
**From fundamental understanding to predicting new nanomaterials for
high capacity hydrogen storage and fuel cell technologies
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T. Yildirim^{1,2} and J. E. Fischer¹

¹Department of Materials Science and Eng., University of Pennsylvania,
Philadelphia, PA 19104

²National Institute of Standards and Technology, NCNR, Gaithersburg, MD 20899

Program Scope:

This is an add-on BES proposal to Jack Fischer's existing grant on "Carbon Nanotubes: Properties and Applications", which will focus on achieving fundamental understanding of the chemical and structural interactions governing the storage and release of hydrogen in a wide spectrum of candidate materials. Even though we have just started our theory and modeling efforts coupled closely to neutron experiments at NIST, we have already obtained significant results that will be briefly discussed in this abstract. The main purpose of our proposal is to launch a broad modeling effort, in the framework of this BES grant. The goals are

- To provide fundamental understanding of how the most of the candidate materials (MOF's, alanates, destabilized chemical hydrides, etc) interact with H₂ chemically, structurally and energetically; and
- To provide timely feedback and guidance from theory to *de novo* materials design and targeted syntheses throughout the DOE programs.

We expect that this new modeling initiative will have a major impact on the extensive experimental work at NIST, where senior staffs are coupled to essentially all of the EERE Centers of Excellence.

Recent Progress:

(a) High-Temperature Molecular Dynamics Study and Normal Mode Analysis of Ti-decorated C₆₀ and SWNT for Room-Temperature Hydrogen Storage Media

There is accumulating experimental and computational evidence that Ti additions to low-capacity storage materials can have dramatic beneficial effects on H₂ capacity. We recently showed that a single Ti could adsorb four H₂ molecules with interaction strength intermediate between chemi- and physisorption, precisely what is needed for reversible room temperature storage. This recent discovery opens a totally new way of engineering nanostructured materials by tuning the interaction centers in high-surface area materials and will be one of the main focuses of this project. We are currently studying several important questions such as "metal clustering" or "segregation" in Ti-decorated nanostructures using high-temperature molecular dynamics simulations and normal-mode analysis.

We have calculated normal modes (i.e. phonons) of several C₆₀Ti_yH_x (y=0,1,6, x=0,2,4, and 8) clusters and the corresponding Neutron and Raman intensities. We found that all modes are positive suggesting that the predicted Ti-decorated C60 structures are at least metastable phases. Hence if one could synthesize them, they will stay in that way below some critical temperature. The calculated phonon-spectrums will be also in valuable in confirming that any attempted synthesis was successful or not via Raman

and/or Infrared and/or Neutron INS measurements and comparing the results with our calculations. Among many unique modes of $C_{60}TiH_x$, we found that the first three lowest energy modes all involve the TiH_x group vibrating as a whole as shown in the left panel to Figure 1. The lowest energy mode is the one where the TiH_x group oscillates towards the nearest neighbor hexagon centers (shown as red arrow). The second lowest energy mode is the similar one but this time the TiH_x group vibrates along the bridge bond (rather than towards hexagons – see blue arrow in Fig. 1). And finally, the third lowest energy mode is the radial oscillation of the TiH_x group (black arrow in Fig. 1). We note that these modes have low energies not due to the weak interaction of the C_{60} and TiH_x group but rather due to large mass of the TiH_x group. The fact that these modes are positive suggests that proposed structures form stable local energy minima. In order to test the stability and metal-segregation in these systems further, we are currently performing high-temperature first-principles dynamics simulations. Within the MD simulation time, we have found that the diffusion of metal is very small (to be more precise, we have not observed any diffusion within the MD simulation time of 1 ps and temperatures up to 800 K). Hence, it is very likely that if Ti-decorated C_{60} and SWNT systems can be synthesized, they will preserve their initial structures during the hydrogen charging and discharging cycles. The right panel in Figure 1 shows the Ti-Ti distance during the MD simulation at 800 K for a pair of two TiH_2 group bonded to two nearest neighbor bridge sites on a C_{60} molecule. From this simulation, no the evidence for clustering has been observed.

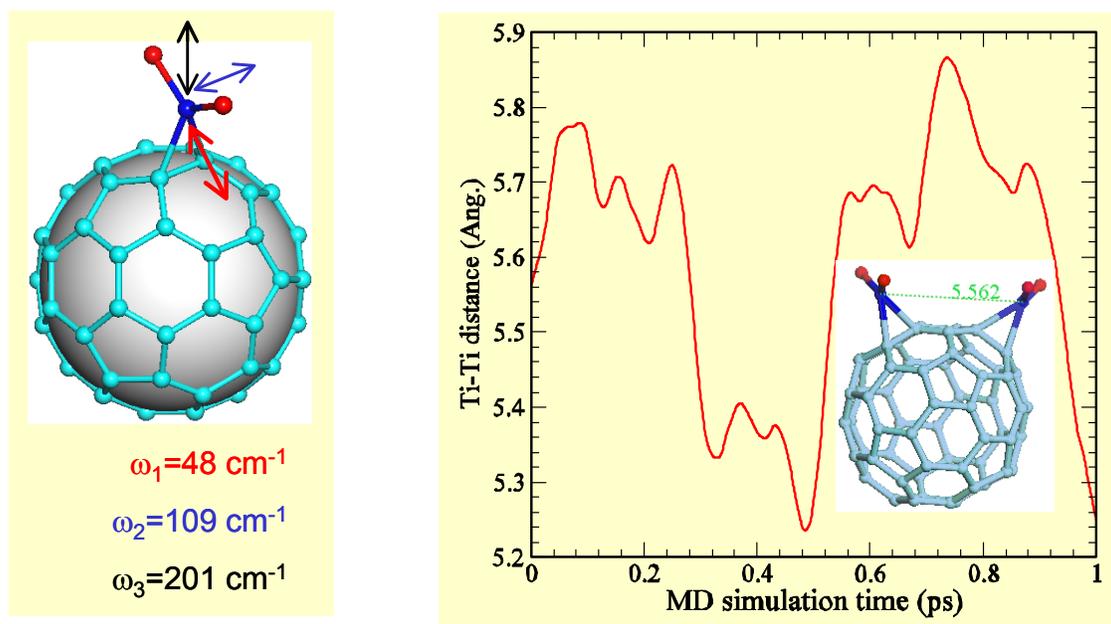


Figure 1. LEFT: The three lowest energy modes of a $C_{60}TiH_2$ cluster. The mode energies given at the bottom are all positive, indicating that the system is in a local minima structure. RIGHT: The Ti-Ti distance as a function of MD simulations at 800 K for a $C_{60}(TiH_2)_2$ cluster as shown in the inset. No evidence for clustering is observed within the MD simulation time length.

(b) Ti-enhanced kinetics of hydrogen adsorption and desorption in NaAlH₄ surfaces (submitted Phys. Rev. B see cond-mat/0604472)

In this work, we report a first-principles study of the energetics of hydrogen absorption and desorption (i.e. H-vacancy formation) on pure and Ti-doped sodium alanate (NaAlH₄) surfaces. We find that the Ti atom facilitates the dissociation of H₂ molecules as well as the adsorption of H atoms. In addition, the dopant makes it energetically more favorable to create H vacancies by saturating Al dangling bonds. Interestingly, our results show that the Ti dopant brings close in energy all the steps presumably involved in the absorption and desorption of hydrogen, thus facilitating both and enhancing the reaction kinetics of the alanates. We also discuss the possibility of using other light transition metals (Sc, V, and Cr) as dopants.

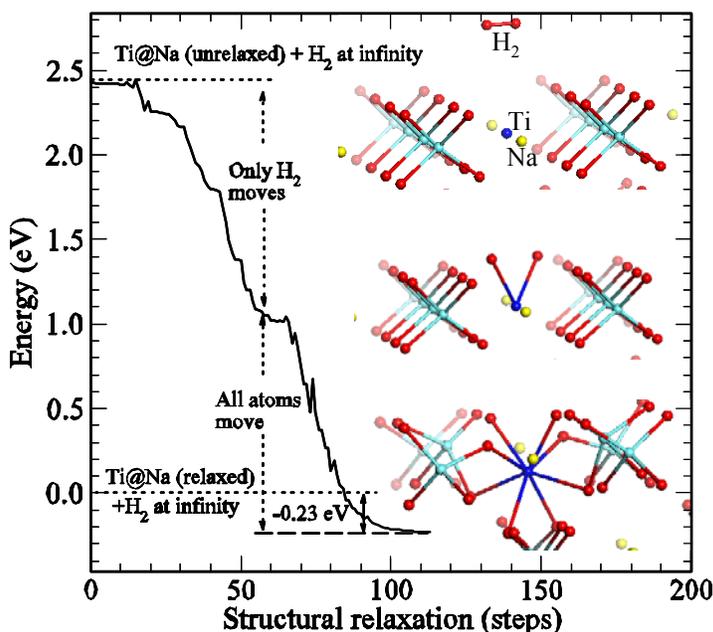


Figure 2: Energy versus structural relaxation step for the H₂ dissociation and absorption by the Ti@Na surface. The starting point is the unrelaxed Ti@Na surface with an H₂ molecule close to it, which is taken as the zero of energy. In the first part of the relaxation, only the H₂ molecule is allowed to move; then, all the atomic positions are relaxed. Given for reference is the result for the relaxed Ti@Na plus an H₂ located at infinity. The insets show the various steps of the absorption process.

(c) H₂ and CH₄ adsorption in MOF5: A High-Pressure Volumetric and INS Study

We measured the H₂ and CH₄ adsorption isotherms in MOF5 over a large temperature range (30-300 K) and pressure range (up to 65 bar) using a home-built, fully computer-controlled Sieverts apparatus. We found that in a volumetric method, properly choosing the real gas equation of state is of critical importance for obtaining reliable isotherm data. For H₂ and CH₄, the widely used van der Waals equation of state (EOS) is not adequate and the modified Benedict-Webb-Rubin (MBWR) EOS should be used in the data reduction. With the sample mass and bulk density known, the skeleton density and the specific pore volume of MOF5 were also measured and found to be ~1.78 g/cc and 66.2 % respectively. The absolute adsorption, excess adsorption and effective adsorption were then all experimentally determined. At low temperature, the maximal excess adsorption capacities of H₂ and CH₄ in MOF5 are found to be 10.3 wt% and 51.7 wt% respectively. From the isotherm data, the isosteric heat of adsorption (Q_{st}) was estimated. The excess Q_{st}'s for the initial H₂ and CH₄ adsorption in MOF5 are ~4.8 KJ/mol and ~12.2 KJ/mol, respectively. When the amount adsorbed is large, Q_{st}

increases with increasing amount adsorbed, a result of cooperative interactions between adsorbed molecules.

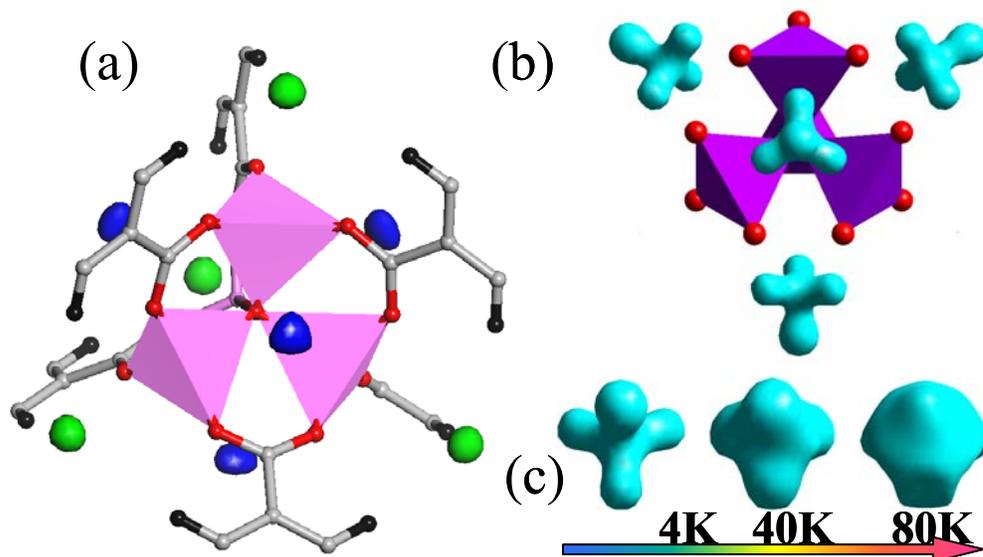


Figure 3. (a) First two hydrogen absorption sites in MOF5 as directly measured by neutron scattering. (b) The methane absorption sites in MOF5. Light-blue are actual experimental scattering density of CH_4 absorbed in MOF5. (c) Temperature evaluation of the CH_4 orientation as T increases from 4K to 80 K.

Finally, we also performed several neutron scattering measurements to study the H_2/CH_4 interactions in MOF-host lattice as shown in Fig. 3. We successfully identified the absorption sites as a function of gas-loading concentration. We also measured and calculated the elementary excitations such as ortho-para transition of H_2 and “rotational tunnel splitting of methane” in MOF, which gives very detailed information about the H_2 -MOF interactions.

(d) Unusually Short Hydrogen-Hydrogen Pairing in LaNiInH_x

A recent neutron powder diffraction study of the $R\text{NiIn-D}_2$ systems ($R = \text{La}, \text{Ce}, \text{Nd}$) [J. Alloys Comp. 330-332 (2002) 132] showed an unusual double H occupancy in the trigonal bipyramidal $R_3\text{Ni}_2$ sites (see Fig. 4), leading to the formation of hydrogen pairs with the shortest documented interatomic $\text{H}\cdots\text{H}$ separation (1.56-1.63 Å) for intermetallic hydrides, *raising several important fundamental questions and possible practical applications related to hydrogen storage.*

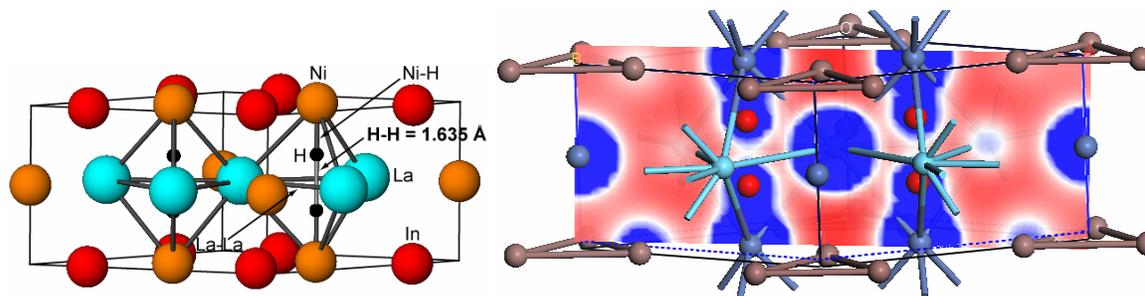


Figure 4. (LEFT) Crystal structure of $\text{LaNiInH}_{1.333}$ (RIGHT) Calculated charge density contour indicating that H atoms are strongly hybridized with Ni (blue color) and there is no bonding between two hydrogen atoms (white region).

In order to understand the nature of bonding, structure and dynamics in these interesting intermetallic hydrides, RNiIn-H_x , we have performed (a) inelastic neutron scattering measurement for $x=1.333$ and 0.666 and (b) first-principles structure and dynamics calculations for three different values of hydrogen concentration. Both INS spectrum and calculations suggest that in $\text{LaNiInH}_{0.666}$, H atoms are on different sites. Charge and bond-population analysis indicate that the bonding in these interesting system is a combination of ionic and covalent. There is a little H—H chemical bonding (if any) as shown in Figure 4. The neutron vibrational spectrum shows only the modes where H vibrates in the ab-plane. Somehow the high-energy vibrations along the c-axis are missing (probably due to anharmonic behavior which results in large rms displacement, and therefore large temperature-factor)! Comparison between experiment and calculations indicate that the force constant between H—H is about 10% of the Ni-H force constant, consistent with the charge density plot shown in Fig. 4.

Future Plans:

Based on the current results discussed above, we will continue to use the following unique approaches to solve the outstanding problems in hydrogen storage field:

- Major emphasis will be placed on fundamental issues, such as understanding the mechanism of hydrogen interaction in different candidate materials, by employing a powerful combination of first-principles modeling and closely coordinated neutron scattering experiments to develop and test intermolecular potential surfaces, etc.
- A major focus will be on nanoscale materials and the practicality of exploiting metastable states, in contrast to traditional theory which goes to great lengths to avoid local minima in atomic configuration energies. This approach is much more consistent with the manner in which many of these materials are synthesized, e.g. ball-milling to realize Ti-doped aluminates, in which high energy nonequilibrium methods are a prerequisite to obtain the targeted phase.
- Theory and experiment will be done under the same roof at NIST. Frequent interactions *via* group meetings, web-conference and email will be programmed.

In particular, in the rest of the project, we will try to accomplish the following objectives:

- Study hydrogen sorption properties of Ti and other transition metal coated carbon, boron-nitride and TiS_2 nanotubes. Determine trends in binding energies, geometries and hydrogen sorption capacity as a function of tube type, radius, transition metal and coverage.
- Apply Ti doping/activation to other promising materials, e.g sodium alanates and borates and novel clusters such as metcarb (i.e. Ti_{12}C_8).
- Establish the stability and energetics of MOF materials doped with alkali and transition metals (Li being particularly attractive). Identify metal absorption sites and their interactions with high-energy molecules such as hydrogen and methane.
- In parallel with the theory effort, synthesize and characterize the most promising doped nanostructured materials predicted by the modeling. Perform high-pressure hydrogen adsorption isotherms to determine capacity and kinetics. Use neutron scattering to determine the location of interaction centers, hydrogen dynamics and the nature of bonding.

Publications in 2006 (related to this project)

1. *Ti-enhanced kinetics of hydrogen absorption and desorption in NaAlH_4 surfaces*, J. Iniguez and T. Yildirim (PRB, submitted 2006, cond-mat/0604472).
2. *Structure, Dynamics and Rotational Tunneling of Methane in MOF*, W. Zhou and T. Yildirim (in preparation, 2006.)
3. *Unusually Short Hydrogen-hydrogen distance in LaNiInH_x* , T. Yildirim, J. Iniguez, T. J. Udovic, V. A. Yartys, PRB rapid comm. (in preparation, 2006).
4. *Lattice Dynamics of MOF5; A combined neutron scattering and first-principles study*, W. Zhou and T. Yildirim (in preparation, 2006.)
5. *H_2 and CH_4 adsorption in MOF5: A High-Pressure Volumetric Study*, W. Zhou, M. R. Hartman and T. Yildirim (in preparation, 2006).
6. *Normal Mode Analysis and First-Principles Molecular Dynamics Study of $\text{C}_{60}\text{Ti}_y\text{H}_x$ Clusters for Room Temperature Reversible Hydrogen Storage*, J. Iniguez, W. Zhou and T. Yildirim (in preparation, 2006.)

Invited Talks in 2006 (related to this project)

1. *From fundamental understanding to predicting new nanomaterials for high capacity hydrogen storage technologies*, T. Yildirim, APS March Meeting, Baltimore 2006.
2. *Combined Neutron Scattering and First-Principles Study of Novel Hydrogen Storage Materials*, T. Yildirim, MRS Spring Meeting, San Francisco 2006.
3. *Magic Role of Ti in Novel Hydrogen Storage Materials*, T. Yildirim, the XV International Materials Research Congress (IMRC), Cancún, Aug. 20 -24, 2006.
4. *Neutron Scattering and First-Principles Characterization of Novel Hydrogen Storage Materials*, T. Yildirim, American Conference on Neutron Scattering St. Charles, IL, June 18-22, 2006.