

## IV.I.12 First Principles Based Simulation of Hydrogen Interactions in Complex Hydrides

PI: Qingfeng Ge

Department of Chemistry and Biochemistry,  
Southern Illinois University Carbondale,  
1245 Lincoln Drive, Carbondale, IL 62901,  
qge@chem.siu.edu

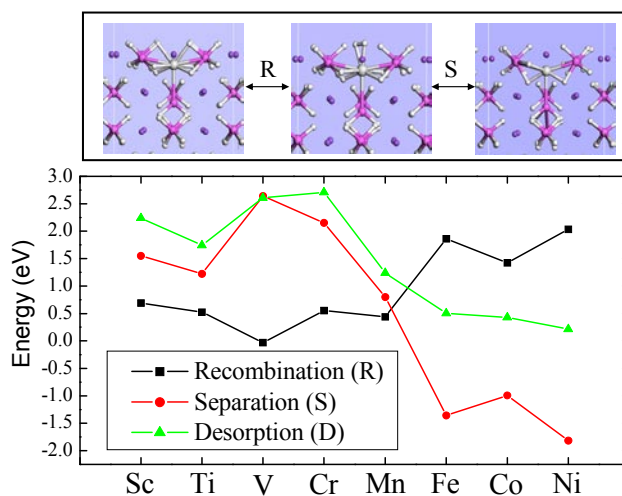
Contract Number: DE-FG02-05ER46231  
Date of Report: April 24, 2009 for Fiscal Year  
2008

### Summary of Accomplishments

Our overall goal is to develop a multiscale approach to model desorption and adsorption of hydrogen in complex metal hydrides. We predicted the  $\text{TiAl}_3\text{H}_x$  complex as the precursor for forming  $\text{TiAl}_3$  alloy observed in Ti-doped  $\text{NaAlH}_4$ . We then showed that doped 3d transition metals form similar interstitial structures, and examined the effect of doped transition metals on reversible hydrogen release/uptake from  $\text{NaAlH}_4$ . We also explored effect of hydrogen spillover in rehydriding  $\text{Li}_3\text{N}$  in collaboration with an experimental group.

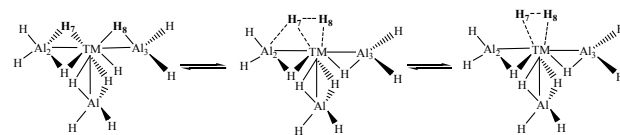
#### (a) Effect of Doped Transition Metal on Reversible Hydrogen Release/Uptake from $\text{NaAlH}_4$

Periodic density function theory calculations with plane-wave basis set and projector-augmented wave potentials have been carried out to investigate the stability and hydrogen interaction in the  $\text{NaAlH}_4(001)$  surfaces doped with 3d transition metal (TM) elements. A complex structure,  $\text{TMAI}_3\text{H}_{12}$ , in which the TM atom occupies the interstitial position formed from three  $\text{AlH}_4^-$  groups, is the most stable structure for  $\text{TM} = \text{Sc}$  to  $\text{Co}$ . The stability of the complex structure, as well as the hydrogen desorption energies from different positions of the complex structure, was found to follow the 18-electron rule in general. The hydrogen desorption process has been considered as a stepwise process: the H atoms first recombine (R) on the TM site to form dihydrogen as an intermediate and the intermediate is then separated (S) from the TM site. These steps as well as the associated energy costs for each TM were plotted in Figure 1. The electron-deficient  $\text{TMAI}_3\text{H}_x$  tends to get more electrons by coordinating with the surrounding Al–H bonds and H–H bond, or by losing the “outside” hydrogen atoms. On the other hand, the electron-rich complex loses its excess electrons easily by releasing  $\text{AlH}_x$ , which resulted in the formation of



**FIGURE 1.** Variation of recombination, separation, and desorption energy of  $\text{H}_7\text{-H}_8$  in  $\text{TMAI}_3\text{H}_{12}$  with TM.

a new catalytic center, or by desorbing  $\text{H}_2$ . By cycling between the electron-deficient and electron-rich states,  $\text{TMAI}_3\text{H}_x$  acted as an active center in the reversible hydrogen release/uptake processes. Electronic structure analysis revealed that the electron transfer between hydrogen and Al groups mediated by the d-orbitals of TMs played important roles in hydrogen release/uptake from alanate-based materials. As shown in scheme 1, the exchange of ligands can be described as a  $\sigma$ -bond metathesis process catalyzed by TM through a dihydrogen complex. Early TMs are more efficient to reduce hydrogen desorption energy and break H–H and Al–H bonds as a result of balanced electron accepting/backdonating abilities, making them better candidates as catalysts. The present analyses are consistent with the experimental observations. (*Chemistry – A European Journal*, 15, 1685 (2009))



**SCHEME 1.** The two-step  $\sigma$ -bond metathesis process with four-membered intermediate ( $\text{TM-Al}_2\text{-H}_7\text{-H}_8$ ).

#### (b) Ti-Doped $\text{LiBH}_4(001)$ , (100), and (010) Surfaces

Density function theory studies have been carried out to investigate the energetics and structures of Ti-doped  $\text{LiBH}_4(001)$ , (100), and (010) surfaces. We

examined possibilities of Ti occupying various positions at these surfaces, including substitution, surface adsorption, and interstitial insertion. Among all possible structures, a Ti atom prefers energetically to occupy the interstitial positions consisting of three or four  $\text{BH}_4^-$  hydrides. The most stable species in the three surfaces have a similar local structure, as shown in Figure 2, and can be described as  $\text{TiB}_2\text{H}_8\text{-nBH}_4$  ( $n=1,2$ ). Furthermore, these complex structures and their transformation are localized. Molecular orbital analysis of the local structure showed that the structural stability can be attributed to the symmetry-adapted orbital overlap between Ti and “inside” hydrogen atoms. The hydrogen desorption energies from many positions of these local complex structures were found to decrease significantly with respect to that from the clean surface, which is consistent with the experimental observations. The most favorable hydrogen desorption pathways led to the formation of the dehydrogenation product in a triplet state. Consequently, the triplet  $\text{TiB}_2\text{H}_8\text{-BH}_4$  in (001) and  $\text{TiB}_2\text{H}_8\text{-2BH}_4$  in (010) will desorb a hydrogen molecule, while the quintet  $\text{TiB}_2\text{H}_8\text{-BH}_4$  in (100) will desorb atomic hydrogen. Detailed electronic structure analysis revealed that the electron backdonation from the d orbitals of Ti to the antibonding orbitals of  $\text{BH}_4^-$  in  $\text{TiB}_2\text{H}_8\text{-nBH}_4$  ( $n=1,2$ ) is not as significant as those to the antibonding orbitals of  $\text{AlH}_4^-$  in  $\text{TiAl}_3\text{H}_{12}$ . Consequently, the B–H bonds in  $\text{TiB}_2\text{H}_8\text{-nBH}_4$  ( $n=1,2$ ) were not as highly activated as the Al–H bonds in  $\text{TiAl}_3\text{H}_{12}$ . (submitted)

### (c) Hydrogen Spillover Enhanced Hydriding Kinetics of Palladium-Doped Lithium Nitride

Hydrogen storage in complex metal hydrides often suffers from unsatisfied hydriding kinetics of the corresponding complex metals under moderated conditions, partly due to the kinetic barrier associated with the breaking of H–H bond. Therefore, doping catalysts for H–H bond breakage becomes a feasible strategy to improve the hydriding kinetics because hydrogen adatoms can efficiently spillover from catalyst to complex metals. To implement this strategy, Dr. Tao Xu of Northern Illinois University, our experimental collaborator, developed a unique method to uniformly dope catalytic metal in the storage complex via synthesis of the eutectic of the catalytic metal and the precursory storage material. This method eliminates the use of support materials for catalysts, while still maintains the

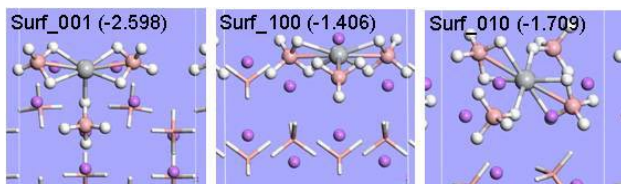


FIGURE 2. The DFT-GGA relaxed structures of Ti doped  $\text{LiBH}_4$  surfaces.

large surface area and uniformity of the catalysts. Our results demonstrated that  $\text{Li}_3\text{NPd}_{0.05}$  with nanoscopic Pd uniformity can be prepared through nitridization of  $\text{LiPd}_{0.01}$  eutectic. The synthesized  $\text{Li}_3\text{NPd}_{0.05}$  exhibits an enhanced hydriding kinetics over pure  $\text{Li}_3\text{N}$  for reaction  $\text{Li}_3\text{N} + \text{H}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{LiH}$  under moderate conditions. The experimental measured an activation barrier of  $\sim 28$  kJ/mol for hydriding  $\text{Li}_3\text{NPd}_{0.05}$ . We used a  $\text{Pd}_4$  cluster supported on the (100) surface of  $\text{Li}_3\text{N}$  to analyze the hydrogen adsorption and migration processes and determined the diffusion barrier using the DFT calculations. We focused on the migration of the hydrogen adatom from the supported  $\text{Pd}_4$  to the neighboring N site. Figure 3 shows a potential energy profile for a hydrogen adatom to diffuse from the bridge-bound configuration on the supported  $\text{Pd}_4$  cluster (A) to the N atom in the  $\text{Li}_3\text{N}$  slab (C). As shown in the figure, the overall diffusion process for H from adsorbed on the  $\text{Pd}_4$  cluster to bond to N is energetically favorable, manifested by an energy gain of 0.684 eV. This diffusion process is activated, with a diffusion barrier calculated to be 0.257 eV, i.e.  $\sim 25$  kJ/mol. This result is in good agreement with the value from analysis of the experimental kinetic data and indicates that the hydriding kinetics is limited by H adatom diffusion. (*Journal Physical Chemistry C, ASAP*)

### (d) Phase Transition of $\text{NaAlH}_4$ Followed by Metadynamics

Experimental studies have established that hydrogen release from  $\text{NaAlH}_4$ -based material is accompanied by a series of phase transitions in solid

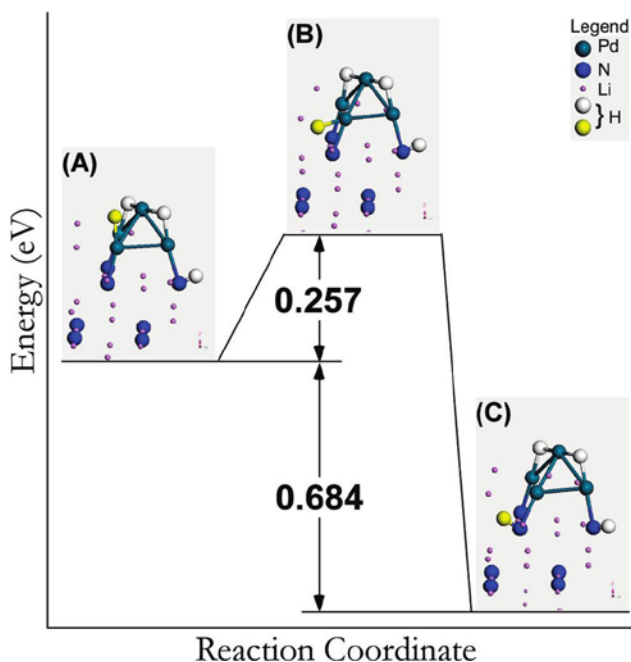
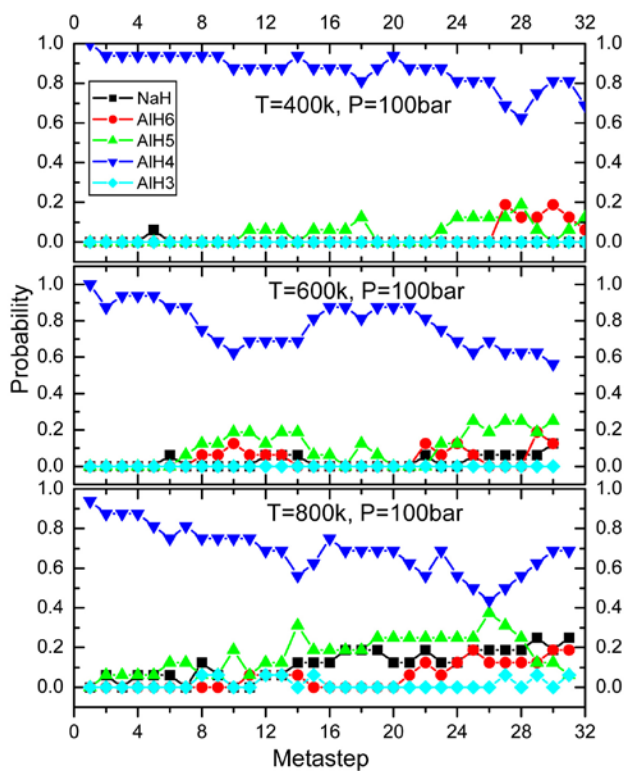


FIGURE 3. Potential energy profile of H adatom diffusion from Pd to N.

state. The process starts with  $\text{NaAlH}_4$ , goes through a  $\text{Na}_3\text{AlH}_6$  intermediates and finishes with  $\text{NaH}$  and  $\text{Al}$ . Traditionally, constant-pressure molecular dynamics can be used to follow the structural transformation in this process. However, the complex potential energy landscape and nature of the system made the traditional MD ineffective. Metadynamics allows the system to escape from free-energy minima and provides a more effective sampling of the potential energy surface. In our simulation, we treated the simulation box edges  $h=(a, b, c)$  as a collective coordinate to explore the structural transformation. These parameters evolve according to the combined driving force derived from stress and a history-dependent Gaussian function. In between the meta steps, the system was allowed to equilibrate by following the regular molecular dynamics trajectory at constant  $T$  and  $P$ . During a metadynamics run, we monitor the change in pairwise distances and use these distances as a measure of formation of certain species.

We run a number of test metadynamics simulations at different temperatures (400, 600, 800 K) with a fixed pressure (100 bar). Figure 4 plots the probabilities of various species formed as system evolves with the metadynamics steps. As shown in Figure 4, more  $\text{NaH}$ ,  $\text{AlH}_6$  and  $\text{AlH}_5$  species are formed with the increased simulation temperatures. The formation of  $\text{NaH}$  causes  $\text{AlH}_4$  to lose its electron and promote polymerization of



**FIGURE 4.** Probabilities of  $\text{NaH}$  and  $\text{AlH}_n$  ( $n=3$  to 5) formation followed by metadynamics.

hydrides through a  $\mu$ -hydrido-bridge bond. The mobile H- may react with the hydrogen atom of electron-deficient polymer, thereby form a hydrogen molecule. This late step remains to be seen in the simulation. (To be published)

## Publications

1. Liu, J.; Han, Y. & Ge, Q. Effect of Doped Transition Metal on Reversible Hydrogen Release/Uptake from  $\text{NaAlH}_4$ , *Chem. Eur. J.* 15, 1685 (2009), (DOI:10.1002/chem.200801045).
2. Lin, C; Xu, T.; Yu, J.; Ge, Q. & Xiao, Z. Hydrogen Spillover Enhanced Hydriding Kinetics of Palladium-Doped Lithium Nitride to Lithium Imide, *Journal Physical Chemistry C*, in press (DOI: 10.1021/jp901598b).
3. Liu, J., Aschelman, J., Rajan, L. M., Che, C. & Ge, Q. "A comparative study on the dehydrogenation energetics of  $\text{M}_2\text{H}_6$  ( $M=\text{B}, \text{Al}, \text{Ga}$ ) via density functional theory calculations", in *Materials Issues in a Hydrogen Economy: Proceedings of the International Symposium, Jena, P.*; Kandalam, A.; Sun Q. (eds.), World Scientific Pub Co Inc (2009).
4. Liu, J. & Ge, Q. A First-Principles Study on Structural and Hydrogen Desorption Properties of Ti-doped Lithium Borohydrides, *submitted*.
5. Liu, J. & Ge, Q. A first principles analysis of hydrogen interaction and NMR chemical shift induced by doping Sc in  $\text{NaAlH}_4$ , *J. Alloy & Compd.* 446-447, 267-270 (2007). DOI:10.1016/j.jallcom.2007.01.052.
6. Liu, J. & Ge, Q. A precursor state for formation of  $\text{TiAl}_3$  complex in reversible hydrogen desorption/adsorption from Ti-doped  $\text{NaAlH}_4$ , *Chem. Comm.* 2006, 1822 - 1824, (2006).
7. Liu, J. & Ge, Q. A First-Principles Analysis of Hydrogen Interaction in Ti-doped  $\text{NaAlH}_4$  Surfaces: Structure and Energetics, *J. Phys. Chem. B*, 110, 25863-25868 (2006).
8. Ge, Q. A first principles analysis of hydrogen storage in complex metal hydrides, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.*, 51, 511-512 (2006).

## Presentations

1. Jianjun Liu & Qingfeng Ge, "Quantum Chemistry Based Molecular Dynamics Simulation of Hydrogen Desorption from Ti-doped  $\text{NaAlH}_4$ ", ACTC2008, Evanston, IL, July, 2008 (poster).
2. Jianjun Liu & Qingfeng Ge, "A First-Principles Study on Mechanism of Interaction between Transition Metal and  $\text{NaAlH}_4$ ", 2008 CCC Spring Symposium, Lisle, IL, May 15, 2008 (poster).
3. Jiamei Yu, Jianjun Liu, & Qingfeng Ge, " $\text{TiAl}_3$ : Structure and its interaction with hydrogen", 2008 CCC Spring Symposium, Lisle, IL, May 15, 2008 (poster).

4. J. Yu, J. Liu, & Q. Ge, "TiAl<sub>3</sub>: Structure and its interaction with hydrogen", 235<sup>th</sup> ACS National Meeting, New Orleans, April, 2008 (poster).
5. N. Sullivan, J. Liu, & Q. Ge, "Dissociation and isomerization of B<sub>2</sub>H<sub>x</sub> on Pt (111)", 235<sup>th</sup> ACS National Meeting, New Orleans, April, 2008 (poster).
6. J. Liu, Y. Han & Q. Ge, "Comparison on hydrogen desorption mechanisms for Ti-doped NaAlH<sub>4</sub> and LiBH<sub>4</sub> surfaces", 39<sup>th</sup> Midwest Theoretical Chemistry Conference, Bloomington, IN, June 28–30, 2007 (poster).
7. J. Liu & Q. Ge, "A First Principles Study of Transition Metal Interaction with NaAlH<sub>4</sub>(001)", the International Symposium on Materials Issues in a Hydrogen Economy, Richmond, VA, Nov. 12–15, 2007.
8. J. Liu, J. Aeschleman, N. Sullivan & Q. Ge, "A first principles study of BH<sub>m</sub> (m=0,3) and B<sub>2</sub>H<sub>n</sub> (n=0,6) adsorption on Pt(111)", 39<sup>th</sup> Midwest Theoretical Chemistry Conference, Bloomington, IN, June 28–30, 2007 (poster).
9. J. Yu, J. Liu & Q. Ge, "A first principles study of TiAl<sub>3</sub> clusters and its effect on hydrogen storage", 39<sup>th</sup> Midwest Theoretical Chemistry Conference, Bloomington, IN, June 28–30, 2007 (poster).
10. L. Cheng, J. Liu & Q. Ge, "Hydrogen Adsorption and Dissociation over Mg Clusters", 39<sup>th</sup> Midwest Theoretical Chemistry Conference, Bloomington, IN, June 28–30, 2007 (poster).
11. J. Liu & Q. Ge, "Transition metals catalyzed NaAlH<sub>4</sub>(001) surface for hydrogen storage", 233<sup>rd</sup> ACS National meeting, Chicago, IL, Mar. 25–29, 2007 (oral).
12. L. Cheng, J. Liu & Q. Ge, "Hydrogen adsorption and dissociation over Mg clusters", 233<sup>rd</sup> ACS National meeting, Chicago, IL, Mar. 25–29, 2007 (poster).
13. C. Che, L. Rajan, J. Aeschleman, J. Liu & Q. Ge, "A comparative study for dehydrogenation and dissociation of B<sub>2</sub>H<sub>6</sub>, Al<sub>2</sub>H<sub>6</sub>, and Ga<sub>2</sub>H<sub>6</sub>", 233<sup>rd</sup> ACS National meeting, Chicago, IL, Mar. 25–29, 2007 (poster).
14. Q. Ge, "A first principles analysis of hydrogen storage in metal complex hydrides", 232<sup>nd</sup> ACS National meeting, San Francisco, CA, Sept. 10–14, 2006 (invited talk).
15. J. Liu & Q. Ge, "A first Principles Study of Active Species in Ti-doped Sodium Aluminum Hydride Surfaces", MH2006, Maui, HI, Oct. 1–6, 2006 (oral).
16. J. Liu & Q. Ge, "Identification of Active Species in Ti-doped Sodium Aluminum Hydrides Surfaces", 38<sup>th</sup> Midwest Theoretical Chemistry Conference, Columbus, OH, June 15–17, 2006 (oral).
17. J. Liu & Q. Ge, "Effect of Ti on hydrogenation interaction in Ti-Doped LiBH<sub>4</sub>: a first principles study", 38<sup>th</sup> Midwest Theoretical Chemistry Conference, Columbus, OH, June 15–17, 2006 (poster).

18. C. Che, J. Liu & Q. Ge, "Al<sub>2</sub>H<sub>x</sub>: Structure, Energy and Dehydrogenation", 38<sup>th</sup> Midwest Theoretical Chemistry Conference, Columbia, Missouri, June 15–17, 2006 (poster).
19. J. Liu & Q. Ge, "First-principle study on Ti interaction with NaAlH<sub>4</sub> (001) Surface", 231<sup>st</sup> ACS National meeting, Atlanta, GA, Mar. 26–30, 2006 (poster).
20. Q. Ge, "A first principles analysis of the surface structure and energetics of complex metal hydrides", Gordon Research Conference on Hydrogen-Metal systems, Waterville, ME, July 10–15, 2005 (poster).

## Seminars

1. Department of Chemistry, University of Missouri, Columbia, Oct. 14, 2008.
2. Institute for Fuel Cell Innovation (IFCI), National Research Council Canada (NRC), Vancouver, Canada, July 15, 2008.
3. Pacific Northwest National Laboratory, July 10, 2008.
4. Department of Chemistry & Biochemistry, Northern Illinois University, Feb. 11, 2008.
5. SINOPEC Tianjin University R&D Center for Petrochemical Technology, Tianjin University, Jan. 11, 2008.
6. Department of Chemistry, TsingHua University, Jan. 3, 2008.
7. Institute of New Energy Material Chemistry, Nankai University, June 22, 2007.
8. School of Chemical Engineering and Technology, Tianjin University, June 14, 2007.
9. Department of Chemical Engineering, University of Illinois at Chicago, Mar. 9, 2006.

## Participants

### Postdoc assistant scientist:

Dr. Jianjun Liu (100%)

### Graduate students:

Lei Cheng (25%), Jeremiah Aeschleman, Jiamei Yu (50%), You Han (visiting student from China).

### Undergraduate students:

Lisa M. Rajan, Nichole Sullivan (REU student)