

# Wednesday Morning, October 17, 2007

## Renewable Energy Science & Technology Topical Conference

Room: 602/603 - Session EN+SS+TF-WeM

### Catalysis for Hydrogen Storage and the Hydrogen Economy

Moderator: G. Fisher, Delphi

8:00am EN+SS+TF-WeM1 **Catalysts for Hydrogen Production by Sulfur-Iodine Thermochemical Water Splitting Cycle**, *L.M. Petkovic, D.M. Ginosar, K.C. Burch, H.W. Rollins, S.N. Rashkeev, H.H. Farrell*, Idaho National Laboratory

Thermochemical cycles can be used to split water through a series of chemical reactions where the net result is the production of hydrogen and oxygen at much lower temperatures than direct thermal decomposition. When the primary energy source to drive the cycle is nuclear or solar heat, hydrogen can be produced without the need of fossil fuels and without generating gasses considered to be responsible for global warming. The sulfur-iodine (S-I) thermochemical cycle appears promising for producing hydrogen from water. The S-I cycle consists of three simultaneous reactions: the decomposition of hydroiodic acid (HI) to produce hydrogen and generate iodine for recycle, the decomposition of sulfuric acid to produce oxygen and generate sulfur dioxide for recycle, and a main reaction where incoming water and the recycle chemicals react to regenerate HI and sulfuric acid. Both HI and sulfuric acid decomposition reactions are facilitated by heterogeneous catalysts. The high-temperature, harsh chemical reaction conditions of the sulfuric acid decomposition reaction present a significantly challenging environment for catalytic materials. In this work a number of titania (rutile)-supported platinum-group metal (i.e., Pt, Ir, Pd, Ru, and Rh) catalysts were investigated for this reaction. To develop an understanding of the factors that cause catalyst deactivation, density-functional theory-based first-principles calculations and computer simulations for transition metal particles positioned on titania (rutile) were performed. In addition, experimental determination of the activity and stability of activated carbon catalysts for the HI decomposition reaction will also be presented. Results of activated carbon characterization analyses, including surface area, temperature programmed desorption, Boehm's titration results, and contact pH of the activated carbons will be discussed.

8:20am EN+SS+TF-WeM2 **Trends in Hydrogen Splitting on Transition Metals at 1 Bar**, *M. Johansson, O. Lytken, I. Chorkendorff*, Technical University of Denmark

Despite the fact that the interaction of hydrogen with various metal surfaces has been studied extensively under ultra-high vacuum conditions, there is very little data available for the hydrogen dissociation rate on clean surfaces at pressures on the order of 1 bar. Here we investigate the hydrogen splitting rate for a number of transition metals by measuring the rate of the H-D exchange reaction. Experiments are also carried out in the presence of CO, in order to investigate the mechanism behind CO poisoning of the anode catalyst in proton-exchange membrane fuel cells. The experiments are performed in an apparatus which combines an ultra-high vacuum chamber for sample preparation and surface analysis with a high-pressure cell.<sup>1</sup> Model catalysts are prepared by electron-beam evaporation of metal spots onto a highly ordered pyrolytic graphite (HOPG) substrate. Typically, the spots are 1 mm in diameter and 50 Å thick. The rate of the H-D exchange reaction for each catalyst spot is measured in the high-pressure cell with the help of a combined gas dispenser and gas sampling device. The gas is sampled 0.2 mm from the center of the spot, and the sampled gas is analyzed with mass spectrometry. Measurements were carried out at 1 bar with a gas mixture containing 1 percent D<sub>2</sub> in H<sub>2</sub>, with or without the addition of 10 ppm CO. The temperature was varied in the range 40 - 200 °C. The model catalysts were characterized with Auger Electron Spectroscopy (AES) before and after exposure to gases in the high-pressure cell. In order to take the back-reaction (HD splitting) into account, a simple model for the H-D exchange reaction is used. It is assumed that the sticking probability, S, is the same for H<sub>2</sub>, HD and D<sub>2</sub>. Under the conditions of interest here, S is mainly dependent on the coverage of adsorbed species on the catalyst surface. Once S has been extracted from the experimental data, the dissociative adsorption/desorption rate for pure H<sub>2</sub> at 1 bar can be calculated. So far, the metals Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt have been investigated. The measured values for S are reasonably consistent with data obtained with high hydrogen coverage under vacuum conditions. Metals which bind hydrogen strongly are expected to give lower values for S.

However, S is found not to correlate with the heat of adsorption for hydrogen as determined at low coverage under vacuum conditions. The most active metal for hydrogen splitting is Ru, closely followed by Rh. For these metals, S is close to being independent of temperature. Pt and Pd give comparable values for S in the temperature range investigated, but the temperature dependence is stronger for Pd than for Pt. The activity then decreases in the order Ir, Co and Ni. No measurable activity is found for Cu. The addition of 10 ppm CO lowers the splitting rate significantly on all the metals, also at 200 °C. Among the investigated metals, Pt and Ir are the ones most sensitive to CO poisoning.

<sup>1</sup> M. Johansson, J. Hoffmann Jørgensen, I. Chorkendorff, *Rev. Sci. Instrum.*, 75 (2004) 2082.

8:40am EN+SS+TF-WeM3 **Catalytic Autothermal Reforming of Renewable Fuels at Millisecond Times**, *L. Schmidt*, University of Minnesota **INVITED**

We compare the reforming of different types of biofuels by autothermal reforming at millisecond contact times to produce synthesis gas, hydrogen, and chemicals. Fuels examined are alcohols, esters, carbohydrates, biodiesel, vegetable oil, and solid biomass. Biofuels generally have higher conversions than fossil fuels because the hydroxyl and ester linkages in these fuels produce higher sticking coefficients than for saturated alkanes. Consequently, conversions of all biofuels in these processes are nearly 100%. Highly oxygenated feedstocks tend to produce mostly syngas with little olefins or oxygenated products because surface reactions dominate, and these larger products are formed predominantly by homogeneous reaction processes after all oxygen is consumed. Recent results on production of syngas by reactive flash volatilization of nonvolatile liquids and solids will also be described. We show that, by impinging cold liquid drops or small solid particles onto the hot catalyst surface, the process can be operated in steady state with no carbon formation for many hours. This occurs because, while pyrolysis of vegetable oils and carbohydrates at low temperatures produces carbon, above ~600°C the equilibrium shifts to produce syngas rather than solid carbon.

9:20am EN+SS+TF-WeM5 **Transient Kinetic Analysis of Intermediates in Steam Reforming on Oxide Supported Cu Catalysts**, *Y. Yang, R. Dissekamp*, Pacific Northwest National Laboratory, *C.T. Campbell*, University of Washington, *C. Mims*, University of Toronto, Canada, *D. Mei, J.H. Kwak, J. Szanyi, C.H.F. Peden*, Pacific Northwest National Laboratory

Formate hydrogenation was proposed to be the surface reaction channel forming methanol through reverse water gas shift by previous investigators [Chorkendorff et al., *J. Vac. Sci. Technol. A*, 10(4), 2277 (1992)]. The interconversion and decay of copper formates on a Cu/Gamma-Al<sub>2</sub>O<sub>3</sub> catalyst are studied here using an apparatus that combines in-situ transmission-FTIR of adsorbed species and mass spectrometric detection of reactor effluent during transient kinetic analyses (transmission-FTIR/MS/TKA). At 573 K, ~ 2% CO and 0.07% methanol conversions were obtained by sending 2.5 bar H<sub>2</sub>:CO<sub>2</sub> 3:1 flow at 10 sccm through the reactor. It is also observed that at lower temperature, 353 K - 433 K, surface formate species are formed with the input feed stream as observed by IR. The kinetics of their transient reactivity (e.g., titration) are examined after switching to either a reducing (H<sub>2</sub>), oxidizing (2% N<sub>2</sub>O in He), or inert gas (He, Ar) feed stream. The kinetics of total formate decay at 306, 363, and 433 K under H<sub>2</sub>, He, or Ar gas exposure are observed to be comparable, suggesting that a thermal unimolecular desorption and not hydrogenation alone, is operative. However upon hydrogen exposure it is observed that within the broad formate IR band(s) there is internal species exchange which indicates two types of different formates are formed. Similar studies are presented for a SiO<sub>2</sub> supported polycrystalline Cu sample to help identify the formate species. Methanol steam reforming on both samples were also studied for further understanding of the reverse reaction processes.

9:40am EN+SS+TF-WeM6 **Model Catalysts for Water-Gas Shift Reaction**, *S. Ma, X. Zhao, J.A. Rodriguez, P. Liu, J. Hrbek*, Brookhaven National Laboratory

Gold supported on ceria was shown to be very active catalyst for water-gas shift reaction and low temperature CO oxidation. Both reactions are used to purify hydrogen by removing CO, a poison of fuel cell catalysts, and are therefore of importance in the hydrogen economy. In this presentation we will describe the preparation, characterization and reactivity of an inverse model catalyst, i.e. CeOx nanoparticles supported on the Au(111) surface. Using STM and XPS we found that physical vapor deposition of Ce metal leads to formation of surface intermetallic compounds after annealing. The Ce-Au surface alloys have low reactivity toward oxygen, however, we were able to prepare CeOx by vapor-

deposition of Ce in a moderate oxygen pressure (10-7 torr). Elongated flat ceria nanoparticles are 0.5 nm thick, several nanometers long and anchored mostly to steps. Atomically resolved images of the ceria island show well-ordered CeO<sub>2</sub> (111) surfaces with few defects. Ce 3d photoelectron spectra were used to identify the oxidation state of Ce in oxides prepared by different methods. In general, oxidation at temperatures below 400 K leads to formation of poorly ordered nanoparticles of Ce<sub>2</sub>O<sub>3</sub> and higher temperature annealing in background oxygen is needed to form CeO<sub>2</sub>. Individually, neither Au(111) nor CeO<sub>2</sub>(111) have any activity in the WGS reaction, while both the Au/CeO<sub>2</sub>(111) model catalyst and the CeO<sub>x</sub>/Au(111) inverse model catalyst show significant activity in high pressure experiments. Our photoemission data indicate that Ce<sub>2</sub>O<sub>3</sub> nanoparticles supported on the gold surface dissociate water molecules even below room temperature while the CeO<sub>2</sub> nanoparticles are inactive. As the water dissociation could be the rate limiting step in the WGS reaction, our ability to identify dissociation products under vacuum conditions and to link them with the structural characterization at the atomic level reinforces reaction models in which the oxide support is not a simple spectator and plays an essential role in the WGS process. Acknowledgement: This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

10:40am **EN+SS+TF-WeM9 Double Role of Water in Fuel Cell Oxygen Reduction Reaction.** *H. Ogasawara, L.-Å Näslund, J.B. MacNaughton, T. Anniyev, A. Nilsson*, Stanford Synchrotron Radiation Laboratory

A management of appropriate humidity level is necessary for the fuel cell to operate. The oxygen reduction reaction (ORR) occurs at the triple phase boundary where gas, electrolyte containing water and catalytic metal particle contact forms humid and dry region on the surface of the catalyst. Using XPS and XAS, we have demonstrated active site poisoning by water, where the activation of oxygen to the adsorbed atomic phase occurs rapidly in the dry region, but not in the humid region. On the contrary, there is a promoter effect of water on the reduction of adsorbed atomic oxygen in the formation of a water-hydroxyl surface complex.

11:20am **EN+SS+TF-WeM11 Adsorption and Dehydrogenation of Carborane on Pt(111).** *A. Tillekaratne, M. Trenary*, University of Illinois at Chicago

The techniques of reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) have been used to explore the dehydrogenation on a Pt(111) surface of 1,2-dicarba-closo-dodecaborane, C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, also known simply as carborane. Complex hydrides, such as the boranes and carboranes, are of interest as possible hydrogen storage materials because of their high hydrogen content. Many hydrides are quite stable and catalysts are needed to promote the release of hydrogen at low temperatures. The carbon and boron atoms of the C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> carboranes occupy the vertices of a slightly distorted icosahedron and have a hydrogen weight percentage of 8.3. There are three isomers of these icosahedral carboranes, of which the ortho form (the 1,2 isomer) is the most readily available. The icosahedral structure of the boron-carbon cage structure of carborane is also adopted by the boron-rich solid boron carbide. The similarity in the structures of carborane and boron carbide has led to the successful use of carborane as a precursor gas for the growth of boron carbide thin films. However, the detailed mechanism by which carborane dehydrogenates to form boron carbide has not been previously investigated. At submonolayer coverages at 85 K the RAIRS spectrum of carborane displays strong B-H stretching vibrations near 2600 cm<sup>-1</sup>, and a weak C-H stretch at 3090 cm<sup>-1</sup> that indicate molecular adsorption at low temperature. The molecule is stable on the surface up to 250 K, where it is transformed into a new intermediate with a strongly red-shifted B-H stretch vibration at 2507 cm<sup>-1</sup>. This intermediate is stable up to 400 K, above which no B-H stretch vibrations are observed. Hydrogen is released in stages as the carborane monolayer is heated from 85 to 800 K, which is also indicative of the formation of partially hydrogenated surface intermediates. Further analysis of the data may permit definitive identification of the surface intermediates formed during the course of carborane dehydrogenation on the Pt(111) surface.

11:40am **EN+SS+TF-WeM12 Short Range Order of Ti Dopants in Al(111): Implications for Hydrogen Storage.** *E.M. Muller*, Brookhaven National Laboratory, *C.V. Ciobanu*, Colorado School of Mines, *P. Zahl, P. Sutter*, Brookhaven National Laboratory

Complex metal hydrides can potentially satisfy the need for lightweight, high-capacity hydrogen storage materials, a key requirement for the Hydrogen Economy. However, for most known complex hydrides the solid-state reactions involved in hydrogen release are not reversible, and their rates are low under moderate ambient conditions. The discovery that small amounts of Ti make the decomposition of sodium alanate (NaAlH<sub>4</sub>) to NaH

and Al reversible at moderate temperatures and pressures<sup>1</sup> has demonstrated doping with catalysts as a promising route to induce reversible hydrogen storage and fast reaction kinetics. A fundamental understanding of the catalytic effect of Ti in NaAlH<sub>4</sub> could form the basis for rational strategies to optimize a broader class of complex hydride hydrogen storage materials. We combine experiments on single crystal model surfaces and density-functional theory (DFT) to establish the role of near-surface Ti in the rehydrogenation of NaH and Al to NaAlH<sub>4</sub>. A likely primary effect of Ti is the formation of catalytically active surface sites enabling the facile dissociative chemisorption of H<sub>2</sub> on Al, which itself has very low affinity to H<sub>2</sub>. Using chemically specific scanning tunneling microscopy and DFT we identify the stable configurations of Ti atoms incorporated into Al(111) surfaces as a first step to identifying potential catalytically active sites. Surprisingly, despite a higher surface energy of Ti (i.e., a driving force for diffusion into sub-surface sites), our observations show a pronounced stabilization of Ti at the Al surface where its catalytic effects are maximized. STM shows a large population of a specific Ti-atom pair complex, which has been predicted to catalyze H<sub>2</sub> dissociation.<sup>2</sup> We discuss the origin of this pairing, and the interaction of atomic and molecular hydrogen interactions with these surface Ti complexes.

<sup>1</sup> B. Bogdanovic and M. Schwickardi. *J. Alloys Comp.* 253-254, 1 (1997).

<sup>2</sup> E. Muller, E. Sutter, P. Zahl, C.V. Ciobanu and P. Sutter., *Appl. Phys. Lett.* 90, 151917 (2007).

12:00pm **EN+SS+TF-WeM13 Alane Formation on Al(111) and Ti-doped Al(111).** *S.C. Chaudhuri*, Washington State University, *J.-F. Veyan, S.C. Schaeffer*, Rutgers, The State University of New Jersey, *J.T. Muckerman*, Brookhaven National Laboratory, *Y.J. Chabal*, Rutgers, The State University of New Jersey

Complex metal hydrides, such as NaAlH<sub>4</sub>, are candidates for hydrogen storage because they can reversibly release and recapture hydrogen under near ambient conditions. Surface processes in the hydrogen storage reaction in NaAlH<sub>4</sub>, starting from a depleted phase consisting of NaH and metallic Al, and proceeding via cryolite Na<sub>3</sub>AlH<sub>6</sub> to the hydrogen-rich NaAlH<sub>4</sub>, are considered as the basis for understanding reversible hydrogen storage in the chosen prototype system. Since metallic Al, particularly when doped with other metals, appear key to H<sub>2</sub> dissociation, we have undertaken a comprehensive study of H interaction with Al(111) and Ti-doped Al(111) surfaces to better understand the atomic scale mechanisms underlying this reversible hydrogen storage behavior. We have combined in-situ infrared absorption spectroscopy with first principles calculations to investigate the reaction of atomic hydrogen reacts with Al surfaces. As previously observed,<sup>1</sup> IR spectra show that alanes are formed upon H exposure. Alanes are highly mobile species at or near room temperature and desorb from Al(111) surfaces at higher temperatures mainly as AlH, AlH<sub>3</sub> and Al<sub>2</sub>H<sub>6</sub>.<sup>2</sup> Using FT-IR we show that the size of the alanes formed on Al(111) depend on the temperature of the sample. For low temperatures (Å90K), small alanes such as AlH<sub>3</sub> and Al<sub>2</sub>H<sub>6</sub> are predominant. At higher temperatures (Å250K), bigger alanes are formed. When the Al(111) surfaces are doped with 5% Ti, the Ti containing sites are reactive, dissociating molecular hydrogen, and thus act as a pump to generate hydride species on Al surfaces that subsequently convert into alanes. LEED is used to test the validity of first principles calculations predicting that Ti atoms occupy hollow sites on the Al(111) surface. Using TPD, the nature of desorbed species from Al(111) and Ti-doped Al(111) surfaces have been analyzed as a function of the sample temperature after either atomic H or H<sub>2</sub> exposures. This presentation summarizes hydrogen dissociation on Ti/Al(111), and alane formation and mobility on both Al(111) and Ti/Al(111) surfaces.

<sup>1</sup> Eden P. Go, Konrad Thuermer, Janice E. Reutt-Robey, *Surf. Sci.* 437 (1999) 377

<sup>2</sup>Hara, M.; Domen, K.; Onishi, T.; Nozoye, H., *J. Phys. Chem.*, 95, (1), (1991) 6-7

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Anniyev, T.: EN+SS+TF-WeM9, 2

## — B —

Burch, K.C.: EN+SS+TF-WeM1, 1

## — C —

Campbell, C.T.: EN+SS+TF-WeM5, 1

Chabal, Y.J.: EN+SS+TF-WeM13, 2

Chaudhuri, S.C.: EN+SS+TF-WeM13, **2**

Chorkendorff, I.: EN+SS+TF-WeM2, 1

Ciobanu, C.V.: EN+SS+TF-WeM12, 2

## — D —

Disselkamp, R.: EN+SS+TF-WeM5, 1

## — F —

Farrell, H.H.: EN+SS+TF-WeM1, 1

## — G —

Ginosar, D.M.: EN+SS+TF-WeM1, 1

## — H —

Hrbek, J.: EN+SS+TF-WeM6, **1**

## — J —

Johansson, M.: EN+SS+TF-WeM2, 1

## — K —

Kwak, J.H.: EN+SS+TF-WeM5, 1

## — L —

Liu, P.: EN+SS+TF-WeM6, 1

Lytken, O.: EN+SS+TF-WeM2, 1

## — M —

Ma, S.: EN+SS+TF-WeM6, 1

MacNaughton, J.B.: EN+SS+TF-WeM9, 2

Mei, D.: EN+SS+TF-WeM5, 1

Mims, C.: EN+SS+TF-WeM5, 1

Muckerman, J.T.: EN+SS+TF-WeM13, 2

Muller, E.M.: EN+SS+TF-WeM12, 2

## — N —

Näslund, L.-Å.: EN+SS+TF-WeM9, 2

Nilsson, A.: EN+SS+TF-WeM9, 2

## — O —

Ogasawara, H.: EN+SS+TF-WeM9, 2

## — P —

Peden, C.H.F.: EN+SS+TF-WeM5, 1

Petkovic, L.M.: EN+SS+TF-WeM1, **1**

## — R —

Rashkeev, S.N.: EN+SS+TF-WeM1, 1

Rodriguez, J.A.: EN+SS+TF-WeM6, 1

Rollins, H.W.: EN+SS+TF-WeM1, 1

## — S —

Schaäfer, S.C.: EN+SS+TF-WeM13, 2

Schmidt, L.: EN+SS+TF-WeM3, **1**

Sutter, P.: EN+SS+TF-WeM12, 2

Szanyi, J.: EN+SS+TF-WeM5, 1

## — T —

Tillekaratne, A.: EN+SS+TF-WeM11, 2

Trenary, M.: EN+SS+TF-WeM11, 2

## — V —

Veyan, J.-F.: EN+SS+TF-WeM13, 2

## — Y —

Yang, Y.: EN+SS+TF-WeM5, 1

## — Z —

Zahl, P.: EN+SS+TF-WeM12, 2

Zhao, X.: EN+SS+TF-WeM6, 1