

IV.I.24 From Fundamental Understanding to Predicting New Nanomaterials for High-Capacity Hydrogen Storage

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Project Scope

The main scope of this BES proposal is to 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. The goals are:

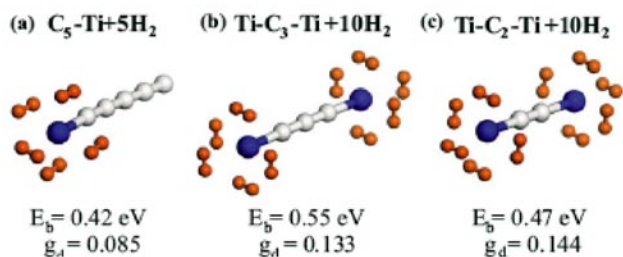
- To provide fundamental understanding of how the most of the candidate materials (MOFs, alanates, destabilized chemical hydrides, etc) interact with H₂ chemically, structurally and energetically; and
- To provide timely feedback and guidance from theory to de novo materials design and targeted syntheses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

Below we present a brief summary of the selected twelve papers which have already been published during 2008-April 2009. The first six of these are resulted from the initial phase of our project which was funded as an add-on DOE BES proposal to Prof. Jack's Fischer's existing grant "Carbon Nanotubes: Properties and Applications" (DE-FG02-98ER45701). In the last six publications, we acknowledge the new grant number, DOE-BES-08ER46522, which has been started on 8-15-2008. At the end of the report, we give the total list of publications and people working on the project.

Research Accomplishments

1. Functionalization of Carbon-Based Nanostructures with Light Transition-Metal Atoms for Hydrogen Storage, E. Durgun, S. Ciraci, and T. Yildirim, *Phys. Rev. B*, **77**, 085405 (2008).

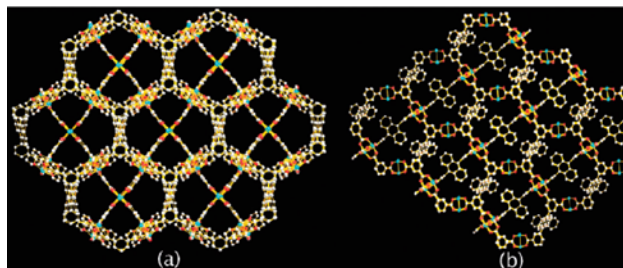
In this work, we extend our previous study further to investigate the hydrogen uptake by light transition-metal atoms decorating various carbon-based nanostructures in different types of geometry and



dimensionality, such as carbon linear chain, graphene, and nanotubes. Using first-principles plane-wave method we show that not only outer but also inner surface of a large carbon nanotube can be utilized to bind more transition-metal atoms and hence to increase the storage capacity. We also found that scandium and vanadium atoms adsorbed on a carbon nanotube can bind up to five hydrogen molecules. Similarly, light transition-metal atoms can be adsorbed on both sides of graphene and each adsorbate can hold up to four hydrogen molecules yielding again a high-storage capacity. Interestingly, our results suggest that graphene can be considered as a potential high-capacity H₂ storage medium. We also performed transition state analysis on the possible dimerization of Ti atoms adsorbed on the graphene and single-wall carbon nanotube.

2. Metal-Organic Framework from an Anthracene Derivative Containing Nanoscopic Cages Exhibiting High Methane Uptake, Shengqian Ma, Daofeng Sun, [Jason M. Simmons](#), Christopher D. Collier, Daqiang Yuan, and Hong-Cai Zhou, *J. Am. Chem. Soc.* **130**, 1012 (2008).

A microporous metal-organic framework, PCN-14, based on an anthracene derivative, 5,5-(9,10-anthracenediyl)di-isophthalate (H₄adip), was synthesized under solvothermal reaction conditions. X-ray single crystal analysis revealed that PCN-14 consists of nanoscopic cages suitable for gas storage. N₂-

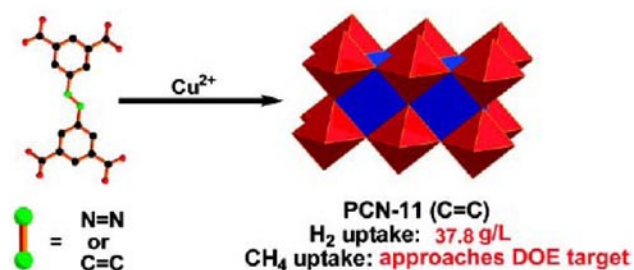


Different views of PCN-14, which exhibits record high methane absorption at room temperature.

adsorption studies of PCN-14 at 77 K reveal a Langmuir surface area of 2,176 m²/g and a pore volume of 0.87 cm³/g. Methane adsorption studies at 290 K and 35 bar show that PCN-14 exhibits an absolute methane-adsorption capacity of 230 v/v, 28% higher than the DOE target (180v/v) for methane storage.

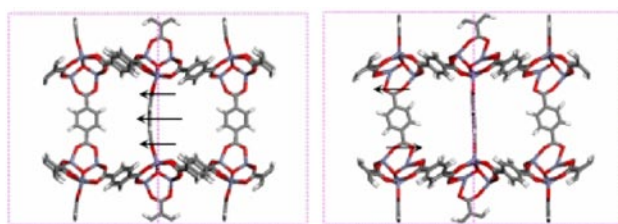
3. Metal-Organic Frameworks Based on Double-Bond-Coupled Di-Isophthalate Linkers with High Hydrogen and Methane Uptakes, Xi-Sen Wang, Shengqian Ma, Karsten Rauch, Jason M. Simmons, Daqiang Yuan, Xiaoping Wang, Taner Yildirim, William C. Cole, Joseph J. López, Armin de Meijere, and Hong-Cai Zhou, *Chem. Mater.* **20**, 3145 (2008).

Utilization of double-bond-coupled di-isophthalate ligands, H₄aobtc and H₄sbtc, in reactions with Cu(NO₃)₂ yielded two isostructural microporous MOFs, PCN-10 and PCN-11, respectively. Upon guest removal, both MOFs contain two types of pores, open metal sites, and retain enduring porosity. In particular, both contain nanoscopic cages that are particularly suitable for gas storage. At 760 Torr, 77 K, the excess hydrogen uptake of PCN-10 is 2.34 wt% (18.0 g/L) and that of PCN-11 is as high as 2.55 wt% (19.1 g/L). Gas adsorption experiments suggest that MOFs containing CdC double bonds are more favorable than those with NdN double bond in retaining enduring porosity after thermal activation, although the NdN double bond has slightly higher H₂ affinity. When the pressure is increased, the excess adsorption at 77 K saturates around 20 atm and reaches values of 4.33% (33.2 g/L) and 5.05% (37.8 g/L) for PCN-10 and PCN-11, respectively. In addition, PCN-11 exhibits an excess methane uptake of 171 cm³(STP)/cm³ at 298 K and 35 bar, approaching the DOE target of 180 v(STP)/v for methane storage at ambient temperatures. Thus, PCN-11 represents one of the few materials that are applicable to both hydrogen and methane storage applications.



4. Origin of the Exceptional Negative Thermal Expansion in Metal-Organic Framework-5, Wei Zhou, Hui Wu, and Taner Yildirim, J.R. Simpson and A.R. Hight Walker, *Phys. Rev. B*, **78**, 054114 (2008).

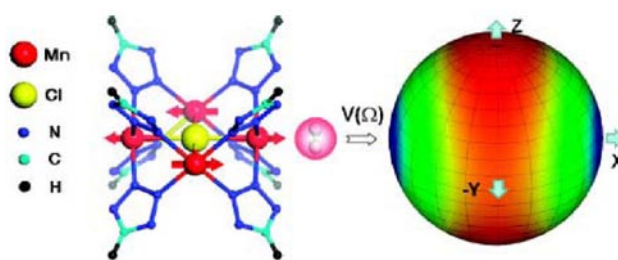
Metal-organic framework-5 possesses an exceptionally large negative thermal-expansion (NTE)



coefficient. Our direct experimental measurement, in the temperature range of 4 to 600 K, shows that the linear thermal-expansion coefficient is $\sim -16 \times 10^{-6} \text{ K}^{-1}$. From first-principles lattice dynamics calculations, we deciphered the origin of this large NTE behavior. We found that almost all low-frequency lattice vibrational modes (below $\sim 23 \text{ meV}$) involve the motion of the benzene rings and the ZnO₄ tetrahedra as rigid units and the carboxyl groups as bridges. These rigid-unit modes exhibit various degrees of phonon softening and thus are directly responsible for the large negative thermal expansion in MOF-5.

5. Nature and Tunability of Enhanced Hydrogen Binding in Metal-Organic Frameworks with Exposed Transition Metal Sites Wei Zhou and Taner Yildirim, *J. Am. Chem. Soc.* **112**, 8132 (2008).

Metal-organic framework (MOF) compounds with exposed transition-metal (TM) sites were recently found to exhibit significantly larger experimental heats of adsorption of H₂ than classical MOFs, thus attracting greater attention. Here we show that the hydrogen binding in Mn₄Cl-MOF is not of the expected Kubas type because there is (a) no significant charge transfer from TM to H₂, (b) no evidence of any H₂-σ* Mn-d orbital hybridization, (c) no significant H-H bond elongation, and (d) no significant shift in H-H stretching mode frequency. We make predictions for the magnetic superexchange interactions in Mn₄Cl-MOF and determined low- and high-spin states of the Mn ion as local minima with very different hydrogen binding energies. We show that, by replacing Cl with F or Br, one can tune the H₂ binding energy. We further

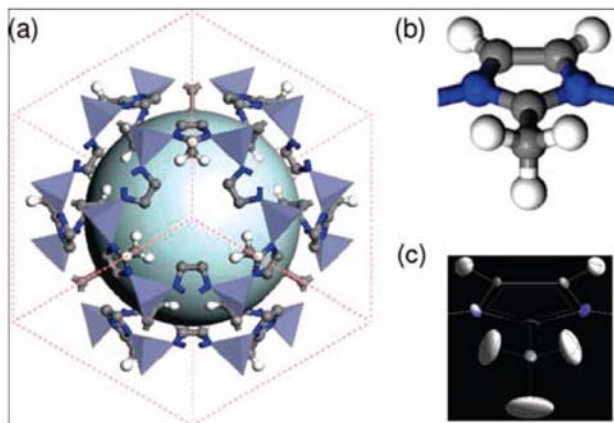


Contour plot of the orientation dependence of the binding energy of H₂ on Mn₄Cl-MOF cluster in (θ, φ) space. The red and blue regions represent strong and weak binding energies, respectively.

reveal that the major contribution to the overall binding comes from the classical Coulomb interaction which is not screened due to the open-metal site and explains the relatively high binding energies and short H₂-TM distances observed in MOFs with exposed metal sites compared to traditional ones. Finally, we show that the orientation of H₂ has a surprisingly large effect on the binding potential, reducing the classical binding energy by almost 30%.

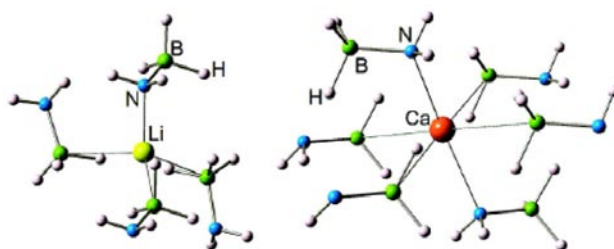
6. Quasi-Free Methyl Rotation in Zeolitic Imidazolate Framework-8, W. Zhou, H. Wu, T.J. Udovic, J.J. Rush, and Taner Yildirim, *J. Phys. Chem. A*, **112**, 12602 (2008).

The reorientational motion of the methyl group is an intriguing physics phenomenon. It can be well described by classical random jumps at high temperature, whereas at low temperature it is dominated by quantum-mechanical rotational tunneling. Using neutron inelastic scattering and diffraction, we have studied the quantum methyl rotation in ZIF-8. The rotational potential for the CH₃ groups in ZIF-8 is shown to be primarily 3-fold in character. The ground-state tunneling transitions at 1.4 K of 334 ± 1 μ eV for CH₃ groups in hydrogenated ZIF-8 and 33 ± 1 ueV for CD₃ groups in deuterated ZIF-8 indicate that the barrier to internal rotation is small compared to almost all methylated compounds in the solid state and that methyl-methyl coupling is negligible.



7. Alkali and Alkaline-Earth Metal Amidoboranes: Structure, Crystal Chemistry, and Hydrogen Storage Properties, Hui Wu, Wei Zhou and Taner Yildirim, *J. Am. Chem. Soc.*, **130**, 14834 (2008).

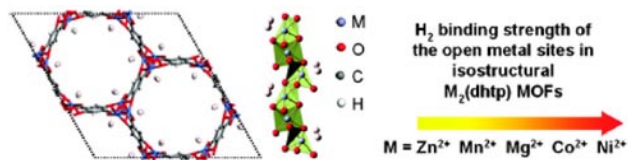
Alkali- and alkaline-earth metal amidoboranes, a new class of compounds with rarely observed [NH₂BH₃]- units, have been recently reported to significantly improve the dehydrogenation properties of ammonia borane. We successfully prepared solvent-



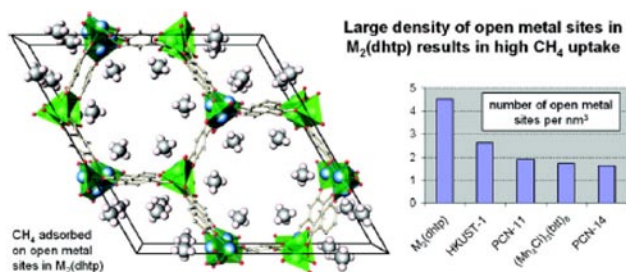
free lithium amidoborane LiNH₂BH₃ and calcium amidoborane Ca(NH₂BH₃)₂, and for the first time determined their structures, using a combined X-ray diffraction and first-principles molecular dynamics simulated annealing method. Through detailed structural analysis and first-principles electronic structure calculations, the improved dehydrogenation properties are attributed to the different bonding nature and reactivity of the metal amidoboranes compared to NH₃BH₃.

8. Enhanced H₂ Adsorption in Isostructural Metal-Organic Frameworks with Open Metal Sites: Strong Dependence of the Binding Strength on Metal Ions, Wei Zhou, Hui Wu, and Taner Yildirim, *J. Am. Chem. Soc.* **130**, 15268 (10/25/2008).

MOFs with open metal sites exhibit much stronger H₂ binding strength than classical MOFs. Yet, how the binding strength varies with different open metal species was previously unknown. We conducted a systematic study of the H₂ adsorption on a series of isostructural MOFs, M₂(dhtp) (M=Mg, Mn, Co, Ni, Zn). The experimental Q_{st} for H₂ of these MOFs range from 8.5 to 12.9 KJ/mol, with increasing Q_{st} in the following order: Zn, Mn, Mg, Co, and Ni. The H₂ binding energies derived from DFT calculations follow the same trend. We also found a strong correlation between the metal ion radius, the M-H₂ distance and the H₂ binding strength, which provides a viable, empirical method to predict the relative H₂ binding strength of different open metals.



The c-axis view of the unit cell of MOF-74, showing the one-dimensional pore geometry.



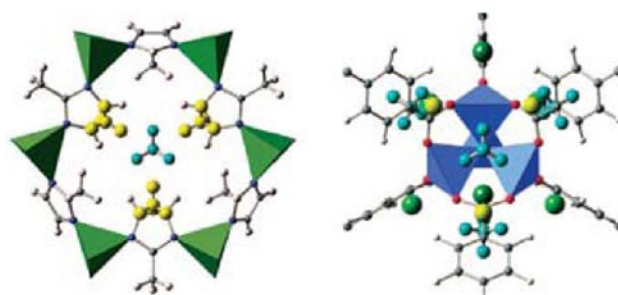
Methane absorbed in MOF-74 as obtained from neutron diffraction.

9. High-Capacity Methane Storage in Metal-Organic Frameworks $M_2(\text{dhtp})$: The Important Role of Open Metal Sites, Hui Wu, Wei Zhou, and Taner Yildirim, *J. Am. Chem. Soc.* **131**, 4995 (03/10/2009).

We found that metal-organic framework (MOF) compounds $M_2(\text{dhtp})$ (open metal $M=\text{Mg, Mn, Co, Ni, Zn}$) possess exceptionally large densities of open metal sites. By adsorbing one CH_4 molecule per open metal, these sites alone can generate very large methane storage capacities, 160-174 $\text{cm}^3(\text{STP})/\text{cm}^3$, approaching the DOE target of 180 $\text{cm}^3(\text{STP})/\text{cm}^3$ for material-based methane storage at room temperature. Our adsorption isotherm measurements at 298 K and 35 bar for the five $M_2(\text{dhtp})$ compounds yield excess methane adsorption capacities ranging from 149 to 190 $\text{cm}^3(\text{STP})/\text{cm}^3$ (derived using their crystal densities), indeed roughly equal to the predicted, maximal adsorption capacities of the open metals (within 10%) in these MOFs. Among the five isostructural MOFs studied, $\text{Ni}_2(\text{dhtp})$ exhibits the highest methane storage capacity, $\sim 200 \text{ cm}^3(\text{STP})/\text{cm}^3$ in terms of absolute adsorption, potentially surpassing the DOE target by $\sim 10\%$. Our neutron diffraction experiments clearly reveal that the primary CH_4 adsorption occurs directly on the open metal sites. Initial first-principles calculations show that the binding energies of CH_4 on the open metal sites are significantly higher than those on typical adsorption sites in classical MOFs, consistent with the measured large heats of methane adsorption for these materials. We attribute the enhancement of the binding strength to the unscreened electrostatic interaction between CH_4 and the coordinatively unsaturated metal ions.

10. Methane Sorption in Nanoporous Metal-Organic Frameworks and First-Order Phase Transition of Confined Methane, Hui Wu, Wei Zhou and Taner Yildirim, *J. Phys. Chem. C*, **113**, 3029 (2009).

Using neutron powder diffraction, we have directly determined the methane sorption sites in two prototypical MOF materials: ZIF-8 and MOF-5. The primary methane adsorption sites are associated with the organic linkers in ZIF-8 and the metal oxide clusters in MOF-5. Methane molecules on these primary sites possess well-defined orientations, implying relatively

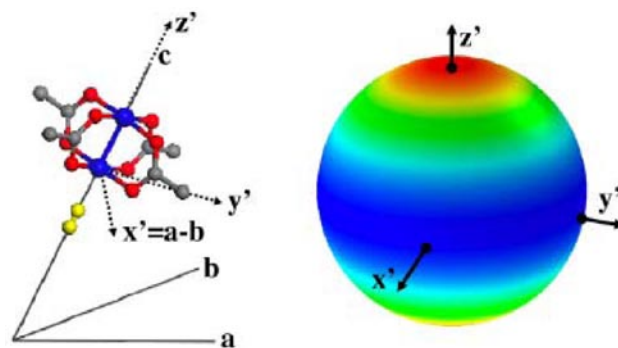


Methane adsorption sites in ZIF-8 and MOF-5 as revealed by neutron diffraction.

strong binding with the framework. With higher methane loading, extra methane molecules populate the secondary sites and are confined in the framework. The confined methanes are orientationally disordered and stabilized by the intermolecular interactions. An unusual reversible methane-induced structural phase transition in MOF host lattice is observed at $\sim 60 \text{ K}$ in both ZIF-8 and MOF-5 due to strong intermolecular interaction between confined methane molecules in the pores of the host lattice.

11. Hydrogen Adsorption in HKUST-1: a Combined Inelastic Neutron Scattering and First-Principles Study, Craig M Brown, Yun Liu, Taner Yildirim, Vanessa K. Peterson, and Cameron J Kepert, *Nanotechnology* **20**, 204025 (2009).

In this paper, we present combined inelastic neutron scattering measurements and detailed first-principles calculations aimed at unraveling the nature of hydrogen adsorption in HKUST-1, a metal-organic framework with unsaturated metal centers. We reveal that, in this system, the major contribution to the overall binding comes from the classical Coulomb interaction which is not screened due to the open metal site; this explains the relatively high binding energies and short H_2 -metal distances observed in MOFs with exposed metal sites as compared to traditional ones. Despite the short



Orientalional potential of hydrogen molecule absorbed in HKUST-1, indicating quasi-two dimensional potential.

distances, there is no indication of an elongation of the H–H bond for the bound H₂ molecule at the metal site. We find that both the phonon and rotational energy levels of the hydrogen molecule are closely similar, making the interpretation of the inelastic neutron scattering data difficult. Finally, we show that the orientation of H₂ has a surprisingly large effect on the binding potential, reducing the classical binding energy by almost 30%. The implication of these results for the development of MOF materials for better hydrogen storage is discussed.

12. Size Effects on the Hydrogen Storage Properties of Nanoscaffolded Li₃BN₂H₈, Hui H. Wu, W. Zhou, K. Wang, T.J. Udovic, J.J. Rush, T. Yildirim, L.A. Bendersky, A.F. Gross, S.L. Van Atta, J.J. Vajo, F.E. Pinkerton, and M. S. Meyer, *Nanotechnology* **20**, 204002 (2009).

The use of Li₃BN₂H₈ complex hydride as a practical hydrogen storage material is limited by its high desorption temperature and poor reversibility. While certain catalysts have been shown to decrease the dehydrogenation temperature, no significant improvement in reversibility has been reported thus far. In this study, we demonstrated that tuning the particle size to the nanometer scale by infiltration into nanoporous carbon scaffolds leads to dramatic improvements in the reversibility of Li₃BN₂H₈. Possible changes in the dehydrogenation path were also observed in the nanoscaffolded hydride.

Publications

**(DE-FG02-08ER46522,
Duration: 08/15/2008 – 04/30/2009)**

- “High-Capacity Methane Storage in Metal-Organic Frameworks M₂(dhtp): The Important Role of Open Metal Sites”, Hui Wu, Wei Zhou, and Taner Yildirim, *J. Am. Chem. Soc.* **131**, 4995 (03/10/2009).
- “Hydrogen adsorption in HKUST-1: a combined inelastic neutron scattering and first-principles study”, C.M. Brown, Y. Liu, T. Yildirim, V.K. Peterson and C.J. Kepert, *Nanotechnology* **20**, 204025 (2009).
- “Size effects on the hydrogen storage properties of nanoscaffolded Li₃BN₂H₈”, H. Wu, W. Zhou, K. Wang, T.J. Udovic, J.J. Rush, T. Yildirim, L.A. Bendersky, A.F. Gross, S.L. Van Atta, J.J. Vajo, F.E. Pinkerton and M.S. Meyer, *Nanotechnology* **20**, 204002 (2009).
- “Methane Sorption in Nanoporous Metal-Organic Frameworks and First-Order Phase Transition of Confined Methane”, W. Hui, W. Zhou, and T. Yildirim, *J. Phys. Chem* **113**, 3029 (2009).
- “Enhanced H₂ Adsorption in Isostructural Metal-Organic-Frameworks with Open Metal Sites: *Strong Dependence of the Binding Strength on Metal Ions*”,

W. Zhou, H. Wu, and T. Yildirim, *J. Am. Chem. Soc.* **130**, 15268 (2008).

6. “Alkali and Alkaline-Earth Metal Amidoboranes: Structure, Crystal Chemistry, and Hydrogen Storage Properties”, H. Wu, W. Zhou, and T. Yildirim, *J. Am. Chem. Soc.* **130**, 14834 (2008).

Publications

**DE-FG02-98ER45701,
Duration: 08/15/2008 – 07/01-2006)**

- “Origin of the exceptional negative thermal expansion in metal-organic frameworks-5 Zn4O(1,4-benzenedicarboxylate)(3), W. Zhou, H. Wu, T. Yildirim, *Phys. Rev. B* **78**, 054114 (2008).
- “Quasi-Free Methyl Rotation in Zeolitic Imidazolate Framework-8”, W. Zhou, H. Wu, T.J. Udovic, J.J. Rush, and T. Yildirim, *J. Phys. Chem. A* **112**, 12602 (2008).
- “Structural variations and hydrogen storage properties of Ca5Si₃ with Cr5B₃-type structure”, W. Hui, W. Zhou, T.J. Udovic, J.J. Rush, T. Yildirim, *Chem. Phys. Lett.* **460**, 432 (2008).
- “Nature and tunability of enhanced hydrogen binding in metal-organic frameworks with exposed transition metal sites”, W. Zhou and T. Yildirim, *J. Phys. Chem. C* **112**, 8132 (2008).
- “Metal-organic frameworks based on double-bond-coupled di-isophthalate linkers with high hydrogen and methane uptakes”, X.S. Wang, S.Q. Ma, K. Rauch, J.M. Simmons, D.Q. Yuan, X.P. Wang, T. Yildirim, W.C. Cole, J.J. Lopez, A. de Meijere, H.C. Zhou, *Chem. Mater.* **20**, 3145 (2008).
- “Metal-Organic Framework from an Anthracene Derivative Containing Nanoscopic Cages Exhibiting High Methane Uptake”, Shengqian Ma, Daofeng Sun, Jason M. Simmons, Christopher D. Collier, Daqiang Yuan, and Hong-Cai Zhou, *J. Am. Chem. Soc.* **130**, 1012 (2008).
- “Structures and Crystal Chemistry of Li₂BNH₆ and Li₄BN₃H₁₀”, Hui Wu, Wei Zhou, Terrence J. Udovic, John J. Rush, and Taner Yildirim, *Chem. Mater.* **20**, 1245 (2008).
- “Crystal Chemistry of Perovskite-Type Hydride NaMgH₃: Implications for Hydrogen Storage”, Hui Wu, Wei Zhou, Terrence J. Udovic, John J. Rush, and Taner Yildirim, *Chem. Mater.* **20**, 2335 (2008).
- “Functionalization of carbon-based nanostructures with light transition-metal atoms for hydrogen storage”, E. Durgun, S. Ciraci, and T. Yildirim, *Phys. Rev. B* **77**, 085405 (2008).
- “Neutron vibrational spectroscopy of the Pr₂Fe₁₇-based hydrides”, T.J. Udovic, W. Zhou, W. Wu, C. M. Brown, J.J. Rush, T. Yildirim, E. Mamontov, O. Isnard, *J. Alloys and Comp.* **446**, 504 (2007).

17. “Neutron vibrational spectroscopy and first-principles calculations of the ternary hydrides $\text{Li}_4\text{Si}_2\text{H(D)}$ and $\text{Li}_4\text{Ge}_2\text{H(D)}$: Electronic structure and lattice dynamics”, H. Wu, W. Zhou, T.J. Udovic, J.J. Rush, T. Yildirim, M.R. Hartman, R.C. Bowman, and J.J. Vago, *Phys. Rev. B* **76**, 224301 (2007).
18. “Hydrogen and Methane Adsorption in Metal-Organic Frameworks: a High-Pressure Volumetric Study”, Wei Zhou, Hui Wu, M.R. Hartman, Taner Yildirim, *J. Chem. Phys. C*, **111**, 16131 (2007).
19. “Hydrogen Storage in a Prototypical Zeolitic Imidazolate Framework-8”, Hui Wu, Wei Zhou, and Taner Yildirim, *JACS* **129**, 5314 (2007).
20. “Vibrational properties of TiH_n complexes adsorbed on carbon nanostructures”, Jorge Iniguez, Wei Zhou and Taner Yildirim, *Chem. Phys. Lett.*, **444**, 140 (2007).
21. “Hydrogen-related catalytic effects of Ti and other light transition metals on NaAlH_4 surfaces”, J. Iniguez and T. Yildirim, *J. Phys. Condes. Matter* **19**, 176007 (2007).
22. “Hydrogen absorption properties of metal-ethylene complexes”, W. Zhou, T. Yildirim, E. Durgun, S. Ciraci, *Phys. Rev. B* **76**, 085434 (2007).
23. “Structure and interstitial deuterium sites of beta-phase ZrNi deuteride”, H. Wu, W. Zhou, T.J. Udovic, J.J. Rush, T. Yildirim, Q. Huang, and R.C. Bowman, *Phys. Rev. B* **75**, 064105 (2007).
24. “Structure and Vibrational Spectra of Calcium Hydride and deuteride”, H. Wu, W. Zhou, T.J. Udovic, J.J. Rush, T. Yildirim, *J. Alloys Comp.* **436**, 51 (2007).
25. “Lattice dynamics of metal-organic frameworks: Neutron inelastic scattering and first-principles calculations”, W. Zhou and T. Yildirim, *Phys. Rev. B*, **R74**, 180301 (2006).
26. “Hydrogen storage capacity of titanium met-cars”, N. Akman, E. Durgun, T. Yildirim, and S. Ciraci, *J. Phys. Condes. Matter.* **18**, 9509 (2006).
27. “Transition-Metal-Ethylene Complexes as High-Capacity Hydrogen-Storage Media”, E. Durgun, S. Ciraci, W. Zhou, and T. Yildirim, *Phys. Rev. Lett.* **97**, 226102 (2006).
28. “Structure and hydrogen bonding in CaSiD_{1+x} : Issues about covalent bonding”, H. Wu, W. Zhou, T.J. Udovic, J.J. Rush, and T. Yildirim, *Phys. Rev. B* **74**, 224101 (2006).

People Working on The Project

1. **Jamie Ford (UPENN)**: Jamie has recently joined our hydrogen storage program, starting April 1, 2009. He is fully supported by this grant. Since UPENN received the DOE grant money in Dec. 2008, we were not able to hire someone earlier. Currently, we are about to hire a 2nd person to work on this project.
2. **Jason M. Simmons (NRC postdoc at NIST)**: Jason was employed at UPENN during the initial phase of this proposal (2007) but then he got NIST NRC postdoctoral research grant and therefore his salary is no longer supported by this DOE grant. He works part time on this project using Sievert equipment, chemicals, etc which are funded by this grant.
3. **Wei Zhou (University of Maryland and NIST)**: Wei got his PhD from UPENN on 2005. During 2005-2007, he worked as PostDoct with Dr. Yildirim and funded by DOE UPENN-Drexel-NIST EERE. Since 2007, Wei joined NIST permanently and works with Dr. Yildirim on this project as a valuable collaborator.
4. **Prof. Salim Ciraci (Bilkent, Turkey)**: We have a long term international collaboration for the computational portion of this work with Prof. Salim Ciraci at Bilkent University, Ankara, Turkey. Prof. Ciraci or someone from his group usually visit us during the summer for a month. This visit is supported by the DOE grant (i.e. per diem, hotel, rental car, etc).