IV.I.7 Elucidation of Hydrogen Interaction Mechanisms with Metal-Doped Carbon Nanostructures

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Project Overview

This research work is aimed at obtaining a fundamental understanding of the nanoscale level of hydrogen sorption behavior of light-metal hydride material catalyzed by carbon nanostructures. The experimental work is closely linked to relevant modeling studies of these materials. Advances in hydrogen storage technology based on carbon nano-structures and particularly metal-doped carbon nanotube require the development of a basic understanding of their physicochemical properties and the manner in which these properties influence the hydrogen bonding. Our effort is focused on understanding of the hydrogen interaction mechanisms such as physisorption, weak covalent bonding, and chemisorption in these nano-carbon systems.

In the context of hydrogen, carbon nanomaterials have been commonly associated with use as storage materials. We have formulated a novel view; the employment of carbonaceous nanomaterials as catalysts for hydrogen uptake and release. The underlying mechanism relies on the electronegativity of the carbon-based nanomaterials (such as fullerenes and carbon nanotubes) which exerts a destabilizing effect on complex metal hydride systems by withdrawing electrons. The thus generated electron-deficient environment weakens the chemical bonds of hydrogen (e.g., the Al-H bond in $NaAlH_4$). This is a new concept on the catalysis of hydrogen storage reactions involving complex metal hydride materials. All currently considered catalysts (typically Ti or other transition metals) strongly react chemically with the host compounds, which complicates a thorough understanding of their catalysis mechanism.

Experimental work shows carbon nanostructure-catalyzed hydrogen uptake and release for sodium alanate ($NaAlH_4$) and lithium borohydride ($LiBH_4$). A survey of carbon material (fullerene, carbon nanotubes, and graphene) $NaAlH_4$ nanocomposites demonstrated varying degrees of catalytic activity. Partial reversibility of hydrogen was observed for $NaAlH_4$ and $LiBH_4$. C_{60} materials were found to be the best carbon additive for $NaAlH_4$, rehydriding $NaAlH_4$ up to 4.3 wt% over 8 hours with 200 bar hydrogen overpressure. A fullerene- $LiBH_4$ composite demonstrates catalytic properties with not only lowered hydrogen desorption temperatures but regenerative rehydrogenation at a relatively low temperature of 350°C. C_{60} materials were found to be an excellent carbon additive for $LiBH_4$, rehydriding $LiBH_4$ by 4.2 wt% over 12 hours with 120 bar hydrogen overpressure. We believe that a contributing factor to the performance of the C_{60} with both complex hydrides is its dispersibility.

This synergistic approach involving experiment and first-principles theory not only shows that carbon nanostructures can be used as catalysts for hydrogen uptake and release in complex metal hydrides $NaAlH_4$ and $LiBH_4$, but also provides an unambiguous understanding of how the catalysts work. Interaction of $NaAlH_4$ with an electronegative substrate such as carbonaceous graphitic materials affects the ability of Na to donate its charge to AlH_4, consequently weakening the Al-H bond and causing hydrogen to desorb at lower temperatures as well as facilitating the absorption of H_2 to reverse the dehydrogenation reaction. Computation simulations show that the stability of $NaAlH_4$ originates with the charge transfer from Na to the AlH_4 moiety, resulting in an ionic bond between Na^+ and AlH_4^- and a covalent bond between Al and H. Carbon nanostructures with zero, one, and two nanoscale dimensions (fullerene, carbon nanotubes, and graphene) show decreasing relative catalytic activity for hydrogen sorption in $NaAlH_4$ (see Figure 1). Based on our experimental observations and theoretical calculations

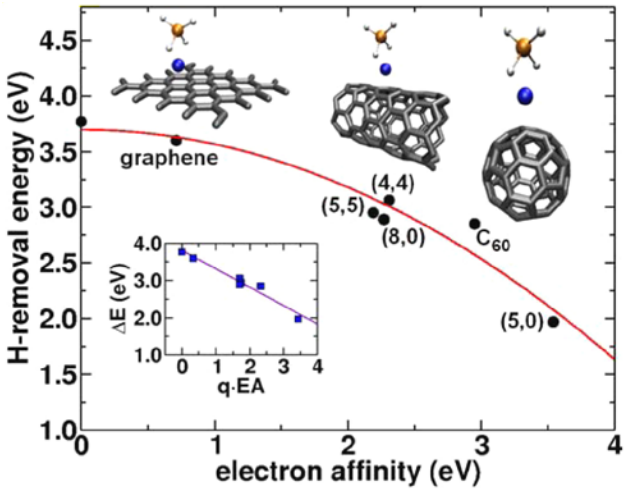

FIGURE 1. Correlation of the carbon substrate electron affinity and the hydrogen removal energy.

it appears the curvature of the carbon nanostructure plays a role in the catalytic process. This model provides a conceptual frame work for carbon nanostructure catalytic effects and a rational extension to a variety of complex hydrides.

The past years effort draws its strength from our synergistic approach, involving systematic experimental measurements complemented by state-of-the-art first-principles theory. This combination enabled us to demonstrate for the first time the surprising catalytic effect of carbon nanostructures on hydrogen uptake and release in sodium alanate and lithium borohydride, and at the same time, to reveal the mechanism at the atomic and electronic level that allows the carbon nanostructures to act as efficient catalysts in this system.

Publications in Which BES Support is Acknowledged

1. Stowe, A.C.; Zidan, R.; Acatrinei, A.I.; Hartl, M.A.; Daemen, L.L.; Lujan, M., Jr.; "Neutron Scattering and Computational Studies of the Structure and Dynamics of $NaMgH_3$" *J. Mat. Sci. Eng. Submitted.*

2. Berseth, P.A.; Harter, A.G.; Zidan, R.; Blomqvist, A.; Araújo, C.M.; Scheicher, R.H.; Ahuja, R.; Jena, P. "Carbon nanomaterials as catalysts for hydrogen uptake and release in $NaAlH_4$" *Nano Letters.* **2009**, 9(4), 1501-1505.

3. Vennila, R.S.; George, V.D.L.; Saxena, S.K.; Liermann, H.-P.; Liu, H.Z.; Stowe, A.C.; Berseth, P.; Anton, D.; Zidan, R. "Structural Study of Ball-Milled Sodium Alanate under High Pressure" *J. Alloys Comp.* **2009**, 473, 576–578.

4. Wellons, M.S.; Berseth, P.A.; Zidan, R. "Fullerene as a catalyst for hydrogen uptake and release in $LiBH_4$" *J. Nanotechnology, Special issues: Nanoscale phenomena in hydrogen storage.* Accepted, on line April **2009**.

5. Corey, R.L.; Ivancic, T.M.; Shane, D.T.; Carl, E.A.; Bowman, R.C., Jr.; Bellosta von Colbe, J.M.; Dornheim, M.; Bormann, R.; Huot, J.; Zidan, R.; Stowe, A.C.; Conradi, M.S. "Hydrogen Motion in Magnesium Hydride by NMR" *J. Phys. Chem. C.* **2008**, 112(49), 19784-19790.

6. Stowe, A.C.; Berseth, P.A.; Farrell, T.P.; Laughlin, L.; Anton, D.; Zidan, R. "Investigation of the thermodynamics governing metal hydride synthesis in the molten state process" *J. Alloy. Comp.* **2008**, 465(1-2), 41-46.

Personnel Commitments for FY 2008 to Nearest +/- 10%

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