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 TiAl$_3$H$_x$ complex as the precursor for forming TiAl$_3$ alloy observed in Ti-doped 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 NaAlH$_4$. We also explored effect of hydrogen spillover in rehydriding Li$_3$N in collaboration with an experimental group.

(a) Effect of Doped Transition Metal on Reversible Hydrogen Release/Uptake from 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 NaAlH$_4$(001) surfaces doped with 3d transition metal (TM) elements. A complex structure, TMAl$_3$H$_{12}$, in which the TM atom occupies the interstitial position formed from three AlH$_4^-$ groups, is 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 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 TMAl$_3$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 AlH$_x$, which resulted in the formation of a new catalytic center, or by desorbing H$_2$. By cycling between the electron-deficient and electron-rich states, TMAl$_3$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 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 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))

(b) Ti-Doped LiBH$_4$(001), (100), and (010) Surfaces

Density function theory studies have been carried out to investigate the energetics and structures of Ti-doped 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 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 TiB$_2$H$_n$-nBH$_4$ (n=1,2). Furthermore, these complex structures and their transformation are localized. Molecular orbital analysis of the local structures 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$_2$H$_n$-BH$_4$ in (001) and TiB$_2$H$_n$-2BH$_4$ in (010) will desorb a hydrogen molecule, while the quintet TiB$_2$H$_n$-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 BH$_4^-$ in TiB$_2$H$_n$-nBH$_4$ (n=1,2) is not as significant as those to the antibonding orbitals of AlH$_4^-$ in TiAl$_x$H$_{12-2x}$. Consequently, the B–H bonds in TiB$_2$H$_n$-nBH$_4$ (n=1,2) were not as highly activated as the Al–H bonds in TiAl$_x$H$_{12-2x}$ (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 large surface area and uniformity of the catalysts. Our results demonstrated that Li$_3$NPd$_{0.03}$, with nanoscopic Pd uniformity can be prepared through nitridization of LiPd$_{0.03}$ eutectic. The synthesized Li$_3$NPd$_{0.03}$ exhibits an enhanced hydriding kinetics over pure Li$_3$N for reaction Li$_3$N + H$_2$ ⇌ Li$_3$NH + LiH under moderate conditions. The experimental measured an activation barrier of $\sim$28 kJ/mol for hydriding Li$_3$NPd$_{0.03}$. We used a Pd$_4$ cluster supported on the (100) surface of Li$_3$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 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 Pd$_4$ cluster (A) to the N atom in the Li$_3$N 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. $\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.

(d) Phase Transition of NaAlH$_4$ Followed by Metadynamics

Experimental studies have established that hydrogen release from NaAlH$_4$-based material is accompanied by a series of phase transitions in solid
state. The process starts with NaAlH₄, goes through a Na₃AlH₆ intermediate, and finishes with NaH and 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 NaH, AlH₅, and AlH₆ species are formed with the increased simulation temperatures. The formation of NaH causes AlH₄ to lose its electron and promote polymerization of hydrides through a µ-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**


**Presentations**


8. J. Liu, J. Aeschleman, N. Sullivan & Q. Ge, “A first principles study of BH2 (n=0,3) and B2H6 (n=0,6) adsorption on Pt(111)”, 39th Midwest Theoretical Chemistry Conference, Bloomington, IN, June 28–30, 2007 (poster).


Seminars

5. SINOPEC Tianjin University R&D Center for Petrochemical Technology, Tianjin University, Jan. 11, 2008.
8. School of Chemical Engineering and Technology, Tianjin University, June 14, 2007.

Participants

Postdoc assistant scientist:
Dr. Jianjun Liu (100%)  
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Lei Cheng (25%), Jeremiah Aeschleman, Jiamei Yu (50%), You Han (visiting student from China).
Undergraduate students:
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