Ab Initio Studies of Complex Metal Hydrides as Hydrogen Storage Materials

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LA-SiGMA
Louisiana Alliance for Simulation-Guided Materials Applications

NSF

Summary

In collaboration with the Louisiana-Alliance for Simulation Guided Materials Applications team (LA-SiGMA), this project focuses on using an atomically-detailed theory-guided computational approach to develop fundamental information that would help us gain insight into critical areas in kinetics, thermodynamics, and novel nanomaterial design for energy applications.

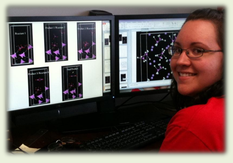
- **Complex Metal Hydrides (CMHs) based on light elements such as Al or Mg hold great promise as hydrogen storage systems due to their inherent high hydrogen content and demonstrated reversibility for hydrogen release and uptake.**
- **This work focuses on a preliminary study of the effect of 3d transition metals on alloyed CMHs and kinetics of pure and doped CMHs for hydrogen storage applications.**
- **Complete microscopic understanding of the rate-limiting processed for hydrogen storage will help us identify new and improved catalysts.**

LA-SiGMA RET Program at LATech

Structure and kinetics of pure and modified $LiAlH_4$

By **Jeanine Edgecombe**

Simsboro High School, Simsboro, LA



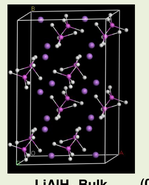
- Structure and kinetics of **pristine and modified $LiAlH_4$** are investigated using **PBE/USPP**.
- **Ti and Ni dopants in (0 1 0) surface** are studied by replacing lithium atom with the transition metal, as well as placing transition metal between aluminum atoms.
- **Addition energy** of X (X = Ti, Ni) was calculated:

$$\Delta E_{add} = E_{coh}\frac{(XLiAlH_4)}{N} - E_{coh}\frac{(LiAlH_4)}{N}$$

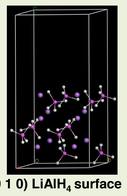
ΔE_{add} (Ti) = -0.08 eV

ΔE_{add} (Ni) = -0.07 eV

- Results have shown that even though nickel is added to system with less energy, the **Ti-doped system binds with more hydrogen** at the end of reaction.

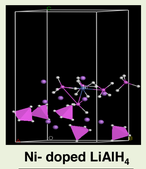


$LiAlH_4$ Bulk

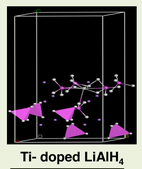


(0 1 0) $LiAlH_4$ surface

Al Li H



Ni- doped $LiAlH_4$

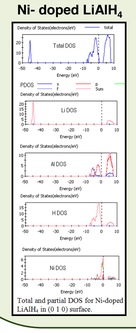


Ti- doped $LiAlH_4$

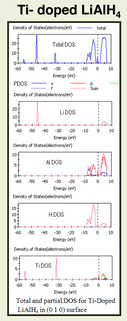
Table 1. Calculated structural parameters of $LiAlH_4$ unit cell.

	Calc. (Å)	Expt. (Å)
Lattice Parameters	a= 4.877 b= 7.864 c= 7.815 α = γ=90° β=111.8°	a=4.817 b=7.802 c=7.821 α = γ=90° β=112.3°

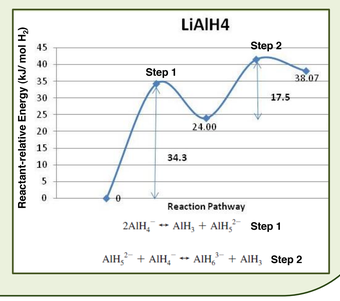
The calculated formation energy of $LiAlH_4$ is 121.57 kJ/mol.



Total and partial DOS for Ni-doped $LiAlH_4$ in (0 1 0) surface.



Total and partial DOS for Ti-Doped $LiAlH_4$ in (0 1 0) surface



Hydrogen Storage Materials

Structure and kinetics of pure and modified $NaMgH_3$

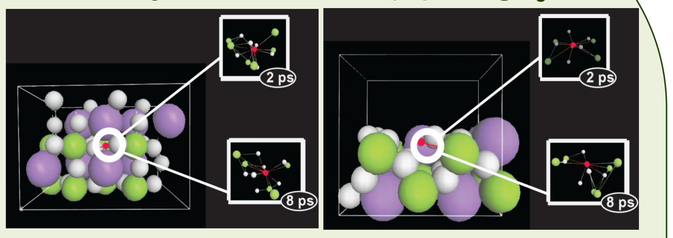
By **Fernando Soto**

Louisiana Tech University

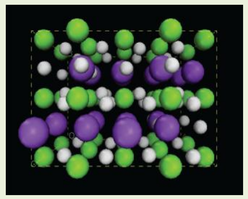
METHODOLOGY

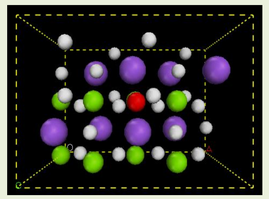
Plane-Wave Density Functional Theory with the Generalized Gradient Approximation (GGA) exchange and Perdew and Wang (PW91) correlation functional with Molecular Dynamics (MD) to elucidate the effect of 3*d* transition metals on the thermodynamics and kinetics of pure and doped CMHs models for hydrogen storage application.

Dynamic Results: (Ti)$NaMgH_3$



Bulk and Surface Models

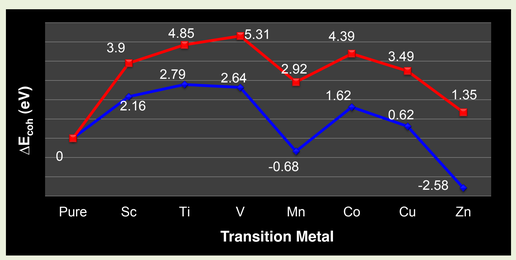




Dopant Sites

- **Bulk model Na @ Na site is replaced with 3*d* dopants**
- **3d→@ Na site**
- **3d →@ Hollow site**
- **3d →@ Bridge site (Top of Na)**
- **3d →@ top of Hollow Site**
- **3d →@ Mg Site**

- **Most favorable models: Ti @ Na site and Ti @ Hollow site**
- **Ti@ Top Hollow site and Ti @ Top Na site have same cohesive energy**
- **Ti@ Mg site is more favorable than @ Top Hollow and Top Na site**
- **More favorable to remove hydrogen from Doped model than from Pure model**



Cohesive Energy Results. Bulk substitution of transition metal in $NaMgH_3$ (blue), pure crystalline transition metal (red).

Remark

The cohesive energies of the 3*d* block elements in the bulk follow a strong correlation with the cohesive energies of their metallic elements counterpart.

LA-SiGMA REU Program at LATech

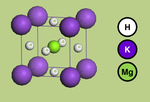
Structure and dehydrogenation kinetics of pure and modified $KMgH_3$

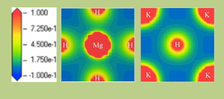
By **Matthew Wespetal**

Grove City College, Pennsylvania

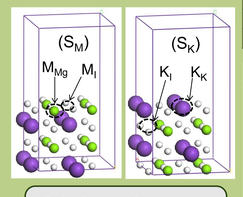
- DFT is used to investigate **Ti-doped models of $KMgH_3$** and 2 reaction mechanisms for **H_2 desorption** from Mg-H complexes in the (1 0 0) surface of **$KMgH_3$**.
- **Sites favorable to Ti-doping and the stability** of the Ti-doped structures are determined
- **Energy of dehydrogenation** is used to compare desorption of hydrogen from doped and pristine models.
- **Ti acts as a catalyst** in $KMgH_3$, reducing the energy of dehydrogenation
- The **formation of a magnesium complex on the surface** may precede **H_2 desorption** from the metal hydride.

We doped two (1 0 0) surface models (40 atoms) for energy calculations:



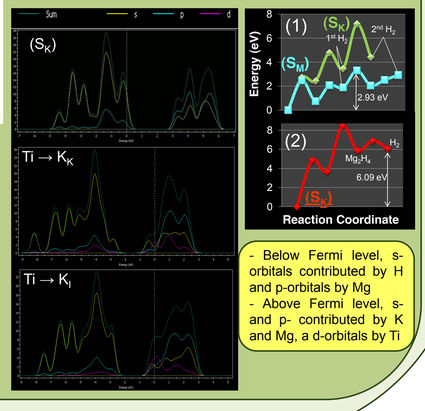


$KMgH_3$ has a stable perovskite (Pm3m) structure.



Dehydrogenation energy:
(S_M) 130.144 kJ/mol H
(S_K) 118.971 kJ/mol H

Ti dopant	Energy required to dope (eV/Ti)	Dehydrogenation (average, kJ/mol H)
Ti → M_{Mg}	2.92	103.35
Ti → M_I	4.20	64.69
Ti → K_K	3.12	43.68
Ti → K_I	3.84	33.08



- Below Fermi level, s-orbitals contributed by H and p-orbitals by Mg
- Above Fermi level, s- and p- contributed by K and Mg, a d-orbitals by Ti

2 possible dehydrogenation reaction pathways:

(1) Mg_3H_8-MgH_3 forms on the surface and releases $2H_2$, leaving Mg_4H_7; the overall activation barrier for one H_2 is 2.07 eV and for two is 3.31 eV.

(2) $2MgH_2$ desorb from the surface, forming Mg_2H_4, and H_2 desorbs from the resulting MgH_5^{3-} in the surface; the overall activation barrier for one H_2 is 8.47 eV.

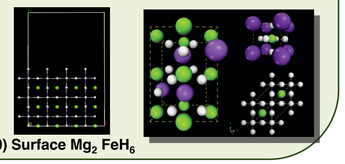
Other materials

Structure, thermodynamics and kinetics of Hydride Materials for Energy Storage

By **Dwayne Teamer and Ashley Matthews**

Louisiana Tech University

The goal for the research is to predict **new catalysts** that work in other systems.
The effects of **imperfect surfaces** and **interfaces** on the **kinetics of hydrogen dissociation** and **diffusion** also need to be understood.

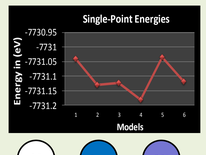


(100) Surface Mg_2FeH_6

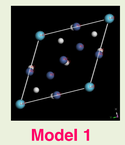
Collaboration: LATech - LSU

In collaboration with Dr. Randall Hall (LSU)

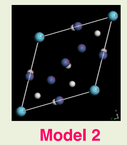
- **We have investigated the energetics of hydrogen site occupation in $LaNi_5H_6$ for six different models.**
- **We find that the minimum occurs for model 4.**



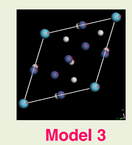
H La Ni



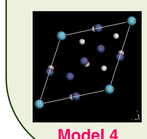
Model 1



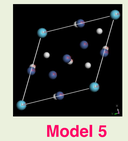
Model 2



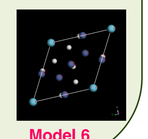
Model 3



Model 4



Model 5



Model 6

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