

## Surface Science

### Room 202 - Session SS1-MoM

#### Catalytic Chemistry of Hydrocarbons

**Moderator:** M. Trenary, University of Illinois at Chicago

8:20am **SS1-MoM1 Transition States of Hydrogenation and  $\beta$ -Hydride Elimination in Alkyl Groups on the Pt(111) Surface**, P.P. Ye, A.J. Gellman, Carnegie Mellon University

Substituent effects have been used to probe the characteristics of the transition states to hydrogenation of alkyl groups and the transition state to  $\beta$ -hydride elimination in alkyl groups on the Pt(111) surface. Eight different alkyl and fluoroalkyl groups have been formed on the Pt(111) surface by dissociative adsorption of their respective alkyl and fluoroalkyl iodides. Co-adsorption of hydrogen and subsequent heating of the surface results in hydrogenation of the alkyl groups to alkanes which desorb into the gas phase. The influence of the substituents on the activation barriers to hydrogenation has been correlated to the field and polarizability substituent constants of the alkyl groups in the form of a linear free energy relationship. Increasing both the field and polarizability constants of the alkyl groups increases the barrier to reaction. These substituent effects indicate that the  $\alpha$ -carbon in the transition state is cationic with respect to the initial state of alkyl group and that the reactant has greater charge density on the  $\alpha$ -carbon than the transition state. In the absence of adsorbed hydrogen, alkyl groups on Pt(111) dehydrogenate via  $\beta$ -hydride elimination. In the fluorinated alkyl groups this then leads to the deposition of hydrogen on the surface and the hydrogenation of the intact fluoroalkyl groups to form fluoroalkanes. The desorption kinetics of the product fluoroalkanes serves as a measure the kinetics of the  $\beta$ -hydride elimination. The field effects of the fluorinated substituents increase the barriers to  $\beta$ -hydride elimination. The interpretation of this effect is that the  $\beta$ -carbon atom in the transition state is cationic with respect to the reactant. This is consistent with observations made on the Cu(111) surfaces although the substituent effect is smaller on the Pt(111) surface indicating a difference in the nature of the transition states on the two surfaces.

8:40am **SS1-MoM2 Surface Science Insights on the Enantioselective Hydrogenation of Activated Ketones on Chirally-Modified Platinum**, S. Lavoie, P.H. McBreen, Université Laval, Canada

The asymmetric hydrogenation of  $\alpha$ -ketoesters on chirally-modified platinum catalysts, the Orito reaction, involves a complex set of interrelated interactions. These include the chemisorption of the chiral modifier and the ketoester on the metal surface, as well as the modifier-ketoester interactions responsible for enantiodifferentiation. In order to isolate the key modifier-ketoester interactions, RAIRS studies were performed on a range of aromatic-carbonyl co-adsorption systems of progressively increasing complexity. All effective modifiers for the Orito reaction contain both an extended aromatic function and a function capable of conventional H-bonding. It is generally accepted that the aromatic function serves to anchor the chiral modifier to the platinum surface, and that it may also play a steric role in inducing asymmetry. However, evidence will be presented for a key additional role for the aromatic anchor. Using results for the Pt(111) surface, it will be shown that the modifier-ketoester interaction may be described in terms of two distinct H-bonds, one of which is to the chemisorption activated aromatic system. It will be shown that such a two-point H-bonding interaction can account for most observations in the catalysis literature concerning the Orito reaction.

9:00am **SS1-MoM3 Electronic States of Adsorbed Molecules and Vibrational Excitation by Inelastically Tunneled Electrons from STM Tip**, M. Kawai, RIKEN and University of Tokyo, Japan

INVITED

The inelastic tunneling process of electrons between the tip of an STM and the target molecule can lead to various dynamical processes at surfaces such as desorption, lateral hopping, rotation and chemical reaction via the excitation of vibrational modes of adsorbed molecules. The vibrational mode that are excited through the process could be defined through the response of the molecular motion to the applied bias voltage, i.e. action spectrum. Action spectra for hopping motion of *cis*-2-butene on Pd(110), cleavage of dimethyl-disulfide on Cu(111) and hopping motion of cleaved product methyl-thiol show clear thresholds in bias voltage that are equivalent to certain vibration modes, the excitation mechanism of which can be understood by the resonant tunneling mechanism. When the

electron jumps into or out of a certain molecular orbital, molecules will temporarily go through the negative or positive ion state. And vibration states can be excited, during the relaxation process. Inelastic process that leads to vibrational excitation has attracted much attention of since the conductivity of molecules bridging the electrodes is found to be strongly affected when they are vibrationally excited. Considering that the conduction electrons passes through the electronic state crossing the Fermi level or hopping through the HOMO or LUMO state of the molecule, the electronic state of adsorbate should play a crucial role in the molecular electronics as well as the chemical reactions at surfaces.

9:40am **SS1-MoM5 The Reaction Pathway for the Synthesis of Vinyl Acetate on Pd(111)**, W.T. Tysoe, F. Calaza, D. Stacchiola, UW-Milwaukee

The palladium-catalyzed synthesis of vinyl acetate from acetic acid, ethylene and oxygen is studied on Pd(111) single crystal surfaces. The rate of reaction between gas-phase ethylene and adsorbed acetate species is followed using infrared spectroscopy by measuring the time dependence of the intense OCO acetate mode at 1414  $\text{cm}^{-1}$ . The acetate removal kinetics are modeled by assuming that ethylene adsorption is blocked by acetate species. Temperature-programmed reaction confirms that vinyl acetate is formed in the reaction. The reaction pathway is explored by comparing the reaction rates of  $d_2$ ,  $1,1-d_2$ ,  $1,2-d_2$  and normal ethylene with surface acetates.  $d_2$  ethylene reacts about six times more slowly than  $C_2H_4$  indicating that hydrogen is involved in the rate-limiting step. The reaction rates are different for  $1,1-C_2H_4$  and  $1,2-C_2H_4$ . This indicates that vinyl acetate formation occurs via the insertion ethylene into the surface acetate species to form an acetoxyethyl-palladium intermediate, which then reacts to form vinyl acetate via a  $\beta$ -hydride elimination reaction, rather than by vinyl formation and addition to the acetate species to form vinyl acetate. The different reactivities of the isotopomers is rationalized by making the reasonable assumption that ethylene adsorption is blocked by the acetoxyethyl-palladium intermediate. When reaction is carried out using  $1,1-C_2H_4$ , the intermediate can be formed with exclusively deuterium atoms in the  $\beta$ -position, slowing its rate of decomposition, blocking ethylene adsorption, and slowing the reaction rate. Reaction with  $1,2-C_2H_4$  results in one hydrogen being in the  $\beta$ -position, allowing it to decompose more rapidly. Final conformation of this pathway comes from detecting the acetoxyethyl-palladium intermediate using infrared spectroscopy when reaction is carried out using  $C_2H_4$ .

10:00am **SS1-MoM6 Vinyl Acetate Synthesis on Pd-based Catalysts: Structure Sensitivity and Active Site Identification**, D. Kumar, M.S. Chen, Y.F. Han, C.-W. Yi, K. Luo, D.W. Goodman, Texas A&M University

The synthesis of vinyl acetate (VA) is a very important industrial reaction and is produced by acetoxylation of ethylene over Pd-Au catalysts. Historically this highly selective reaction has been studied using conventional kinetic techniques; however, there is no consensus regarding a reaction mechanism. A combination of surface science techniques and kinetic measurements has been used in the current study to address the structure sensitivity and the active ensemble for the reaction. VA synthesis was carried out over Pd and Pd-Au high-surface-area and model planar catalysts and the reaction rates found to be:  $\text{Pd}(100) < 5 \text{ wt\% Pd/SiO}_2(d_{\text{Pd}}=4.0\text{nm}) < 1 \text{ wt\% Pd/SiO}_2(d_{\text{Pd}}=2.5\text{nm})$ . A particle size dependence of the reaction rates implies a degree of structure sensitivity. Furthermore, the addition of Au to Pd/SiO<sub>2</sub> catalysts leads to a significant increase in the reaction rate and selectivity with the latter related directly to a change in the reaction order with respect to ethylene. Infrared reflection absorption spectroscopy (IRAS) of CO on Pd/Au(100) and Pd/Au(111) confirms that Pd is present as isolated monomers on a Au-rich surface. A pair of Pd monomers is the optimum active site for the adsorption of ethylene and acetate species, and leads to the formation of VA. The spacing between the two active Pd monomer pairs is crucial on Au(100) and Au(111), evident by the relative rates of VA synthesis on Pd/Au model catalysts, i.e.  $\text{Pd/Au}(111) < \text{Pd/Au}(100)$ .

10:20am **SS1-MoM7 Selective Oxidation of Hydrocarbons on Chemisorbed Oxygen Covered Au(111)**, X. Deng<sup>1</sup>, C.M. Friend, Harvard University

Chemisorbed oxygen covered Au(111) has been found to be active for the partial oxidation of hydrocarbons. Specifically, chemisorbed oxygen on a herringbone-Au(111) was deposited via electron-induced dissociation of NO<sub>2</sub>. Several hydrocarbons, including cyclohexene and styrene, were

<sup>1</sup> Morton S. Traum Award Finalist

# Monday Morning, October 31, 2005

studied on the O/Au surface by using temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). The primary products are styrene epoxide and benzene for styrene and cyclohexene oxidation, respectively. HREELS was performed to identify the intermediates of the reactions. In combination with the observed isotope effects, the reaction mechanisms on O/Au(111) were proposed and compared with those on O/Ag(110).

10:40am **SS1-MoM8 Reactivity Studies of Molybdenum Carbide Nanoparticles formed on Au(111) using Reactive-Layer Assisted Deposition**, *D.V. Potapenko*, BNL; *J.M. Horn, M.G. White*, BNL and SUNY at Stony Brook

The chemical properties of MoC@sub x@ nanoparticles prepared by a novel method on the Au(111) support have been studied using cyclohexene, cyclohexane and benzene as test molecules. The surfaces have been prepared by depositing Mo by physical vapor deposition (PVD) on a reactive layer of ethylene, which was physisorbed on a Au(111) substrate at low temperatures (85 K). STM imaging shows that the resulting MoC@sub x@ particles have a narrow size distribution and preferentially nucleate near the 'elbow' sites on the reconstructed (22 x @sr@3)-Au(111) surface. Auger and XPS indicate that the MoC@sub x@ particles are near stoichiometric (x = 1). Also we have found that in the thermodynamically stable state MoC@sub x@ particles are partially encapsulated by gold from the support. Thermal programmed desorption (TPD) studies have shown that cyclohexene undergoes three different reactions on bare (not encapsulated by Au) MoC@sub x@ nanoparticles: hydrogenation to cyclohexane, partial dehydrogenation with benzene formation, and complete dehydrogenation with surface carbon deposition. In contrast, interaction of cyclohexene with Au-encapsulated MoC@sub x@ nanoparticles exhibits a very high (at least 95 %) selectivity toward partial dehydrogenation to benzene. The found selectivity is higher than that for cyclohexene reactions on either C/Mo(110) or Pt(111) surfaces. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract No. DE-AC02-98CH10886.

11:00am **SS1-MoM9 The Mechanism of Partial Oxidation of Styrene on Ag(111)**, *A. Klust, R.J. Madix*, Stanford University

The partial oxidation of olefins on Ag surfaces has been a long standing problem in surface science and is of great commercial interest. In particular, the nature of reaction intermediates has been subject of intense debate. One candidate for the reaction intermediate is the oxametallacycle where both ends of a -C-C-O- chain are attached to the Ag surface (see e.g. [1]). We present a temperature programmed reaction spectroscopy (TPRS) and x-ray photoelectron spectroscopy (XPS) study of the partial oxidation of styrene on Ag(111). The reaction products are CO@sub 2@, H@sub 2@O, styrene oxide, benzene, and benzoic acid. XPS gives evidence for two different intermediate structures that we assign to an oxametallacycle and to benzoate. The oxametallacycle seems to be the precursor for the formation of the styrene oxide as well as for the formation of the benzoate while the benzoate itself leads to the formation of CO@sub 2@, benzene, and benzoic acid. The results are explained in the framework of a model based on the asymmetry of the oxametallacycle caused by the phenyl ring of styrene. @FootnoteText@ @footnote 1@ S. Linic and M. A. Barteau, *J. Am. Chem. Soc.* 125 (2003) 4034.

11:40am **SS1-MoM11 Catalytic Hydrodechlorination of Chlorobenzene and Chlorotoluene Isomers on the Pt(111) Surface**, *B.M. Haines*, University of Michigan; *D.A. Fischer*, National Institute of Standards and Technology; *J.L. Gland*, University of Michigan

The catalytic hydrodechlorination of chlorobenzene on the Pt(111) surface has been characterized using temperature programmed reaction spectroscopy (TPRS) and fluorescence yield near edge spectroscopy (FYNES) above the carbon K edge. Thermal hydrodechlorination, dehydrogenation and rehydrogenation result in the formation of benzene, HCl, and H@sub 2@ when chlorobenzene is heated on platinum. The effects of methyl substituents on hydrodechlorination were probed using the isomers of chlorotoluene. The chlorobenzene monolayer adsorbs on the Pt(111) surface with the plane of the ring at a 45° angle from the surface as indicated by FYNES. The monolayer partially desorbs at 196 K and the remaining chlorobenzene then undergoes dechlorination via two reaction channels at 270 K and at 420 K as shown by TPRS. Comparison of the integrated peak areas for these two channels yields a 3:2 (270 K: 420 K) ratio. Temperature programmed-FYNES show that a stable cyclohexadiene intermediate is formed above 250 K that is coadsorbed in a 3:2 ratio with molecular chlorobenzene. The remaining molecular chlorobenzene is

dechlorinated in the 420 K range to form additional adsorbed cyclohexadiene. For chlorotoluene, substituent effects dominate activation of the C-Cl bond through the ring and dehydrogenation of the methyl group at low temperatures.

## Author Index

### Bold page numbers indicate presenter

— C —

Calaza, F.: SS1-MoM5, **1**

Chen, M.S.: SS1-MoM6, **1**

— D —

Deng, X.: SS1-MoM7, **1**

— F —

Fischer, D.A.: SS1-MoM11, **2**

Friend, C.M.: SS1-MoM7, **1**

— G —

Gellman, A.J.: SS1-MoM1, **1**

Gland, J.L.: SS1-MoM11, **2**

Goodman, D.W.: SS1-MoM6, **1**

— H —

Haines, B.M.: SS1-MoM11, **2**

Han, Y.F.: SS1-MoM6, **1**

Horn, J.M.: SS1-MoM8, **2**

— K —

Kawai, M.: SS1-MoM3, **1**

Klust, A.: SS1-MoM9, **2**

Kumar, D.: SS1-MoM6, **1**

— L —

Lavoie, S.: SS1-MoM2, **1**

Luo, K.: SS1-MoM6, **1**

— M —

Madix, R.J.: SS1-MoM9, **2**

McBreen, P.H.: SS1-MoM2, **1**

— P —

Potapenko, D.V.: SS1-MoM8, **2**

— S —

Stacchiola, D.: SS1-MoM5, **1**

— T —

Tysoe, W.T.: SS1-MoM5, **1**

— W —

White, M.G.: SS1-MoM8, **2**

— Y —

Ye, P.P.: SS1-MoM1, **1**

Yi, C.-W.: SS1-MoM6, **1**