FINAL REPORT
January 1, 2007 – June 30, 2013
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CENTER FOR HYDROGEN STORAGE

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INTRODUCTION

Developing safe, cost-effective, and practical means of hydrogen storage is essential for the advancement of hydrogen and fuel cell technologies. There is much interest in certain destabilized metal hydrides and in metal organic frameworks which have great potential for hydrogen storage.

The main goals of this project were to (1) Establish a Center for Hydrogen Storage Research at Delaware State University for the preparation and characterization of selected complex metal hydrides and the determination their suitability for hydrogen storage. (2) Develop methods for the synthesis, characterization, and modeling of complex hydrides using $LiBH_4/MgH_2$ as a model system. (3) Identify the most promising types of complex hydrides destabilized hydrides and demonstrate the optimum temperature/pressure range and sorption kinetics of the hydrides under a variety of conditions. (4) Determine their cyclic stability and develop improved sorption catalysts. (5) Perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures. (6) Extend the studies to include several new destabilized systems that have been predicted, based on first principles calculations, to have good potential for hydrogen storage. (7) Extend the studies to include carbon-based materials such as metal organic frameworks (MOFs) that also have great potential for hydrogen storage.

SUMMARY OF ACCOMPLISHMNENTS

All of the major goals of this project have been accomplished. During the most recent six month period (January 1, 2013 – June 30, 2013) the following goals were accomplished:

We have developed a reactive ball milling method for synthesizing RbH, a new catalyst for the $MgH_2/LiNH_2$ system. Mixtures with an initial molar composition of ($2LiNH_2 + MgH_2$) were studied with and without the presence of 3.3 mol% RbH and KH dopants. XRD analyses showed that the KH catalyst appears in the dehydrogenated pattern along with $Li_2Mg(NH)_2$ but the RbH does not. This is due to the low decomposition temperature of RbH. TPD analyses showed that the RbH and KH doped samples had about the same onset temperature. Both of these catalyzed mixtures desorbed hydrogen about 90 degrees lower than the un-catalyzed mixture. PCT isotherms were constructed for the catalyzed and un-catalyzed mixtures. Desorption enthalpies determined from van't Hoff plots showed that the enthalpies for the catalyzed mixtures were both ~42 kJ/mol whereas the enthalpy for the un-catalyzed mixture was 65 kJ/mol. The dehydrogenation kinetics of the doped and un-catalyzed mixtures was compared at 210^oC. In each case a constant pressure thermodynamic driving force was applied in which the ratio of the plateau pressure to the applied hydrogen pressure was set at 10. This ratio has been designated as the N-Value. Under these conditions, the RbH doped mixture desorbed hydrogen about twice as fast as the KH doped mixture and about 60 times faster than the un-doped mixture. Modeling studies were done using two different methods. Both methods showed that diffusion is the rate-controlling process. The faster kinetics of the RbH doped mixture can be explained, in part, based on the fact that the larger atomic size of Rb expands the lattice and allows for faster diffusion than that in the KH doped sample.

We have also developed a rapid solvothermal method for synthesizing IRMOF-8. We have functionalized IRMOF-8 by adding $–NO_2$ groups to the linker. It was found that functionalization decreased the surface area and decreases the amount of gas adsorption. However functionalization increased the enthalpy for adsorption of H_2, CH_4 and CO_2 on IRMOF-8. Sticking efficiencies of the various gases were increased as a result of NO_2 functionalization. Sticking efficiencies were determined based on a newly developed parameter called the sticking factor (θ). Results showed that θ increases with ΔH and molecular weight. Also θ decreases with increasing temperature.

The research done under this grant since 2007 has resulted in 17 publications in refereed journals and 20 papers presented at international research conferences. A complete listing of the publications and presentations is given on the following pages. This includes one Patent Application. The research has also enabled four graduate students to receive PhDs. The list of students as well as their dissertation titles is given.

PUBLICATIONS

January 1, 2009 – June 30, 2013

Samuel Orefuwa, Esosa Iriowen, Hongwei Yang, Bryan Wakefield and Andrew Goudy, "Effects of Nitro-Functionalization on the Gas Sorption Properties of Isoreticular Metal-Organic Framework-Eight (IRMOF-8)", Micropor. Mesopor. Mater., 177 (2013) 82-90

Durojaiye T, Hayes, J, and Goudy A, "Rubidium Hydride – A Highly Effective Dehydrogenation Catalyst for the lithium amide/magnesium hydride system" J. Phys Chem C, 117 (2013) 6554 - 6560

A.A. Ibikunle, S.T. Sabitu, A.J. Goudy, "Kinetics and Modeling Studies of the $CaH_2/LiBH_4$, $MgH_2/LiBH_4$, $Ca(BH_4)_2$ and $Mg(BH_4)_2$ Systems" J. Alloys Compds, 556 (2013) 45 - 50

Andrew Goudy, Adeola Ibikunle, Saidi Sabitu and Tolulope Durojaiye, "Thermodynamics and Kinetics of Complex Borohydride and Amide Hydrogen Storage Materials" Materials Challenges in Alternative and Renewable Energy II, in Ceramic Transactions, Vol 239, Edited by George Wicks, Wiley, 2013, ISBN: 978-1-118-58098-1.

Saidi Sabitu and Andrew Goudy, "Dehydrogenation kinetics and modeling studies of MgH_2 enhanced by NbF_5 catalyst using constant pressure thermodynamic forces" Int. J. Hyd. Energy 37 (2012) 12301 – 12306

Adeola Ibikunle and Andrew Goudy, "Kinetics and Modeling Study of a $Mg(BH_4)_2/Ca(BH_4)_2$ Destabilized System" Int. J. Hyd. Energy 37 (2012) 12420 – 12424

Saidi Sabitu and Andrew Goudy, "Dehydrogenation kinetics and modeling studies of $2LiBH_4 + MgH_2$ enhanced by NbF_5 catalyst" J. Phys. Chem. C 116 (2012) 13545−13550

Saidi Temitope Sabitu and Andrew Goudy, "Dehydrogenation kinetics and modeling studies of MgH_2 enhanced by transition metal oxides catalysts using constant pressure thermodynamic driving forces", Metals 2 (2012) 219-228.

Durojaiye T, Goudy A, "Desorption kinetics of lithium amide/magnesium hydride systems at constant pressure thermodynamic driving forces", Int. J. Hyd. Energy, 37 (2012) 3298-3304.

Samuel A. Orefuwa, Hongwei Yang, and Andrew J. Goudy, "Rapid Solvothermal Synthesis of an Isoreticular Metal Organic Framework with Permanent Porosity for Hydrogen Storage", Micropor. Mesopor. Mater., 153 (2012) 88–93.

Hongwei Yang, Samuel Orefuwa and Andrew Goudy, "Study of Mechanochemical Synthesis in the Formation of the Metal-Organic Framework $Cu_3(BTC)_2$ for Hydrogen Storage", Micropor. Mesopor. Mater., 143 (2011) 37-45.

S.T. Sabitu, O. Fagbami, A.J. Goudy, "Kinetics and Modeling Study of Magnesium Hydride with Various Additives at Constant Pressure Thermodynamic Driving Forces", J. Alloys Compds, 509S (2011) S588-S591.

T. Durojaiye, A. Ibikunle and A. J. Goudy, "Hydrogen Storage in Destabilized Borohydride Materials" Int. J. Hyd. Energy, 35 (2010) 10329-10333

Hongwei Yang, Adeola Ibikunle and Andrew J. Goudy, "Effects of Ti-based additives on the hydrogen storage properties of a $LiBH_4$ / CaH_2 destabilized system" Advances in Materials Science and Engineering, vol. 2010, Article ID 138642, 7 pages, 2010. doi:10.1155/2010/138642.

S. T. Sabitu, G. Gallo and A. J. Goudy, "Effect of TiH_2 and Mg_2Ni additives on the hydrogen storage properties of magnesium hydride" J. Alloys Compds, 449 (2010) 35-38

H. Yang, A. Ojo, P. Ogaro and A. J. Goudy, "Hydriding and Dehydriding Kinetics of Sodium Alanate at Constant Pressure Driving Forces" J. Phys Chem C, 113 (2009) 14512-14517.

A. Ibikunle, A. J. Goudy, and H. Yang Hydrogen Storage in a CaH_2 / $LiBH_4$ Destabilized Metal Hydride System, J. Alloys Compds, 475 (2009) 110-115.

US PATENT APPLICATION

Andrew Goudy, Tolulope Durojaiye and Jalaal Hayes, "A Rubidium Hydride Catalyzed Lithium Amide/Magnesium Hydride System for Hydrogen Storage Applications", EFS ID: 15658884, Application No. 61817886, May 1, 2013.

PHD THESES COMPLETED

S. Abidemi Orefuwa, " A Study of an Isoreticular Metal-Organic Framework (IRMOF-8) For Gas Storage: Synthesis, Functionalization and Nanoconfinement", Delaware State University, 2013

Tolulope Olumide Durojaiye, "Thermodynamic and Kinetic Enhancement of $LiNH_2$-MgH_2 Systems Using Non-Transition Metal Dopants for Hydrogen Storage", Delaware State University, 2013

Adeola Ahmed Ibikunle, "Destabilized Borohydride as Potential Hydrogen Storage Materials", Delaware State University, 2012

S. Temitope Sabitu, "Thermodynamics, Kinetics and Modeling Studies of Magnesium Hydride Enhanced by Catalysts for Hydrogen Storage Applications", Delaware State University, 2012

PRESENTATIONS AT RESEARCH CONFERENCES

J. Hayes, T. Durojaiye and A. J. Goudy, "Effects of Alkali Metal Hydrides on $2LiNH_2/MgH_2$ System", Gordon Conference, 2013.

E. Iriowen, S. A. Abidemi, H. Yang and A. J. Goudy, "Sticking Efficiencies of Different Gases on Metal Organic Frameworks", Gordon Conference, 2013.

Andrew Goudy, Saidi Sabitu, Adeola Ibikunle, Tolulope Durojaiye, "Kinetics Studies on Some Complex Borohydride and Amide Hydrogen Storage Materials", NanoSciences & Technologies Conference, October, 2012.

Adeola Ibikunle, Saidi Sabitu and Andrew Goudy, "Kinetics and Modeling Studies of Some Alkaline Earth Borohydrides at Constant Pressure Thermodynamic Forces", ACS National Meeting, Philadelphia, PA, August, 2012

Hongwei Yang, Samuel Orefuwa and Andrew Goudy, "Solvent-Assisted Mechanochemical Synthesis of Metal-Organic Framework $Cu_3(BTC)_2$ for Hydrogen Storage" MRS Spring meeting, April 9 – April 13, 2012, San Francisco, CA.

Andrew Goudy, "Thermodynamics and Kinetics of Complex Borohydride and Amide Hydrogen Storage Materials", Materials Challenges in Alternative & Renewable Energy, Clearwater Beach, FL, 2012.

Andrew Goudy, "Thermodynamics, Kinetics and Modeling Studies on Hydrogen Storage Materials", Low Carbon Earth Summit, October 2011

Samuel Orefuwa, Hongwei Yang, Dante Alexander, Bryan Wakefield and Andrew Goudy, "Characterization and Hydrogen Enthalpy of a Novel IRMOF-8-NO_2 prepared by a Rapid Solvothermal method", Gordon Conference, July, 2011

Tolulope Durojaiye and Andrew Goudy, "Desorption Kinetics of $LiNH_2/MgH_2$ Systems at Constant Pressure Thermodynamic Driving Forces", Gordon Conference, July, 2011.

Synthesis of New Naphthalene Linkers for the Incorporation in Hydrogen Storing Metal Organic Frameworks Bryan Wakefield, Andrew Goudy, Samuel Orefuwa, Lewis Q. Lott, Dante Alexander, Andre Kerr, ACS Meeting, Washington, DC, 2011

Hongwei Yang and Andrew Goudy, "Mechanochemical synthesis of the metal-organic framework $Cu_3(BTC)_2$ for hydrogen storage: An efficient and environmentally benign approach", 15th Annual Green Chemistry and Engineering Conference + 5th International Conference on Green and Sustainable Chemistry, Washington, DC, June 2011

S. T. Sabitu, O. Fagbami and A. J. Goudy, "Kinetics and Modeling Study of Magnesium Hydride with Various Additives at Constant Pressure Thermodynamic Driving Forces", International Symposium on Metal-Hydrogen Systems – Fundamentals and Applications, July 19-23, 2010

A. J. Goudy*; A. Ibikunle; and T. Durojaiye , "Hydrogen Storage in Destabilized Borohydride Materials", Symposium FB "Materials and Process Innovations in Hydrogen Production and Storage" of the 5th Forum on New Materials of CIMTEC 2010, June 13-18, 2010.

Andrew Goudy and Saidi Sabitu "Improved Hydrogen Storage in Magnesium Hydride Catalyzed by TiH_2 and Mg_2Ni", NHA Hydrogen Conference and Expo, Long Beach, CA, May 3-6, 2010

Hongwei Yang and Andrew Goudy, "Kinetic and Modeling Study of Sodium Alanate at Constant Pressure Thermodynamic Driving Forces", MRS Fall meeting, November 30 - December 3, 2009, Boston, MA.

Adeola Ibikunle, Tolulope Durojaiye and Andrew Goudy, "Hydrogen Storage in Modified $LiBH_4$ Metal Hydride Materials" NOBCChE Southeast Regional Meeting, University of Maryland, November 2009

Saidi T. Sabitu, George Gallo and Andrew J. Goudy, "Thermodynamic studies on the interactions of TiH_2 and Mg_2Ni with MgH_2 for high capacity hydrogen storage" NOBCChE Southeast Regional Meeting, University of Maryland, November 2009

O. Fagbami and A. J. Goudy, "Thermodynamic and Kinetics Measurements MgH_2 for Hydrogen Storage", Posters on the Hill, Capitol Building, Washington, DC, May 5, 2009

A. J. Goudy, A. Ibikunle and T. Durojaiye, "Hydrogen Storage in $LiBH_4$ Destabilized Metal Hydride Materials", Gordon Conference, Lucca, 2009.

O. Fagbami and A. J. Goudy, "Thermodynamic and Kinetics Measurements on Magnesium Hydride", 11th Undergraduate Research Symposium in the Chemical and Biological Sciences, UMBC, Baltimore, MD, October 11, 2008.