Final Report

First Principles Based Simulation of Reaction-induced Phase Transformation in Materials for Hydrogen Storage and other Applications

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I. Project Summary

This major part of this proposal is simulating hydrogen interactions in the complex metal hydrides. Over the period of DOE BES support, key achievements include (i) Predicted $TiAl_3H_x$ as a precursor state for forming $TiAl_3$ through analyzing the Ti-doped $NaAlH_4$ and demonstrated its catalytic role for hydrogen release; (ii) Explored the possibility of forming similar complex structures with other 3d transition metals in $NaAlH_4$ as well as the impact of such complex structures on hydrogen release/uptake; (iii) Demonstrated the role of $TiAl_3$ in hydriding process; (iv) Predicted a new phase of $NaAlH_4$ that links to Na_3AlH_6 using first-principles metadynamics; (v) Examined support effect on hydrogen release from supported/encapsulated $NaAlH_4$; (vi) Expanded research scope beyond hydrogen storage. The success of our research is documented by the peer-reviewed publications.

II. Background and Objectives

Climate change resulting from CO_2, produced from consumption of fossil fuel, has become an imminent threat to humankind. Consequently, developing a practical alternative is an urgent challenge. As an energy carrier, hydrogen is a promising alternative to fossil fuel. Similar to electricity, hydrogen needs to be produced using a different energy source, such as solar or nuclear. Once hydrogen is produced, a hydrogen-based energy system with a competitive fuel cell technology only produces water and, therefore, is pollution-free.

For on-board applications, the hydrogen storage systems are required to provide the needed quantity of hydrogen with acceptable volume, weight, cost, and safety risk compared to the current gasoline-driven combustion engine. The available hydrogen storage modalities – including compressed gaseous hydrogen, cryogenic liquid hydrogen, and metal hydrides– each meet some, but not all, of the requirements for critical applications, as shown in Fig. 1.[1] Therefore, developing a compact and efficient hydrogen-storage technology is the most technically challenging aspect of achieving a hydrogen economy.

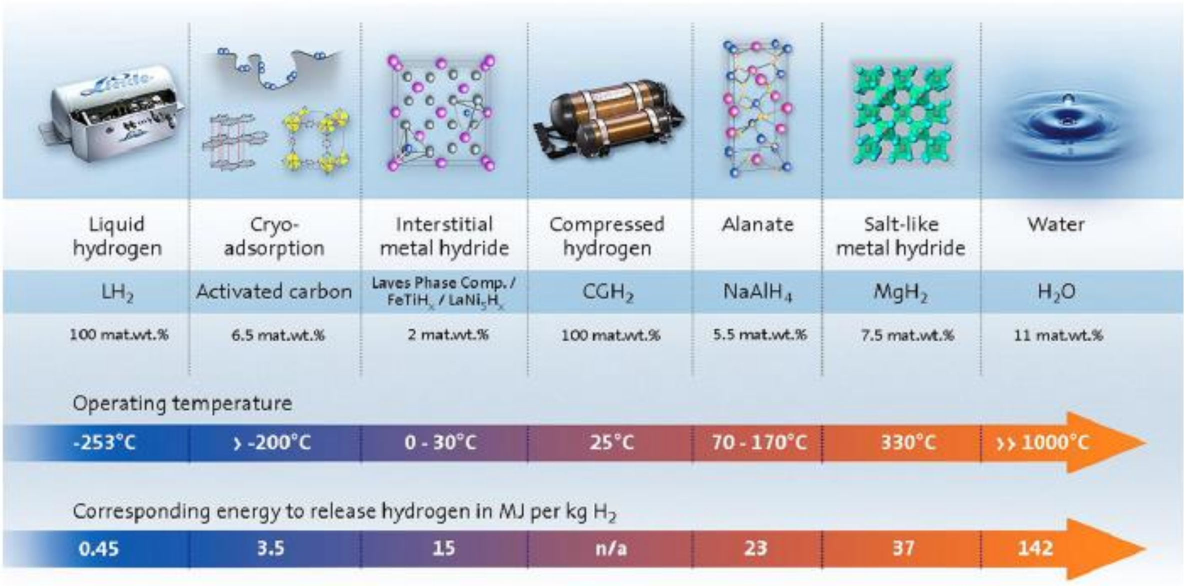


Fig. 1. Available hydrogen storage technology and the corresponding operating conditions.[1]

Solid-state hydrogen storage, using nanoscience and nanotechnology, offers perhaps the best opportunity for meeting the requirements of on-board applications. Nanomaterials can be in the form of thin films or surface coatings, nanowires and nanotubes, or nanoparticles. The unique properties of nanomaterials originate from the increased surface area and quantum effects, both of which relate to the small size. Consequently, the reactivity, strength and electrical characteristics of nanomaterials may be significantly different from those of conventional materials. For example, a particle of size 30 nm has only 5% of its atoms on its surface. When the size is reduced to 3 nm, the particle has 50% of its atoms exposed on the surface. This gives nanoparticles a much greater surface area per unit mass than larger particles. Both surface area and exposed atoms on the surface could be useful for storing hydrogen. The concept of nanoscience and nanoengineering has been actively exploited in improving existing hydrogen storage materials and searching for new hydrogen storage candidates. For example, nanocatalysts have been used to improve the kinetics of hydrogen uptake and release[2, 3] and to improve hydrogen storage capacity through spillover.[4] Novel building blocks have been proposed to maximize the hydrogen capacity and optimize the strength of hydrogen binding.[5] Large-surface area nanomaterials that offer more host atoms/sites for hydrogen and allow easy access to these sites have been synthesized in materials such as metal organic frameworks (MOFs) [6] and covalent organic frameworks (COFs) [7], and show promise as hydrogen storage media.

Depending on the nature of the hydrogen interaction with the storage media, solid state hydrogen storage materials can be categorized into two groups: atomically bound hydrogen in either hydrides or other compounds (amines or imides) and molecularly adsorbed hydrogen in highly porous materials. The two groups can also be combined, e.g., using the high surface area material as a support/scaffold for hydrides or other hydrogen containing compounds. In all the solid state materials that *chemically* store hydrogen, *phase transitions* are inevitable when the materials release and adsorb hydrogen. For example, transitions from a $NaAlH_4$(s) phase to a Na_3AlH_6(s) phase and then to NaH(s) and Al(s) phases occur during hydrogen release from Ti-doped $NaAlH_4$ in sodium alanate based hydrogen storage systems. In the reverse process, a mixture of NaH(s) and Al(s) will have to react with the gaseous hydrogen with the aid of Ti to form $NaAlH_4$(s). Phase transitions are also involved in the simple metal hydrides such as MgH_2. Transition from MgH_2(s) to Mg(s) occurs during hydrogen release whereas the reversal transition from Mg(s) to MgH_2(s) takes place during hydriding. In fact, the *reaction-induced phase transitions* are not limited to the gas-solid reactions involved in hydrogen storage.[8] In the proposed strategy to reduce CO_2 emission using carbon capture and storage,[9] the stored CO_2 in geological formations may react with the rock bed under certain moisture/acidic conditions.[10] This type of reactions will transform CO_2 into minerals, which may have long-term ecological consequences. For the solid-state hydrogen storage materials, the reversibility and long-term mechanical stability are also expected to closely relate to the phase transitions. Therefore, understanding the process is important to the design of practical hydrogen storage systems.

For all hydrogen storage materials, structural information is critical to understanding their properties and performance. However, experimentally determining the structure of materials at the nanometer scale, especially for those materials involving hydrogen, is extremely challenging. Tracking the chemistry of hydrogen is even more difficult. On the other hand, computational chemistry and molecular simulation are advantageous for studies of well-defined systems, including those containing hydrogen. First-principles approaches developed on the basis of density functional theory (DFT)[11, 12] and implemented for both clusters and periodic slabs can handle systems significantly larger than those using traditional *ab initio* methods. The combined predictive power and atomic resolution provide a quantitative characterization of new materials. These methods have been applied to a wide range of problems of practical interest, including materials and structures related to hydrogen storage. Theory and computation can be used not only to understand experimental results, but also to guide the search for, and design of, new hydrogen-storage materials.

The project started with a focus on the effect of doped transition metals, in particular Ti, on hydrogen interactions in complex metal hydrides based hydrogen storage materials. We expanded our efforts on investigating how phase-transitions couple with the reactions at the atomic scale in heterogeneous systems. **Our objectives are to:** *1) understand the nature of hydrogen interactions and determine how hydrogen migrates in hydrides, 2) establish the relationship of structure of nanosized particles to the strength and nature of hydrogen interactions, 3) relate local chemical change to phase transition, 4) develop first-principles based descriptor for phase separation/transition.* In our research, we combined DFT based first-principles methods with molecular dynamics or other simulation tools to unravel the underlying chemical and physical origins that govern the materials-hydrogen interaction. The methodology developed in this study can be applied to a more general process that couples chemical reaction with phase transitions, e.g., CO_2 mineralization involved in carbon capture and storage.

III. Progress report for grant period 9/1/2011-8/31/2014

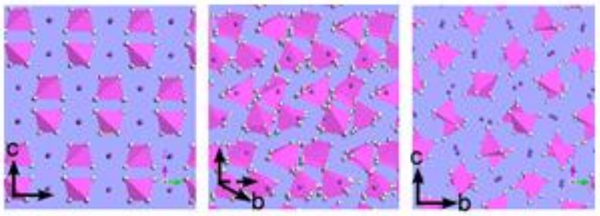
Over this grant period, the notable achievements are:

1. Predicted a new phase of $NaAlH_4$ that links to Na_3AlH_6 using first-principles metadynamics.
2. Examined support effect on hydrogen release from supported/encapsulated $NaAlH_4$.
3. Expansion of research scope beyond complex metal hydrides.

The following texts provide some additional highlights of these achievements.

(a) Using first-principles metadynamics simulation to predict new phases and probe phase transition of $NaAlH_4$ (Liu & Ge, J. Phys.: Condens. Matter 2011).

$NaAlH_4$ is a prototype of complex metal hydrides that can be used for hydrogen storage. Phase stability and transition under normal pressure and at a temperature close to melting point play important roles in understanding complex mechanism of hydrogen release and uptake. We developed a DFT-based metadynamics simulation method and used it to investigate the phase stability and transition of $NaAlH_4$. Our results showed that at a temperature close to melting point, thermal energy may excite the translational motion that is coupled to the low-energy vibrational modes, which will break the original periodicity. An adapted metadynamics simulation scheme which allows the lattice vector to change is proven to be an effective tool to follow the lattice dynamics and phase transition.

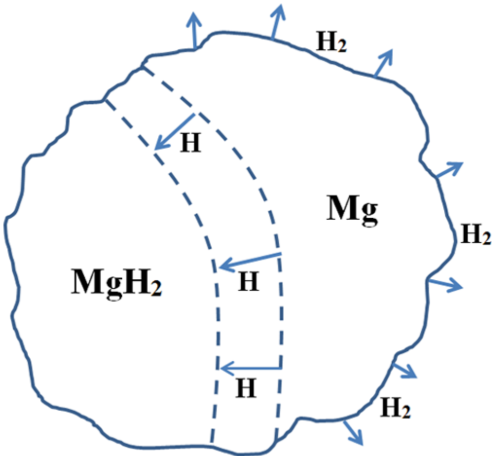


Dynamic Snapshots of $NaAlH_4$

The DFT-based metadynamics simulation showed that *$I4_1/a \rightarrow Cmcm \rightarrow Pbcm$* phase transitions can take place at a temperature close to melting point. These transitions were correlated with the symmetry-lowering process ($D_{2h} \rightarrow C_{2v} \rightarrow C_s$) of the AlH_4^- complex ions. Thermodynamics analysis revealed that the *Cmcm* phase form from the *$I4_1/a$* phase at around the melting point (548 K). These results are in qualitative agreement with a previous Raman scattering measurement showing the transition took place at ~503 K.

Previous experimental studies have demonstrated that the *Cmcm* phase of $NaAlH_4$ may be an important intermediate connecting $NaAlH_4$ (*$I4_1/a$*) with Na_3AlH_6.

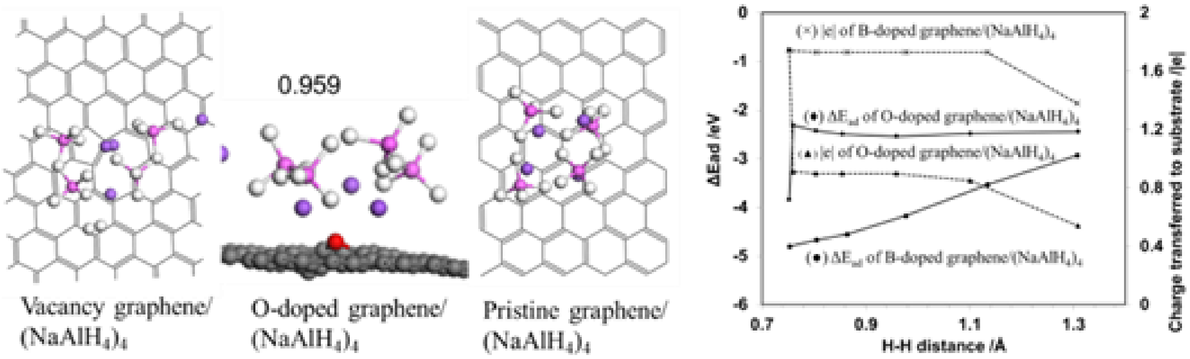
(b) First-Principles Studies on Hydrogen Desorption Mechanism of Mg_nH_{2n} (n=3, 4) (Liu, et al, J. Phys. Chem. C. 2013**).**



In attempt to decrease hydrogen desorption temperature of MgH_2, great efforts have been made to improve kinetic and thermodynamic properties by reducing its cluster size. However, these improvement were further impeded because hydrogen desorption mechanism of MgH_2 clusters is not clear. Density functional theory studies have been performed to investigate hydrogen desorption mechanisms in Mg_nH_{2n} (n=3, 4) systems. In both Mg_3H_x and Mg_4H_x systems, hydrogen desorption barriers are higher than hydrogen transfer ones and the first hydrogen desorption is rate-determining step. Electronic structure analysis showed that many important intermediates in the minimum-energy pathways are the combinations of metallic Mg cluster and ionic MgH_2 hydride, indirectly indicating that phase separation into metallic Mg and ionic MgH_2 hydrides may happen in a large nanoparticle. It is expected that hydrogen desorption mechanism of MgH_2 clusters comprises hydrogen transfer, phase separation, and hydrogen separation.

(c) Effect of defects and dopants in grapheme on hydrogen interaction in grapheme-supported $NaAlH_4$ (Xu & Ge, Int. J. Hydrogen Energy, 2013**).**

Carbon-based materials have attracted great attention over the past few years due to their role as a support for sodium alanate improving the kinetics of H_2 release/uptake. Herein, we used graphene with defects and various dopants to simulate the carbon materials and performed a periodic density functional theory study on the impact of the modifications in the graphene substrates on the hydrogen interaction in, and hydrogen desorption from, the highly dispersed sodium alanate. Our results showed that the impact of various defects and dopants can be categorized in groups: (i) Pristine graphene and pentagon–heptagon (5–7) pairs defective graphene, as well as N- and S- doped graphene substrates show a weak interaction with the supported sodium alanate cluster, as reflected in the geometry change of the supported cluster and charge transfer between the supported cluster and the substrate. These defects and



dopants do not promote H_2 formation and desorption. (ii) Carbon vacancies, as well as B and Cl dopants, cause instantaneous H_2 formation in supported $NaAlH_4$ upon relaxation. (iii) O-, P-, F- and OH- doped graphene substrates led to the formation of a meta-stable di-hydrogen state with a H-H distance of ~ 0.96 Å. There is an activation barrier between the meta-stable di-hydrogen state and the most stable state with H_2 being formed. Furthermore, our results with the optB88-vdW functional show that van der Waals interaction strengthens the binding of the cluster on the substrates by 0.9-1.4 eV over the PBE results but does not alter the relative stability of the system.

IV. Progress report for grant period 9/1/2008-8/31/2011

Over this grant period, we expanded our previous discovery of $TiAl_3H_x$ complex structure and explored its role in catalyzing hydrogen release and uptake in sodium alanate based materials. We actively sought collaboration with experimental groups working on projects related to hydrogen storage. Our main achievements are summarized as the following:

1. Examined 3d transition metal interaction with $NaAlH_4$ based on the interstitial $TMAl_3H_x$ complex structure and explained the experimentally observed reactivity trends of doping transition metal in $NaAlH_4$.
2. Predicted the role of $TiAl_3H_x$ complex in synthesizing $NaAlH_4$ from NaH and Al.
3. Identified super atom nature of selected Ti-Al-H complex and predicted supramolecular structures as hydrogen storage candidates.
4. Examined interaction of Ti interaction with $LiBH_4$ and unraveled the chemical origin of the different consequence of doping Ti in $LiBH_4$ from that in $NaAlH_4$.
5. Implemented metadynamics to follow phase transition and tested the implementation on bimetal oxides ($Ag_2Mo_2O_7$ and Ag_2WO_4). Obtained preliminary results of metadynamics on $NaAlH_4$.
6. Predicted potential energy profile of hydrogen spillover from Pd to N in Pd-doped Li_3N, in collaboration with Dr. Tao Xu's experimental group of Northern Illinois University.
7. Predicted structure and vibrational frequencies of CO adsorption on the LaB_6 surface, complementing the experimental work by Dr. Mike Trenary's group from University of Illinois at Chicago.

In what follows, we provide some additional highlights of our main achievements.

(a) Effect of Doped Transition Metal on Reversible Hydrogen Release/Uptake from $NaAlH_4$ (Liu, et al, Chemistry – A European Journal 2009)

In previous studies, we predicted the interstitial $TiAl_3H_x$ complex in Ti-doped $NaAlH_4$ and proposed the complex $TiAl_3H_x$ as a precursor for forming $TiAl_3$ that was observed experimentally. The existence of the $TiAl_3H_x$ complex structures has been confirmed by independent experimental study.[13] We further proposed the complex structure as an active center in reversible hydrogen desorption/adsorption. Over the prior funding period, we used the same approach and investigated the stability and hydrogen interaction in the $NaAlH_4(001)$ surfaces doped with 3d transition metal (TM) elements. Similar complex structure, $TMAl_3H_{12}$, in which the TM atom occupies the interstitial position formed from three AlH_4^- groups, was found to be the most stable structure for TM = Sc to 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 di-hydrogen 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 Fig 2. The electron-deficient $TMAl_3H_x$ 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 AlH_x, which would result in the formation of a new catalytic center, or by desorbing H_2. By cycling between the electron-deficient and electron-rich states, $TMAl_3H_x$ 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 Fig. 3, the exchange of ligands can be described as a σ-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 abilities of accepting and back-donating electron, making them better candidates as catalysts. The present analyses are consistent with the experimental observations.

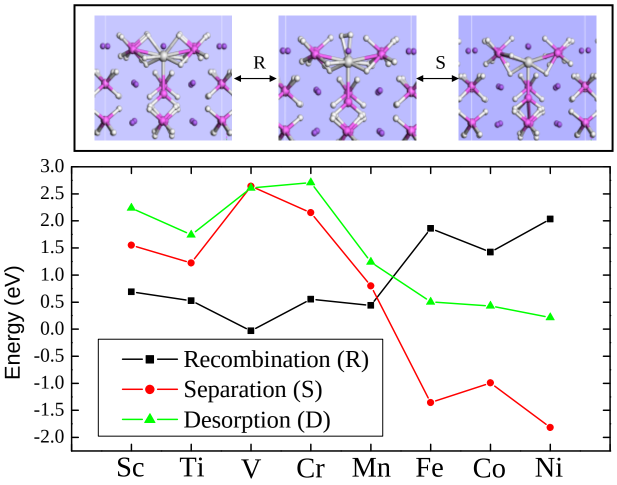


Fig. 2 Variation of recombination, separation, and desorption energy of H_7-H_8 in $TMAl_3H_{12}$ with TM.

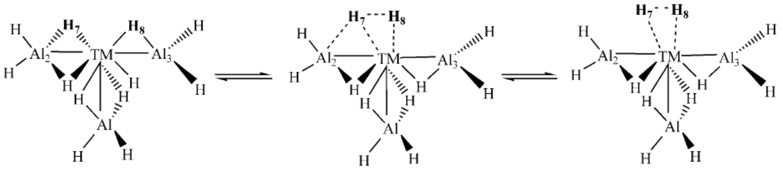


Fig. 3. A proposed ligand exchange mechanism involved in dehydriding and hydriding of TM doped $NaAlH_4$.

(b) Hydride-Assisted Hydrogenation of Ti-Doped NaH/Al . (Liu, et al, Journal of Physical Chemistry C. 2011)

Density-functional theory calculations were performed to study the hydrogenation mechanism of Ti-doped NaH/Al mixture, with emphasis on the role of NaH. Results from $TiAl_3H_x$ (x=0~16) clusters showed that hydrogenation of $TiAl_3$ experienced a structural evolution in which $TiAl_3$ organizes into a distorted tetrahedral skeleton in $TiAl_3H_x$ (x=0~7), but forms a planar T-shape structure in $TiAl_3H_x$ (x=10~16), with $TiAl_3H_8$ and $TiAl_3H_9$ being transition structures between the tetrahedral and planar structures. Moreover, H_2 adsorbs molecularly at the Ti site of $TiAl_3H_x$, and dissociates spontaneously into hydrides when an extra electron was added to the cluster. The electron-assisted dissociation of H_2 is manifested as hydride-assisted hydrogenation of Ti-doped NaH/Al, simulated as $TiAl_3H_x$ supported on the NaH (001) surface. Geometry optimizations and molecular dynamics showed that $TiAl_3H_x$ clusters are active for H_2 dissociation after acquiring hydride from the NaH surface. A series of snapshots from MD trajectories that follow the dissociation the Ti site of the support $TiAl_3H_x$ with two different x values are shown in Fig. 4. Clearly, hydride transfer from NaH to $TiAl_3$ enabled the supported $TiAl_3H_x$ to break the H—H bond in the adsorbed H_2 molecules. The present results suggest a possible mechanism of forming $NaAlH_4$ from NaH and Al in the recycling of Ti-doped $NaAlH_4$ as a hydrogen storage medium

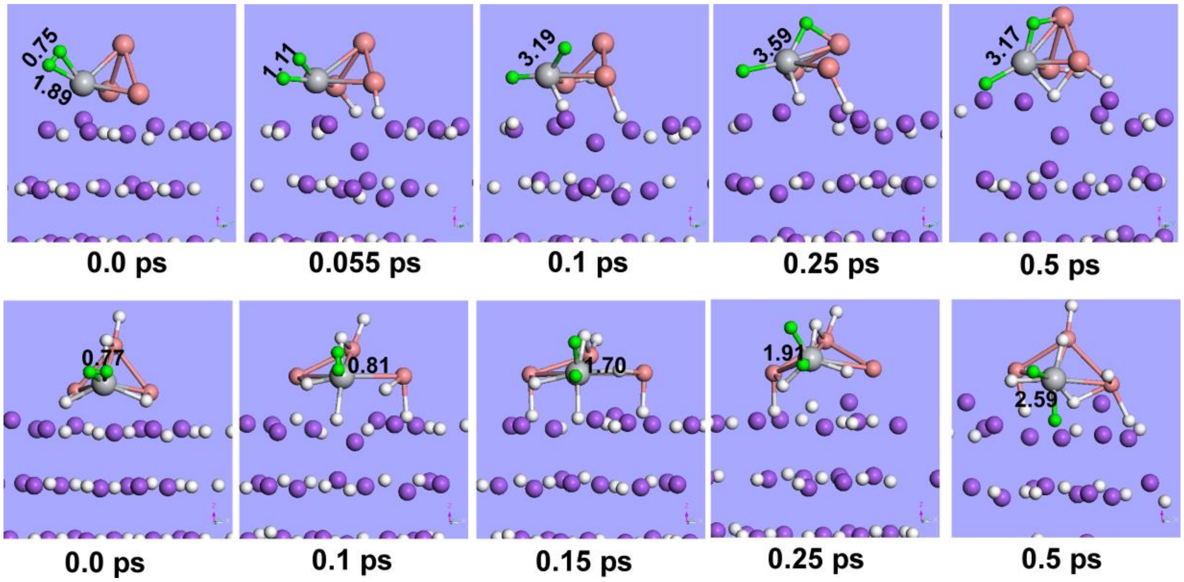


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Fig. 4. Snapshots from ab initio molecular dynamics trajectories for H_2 dissociation on $TiAl_3$ and $TiAl_3H_4$ clusters supported on NaH (001) surface. The purple, white, orange, and gray balls represent Na, H, Al, and Ti atoms, respectively, whereas the green balls correspond to the dissociating H_2.

(c) Transition Metal-Doped Aluminum Hydrides as Building Blocks for Supramolecular Assemblies (Liu, et al, Journal of Physical Chemistry A. 2010)

In this study, we use density functional theory calculations to show that transition metal-doped aluminum hydrides, form stable $TMAl_nH_{2n}$ and $TMAl_nH_{2n+1}$ (TM=Sc, Ti, V, n=3,4) species, in either charged or neutral form. Some selected structures are shown in Fig. 5. To account for the stability of these clusters, we developed a new electron-counting rule, formulated as PSEN (paired skeleton electron number) = 4n, which can characterize both closed-shell and open-shell clusters. Based on this electron-counting rule, the superatomic clusters such as $TiAl_4H_9$ and $TiAl_3H_6$ were identified and can be used to assemble supramolecular structures. Electronic structure analysis showed that the three-centered TM-Al-H bonds in these superatomic clusters contributed to the structural stability. Also, the spin state of a wide range of clusters in their ground state can be predicted by the electron-counting rule.

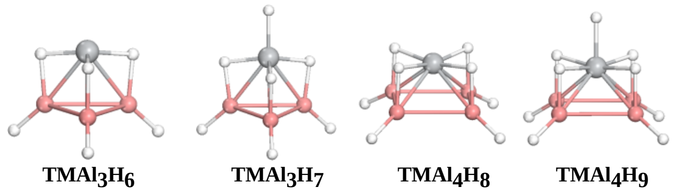

Fig. 5. Stable transition metal aluminum hydride complex.

(d) Implementation and Validation of Metadynamics (Stone, et al, Scripta Materialia, 2010).

Hydrogen release from $NaAlH_4$ is a heterogeneous process that involves solid state phase transitions coupled with the chemical reactions and mass transport. In fact, such reaction-accompanied phase transition process is common to heterogeneous reactions involving volatile species. However, the currently available computational tools *cannot* describe the process directly. On the other hand, metadynamics has been implemented to follow a specific reaction coordinate and phase transitions in crystalline solids. In the present project, we developed a metadynamics program and interfaced to the VASP code. Ultimately, we would couple the system with a reservoir and describe hydrogen release and uptake from the complex-hydride-based materials.

To validate our implementation, we first studied phase transitions of Si, starting from the Si diamond structure, a system that has been studied as a benchmark for metadynamics. Our results are consistent with previous simulation results reported in literature. We then applied our implementation to follow the phase transitions in $Ag_2Mo_2O_7$ and Ag_2WO_4, attempting to understand the low friction coefficient of $Ag_2Mo_2O_7$ at high temperatures. Fig. 6 shows the snapshots following the dynamics trajectories of the two systems at 800 and 1000 K. We identified significant clustering of Ag in $Ag_2Mo_2O_7$ at 800 K whereas no clear phase segregation was observed for Ag_2WO_4 even at 1000 K. The simulation results are qualitatively consistent with the experimental observations

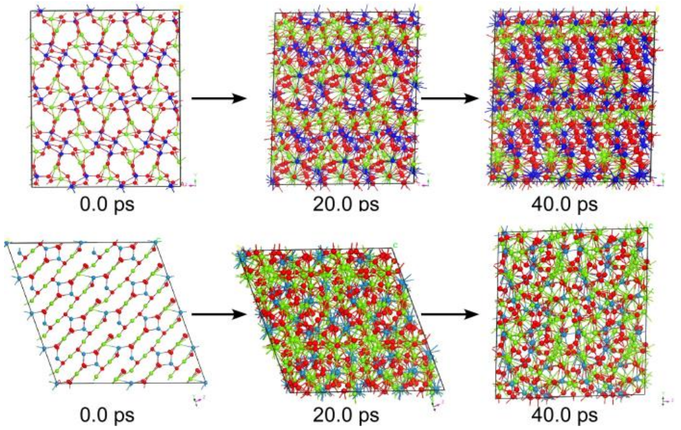

Fig. 6. Snapshots of density functional theory PBE metadynamics simulations of (a) $Ag_2Mo_2O_7$ at 800 K and 1 bar and (b) Ag_2WO_4 at 1000 K and 1 bar. Red, dark blue, light blue, and green balls represent O, Mo, W and Ag, respectively.

(e) Ti-Doped $LiBH_4$(001), (100), and (010) Surfaces (Liu & Ge, Journal of Chemical Theory and Computation 2009).

We completed our density function theory studies on the energetics and structures of Ti-doped $LiBH_4$(001), (100), and (010) surfaces. In this study, we examined possibilities of Ti

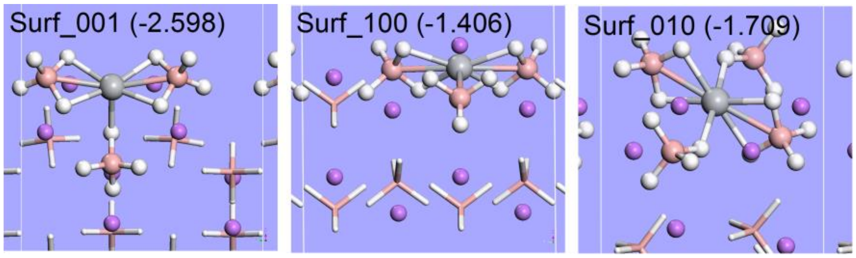

Fig. 7. The DFT-GGA relaxed structures of Ti doped $LiBH_4$ surfaces.

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 BH_4^- hydrides. The most stable species in the three surfaces have a similar local structure, as shown in Fig. 7, and can be described as TiB_2H_8-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 TiB_2H_8-BH_4 in (001) and TiB_2H_8-$2BH_4$ in (010) will desorb a hydrogen molecule, while the quintet TiB_2H_8-BH_4 in (100) will desorb atomic hydrogen. Detailed electronic structure analysis revealed that the electron back-donation from the d orbitals of Ti to the antibonding orbitals of BH_4^- in TiB_2H_8-nBH_4 (n=1, 2) is not as significant as those to the antibonding orbitals of AlH_4^- in $TiAl_3H_{12}$. Consequently, the B–H bonds in TiB_2H_8-nBH_4 (n=1, 2) were not as highly activated as the Al–H bonds in $TiAl_3H_{12}$.

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

(Lin, et al, Journal of Physical Chemistry C, 2009).

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 large surface area and uniformity of the catalysts. Our results demonstrated that $Li_3NPd_{0.03}$ with nanoscopic Pd uniformity can be prepared through nitridization of $LiPd_{0.01}$ eutectic. The synthesized $Li_3NPd_{0.03}$ exhibits an enhanced hydriding kinetics over pure Li_3N for

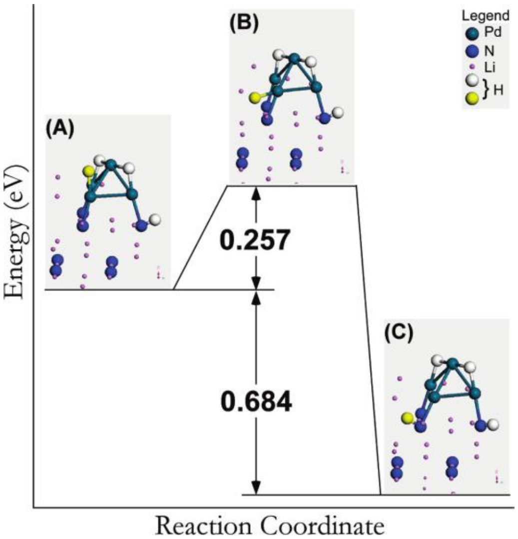

Fig. 8. Potential energy profile of H adatom diffusion from Pd to N.

reaction $Li_3N + H_2 \leftrightarrow Li_2NH + LiH$ under moderate conditions. The experiment measured an activation barrier of ~28 kJ/mol for hydriding $Li_3NPd_{0.03}$. We used a Pd_4 cluster supported on the (100) surface of Li_3N 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 Pd_4 to the neighboring N site. Fig. 8 shows a potential energy profile for a hydrogen adatom to diffuse from the bridge-bound configuration on the supported Pd_4 cluster (A) to the N atom in the Li_3N slab (C). As shown in the figure, the overall diffusion process for H from adsorbed on the 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. ~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.

V. Progress report for grant period 9/1/2005-8/31/2008

Our overall goal of the project was to develop a multiscale approach to model desorption and adsorption of hydrogen in complex metal hydrides. Over this grant period, we analyzed the crystal structures of $LiAlH_4$, $NaAlH_4$, $KAlH_4$ as well as $LiBH_4$ and determined the stability of different crystal surfaces of these hydrides. We then studied the energetics of hydrogen desorption from the surfaces by creating hydrogen vacancies on the surfaces. In Ti-doped $NaAlH_4$, we identified a complex $TiAl_3H_x$ as a precursor state for forming $TiAl_3$ that was observed experimentally – the existence of $TiAl_3H_x$ complex structures has been confirmed by independent experimental study. We further proposed the role of the complex structure in reversible hydrogen desorption/adsorption. We also explored the effect of doping other 3d transition metals on the structure and the interaction of the transition metal with the Al-H bonds in $NaAlH_4$(001). We started to build a database for the next step – kinetic Monte Carlo simulation – by determining a number of key reaction barriers for hydrogen transportation in the hydride and for desorption/adsorption.

In what follows, I will provide some additional highlights of the progress.

(a) Density functional theory analysis of intrinsic surface properties of complex metal hydride (Ge, Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem. 2006).

Since Ti-doped $NaAlH_4$ was demonstrated to reversibly desorb and readsorb hydrogen, there have been intensive interests in alanate-based complex metal hydrides. This class of materials showed great promises for meeting the requirements as on-board hydrogen storage media. In particular, $NaAlH_4$ also serves as a prototype in the study of hydrogen interactions in complex metal hydrides. For $NaAlH_4$, the first two combined reactions give a theoretical reversible hydrogen-storage capacity of 5.6 wt% at temperatures lower than 250°C out of a total hydrogen content of 7.5 wt%. For $LiAlH_4$ and $KAlH_4$, the first two steps would produce a theoretical reversible hydrogen capacity of 7.9% and 4.3%, respectively. The mechanism involves a series of complex steps of heterogeneous reactions and phase transitions. This mechanism is significantly different from the hydrogen storage mechanism in the conventional metal hydrides in which hydrogen atoms are the only mobile species and fill in the interstitial sites of the metal lattice frame.

We created a series of low-index surfaces, including (001), (010), (100), and (101), by constructing slabs from the relaxed bulk $MeAlH_4$ structures. We built all these surfaces without breaking the Al–H bond of the AlH_4^- unit. The thickness of the slab in each case is about 12 Å and the vacuum region separating the slab from its periodic images is larger than 15 Å. The surface energy, in J/m^2, is calculated by the following formula:

$$\sigma_{surf} = \frac{1}{2A}(E_{stoi} - nE_{bulk}) \quad (1)$$

where A is the area of the surface unit cell, E_{stoi} and E_{bulk} are the total energy of a stoichiometric slab and the total energy of one formula $MeAlH_4$ in the bulk, respectively. The number of $MeAlH_4$ formula in the slab is represented by n. The results are summarized the Table 1.

Table 1. DFT-GGA surface energy of $LiAlH_4$, $NaAlH_4$ and $KAlH_4$ (J/m^2)

	(001)	(010)	(100)	(101)
$LiAlH_4$	0.205	0.176	0.160	0.192
$NaAlH_4$	0.146	0.327	0.327	0.246
$KAlH_4$	0.104	0.132	0.157	/

In order for alkali alanates to release hydrogen, the Al – H bonds in these compounds have to be broken. The energy difference between the defective surfaces formed by removing H atoms and the perfect surface, i.e. the vacancy formation energy, will provide a measure of the hydrogen desorption energy. The formation energy of H vacancies can be defined as,

$$\Delta E_{vac} = \frac{1}{2n}(E_{vac} - E_{stoi} + nE_{H_2}) \quad (2)$$

where E_{vac} and E_{stoi} are the total energies of the slab with hydrogen vacancies and the slab of the perfect surface. E_{H_2} is the total energy of a free H_2 molecule calculated in a large box. The formation energy was averaged over the vacancies in the same unit cell and the factor of 2 accounts for the two-sided slab. The calculated energy costs to create the defects are summarized in Table 2.

Table 2. Hydrogen desorption energy (eV) from the surfaces of $LiAlH_4$, $NaAlH_4$ and $KAlH_4$.

	(001)	(010)	(100)	(101)
$LiAlH_4$	1.324	1.472	1.293	1.319
$NaAlH_4$	1.390	1.227	1.308	1.299
$KAlH_4$	1.349	1.369	1.338	/

The energy cost to create a single H vacancy represents the low-limit of the activation energy for hydrogen desorption from an ideal surface. By comparing with the results from our earlier study of $LiBH_4$ system,[14] we found that this energy correlates strongly with the intrinsic H-M bond energy, i.e. H-B >> H-Al (340 vs 284 kJ/mol for gas phase molecules), in the complex hydrides but correlates weakly with the alkali ions.

(b) A precursor state for formation of $TiAl_3$ complex in reversible hydrogen desorption/adsorption from Ti-doped $NaAlH_4$ and the catalytic role of $TiAl_3H_x$ complex.

(Liu & Ge, Chem Comm. 2006)

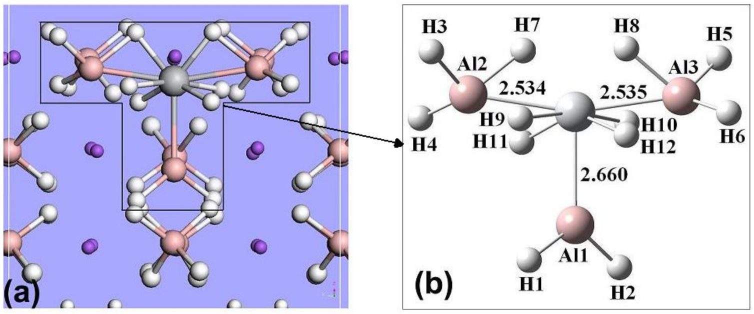

Fig. 9. (a) GGA-relaxed structure of Ti-doped $NaAlH_4$(001) with Ti in the interstitial space; (b) Detailed local structure of the $TiAl_3Hx$ (x=12) complex shown in (a).

Extensive experimental studies of Ti-doped $NaAlH_4$ have led to considerable improvement in the kinetics and cycling performance at the conditions that are relevant to the practical operation of a proton exchange membrane fuel cell. Despite this progress, the mechanism and process by which the $NaAlH_4$ system is catalyzed by a small amount of Ti is not well understood. By systematically examining the stability of doping Ti in different positions in a *surface* model of $NaAlH_4$, we found that Ti energetically favors the interstitial sites formed by three neighboring AlH_4^- units and interacts directly with them in both $NaAlH_4(001)$ and (100) surfaces. In contrast, many previous computational studies adopted *bulk* models of $NaAlH_4$ and focused primarily on substitutional modes of doping. The resulting local structure from the surface interstitial doping corresponds to a formula of $TiAl_3H_x$ with x=12 before hydrogen starts to desorb, as shown in figure 9. The hydrogen desorption energies from many positions of $TiAl_3H_x$ are reduced considerably as compared with that from the corresponding clean, undoped $NaAlH_4$ surfaces. The almost invariant local environment surrounding Ti during dehydrogenation makes the $TiAl_3H_x$ complex a precursor state for the formation of experimentally observed $TiAl_3$ after dehydriding Ti-doped $NaAlH_4$.

The importance of the complex has been explored by analyzing the structural change and energetics as hydrogen is desorbed from the complex. The $TiAl_3H_x$ complex showed an extended effect beyond locally reducing the hydrogen desorption energy. It also facilitates hydrogen desorption at a reduced desorption energy by either transferring the hydrogen to $TiAl_3H_x$ or by reducing the hydrogen desorption energy in neighboring AlH_4^- by linking these AlH_4^- units with the complex structure. We also identified the pathways for forming octahedral AlH_6^{3-} in the vicinity of $TiAl_3H_x$, as illustrated in figure 10: Desorbing hydrogen atoms between Ti and Al atoms causes a symmetrical expansion of Ti-Al bonds which pushes the hydrogen atoms to the next neighbor AlH_4^-, leading to the formation of octahedral AlH_6^{3-}. The interstitial $TiAl_3H_x$ structure that we determined was supported by a recent combined Ti K-edge EXAFS, Ti K-edge XANES, and XRD study of $TiCl_3$-doped $NaAlH_4$.[15] These authors showed that the Ti atoms in the surface interstitial sites that we identified account for 70% of all Ti doped in $NaAlH_4$.

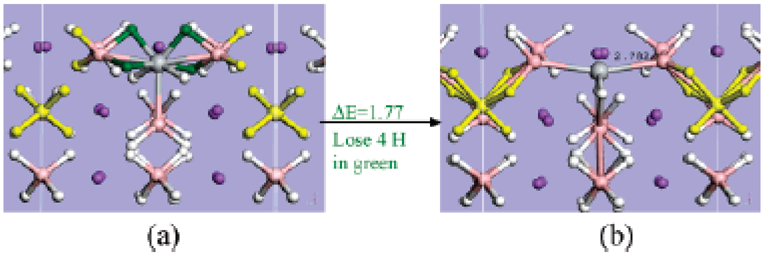

Fig. 10. A possible pathway of forming octahedral structure AlH_6^{3-} in the presence of $TiAl_3H_x$. After desorbing the hydrogen atoms connected with Ti, highlighted in green in part a, an octahedral AlH_6^{3-} structure, highlighted in yellow in part b, starts to form.

(c) Sc-doped $NaAlH_4$ and NMR chemical shielding (Liu & Ge, J. Alloy & Compd, 2007).

Stimulated by the reported ^{27}Al MAS NMR chemical shifts by Bowman and co-workers at the 2006 DOE review meeting, we examined the effect of doping Sc in the $NaAlH_4(001)$ surface and found that Sc occupies the same interstitial site as that of Ti, forming an extended complex structure of $ScAl_3H_{12}$-$2AlH_4$. We also found that hydrogen desorption energies from many positions of the complex were reduced significantly from that of the clean surface. The extended $ScAl_3H_{12}$-$2AlH_4$ structure is more efficient for dehydrogenating $NaAlH_4$ than the similar $TiAl_3H_{12}$ complex that was identified in the Ti-doped $NaAlH_4$ surfaces. We also calculated the NMR chemical shielding on the basis of the complex structure embedded in the periodic slab and found that the Al atoms in direct contact with Sc have very different shileding values from the Al atoms in the center of H tetrahedra. These results may provide an explanation for the ^{27}Al MAS NMR chemical shifts observed experimentally.

(d) Dehydrogenation of B_2H_6, Al_2H_6, and Ga_2H_6 (Liu, J., et al in Materials Issues in a Hydrogen Economy, Jena, P.; Kandalam, A.; Sun Q. (eds.), World Scientific Pub Co Inc, ISBN10: 9812838015; ISBN13: 9789812838018 (**2009**).)

1. Our studies of hydrogen desorption from Ti-doped $NaAlH_4$ indicated that AlH_3 as well as its polymerized derivatives may be important intermediates. Furthermore, this type of binary hydrides has been shown to exist in solid matrices and characterized with various spectroscopic techniques. We studied the M_2H_6 (with M=B, Al, and Ga) molecules as well as their dehydrogenation derivatives, M_2H_x, with x varying from 0 to 5, by using B3LYP hybrid density functionals and a 6-311++(2d,3p) basis set. Based on the optimized minimum energy structure at each x value, we determined reaction energies of sequential dehydrogenation reaction, $M_2H_6 \rightarrow M_2H_x + (6-x)/2\ H_2$, for all M_2H_6 molecules and plotted in figure 11. These reaction energies represent the low limit of dehydrogenation for each individual reaction. Transition state analysis for $M_2H_6 \rightarrow M_2H_4 + H_2$ showed that the elementary step for this unimolecular pathway proceeds through a transition state with a similar structure for all three *hex* hydrides and leads to the formation of an intermediate product state that is less stable than the ground state of M_2H_4.

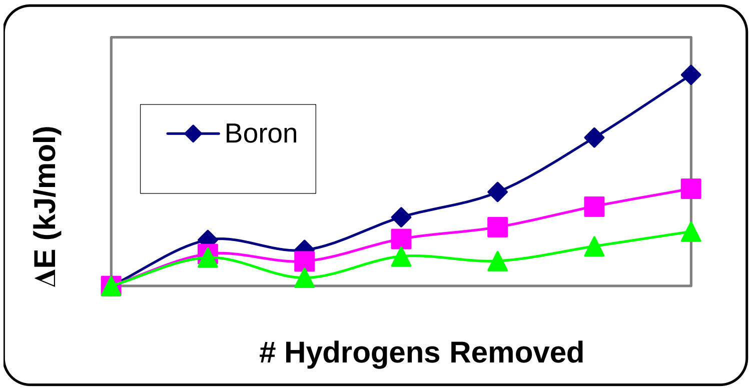

Fig. 11. Energy costs to successively remove hydrogen from M_2H_6 molecules.

VI. Lists of Publications and Presentations

a. Peer-reviewed Publications

1. Zhu, K.; Xia, Y.; Tang, M.; Wang, Z.-T.; Lyubinetsky, I.; **Ge, Q.**; Dohnalek, Z.; Park, K. & Zhang, Z., Low-Temperature Reductive Coupling of Formaldehyde on Rutile TiO_2(110), J. Phys. Chem. C, in press.
2. **Ge, Q.** & M. Gutowski, A Comparative Study of Methanol Adsorption and Dissociation over WO_3 (001) and ReO_3 (001), Topics in Catalysis, 58, 655-664 (**2015**).
3. Zhu, K.; Xia, Y.; Tang, M.; Wang, Z.-T.; Jan B.; Lyubinetsky, I.; **Ge, Q.;** Dohnalek, Z.; Park, K. & Zhang, Z., Tracking Site-Specific C–C Coupling of Formaldehyde Molecules on Rutile TiO_2(110), J. Phys. Chem. C, 119, 14267–14272 (**2015**).
4. Zhang, Z.; Tang, M.; Wang, Z.-T.; Xia, Y.; Park, K. T.; Lyubinetsky, I.; Dohnalek, Z. & **Ge, Q.** Imaging of Formaldehyde Adsorption and Diffusion on TiO_2(110), Topics in Catalysis,

58, 103-113 (**2015**).

5. Ye, J.; Liu, C.-j.; Mei, D. & **Ge, Q.** Methanol Synthesis from CO_2 Hydrogenation over a Pd_4/In_2O_3 Model Catalyst: A Combined DFT and Kinetic Study, J. Catal. 317, 44-53 (**2014**).
6. Ye, J.; Liu, C.-j.; Mei, D. & **Ge, Q.** Active Oxygen Vacancy Site for Methanol Synthesis from CO_2 Hydrogenation on In_2O_3(110): A DFT Study, ACS Catal. 3, 1296-1306 (**2013**).
7. Liu, J.; Tyrrell, J.; Cheng, L. & **Ge, Q.** First-Principles Studies on Hydrogen Desorption Mechanism of Mg_nH_{2n} (n=3, 4), J. Phys. Chem. C. 117, 8099-8104 (**2013**).
8. Xu, L. & **Ge, Q.** Effect of defects and dopants in grapheme on hydrogen interaction in grapheme-supported $NaAlH_4$, Int. J. Hydrogen Energy, 38, 3670-80 (**2013**).
9. Ye, J.; Liu. C.-j.; & **Ge, Q.** "A DFT study of methanol dehydrogenation on the PdIn(110) surface", Phys. Chem. Chem. Phys. 14, 16660-16667 (**2012**).
10. Xia, Y.; Zhang, B.; Ye, J.; **Ge, Q.** & Zhang, Z. "Acetone-Assisted Oxygen Vacancy Diffusion on TiO2(110)", J. Phys. Chem. Lett. 3, 2970 (**2012**).
11. Ye, J.; Liu. C.-j.; & **Ge, Q.** DFT Study of CO_2 Adsorption and Hydrogenation on the In_2O_3 Surface, J. Phys. Chem. C. 116, 7817 (**2012**).
12. Yin, S. & **Ge, Q.** Selective CO_2 hydrogenation on the γ-Al_2O_3 supported bimetallic Co-Cu catalyst, Catalysis Today, 194, 30(**2012**).
13. Karakatsani, S.; **Ge, Q.**; Gladys, M. J.; Held, G. & King, D. A. Coverage-dependent molecular tilt of carbon monoxide chemisorbed on Pt{110}: A combined LEED and DFT structural analysis, Surf. Sci. 606, 383–393(**2012**).
14. Liu, J. & **Ge, Q.** Using first-principles metadynamics simulation to predict new phases and probe phase transition of $NaAlH_4$, J. Phys.: Condens. Matter 23, 345401 **(2011).**
15. Liu, J.; Yu, J. & **Ge, Q.** Hydride-Assisted Hydrogenation of Ti-Doped NaH/Al: A Density-Functional Theory Study, J. Phys. Chem. C. 115, 2522 (**2011**).
16. Liu, J.; Yu, J. & **Ge, Q.** Transition Metal-Doped Aluminum Hydrides as Building Blocks for Supramolecular Assemblies, J. Phys. Chem. A. 114, 12318 (**2010**).
17. Stone, D.; Liu, J.; Singh, D.P.; Muratore, C.; Voevodin, A.A.; Mishra, S.; Rebholz, C.; **Ge, Q.**; & Aouadi, S.M. Layered atomic structures of double oxides for low shear strength at high temperatures, Scripta Materialia, 62, 735 (**2010**).

33. Liu, J. & **Ge, Q.** Hydrogen interaction in Ti-doped $LiBH_4$ for hydrogen storage: A density functional analysis, J. Chem. Theory Comput. 5, 3079 (**2009**).
34. Cheng, L. Mei, D. & **Ge, Q.** Origin of Support Effects on the Reactivity of a Ceria Cluster, J. Phys. Chem. C. 113, 18296 (**2009**).
35. Yorisaki, T.; Tillekaratne, A.; **Ge, Q.**; Oshima, C.; Otani, S.; Trenary, M. Probing the Properties of the (111) and (100) Surfaces of LaB_6 through Infrared Spectroscopy of Adsorbed CO, Surf. Sci. 603, 3011 (**2009**).
36. Lin, C; Xu, T.; Yu, J.; **Ge, Q.** & Xiao, Z. Hydrogen Spillover Enhanced Hydriding Kinetics of Palladium-Doped Lithium Nitride to Lithium Imide, J. Phys. Chem. C. 113, 8513 (**2009**).
37. Liu, J.; Han, Y. & **Ge, Q.** Effect of Doped Transition Metal on Reversible Hydrogen

Release/Uptake from $NaAlH_4$, Chem. Eur. J. 15, 1685 (**2009**).

38. Liu, J. & **Ge, Q.** A first principles analysis of hydrogen interaction and NMR chemical shift induced by doping Sc in $NaAlH_4$, J. Alloy & Compd, 446-447, 267-270 **(2007).**
39. Liu, J. & **Ge, Q.** A First-Principles Analysis of Hydrogen Interaction in Ti-doped $NaAlH_4$ Surfaces: Structure and Energetics, J. Phys. Chem. B, 110, 25863-25868 (**2006**).
40. Liu, J. & **Ge, Q.** A precursor state for formation of $TiAl_3$ complex in reversible hydrogen desorption/adsorption from Ti-doped $NaAlH_4$, Chem. Comm. 1822 – 1824, (**2006**)**.**

b. Book Chapters

2. Liu, J. Tyrrell, J. & **Ge, Q**. "*Computational Nanostructure Design for Hydrogen Storage*", Chap. 22(p. 761-799), in Springer series of Green Energy and Technology, "Energy Efficiency and Renewable Energy through Nanotechnology", Zang, L. (eds.), Springer, ISBN: 978-0-85729-637-5 (**2011**).
3. Liu, J., Aschelman, J., Rajan, L. M., Che, C. & **Ge, Q.** "*A comparative study on the dehydrogenation energetics of M_2H_6 (M=B, Al, Ga) via density functional theory calculations*", (p. 234-243), in Materials Issues in a Hydrogen Economy: Proceedings of the International Symposium, Jena, P.; Kandalam, A.; Sun Q. (eds.), World Scientific Pub Co Inc, ISBN10: 9812838015; ISBN13: 9789812838018 (**2009**).

c. Invited Conference Presentations

1. "*Graphene supported clusters for hydrogen storage and electrocatalysis*", 248th ACS national meeting, San Francisco, CA, August 10-14, **2014** (invited).
2. "*Complex metal hydrides as hydrogen storage materials: Hydrogen interaction and phase transition*", 242nd ACS National Meeting, Denver, CO, Aug., **2011** (invited)
3. "*Understanding and designing hydrogen storage materials based on first principle computational analysis*", 240th ACS national meeting, Boston, Aug. 22-26, **2010** (invited).
4. "*Effect of doped transition metal on hydrogen interaction in $NaAlH_4$ and $LiBH_4$*", 238th ACS national meeting, Washington DC, Aug. 16-20, **2009** (invited).
5. "*From Elementary Steps to Catalytic Reaction Mechanisms*", Plenary lecture at International Symposium on Multiscale Modeling and Simulation of Materials-2009 & International Workshop on Theoretical and Computational Catalysis, Tsinghua University, Beijing, China, July 5-9, 2009 (invited).
6. "*First Principles-Based Simulation of Hydrogen Interactions in Complex Hydrides*", 2009 DOE HYDROGEN PROGRAM and VEHICLE TECHNOLOGIES PROGRAM ANNUAL MERIT REVIEW and PEER EVALUATION MEETING, May 19, **2009** (invited).
7. "Catalysis in hydrogen storage", NIU-ANL-SIU Collaborative Energy Research Symposium, Sept. 24, 2007 (invited)
8. "*First principles based simulation of hydrogen interactions in complex metal hydrides*", DOE Hydrogen Storage Meeting, Division of Materials Science & Engineering, Germantown, MD, Aug. 16-17, 2007 (invited)

9. "*A first principles analysis of hydrogen storage in metal complex hydrides*", 232nd ACS National meeting, San Francisco, CA, Sept. 10-14, 2006 (invited).
10. Lingyun Xu & **Qinfeng Ge**, "Theoretical study of H_2 releasing from sodium alanate on graphene based substrates", 44th Midwest Theoretical Chemistry Conference, Madison, WI, June 7-9, 2012 (poster)
11. Jianjun Liu, Lei Cheng, James Tyrrell & **Qingfeng Ge**, "DFT analysis of hydriding and transforming Mg_mH_n clusters", 243rd ACS National Meeting, San Diego, CA, March 25-29, 2012.
12. Jianjun Liu, **Qingfeng Ge**, "Exploration of hydrogenation mechanism in Ti-doped $NaAlH_4$ by $TiAl_3$ cluster model", 42nd Midwest Theoretical Chemistry Conference, West Lafayette, IN, May 20-22, 2010 (talk).
13. Jiamei Yu & **Qingfeng Ge**, "Hydrogen Spillover Enhanced Hydriding of Lithium Nitride", 41st Midwest Theoretical Chemistry Conference, Carbondale, IL, May 28-30, 2009 (poster).
14. Jianjun Liu & **Qingfeng Ge**, "First-Principles Based Molecular Dynamics Simulations for Phase Transition of $NaAlH_4$", 41st Midwest Theoretical Chemistry Conference, Carbondale, IL, May 28-30, 2009 (poster).
15. Jianjun Liu & **Qingfeng Ge**, "Quantum Chemistry Based Molecular Dynamics Simulation of Hydrogen Desorption from Ti-doped $NaAlH_4$", ACTC2008, Evanston, IL, July, 2008 (*poster*).
16. Jianjun Liu & **Qingfeng Ge**, "A First-Principles Study on Mechanism of Interaction between Transition Metal and $NaAlH_4$", 2008 CCC Spring Symposium, Lisle, IL, May 15, 2008 *(poster*)
17. Jiamei Yu, Jianjun Liu, & **Qingfeng Ge**, "$TiAl_3$: Structure and its interaction with hydrogen"**,** 2008 CCC Spring Symposium, Lisle, IL, May 15, 2008 (*poster*)
18. J. Yu, J. Liu, & **Q. Ge**, *$TiAl_3$: Structure and its interaction with hydrogen*, 235th ACS National Meeting, New Orleans, April, **2008**. (*poster*)
19. N. Sullivan, J. Liu, & **Q. Ge**, *Dissociation and isomerization of B_2H_x on Pt(111)*, 235th ACS National Meeting, New Orleans, April, **2008**. (*poster*)

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