

# Tuesday Morning, November 1, 2011

## Surface Science Division

Room: 109 - Session SS1-TuM

## Chemisorption & Surface Reactions

Moderator: D.A. Chen, University of South Carolina

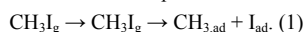
8:00am **SS1-TuM1 XANES and EXAFS Analysis of the Effects of Cobalt Incorporation Into Silica Supports for Fischer-Tropsch Synthesis**, *B.M. Goundie, I.T. Ghampson, M.C. Wheeler, W.J. DeSisto, B.G. Frederick, R.W. Meulenberg*, University of Maine

The growing need for non-petroleum based fuel sources has led to an increase in research into Fischer-Tropsch synthesis (FTS), which can be used to convert biomass into fuels. We have developed several silica supported cobalt catalysts to investigate the role of pore size on phase and reactivity. Cobalt based catalysts produce high molecular weight hydrocarbons in FTS, and there has been increased research into the characterization of such catalysts. The catalysts have been previously characterized using several techniques including x-ray diffraction (XRD), nitrogen porosimetry, and transmission electron microscopy/selected area diffraction (Ghampson IT, et al. Effects of pore diameter on particle size, phase, and turnover frequency in mesoporous silica supported cobalt Fischer-Tropsch catalysts. *Applied Catalysis A – General*. 2010; 388(1-2)).

In this presentation we will discuss x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) measurements of three different MCM-41 supported cobalt catalysts. These materials include incorporation of cobalt into the silica framework (Co-MCM-41), and cobalt impregnated catalysts, via wet impregnation, onto the pure (Co/MCM-41) and cobalt in the framework (Co/Co-MCM-41) supports. We analyzed the XANES and EXAFS at three different stages in the catalyst history: after calcination, after temperature programmed reduction, and after Fischer-Tropsch synthesis. Evidence suggests that the presence of cobalt in the framework affects the reducibility of the cobalt species. The data also suggests mixed phases of cobalt metal and cobalt monoxide in the reduced and post FTS samples. The as prepared samples show only the Co<sub>3</sub>O<sub>4</sub> phase, while the post FT and post TPR show both CoO and Co metal. The good agreement between XAS and XRD measurements demonstrates the use of these techniques to quantitatively determine the cobalt phase composition.

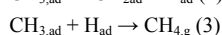
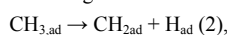
8:20am **SS1-TuM2 Measurement of the C-Pt Bond Energy for Adsorbed Methyl on Pt(111) by Methyl Iodide's Dissociative Adsorption Energy**, *E.M. Karp, T.L. Silbaugh, C.T. Campbell*, University of Washington

Knowing the bond energies of molecular fragments adsorbed to surfaces is an important ingredient in the fundamental understanding needed for rational design of heterogeneous catalysts. This study utilizes the ultrahigh vacuum technique of single crystal adsorption calorimetry to study the energetics of adsorbed methyl (CH<sub>3,ad</sub>) on Pt(111), using measurements of the dissociative adsorption energy of methyl iodide (CH<sub>3</sub>I) on Pt(111). At temperatures above 250 K, adsorbed CH<sub>3</sub>I on Pt(111) is known to undergo C-I bond scission to form CH<sub>3,ad</sub> and adsorbed iodine (I<sub>ad</sub>). At 270 K, the rate of C-I scission is fast relative to the 100 ms time of calorimetric measurement, so that it provides the enthalpy for the net, two-step dissociative adsorption reaction:



The integral heat of Reaction (1) is -224 kJ/mol at a coverage of 0.05 ML. Through the use of a simple thermodynamic cycle and other known adsorption energies, this provides a heat of formation of CH<sub>3,ad</sub> of -63 kJ/mol and a Pt—CH<sub>3</sub> bond energy of 209 kJ/mol.

Mass spectrometer measurements taken during experiments at 300 K and 320 K indicate that methane is produced. Previous studies indicate that at these temperatures, adsorbed methyl both decomposes to form adsorbed methylene (CH<sub>2,ad</sub>) and hydrogen (H<sub>ad</sub>) and reacts with H<sub>ad</sub> to form methane according to the reactions:



where CH<sub>4,g</sub> is gas phase methane. The microcalorimetric measurements performed at 300 K and 320 K, along with information on the rates of Reactions (2) and (3) available in the literature, allowed for the decoupling of Reactions (1)-(3) and an analysis of the energetics of all three reactions as a function of surface coverage, and the heat of formation of CH<sub>2,ad</sub>.

8:40am **SS1-TuM3 A DFT Study of Methanol Reaction Pathways on the Au<sub>13</sub>/TiO<sub>2</sub>(110) Surface**, *S. Hong*, University of Central Florida, *D.A. Chen*, University of South Carolina, *T.S. Rahman*, University of Central Florida

We have performed density functional theory calculations to understand the reaction pathway selection for methanol decomposition on clean and Au<sub>13</sub> deposited TiO<sub>2</sub>(110) surface. We find that when methanol adsorbs on the *clean* and *reduced* TiO<sub>2</sub>(110) surface, it decomposes spontaneously into methoxy, which adsorbs on the O-vac site and desorbs as methyl leaving behind O-br on the TiO<sub>2</sub>(110) surface. On the *stoichiometric* TiO<sub>2</sub>(110) surface, we find that while methanol decomposition has a small activation energy of 0.2 eV, methoxy decomposition (i.e. formaldehyde formation) is not possible because of high activation energy of 3 eV. Nevertheless, once the surface is oxidized formaldehyde formation becomes *spontaneous*, through C-H bond scission by surface oxygen species. These results confirm the experimental results of methyl formation on the *reduced* and formaldehyde formation on the *oxidized* TiO<sub>2</sub>(110) surface. Turning to the case of partially reduced Au/TiO<sub>2</sub>(110) surface, our DFT calculations show that the adsorption of methanol and its intermediate methoxy does not occur on gold sites but on TiO<sub>2</sub> sites. Methoxy, in fact, forms at the Au-titania interface as a result of O-H bond scission by lattice oxygen (O-br), and its optimized tilted structure makes C-H bond scission -- through H abstraction by lattice oxygen near the interface site -- much easier than that for a vertical, non-tilted structure of methoxy in a non-interfacial site. Moreover, depending on the reduction level of the TiO<sub>2</sub>(110) surface, the adsorption site preference for methanol and methoxy species on the Au/TiO<sub>2</sub>(110) surface is: O-vac > interfacial Ti-cus > stoichiometric Ti-cus site. This hierarchy implies that the major product will switch from methyl on the fully-reduced surface, to formaldehyde on the partially-reduced or oxidized Au/TiO<sub>2</sub>(110) surface. This conclusion is in full agreement with experiment.

This work is supported in part by US-DOE under Grant No. DEFG02-07ER15842.

9:00am **SS1-TuM4 Turning Aluminum into a Noble-metal like Catalyst for Low Temperature Molecular Hydrogen Activation**, *I. Chopra*, University of Texas at Dallas, *S. Chaudhuri*, Washington State University, *J.F. Veyan, Y.J. Chabal*, University of Texas at Dallas

There has been an ongoing quest to find cheaper hydrogen activation routes based on aluminum. Despite theoretical suggestions<sup>1,2</sup> it has been difficult to obtain unambiguous experimental evidence for such catalytic activity towards hydrogen activation.

We demonstrate here that aluminum doped with very small amounts of Ti can activate molecular hydrogen at temperatures as low as 90K. The method is based on the ability to introduce a high flux of molecular hydrogen seeded with a *guest molecule to probe the catalytic activity and H<sub>2</sub> dissociation*. Once dissociated, hydrogen forms a complex with adsorbed CO (CO-H), characterized by a substantially and uniquely blue-shifted CO internal frequency. This complex is metastable, and is removed at a temperature (115K). We find that CO does not adsorb even weakly on H-covered Al, and use this finding to clearly show that, once dissociated, hydrogen diffuses away from the catalytic site onto Al sites (i.e. spills over). We use this new method to determine the dependence of the catalytic activity of aluminum surfaces on Ti coverage. Finally we show that the complex with activated hydrogen leads to further reactions at remarkably low temperatures (115K), such as formation of formyl (HCO), formaldehyde (HCHO) or methanol. These results provide the first direct evidence that Ti-doped Al can perform the quintessential first step of molecular hydrogen activation under nearly barrier-less conditions, thereby challenging the monopoly of noble metals in hydrogen activation.<sup>3</sup>

References:

[1] Chaudhuri, S. & Muckerman, J. T. First-principles study of Ti-catalyzed hydrogen chemisorption on an Al surface: A critical first step for reversible hydrogen storage in NaAlH<sub>4</sub>. *Journal of Physical Chemistry B* **109**, 6952-6957 (2005).

[2] Chaudhuri, S., Graetz, J., Ignatov, A., Reilly, J. J. & Muckerman, J. T. Understanding the role of Ti in reversible hydrogen storage as sodium alanate: A combined experimental and density functional theoretical approach. , 11404-11415 (2006). B. Author, Nano. Bio. Info. Sci. **001**, 1234 (3001).

[3] Chopra, I. S., Chaudhuri, S., Veyan, J.-F., and Chabal, Y. J., Nature materials ( submitted ) 2011.

9:20am **SS1-TuM5 On the Role of Hydrogen in Heterogeneously Catalyzed Reactions**, *M. Mavrikakis*, University of Wisconsin Madison  
**INVITED**

Hydrogen is a frequent participant in several heterogeneously catalyzed reactions, including Fischer-Tropsch Synthesis (FTS) of fuels, ammonia synthesis, oxygen reduction reaction (ORR), NO reduction, preferential oxidation of CO in the presence of H<sub>2</sub> (PROX), etc. Having analyzed the detailed aspects of the reaction mechanism for a number of these reactions on various transition metal and alloy surfaces using first-principles methods, some common principles governing the role of hydrogen in a wide range of catalytic transformations begin to emerge. In this presentation, we will discuss these common mechanistic principles by examples, including FTS<sup>1,2</sup>, NO-reduction, ORR<sup>3</sup>, PROX<sup>4,5</sup>, through an analysis of the energetics of alternative elementary reaction steps and the resulting potential energy diagrams. Connections to observations from experimental studies provide an invaluable perspective for the evaluation of our theoretical assessments.

References

1. M. Ojeda, R. Nabar, A. U. Nilekar, A. Ishikawa, M. Mavrikakis, E. Iglesia, *Journal of Catalysis* **272**, 287 (2010).
2. M. Ojeda, A. Li, R. Nabar, A. U. Nilekar, M. Mavrikakis, E. Iglesia, *Journal of Physical Chemistry C* **114**, 19761 (2010).
3. D. C. Ford, A. U. Nilekar, Y. Xu, M. Mavrikakis, *Surface Science* **604**, 1565 (2010).
4. A. U. Nilekar, S. Alayoglu, B. Eichhorn, M. Mavrikakis, *Journal of the American Chemical Society* **132**, 7418 (2010).
5. S. Alayoglu, A. U. Nilekar, M. Mavrikakis, B. Eichhorn, *Nature Materials* **7**, 333 (2008).

10:40am **SS1-TuM9 Prediction of Surface Ensembles in Au-based Bimetallic Alloys using Combined DFT and Monte Carlo Simulations**, *J.A. Stephens, H.C. Ham, G.S. Hwang*, University of Texas at Austin

Bimetallic materials have shown great promise for the development of superior catalysts. The recent surge of new interest in catalysis by gold has led researchers to investigate the effects of adding gold to other metals. While mechanisms underlying the alloying effect are still not understood in detail, recent evidence suggests that the enhanced reactivity of bimetallic catalysts can be attributed to a combination of metal-metal interactions (ligand effect) and unique mixed-metal surface sites (ensemble effect). The ability to accurately predict the arrangements of constituent atoms in a surface alloy is indispensable to unraveling the roles played by the ensemble and ligand effects in the performance of bimetallic model catalysts. We have developed a scheme to predict the equilibrium arrangement of atoms in surface alloys in the presence of adsorbates at finite temperatures. It is based on the Ising model and is capable of reproducing DFT-predicted total energies to within no more than a few meV per surface atom. We have used it successfully to predict the populations of monomers, dimers, and other, larger ensembles in Au-Pd and Au-Pt fcc (111) and (100) surface alloys. The scheme will be presented in detail, as well as what we have learned about the effects of temperature, composition, and the presence of adsorbates on ensemble formation in both fcc (111) and (100) surface alloys. We will also discuss how the atomic arrangements affect the reactivity of gold-based alloy surfaces, particularly towards oxygen reduction and carbon monoxide oxidation.

11:00am **SS1-TuM10 Adsorption and Electron-induced Dissociation of CO<sub>2</sub> on TiO<sub>2</sub>(110)**, *J. Lee, X. Deng, D. Sorescu*, National Energy Technology Laboratory

Adsorption and electron-induced reaction of CO<sub>2</sub> on the TiO<sub>2</sub>(110) surface has been investigated using scanning tunneling microscopy (STM) and dispersion corrected density functional theory (DFT). At low coverage the adsorption of CO<sub>2</sub> takes place at the oxygen vacancy defect. At higher coverage the CO<sub>2</sub> starts to adsorb on the Ti rows. The DFT results show that the CO<sub>2</sub> at the oxygen vacancy defect is in a tilted configuration and the molecular axis is perpendicular to the bridging oxygen row. On the Ti row, the DFT results confirm that the CO<sub>2</sub> adsorbs in a flat configuration with its axis parallel to the bridging oxygen row. Electron injection from the STM tip into the CO<sub>2</sub> at the oxygen vacancy defect induces the dissociation of CO<sub>2</sub>. The oxygen vacancy defect is found to be healed by the O atom released during the CO<sub>2</sub> dissociation process. Statistical analysis shows that the dissociation of CO<sub>2</sub> is a one-electron driven process with a threshold voltage of 1.4 eV above the conduction band minimum of TiO<sub>2</sub>. The formation of a transient negative ion by the injected electron is considered to be the key process in the CO<sub>2</sub> dissociation.

11:20am **SS1-TuM11 Adsorption and Dissociation of Propane-1, 3-diol Molecules on Reduced TiO<sub>2</sub>(110) Surface- A Scanning Tunneling Microscopy Study**, *D. Acharya, X. Lin, B.D. Kay, Z. Dohnálek, Z. Zhang*, Pacific Northwest National Laboratory

Rutile TiO<sub>2</sub>(110) surface is one of the most studied model systems for the fundamental investigations of a variety of processes on metal oxide surfaces, including heterogeneous catalysis, greenhouse gas reforming, solar cells, photodecomposition of organic pollutants, and photoinduced water splitting. It is widely accepted that the surface chemistry of the oxide surfaces are mainly influenced by the defects sites, particularly oxygen vacancies. Here we study the adsorption of propane-1,3-diol molecules on partially reduced rutile TiO<sub>2</sub>(110) surface using variable temperature scanning tunneling microscope (STM). STM images obtained before and after in-situ dose of propane-1,3-diol molecules at room temperature shows that the molecule preferentially binds at the bridging oxygen vacancies via bond scission of one of the OH groups. The hindered rotation of the 3-hydroxypropoxide species was seen at room temperature, while the diffusion and dissociation of the species were observed at elevated temperatures. The experiment was carried out at the Environmental Molecular Science Laboratory, a National Scientific user facility supported by the U.S. Department of Energy, Office of Biological and Environmental Research at Pacific Northwest National Laboratory.

11:40am **SS1-TuM12 Oxygen-Vacancy Assisted Formation of Enolate Species on Reduced CeO<sub>2</sub>(111) Surfaces**, *F.C. Calaza, Y. Xu, D.R. Mullins, S.H. Overbury*, Oak Ridge National Laboratory

Enolate species are key intermediates proposed in a number of important organic reactions heterogeneously catalyzed by metals and metal oxides, but enolate has been difficult to identify on active catalytic surfaces due to difficulties of isolating it in the keto-enol equilibrium.

Reflection absorption infrared spectroscopy (RAIRS) was coupled with density functional theory (DFT) to study the adsorption of acetaldehyde, a simple  $\geq C_2$  aldehyde, on CeO<sub>2-x</sub>(111) surfaces of different extent of oxidation (where  $x = 0 - 0.5$ ). It is found experimentally that the molecule adsorbs weakly on the fully oxidized surface ( $x=0$ ) at low temperatures and desorbs without further reaction near 215 K. The molecule bonds to *c.u.s.* Ce<sup>4+</sup> cations through the oxygen lone pair electrons in the carbonyl group with its C-C bond perpendicular to the surface plane and the acyl hydrogen tilted slightly towards one of the lattice oxygen anions of the first layer.

On the reduced surfaces ( $x=0.1 - 0.4$ ), acetaldehyde interacts more strongly with the surface upon adsorption at low temperatures by losing its carbonyl bond character and adsorbing as 1,1-dioxyethane and forming dimers and polymers. Heating the surface to 400 K leads to desorption of some amount of these strongly adsorbed species as acetaldehyde and the appearance of hydroxyl and yet a different organic species.

The identities and structures of the different intermediates on the CeO<sub>2</sub> and CeO<sub>2-x</sub> surfaces have been determined by their characteristic signatures in RAIRS and by DFT calculations. Our observations for the CeO<sub>2-x</sub> surfaces are consistent with the vacancy-promoted dehydrogenation in the original methyl position of acetaldehyde and the formation of enolate (CH<sub>2</sub>=CHO-Ce). Experiments with isotopically labeled acetaldehyde have verified the vibrational assignments for the enolate species and are in excellent agreement with DFT results. The assignment of the enolate species is furthermore consistent with C 1s XPS and C k-edge NEXAFS results.

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