydrides and Nanoporous Sorbents

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Outline

- **Metal Organic Frameworks**
  - Simulation methods for $\text{H}_2$ adsorption in MOFs
  - Validation and predictions for existing MOFs
  - Where and how $\text{H}_2$ adsorbs in MOFs—volume density of states

- **Metal Hydrides**
  - Thermodynamics of destabilized metal hydrides
  - Calculation methods
  - Reaction enthalpies: Test systems and predictions
  - Entropic contributions & van’t Hoff plots
  - Kinetic issues: Dissociation of $\text{H}_2$ on $\text{Mg}_2\text{Si}$
Why study $\text{H}_2$ adsorption in MOFs?

- Metal organic frameworks have been found to be very good adsorbents for methane.
  - Snurr and collaborators have found that computer simulation results for methane compare very well with experiments, and predicted the structure of a new material with a very large methane adsorption.

- Experiments of $\text{H}_2$ adsorption on MOFs at 77 K (Rosi et al., Rowsell et al.) and 298 K (Rosi et al.) indicate that these materials are promising candidates for meeting the DOE targets.
Metal Organic Frameworks

- Metal-oxide vertices held together with organic linkers
- Easy to synthesize
- Stable under a wide range of temperature and pressures
- Large effective surface area (many sites for adsorption)
- Comparatively light
- Can be tailored by changing metal groups, ligands, & organic linkers

Structure of IRMOF-14
Modeling Hydrogen Adsorption in MOFs

- Structure of the MOFs: rigid framework obtained by XRD experiments
- Solid-fluid potential: standard UFF force field
- Fluid-fluid potential: Buch potential: Spherical, $\varepsilon = 34.7$ K, $\sigma = 2.96$ Å
- Computational technique: grand canonical Monte Carlo
  - Quantum diffraction effects at 77 K treated by path integral Monte Carlo and the Feynman Hibbs effective potential approximation.
Adsorption Isotherms for H₂ on IRMOF-1 at 77K: Comparison with Experiments

(b)

- Simulations: Buch potential
- Simulations: FH Effective Buch Potential
- Wong-Foy et al., JACS, 128, 3494 (2006)
- Ahn group, JPCB, 110, 1099 (2006)
- Rowsell et al. JACS, 126, 5666 (2004)
Adsorption Isotherms for H₂ on IRMOF-1 at 77K: Comparison with Experiments
H$_2$ Adsorption in IRMOF-1 at 298 K

- Experimental data by Rosi et al. (O. Yaghi’s group) published in Science, 300, 1127 (2003)
- Simulation data are predictions, no adjustable parameters
Prediction: Excess Adsorption at 77K
Prediction: Excess Adsorption at 298K
Volumetric Density of States
What are the Properties of Ideal Adsorbents?

- $\Delta G = \Delta H - T\Delta S < 0$.
- Estimate of $\Delta S$: an ideal gas at 100 bar minus one degree of freedom at 298 K: $-T\Delta S \approx 1600$ K (13 kJ/mol).
- One would need high volumetric density of states available in the PES at an energy $U = \Delta H \sim T\Delta S$ to have large adsorption.
- MOF 2 and 3 have sites at almost the right energy, but low volume density of states.
- IRMOFs have a high volume density of states, but for energies that are too weak.
Conclusions—MOFs

- The computer simulations are in fairly good agreement with many experiments on MOFs.
- Problems with experiments have been identified by comparison with simulation data.
- The MOFs we have tested do not meet the DOE requirements at 298K.
  - The volume available for adsorption is large enough.
  - The energy of the adsorption sites is too weak.
- Computer simulations will be useful to estimate the adsorption properties of MOFs yet to be synthesized.
- Stronger adsorption are needed, e.g., unsaturated metals, spillover.
Why Metal Hydrides?

- Metal hydrides can have very high volumetric densities, much higher than liquid H\(_2\).
- Hydrides of period 2 and 3 metals can also have very high gravimetric densities.
So Why Not Metal Hydrides?

- Temperatures required for dehydrogenation
- Reversibility
- Heat management
A useful way to characterize a metal hydride is the temperature at which the material is in equilibrium with 1 bar H₂:

\[ \Delta G = 0 \text{, so } \Delta H = T \Delta S \]

For a large number of simple metal hydrides, \( \Delta S \sim 130 \text{ J K}^{-1} \text{ mol}^{-1} \)

For some complex metal hydrides (e.g. LiBH₄), \( \Delta S \sim 100 \text{ J K}^{-1} \text{ mol}^{-1} \)

\[ 100 < \Delta S < 130 \text{ J K}^{-1} \text{ mol}^{-1} \quad 25 < T < 150 \text{ °C} \]

\[ 30 < \Delta H < 60 \text{ kJ/mol H}_2 \]
Thermodynamics of H₂ Storage in Metal Hydrides

Direct decomposition: MHₓ → M + (x/2) H₂

Some metal hydrides satisfy density requirements but not thermodynamic requirements.
Destabilization of Metal Hydrides


Direct reaction: \[ \text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2 \] \( (\Delta H = 64 \text{ kJ/mol H}_2; 7.7 \text{ wt.} \% \text{ H}) \)

Destabilized reaction:
\[ 2 \text{MgH}_2 + \text{Si} \rightarrow \text{Mg}_2\text{Si} + 2 \text{H}_2 \] \( (\Delta H = 37 \text{ kJ/mol H}_2; 5.0 \text{ wt.} \% \text{ H}) \)

\[ \text{direct} \quad \Delta H \quad \text{destabilized} \]

\[ \text{Mg}_2\text{Si} + 2 \text{H}_2 \]

\[ 2 \text{Mg} + 2 \text{H}_2 + \text{Si} \]

\[ 2 \text{MgH}_2 + \text{Si} \]
Destabilization of LiBH$_4$


Direct reaction: LiBH$_4$ $\rightarrow$ LiH + B + 3/2 H$_2$ ($\Delta H = 82$ kJ/mol H$_2$; 13.91 wt.% H)

Destabilized reaction:
2 LiBH$_4$ + MgH$_2$ $\rightarrow$ MgB$_2$ + 2LiH + 4 H$_2$ ($\Delta H = 67$ kJ/mol H$_2$; 11.56 wt.% H)
Practical Limitations of Destabilized Metal Hydrides

Rapid kinetics are required both for H₂ production and hydrogenation.

However, strong kinetic limitations are observed for hydrogenation in both destabilized systems:

\[
\text{Mg}_2\text{Si} + \text{H}_2 \rightarrow 2 \text{MgH}_2 + \text{Si}
\]
not observed even under extreme conditions

\[
2 \text{LiBH}_4 + \text{MgH}_2 \rightarrow \text{MgB}_2 + 2 \text{LiH} + 4 \text{H}_2
\]
gives ~9 wt.% reversible storage, but only at \(T > 250 \, ^\circ C\) (with Ti used as catalyst with ball-milled materials)

Many schemes can be considered, but thermodynamic data are unavailable for most compounds of interest.

Goals of our work:
- Identify reaction schemes yielding > 7 wt.% H₂ with 30 < ΔH < 60 kJ/mol H₂
- Understand origin of kinetic limitations, specifically for Mg₂Si+H₂

Challenges

Identify other destabilization schemes with favorable thermodynamics
Plane wave Density Functional Theory (DFT) is well suited to treating hydrogen interactions with metals

Examples:
H solubility and diffusion through CuPd alloys (Kamakoti et al., Science 307 (2005) 569)


Our calculations:
- Vienna *ab initio* Simulation package (VASP)
- GGA functional with PAW approach (USPP gives similar results)
- Convergence reached with energy cutoff and *k*-space sampling
- All solid state structures fully optimized within experimental space group
What is Density Functional Theory?

Molecular orbital method is “an approximate solution to an exact equation”

\[ H\Psi = E\Psi; \quad E = E[\Psi] \]

- Many-body problem is impossible to solve exactly

DFT is “an exact solution to an approximate equation”

\[ E = T_s[n] + U[n] + V[n] + E_{xc}[n]; \quad E = E[n(r)] \]

- Exact form of \( E_{xc} \) is unknown
First-Pass Estimation of $\Delta H$: Limitations

- Accuracy of DFT
- Approximate $\Delta H \approx \Delta E$
- All calculations at $T = 0$ K
- Heat capacities needed for finite $T$
- No zero point energy corrections
- Phonon density of states needed to compute free energies & equilibrium pressures
Accuracy of DFT-based Values of $\Delta H$


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.
A DFT-based Database of Reaction Enthalpies

We have optimized the crystal structures of 51 solid materials listed in Wycoff or Pearson comprised of Al, B, Ca, Li, Mg, Si, or H:

Al, Al_{12}Mg_{17}, Al_{2}Ca, Al_{2}Ca_{3}Si_{2}, Al_{2}CaSi_{2}, Al_{2}Li_{3}, AlB_{2}, AlH_{3}, AlLi, AlLi_{3}N_{2}, AlLiSi, AlN, Sc, Sc_{5}Si_{3}, ScB_{2}, ScB_{12}, ScH_{2}, ScN, ScSi, ScSi_{2}, Al_{2}Sc, Al_{3}Sc, AlSc_{2}, Li_{3}ScN_{2}, Ca_{2}LiSi_{3}, Ca_{2}N, CaB_{6}, CaH_{2}, CaLi_{2}, CaLiSi_{2}, CaMg_{2}, CaSi, Li, Li_{12}Mg_{3}Si_{4}, Li_{3}N, Li_{5}N_{3}Si, LiBH_{4}, LiH, LiN_{3}, LiNH_{2}, Mg, Mg_{2}Si, Mg_{3}N_{2}, MgB_{2}, MgB_{4}, MgH_{2}, Si, SiB_{6}, B

Full crystal structure of Ca(AlH_{4})_{2} is not known experimentally.

We used ab initio prediction of Løvvik (Phys. Rev. B 71 (2005) 144111)

LiBH_{4} transforms from Pnma at low T to P6_{3}mc at 384 K

(Soulie et al., J. Alloys Compounds 346 (2002) 200)

Results below are for Pnma form (giving higher ΔH than P6_{3}mc)

Li_{5}N_{3}Si 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.

Using this DFT-based database, we have considered >100 reactions that have not previously be evaluated as potential H_{2} storage schemes.
Six new promising destabilization schemes identified – all have high densities & promising thermodynamics. Most schemes (not shown) are less promising for either storage density or thermodynamic reasons (or both).
# Promising Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>wt.% H₂</th>
<th>ΔH (USPP)</th>
<th>ΔH (PAW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 LiNH₂ + 2 LiH + Si → Li₅N₃Si + 4 H₂ (10/11 Si atoms)</td>
<td>7.16</td>
<td>29.8/19.2</td>
<td>34.2/23.3</td>
</tr>
<tr>
<td>4 LiBH₄ + MgH₂ → 4 LiH + MgB₄ + 7 H₂</td>
<td>12.46</td>
<td>66.8 (o) 57.5 (h)</td>
<td>69.2 (o) 59.9 (h)</td>
</tr>
<tr>
<td>7 LiBH₄ + MgH₂ → 7 LiH + MgB₇ + 11.5 H₂</td>
<td>12.99</td>
<td>69.2-73.1 (o) 59.2-63.1 (h)</td>
<td>71.5-75.5 (o) 61.5-65.5 (h)</td>
</tr>
<tr>
<td>CaH₂ + 6 LiBH₄ → CaB₆ + 6 LiH + 10 H₂</td>
<td>11.69</td>
<td>60.3 (o) 50.4 (h)</td>
<td>62.7 (o) 52.9 (h)</td>
</tr>
<tr>
<td>LiNH₂ + MgH₂ → LiMgN + 2 H₂</td>
<td>8.19</td>
<td>29.7</td>
<td>31.9</td>
</tr>
<tr>
<td>ScH₂ + 2 LiBH₄ → ScB₂ + 2 LiH + 4 H₂</td>
<td>8.91</td>
<td>--</td>
<td>49.7</td>
</tr>
</tbody>
</table>
DFT calculations gave the $T = 0$ enthalpy. Is this enough?

\[ G \approx U_0 + U_{ZP} + U_{vib}^{'}(T) - TS_{vib}(T) + PV \]

DFT total energy

harmonic approximation using PHONON code (Parlinski)

Equilibrium pressure for decomposition reaction given by

\[ P = P_0 \exp\left(-\frac{\Delta G(T)}{RT}\right). \]
Validation of DFT + Phonon Approach

Calculate Van’t Hoff Plots to predict equilibrium pressure for the reaction at any temperature $T$

\[ \Delta H(T=0) \]

PHONON code\(^1\) direct lattice method

$C_v$ and Entropy $S$ → Changes in Gibbs Free Energy $\Delta G$

1. K. Parlinski, Sofware PHONON 2005
Sodium Alanate: $3\text{NaAlH}_4 \rightarrow \text{Na}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2$

2 LiBH₄ + MgH₂ → MgB₂ + 2 LiH + 4 H₂

2 LiBH₄ + MgH₂ → MgB₂ + 2 LiH + 4 H₂

Exp: Vajo et al. JPCB 109, 3719 (2005)
\[2\text{MgH}_2 + \text{Si} \rightarrow \text{Mg}_2\text{Si} + 2\text{H}_2\]
LiNH$_2$ + MgH$_2$ → LiMgN + 2H$_2$

$\Delta G_{\text{DFT}}$ $\Delta G_{\text{DFT}} + 10$ kJ/mol H$_2$

$\Delta G_{\text{DFT}} - 10$ kJ/mol H$_2$
6LiBH$_4$ + CaH$_2$ $\rightarrow$ CaB$_6$ + 6LiH + 10H$_2$

$T(°C)$

Hexagonal LiBH$_4$

Orthorhombic LiBH$_4$

Pressure (bar)

1000/T (K$^{-1}$)

$\Delta G_{DFT}$

$\Delta G_{DFT} + 10$ kJ/mol H$_2$

$\Delta G_{DFT} - 10$ kJ/mol H$_2$
ScH$_2$ + 2LiBH$_4$ → ScB$_2$ + 2LiH + 4H$_2$
Prediction of Vapor Pressures

- \( \text{LiNH}_2 + \text{MgH}_2 \rightarrow \text{LiMgN} + 2\text{H}_2 \)
  - Pressure probably too high
- \( 4\text{LiBH}_4 + \text{MgH}_2 \rightarrow 4\text{LiH} + \text{MgB}_4 + 7\text{H}_2 \)
  - Pressure probably too low
- \( 7\text{LiBH}_4 + \text{MgH}_2 \rightarrow 7\text{LiH} + \text{MgB}_4 + 11.5\text{H}_2 \)
  - Pressure probably too low
- \( 6\text{LiBH}_4 + \text{CaH}_2 \rightarrow \text{CaB}_6 + 6\text{LiH} + 10\text{H}_2 \)
  - Pressure probably too low
- \( \text{ScH}_2 + 2 \text{LiBH}_4 \rightarrow \text{ScB}_2 + 2 \text{LiH} + 4 \text{H}_2 \)
  - Just about right! ~1 bar @ 50 °C

Experiments on these materials are needed!
Strong kinetic limitations observed in destabilized reactions studied to date:

\[ \text{Mg}_2\text{Si} + \text{H}_2 \rightarrow 2\text{MgH}_2 + \text{Si} \]

\[ \text{Mg}_2\text{Si} + 2\text{H}_2 \rightarrow 2\text{MgH}_2 + \text{Si} \]

No evidence for hydrogenation
H₂ Dissociation on Mg₂Si Surfaces

One possible kinetic barrier to Mg₂Si + H₂ → MgH₂ + Si is the dissociation of H₂ on surfaces of Mg₂Si
Large barriers to H₂ dissociation are known to exist on Mg(0001)

This hypothesis can be disproved if facile pathways for H₂ dissociation are identified

Our strategy is to compute the most favorable binding sites for H-atoms and H₂ on Mg₂Si(\{\bar{1}10\}) and then to find possible dissociation pathways using the Nudged Elastic Band method* within VASP. The Mg₂Si(\{\bar{1}10\}) surface is very likely to be present in equilibrium Mg₂Si crystals. It is lower in surface energy than other low index surfaces.

**H$_2$ Dissociation on Mg$_2$Si($\bar{1}10$)**

Energy barrier to H$_2$ dissociation is 45 kJ/mol (39 kJ/mol after ZP corrections)


Dissociation of H$_2$ is facile at room temperature
H₂ Dissociation on Mg₂Si

H₂ dissociation rates can be estimated using Transition State Theory

TST dissociation rate/surface site at P_{H₂} = 1 bar:
- T = 20 °C → rate is > 1 s⁻¹
- T = 300 °C → rate is > 1000 s⁻¹

H₂ dissociation appears to be facile on Mg₂Si(\bar{1}10)
so H₂ dissociation is not the rate limiting step in Mg₂Si hydrogenation

Many other atomic-scale processes must still be considered
before a complete description of the overall hydrogenation
reaction is available
- Oxide overlayer formation?
- Formation of MgH₂ from the hydrogenated surface?
- Segregation of MgH₂ and Si?
Oxide Formation on the Mg$_2$Si Surface: 2/3 Monolayer Coverage

Energy barrier to H$_2$ dissociation is 92 kJ/mol (80 kJ/mol after zero point energy corrections)
Energetics of Oxide Formation On Mg$_2$Si

Adsorption Energy per O (kJ/mol) vs Oxygen Coverage (ML)
What is the Extent of Oxide Formation?

Surface Energy (meV/Å²) vs. O₂ pressure at 300 K (atm)

\[
\gamma = \frac{1}{2A} \left[ E^{\text{slab}} - \frac{1}{2} N O E^{\text{O}_2} - N_{\text{Mg}_2\text{Si}} E^{\text{bulk}}_{\text{Mg}_2\text{Si}} - N O \mu_O(p,T) \right]
\]
Energy barrier to H$_2$ dissociation on the 7/4 ML oxide surface is 195 kJ/mol.
Conclusions—Metal Hydrides

- Destabilized metal hydrides are perhaps the most promising known materials for achieving high density reversible storage of H₂.
- Our DFT-based database has allowed several hundred additional reactions to be screened based on reaction enthalpy.
- Six promising examples have been identified, plus a larger number of metastable reaction schemes.
- Entropic terms may be included through calculating the phonon density of states.
- Calculated van’t Hoff plots are in reasonable agreement with experiments.
Conclusions—Metal Hydrides

- Facile dissociation of $H_2$ should be observed on the clean $Mg_2Si$ surface.
- Surface oxide formation is very exothermic.
- Surface oxides inhibit adsorption and dissociation of $H_2$ on $Mg_2Si$.
- Calculations are in accord with experiments indicating that ball milling under a hydrogen atmosphere is required to hydrogenate $Mg_2Si$. (Janot et al., Intermetallics, 14, 163 2006)
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