

## Surface Science

### Room 327 - Session SS1-TuM

#### Catalysis II: Hydrocarbons at Metal Surfaces

Moderator: B.E. Koel, University of Southern California

8:20am **SS1-TuM1 Adsorption Energies of Small Alkane Molecules on MgO(100) and on Pd Nanoparticles on MgO by Temperature Programmed Desorption**, *S.L. Tait, Jr.*, University of Washington; *Z. Dohnalek, B.D. Kay*, Pacific Northwest National Laboratory; *C.T. Campbell*, University of Washington

Catalysts consisting of Pd nanoparticles supported on oxides are active in a variety of important reactions involving small alkanes. Molecular beams and temperature programmed desorption (TPD) were used to study the adsorption of small alkane molecules,  $C_nH_{2n+2}$  ( $n=1-10$ ), on the MgO(100) surface and on Pd nanoparticles on MgO(100) at low temperatures (24 K), a regime little explored for such well-defined model catalysts. High quality MgO films are grown on the Mo(100) surface, producing an MgO(100) surface with defect densities comparable to those obtained by UHV-cleavage of MgO crystals. Hydrocarbon molecules are deposited on the surface by a highly collimated molecular beam with a well-defined kinetic energy. King and Wells style sticking measurements are made by quadrupole mass spectrometer (QMS) during deposition. The initial sticking probability increases with alkane chain length until it reaches unity for octane ( $n=8$ ). The sample is heated at a controlled rate and desorption products are observed by line-of-sight QMS. The adsorption energies and kinetic prefactors for desorption are extracted from these TPD data. Adsorption energy increases non-linearly with alkane chain length. The alkanes bind more strongly to Pd particles than to MgO(100). We plan to present preliminary results also concerning Pd particle size effects in alkane adsorption and dissociation. Pacific Northwest National Laboratory is a multiprogram National Laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830. SLT supported by a UW/PNNL Joint Institute for Nanotechnology fellowship.

8:40am **SS1-TuM2 Reactions of Aliphatic Alcohols on WO<sub>3</sub>(001) Surfaces**, *B.G. Frederick, S. Ma*, University of Maine

Interactions of ethanol and isopropanol with WO<sub>3</sub>(001) thin film surfaces, epitaxially grown on a sapphire substrate, were studied with calibrated thermal desorption spectroscopy (CTDS). The reactivity of reduced and oxidized WO<sub>3</sub> surfaces, as characterized by XPS and UPS, were compared in order to understand the surface structure dependence. Coverage dependent desorption spectra show that alcohol molecules diffuse rapidly on the WO<sub>3</sub> thin film surfaces. Ethanol and isopropanol desorb molecularly between 200 and 450 K with evolution of water. The remaining alkoxy intermediates decompose via  $\beta$ -H elimination, followed by C-O bond scission, to produce ethylene and propylene, respectively. We suggest that diffusion and competition between reaction rates of dehydroxylation vs. associative molecular desorption of alcohol control the alkoxy coverage that determines the selectivity toward alkene under these low coverage conditions.

9:00am **SS1-TuM3 Dissociative Adsorption of Cyclohexene on Pt(111) at 300 K studied by Single-Crystal Microcalorimetry and Sticking Probability Measurements**, *H. Ihm, H.M. Ajo, D.E. Moilanen, C.T. Campbell*, University of Washington

The dehydrogenation reaction of cyclohexene to benzene on platinum surfaces is of fundamental interest due to the importance of the surface chemistry occurring in hydrocarbon conversion. There have been many studies to understand its reaction, mechanism, energetics, and kinetics using experimental and theoretical methods. They agree that cyclohexene on Pt(111) converts to cyclohexenyl between 200-250 K and further converts to benzene between 300-350 K.<sup>1,2</sup> There have been studies to estimate reaction (activation) energies from cyclohexene to cyclohexenyl or benzene, but these were in a limited coverage regime and either by indirect experimental measurements or by theoretical calculation.<sup>1,3</sup> Here, we report direct calorimetric measurements of the heats of reactive adsorption of cyclohexene on Pt(111) at 300 K as a function of coverage. These calorimetry measurements were performed by using a pyroelectric detector and a pulsed cyclohexene molecular beam impinging onto a 1  $\mu$ m thick Pt(111) sample. We also measured the sticking probability as a function of coverage. The sticking probability is initially high (0.86) and stays constant

up to 0.7 ML then decreases linearly to 0 at 1 ML. The flux of the cyclohexene molecular beam was measured with a liquid-nitrogen cooled quartz crystal microbalance. Work supported by NSF.  
<sup>1</sup>FootnoteText@footnote 1@ F.C. Henn, A.L. Diaz, M.E. Bussell, M.B. Hugenschmidt, M.E. Domagala, and C.T. Campbell, J. Phys. Chem. 1992, 96, 5965-5974.  
<sup>2</sup>Footnote 2@ W.L. Manner, G. S. Girolami, and R.G. Nuzzo, J. Phys. Chem. B 1998, 102, 10295-10306.  
<sup>3</sup>Footnote 3@ B.E. Koel, D.A. Blank, and E.A. Carter, J. Molecular Catal. A: Chemical 131 (1998) 39-53.

9:20am **SS1-TuM4 The Reaction of 1-chloro-2-methyl-2-propanol (Cl@super t@BuOH) on Oxygen-covered Ag(110): C-Cl Bond Cleavage in Epoxide Formation**, *H. Piao, K. Adib*, Brookhaven National Laboratory; *M. Enever*, University of Delaware; *Z. Chang*, Brookhaven National Laboratory; *D.R. Mullins*, Oak Ridge National Laboratory; *J. Hrbek*, Brookhaven National Laboratory; *M.A. Barteau*, University of Delaware

Synchrotron-based Temperature Programmed X-ray Photoelectron Spectroscopy in combination of Temperature Programmed Desorption has been used to explore the C-Cl scission in the reaction of Cl@super t@BuOH on oxygen-covered Ag(110) surface to produce isobutylene oxide (IBO). Although the C-Cl bond cleavage is involved in the rate-determining step for the evolution of IBO, the mechanism was not fully understood. This motivated the surface reaction mechanism study to determine whether the surface chlorohydrin reaction follows an S@sub N@1 reaction or a concerted S@sub N@2 path. Using experimental data we also developed a kinetic model for surface reaction chemistry. The combination of experimental and theoretical results indicates that Cl@super t@BuO decomposition does not occur by an S@sub N@2 process that releases IBO directly into the gas phase. Instead, C-Cl scission deposits organic intermediates or products on the surface, and that the appearance of these products in the gas phase lags the appearance of atomic chlorine on the surface. Therefore, we can conclude that the production of IBO is the result of a process involving two kinetically significant steps: C-Cl scission that deposits Cl atoms and IBO molecules on the Ag(110) surface followed by desorption of molecularly adsorbed IBO. Low barrier and pre-exponential for the second step on the high coverage surface indicate that the rate of C-Cl scission may be influenced by other factors, e.g., the availability of surface adsorption sites for Cl adatoms.

9:40am **SS1-TuM5 Surface Chemistry of Hydrocarbon Fragments on Transition Metals: Towards Understanding Catalytic Processes**, *F. Zaera*, University of California, Riverside  
**INVITED**

An overview of our efforts to elucidate the mechanistic details of the surface chemistry of hydrocarbons on transition metal surfaces will be presented. Particular emphasis will be placed on the similarities and differences between surface and organometallic systems, and on the relevance of this chemistry to catalysis. The methods developed in our laboratory for the clean production of catalytically-relevant but unstable surface moieties on well-characterized metal surfaces will be described, and the main thermal decomposition pathways of those intermediates will be discussed. An argument will be presented for the definition of catalytic selectivities based on subtle changes in the regioselectivity for early dehydrogenation rates. For instance, the unique ability of platinum in promoting isomerization and cyclization reactions appears to correlate with its preference to catalyze gamma-hydride elimination steps; nickel, in contrast, facilitates dehydrogenation at the alpha position, and catalyzes hydrogenolysis instead. The additional mechanistic complications in hydrocarbon reforming under catalytic conditions introduced by the presence of strongly bonded carbonaceous deposits on the surface of the active catalyst will be addressed. The working reforming metal catalyst is likely to display a bifunctional character, with rapid hydrogenation-dehydrogenation steps taking place on the hydrocarbon-covered surface and more demanding skeletal rearrangement steps occurring on patches of bare metal. Finally, some details behind the imparting of enantioselectivity to metal catalysts via the adsorption of chiral modifiers will be introduced.

10:20am **SS1-TuM7 Fluorinated Carboxylic Acids Deprotonation on the Cu(100) Surface**, *B. Immaraporn*, Fritz-Haber Institute, Germany; *P. Ye, A.J. Gellman*, Carnegie Mellon University

The kinetics of acid deprotonation on the Cu(100) surface have been studied using four different fluorinated carboxylic acids (CF@sub 2@HCO@sub 2@H, CF@sub 3@CO@sub 2@H, C@sub 2@F@sub 2@HCF@sub 2@CO@sub 2@H, and CF@sub 3@CF@sub 2@CO@sub 2@H). All four acids adsorb molecularly on Cu(100) at 90 K and then undergo deprotonation to form carboxylates during heating below 300 K. Temperature programmed reaction spectroscopy and x-ray photoemission spectroscopy were used to verify that the acids deprotonate on the

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Cu(100) surface. Work function measurements were used to study the deprotonation kinetics during heating and estimate the activation energy barriers ( $\Delta E_{\text{OH}}$ ) to deprotonation. The nature of the transition state to acid deprotonation on Cu(100) was probed by analysis of linear free energy relationships (LFER) or correlations of with  $\sigma_F$ . The field reaction constant,  $\rho_F$ , or the slope of the LFER was found to be  $\rho_F = 57 \pm 9$  kJ/mol in the limit of zero coverage and  $\rho_F = 22 \pm 2$  kJ/mol at 0.5 ML coverage. These values of  $\rho_F$  can be compared to the values of  $\rho_F = 104$  kJ/mol for acid deprotonation in the gas phase. This comparison suggests that the transition state for acid deprotonation on Cu(100) must be anionic with respect to the reactant  $\text{RCO}_2\text{H}(\text{ad})$  ( $\rho_F[\text{RCO}_2\text{H}(\text{ad})] = 22 \pm 2$  kJ/mol at 0.5 ML coverage). These values of  $\rho_F$  can be compared to the values of  $\rho_F = 104$  kJ/mol for acid deprotonation in the gas phase.

## 10:40am SS1-TuM8 Enantioselective Reactivity of R-2-bromobutane on Cu(531), D.M. Rampulla, A.J. Gellman, Carnegie Mellon University

Enantioselective reactions are integral to most biological chemistry and large-scale pharmaceutical production. The difficult aspect of enantioselective reactions is that they require chiral media such as solvents, surfaces, or catalysts. Enantioselective heterogeneous catalysis is a promising method for the preparation of chiral compounds but requires catalytic surfaces with inherently chiral structure. The stepped and kinked high Miller index surfaces of metals are naturally chiral and have been shown to interact enantiospecifically with chiral adsorbates. Enantioselective desorption of small chiral molecules from such surfaces has been demonstrated and studied, but enantioselective reactivity on naturally chiral metal surfaces has not been explored. Temperature Programmed Reaction Spectroscopy (TPRS) has been used to study the decomposition of R-2-bromobutane on the chiral Cu(531)R and Cu(531)S surfaces. R-2-bromobutane debrominates to produce a chiral R-2-butyl intermediate. The R-2-butyl group decomposes by  $\beta$ -hydride elimination to form cis- and trans-2-butene and 1-butene. The hydrogen released by  $\beta$ -hydride elimination can also hydrogenate the R-2-butyl intermediate to form butane. In addition to reaction temperatures that are indicative of enantioselective kinetics, the reaction yield is influenced by the chirality of the Cu(531) surfaces.

## 11:00am SS1-TuM9 Coupled Experimental and Theoretical Study of Weakly Adsorbed Molecules on Metal Surfaces, H. Ogasawara, H. Ostrom, B. Brena, Stockholm University, Sweden; D. Nordlund, Uppsala University, Sweden; M. Nyberg, L. Petersson, Stockholm University, Sweden; A. Nilsson, Stanford Linear Accelerator Center

The heat of adsorption is often treated as an indicator of the strength of adsorbate-substrate interaction. We present the combined experimental and theoretical study of weakly adsorbed systems on metal surfaces. We studied the electronic structure of water and hydrocarbons which are often considered as weakly bound species. We observed significant electron sharing between the adsorbate and metal surface and involvement of both bonding and antibonding molecular orbitals in the molecule-metal bond. These findings are a key to understand the O-H or C-H bond activation mechanism. We also present computational details how we computed the adsorption structure of these systems.

## 11:20am SS1-TuM10 H<sub>2</sub> Production from Ethanol Over Au/Rh/CeO<sub>2</sub> Catalysts, H. Idriss, P.Y. Sheng, The University of Auckland, New Zealand

The reactions of ethanol over oxides and metal-oxides surfaces are receiving increasing attention because of the potentially efficient production of hydrogen by oxidation and steam reforming. Ethanol (now viewed as a bio-fuel with potential for making hydrogen) has received considerable attention in the past because it is a simple probe molecule in studying surface reactions on metals and oxides. We have previously investigated the decomposition of ethanol on M/CeO<sub>2</sub> surfaces (M = Rh, Pt, Pd and Au). In this work we show that the addition of Au to Rh, for the reaction of ethanol, enhances both the production of H<sub>2</sub> and the total oxidation to CO<sub>2</sub>. The reaction of ethanol was conducted by TPD, IR and in steady state catalytic conditions, while catalysts were investigated by XRD and XPS. Among the key results of this work are the following. 1. Addition of Au resulted in the total suppression of adsorbed CO when compared to Rh/CeO<sub>2</sub> catalyst (IR), at low temperatures. 2. The presence of Rh enhanced the production of H<sub>2</sub> and the total decomposition of ethanol when compared to Au/CeO<sub>2</sub> catalyst (steady state reactions). The CO<sub>2</sub> to CO ratios were found equal to 25 for Au/CeO<sub>2</sub>, 5.6 for Rh-

Au/CeO<sub>2</sub>, and 1.8 for Rh/CeO<sub>2</sub>, catalysts (TPD). The reaction pathway for ethanol on the bimetallic system will be discussed and compared to that on the mono-metallic catalysts. Sheng, P.-Y., Yee, A., Bowmaker, G. A., Idriss, H. J. Catal. 2002, 208, 393; and references therein. Cavallaro, S. Freni, S. Int. J. Hydrogen Energy, 1996, 21, 465. Gates, S.M., Russell, J.N., Yates, J.T., Surf. Sci., 1986, 171, 111. Idriss, H., Seebauer, E.G., J. Mol. Catal. A, 2000, 152, 201. Diagne, C., Idriss, H., Kiennemann, A., Catal. Commun. 2002, 3, 565.

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