## Tuesday Afternoon, October 3, 2000

### Surface Science Room 208 - Session SS1-TuA

#### Mechanisms and Control of Surface Reactions Moderator: A.V. Teplyakov, University of Delaware

#### 2:00pm SS1-TuA1 Bestowing Chirality: The Ultimate Control of a Surface Reaction, *R. Raval*, University of Liverpool, UK INVITED

Enantioselective surface reactions represent the ultimate expression of selectivity in catalysis, involving stereodirecting processes where only one optical component of a product is formed. A case in point is the hydrogenation of b-ketoesters, which occurs readily on metal surfaces, but with no stereoselectivity so that both optical products are produced. However, catalytic studies show that this reaction pathway can be rigidly controlled if the metal is first modified by pre-adsorption of particular chiral molecules. But how is stereocontrol is achieved by the presence of these chiral modifiers?. Here, we report surface spectroscopic results from chirally modified metal surfaces created under controlled environments. We show that the adsorbed modifiers display rich and complex phase diagrams in which the chemical nature and 2-dimensional organisation of the chiral molecules is a dynamic function of surface coverage and temperature. Of particular interest is that at certain points of the phase diagram, extended supramolecular assemblies of the chiral molecules impose growth directions that destroy existing symmetry elements of the underlying metal and, thus, directly bestow chirality to the achiral metal surface! These supramolecular assemblies also create chiral channels and chiral spaces at the metal surface that we believe are responsible for imparting enantioselectivity by forcing the reactant molecules to dock in one particular orientation, which subsequently directs the hydrogen attack. Our work shows that it is possible to sustain a single chiral domain across an extended surface. The implications of creating structured chiral metal surfaces go beyond catalysis, with potential applications in molecular electronics, non-linear optics and molecular recognition, and we conside general principles which govern the expression of true extended chirality in 2-dimensional space.

#### 2:40pm SS1-TuA3 Artificial Control of Catalytic Functions for Reaction Selectivity by Thickness-extensional Mode Resonance Oscillation of Acoustic Wave, Y. Inoue, Y. Yukawa, N. Saito, H. Nishiyama, Nagaoka University of Technology, Japan

Thickness-extensional mode resonance oscillation (TERO) of bulk acoustic waves generated by a piezoelectric effect was applied to a 100 nm Ag or Pd film catalyst deposited on a positively polarized ferroelectric single crystal of z-cut LiNbO3 (z-LN), and the TERO effects on reaction selectivity of the catalyst surfaces were studied. For ethanol decomposition on Ag and Pd, TERO with a resonance frequency of 3.5MHz caused remarkable increases in ethylene production without changing acetaldehyde production. The increased activity decreased to an original low level with turning TERO off. Increases in selectivity for ethylene production with TERO were from 56 to 86% for Ag and 31 to 97% for Pd. The activation energy of ethylene production was lowered significantly by the TERO. For comparison, x-cut LiNbO3 (x-LN) having thickness-shear mode resonance oscillation (TSRO) was employed as a ferroelectric substrate, for which no significant activity enhancements for both ethylene and acetaldehyde production were observed with the resonance oscillation. Laser Doppler measurements showed that TERO caused large dynamic lattice displacement vertical to the surface. The surface potential and photoelectron emission behavior varied with the TERO. TERO has been shown to have influences on the work function of the catalyst surfaces, which permits to change the catalytic functions with selectivity.

#### 3:00pm SS1-TuA4 Surface Science Models of Sulfided NiW, CoW, NiMo and CoMo Hydrodesulfurization Catalysts, *L. Coulier, G. Kishan,* Eindhoven University of Technology, The Netherlands; *J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands, Netherlands

Industrial catalysts used in the hydrotreating of crude oil can successfully be modeled using silicon single crystals as the planar support for the catalytically relevant sulfides. Wet chemical deposition techniques on the basis of spin coating enable the preparation of these catalysts via industrially relevant chemistry. The catalytic behavior of these models in the desulfurization of thiophene to butenes has been measured in a batch reactor. Clear relations between the order in which the elements convert to sulfides and the catalytic activity have been observed: The key step in the preparation is to retard the sulfidation of Ni and Co with respect to that of Mo and W. To this end, stabilizing chelating agents may be added in the preparation stage.

#### 3:20pm SS1-TuA5 Chemistry of Thiophene, H@sub 2@S, and SO@sub 2@ on Carbide-Modified Mo(110) and Mo@sub 2@C Powders, J. Dvorak, T. Jirsak, J.C. Hanson, J.A. Rodriguez, Brookhaven National Laboratory

The most widely used catalysts in hydrodesulfurization (HDS) reactions consist of a mixture of cobalt and molybdenum sulfide on an alumina support. More stringent environmental legislations stress the need to develop a new generation of HDS catalysts that lead to the ultimate goal of clean burning fuels. Recently, it has been shown that molybdenum-carbide catalysts have the potential to replace sulfided Mo catalysts in industrial HDS reactors. We have investigated the chemistry of a series of Scontaining molecules on carbide-modified Mo(110) [i.e. MoC@sub x@] and Mo@sub 2@C powders using synchrotron-based photoemission, x-ray absorption near-edge spectroscopy and time-resolved x-ray diffraction. Thiophene adsorbs molecularly on MoC@sub x@ at 100 K. By 200 K, upon desorption of the thiophene multilayer, chemisorbed thiophene and its decomposition products (S and C@sub x@H@sub y@ fragments) coexist on the MoC@sub x@ surface. At 250 K, no C-S bonds are left. H@sub 2@S and SO@sub 2@ are also very reactive on MoC@sub x@, with the cleavage of H-S and S-O bonds taking place at temperatures well below 300 K. For these systems, the chemistry observed on carbide-modified Mo(110) is quite similar to that seen on Mo@sub 2@C powders.

#### 3:40pm SS1-TuA6 Selective Surface Reactions of Single Crystal Metal Carbides: Alkene Production from Short Chain Alcohols on Titanium Carbide and Vanadium Carbide, *R.L. Guenard*, *L.C. Fernández-Torres, S.S. Perry*, University of Houston; *P. Fantz, S.V. Didziulis,* The Aerospace Corporation

The reaction of short chain alcohols on the (100) surface of single crystal vanadium carbide (VC) and titanium carbide (TiC) have been studied using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and x-ray photoelectron spectroscopy (XPS). The short chain alcohols form an alkoxide upon adsorption at 153K on both VC(100) and TiC(100). The alkoxide intermediate selectively reacts with the carbides to produce an alkene and water. Specific isotopic labeling revealed @gamma@ C-H bond scission as a key step in alkene formation. A comparison of the TPD intensities of reaction products on both surfaces indicates that VC(100) has a higher reactivity towards alcohols, with an approximately four-fold higher reaction yield as compared to TiC(100). This difference in reactivity is accounted for by a difference in the electronic structure of these carbide surfaces. This study implicates potential pathways of lubricant degradation in tribological applications and highlights the possible need for passivating additives for carbides used in such applications.

#### 4:00pm SS1-TuA7 Alkylidenes on Molybdenum Carbide; Stable Carbenes on the Surface of a Catalytically Active Material, E.M. Zahidi, H. Oudghiri-Hassani, P.H. McBreen, Laval University, Canada

Molybdenum carbide competes well with platinum and ruthenium as a catalyst for various hydrocarbon transformation reactions. This reactive material can activate both CC and CH bonds. Yet, the present study shows that it is possible to form a layer of thermally stable carbenes on the carbide surface. Dissociative chemisorption of ketones leads to the formation of surface alkylidene groups which are stable to above 900 K. Extensive RAIRS, photoemission and XPS results will be used to describe the mechanism for the formation of these groups, and to outline their stability and their high temperature surface chemistry. This novel method for coupling relatively complex organic species to reactive surfaces may find application in the preparation of surface alkylidenes is also of direct interest for heterogeneous metathesis chemistry.

#### 4:20pm SS1-TuA8 Radical Rearrangement as a Probe of Partial Oxidation Mechanisms: Reaction of (Bromomethyl)cyclopropane on Oxygen-Covered Mo(110), J.A. Levinson, M.A. Sheehy, L.J. Deiner, I. Kretzschmar, C.M. Friend, Harvard University

Rearrangement reactions were used to study the transient intermediates formed during partial oxidation on oxygen-covered (0.75 ML) Mo(110) surfaces using (bromomethyl)cyclopropane. Using temperature programmed reaction spectroscopy, a competition between desorption and reaction was observed, with 1,3-butadiene, butene, ethylene, water, and dihydrogen as reaction products; these were evolved between 450 and 600 K. No cyclic or three-carbon species were observed in the mass spectroscopic data. Two linear analogues, 4-bromo-1-butene and 3-buten-

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1-ol, were also studied and produced similar product spectra. Coadsorption experiments with deuterated species revealed that the hydrogen incorporated into butene and ethylene arises at the time of reaction from the reaction intermediate. Mass spectra indicated that there may be both alkyl and alkoxide species at the surface for the Br-containing compounds, as the hydrocarbon products are evolved at two temperatures. X-ray photoelectron spectroscopy experiments are in progress to determine the surface bonding and the temperature of C-Br bond scission. Fourier transform infrared spectroscopy was used to determine conformational and structural changes in the surface intermediates as a function of temperature. For (bromomethyl)cyclopropane, a double bond appears near 400 K. These data imply that a ring-opened intermediate forms following C-Br bond scission, which is then followed by H-elimination or incorporation. The use of isotopically labeled oxygen on Mo(110) revealed that the alkoxide species for the Br-compounds bind through surface oxygen, whereas the alcohol binds through its original hydroxyl group. Lowering reactant coverage reduces butene and butadiene formation and favors ethylene production. Variation of oxygen coverage from saturation to clean Mo(110) surfaces causes selective product formation to convert to non-selective decomposition.

#### 4:40pm SS1-TuA9 Reaction Kinetics on Supported Model Catalysts: A Molecular Beam / In-Situ IRAS Study of the CO Oxidation on Pd/Al@sub 2@O@sub 3@, J. Libuda, I. Meusel, J. Hoffmann, J. Hartmann, H.-J. Freund, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

We have employed molecular beam techniques combined with timeresolved in-situ IR reflection absorption spectroscopy to study the CO oxidation kinetics on oxide-supported model catalysts. As model systems we have used Pd particles of different size and morphology grown under UHV conditions on a well-ordered alumina film on NiAl(110). Previously, these systems have been characterized in detail with respect to their geometric and electronic structure. Sticking coefficient measurements demonstrate that - contrary to what is observed for densely packed Pd single crystal surfaces - at room temperature and above the Pd crystallites rapidly incorporate a large amount of oxygen. This subsurface and bulk oxygen is not accessible to CO oxidation at low temperature. Once the bulk reservoir is saturated, stable oxidation rates are obtained. Taking advantage of the single-scattering conditions in a molecular beam experiment, we quantitatively address effects which are specific for supported metal catalysts, such as support mediated adsorption. Also, activation energies for the LH reaction step as a function of adsorbate coverage are derived. Various coverage regimes are considered, in particular the limiting cases of high CO or O coverage. The transient behavior and the steady-state CO@sub 2@ production rate are probed over a wide range of reactant fluxes and CO/oxygen flux ratios. In particular, we discuss the origin of the different transient behavior of the oxidation rate on supported Pd particles. Time-resolved IR absorption spectroscopy is employed during the reaction to monitor changes in the occupation of different adsorption sites in transient beam experiments and under steady-state conditions.

# 5:00pm SS1-TuA10 Dissociative Chemisorption of Chloromethanes on Ir(110), Ir(111) and Oxygen Modified Ir(111), *R.J. Meyer, C.T. Reeves, D.J. Safarik, D.T. Allen, C.B. Mullins,* University of Texas at Austin

Chlorinated hydrocarbons are a primary component of the waste streams from the manufacture of many commodity chemicals. Noble metal catalysts, including iridium on alumina, have been shown to be active for both oxidative and reductive catalytic treatment methods. However, the causes of deactivation and mechanisms by which these reactions proceed are not precisely known. Dissociative chemisorption of CH@sub 3@Cl, CH@sub 2@Cl@sub 2@, CHCl@sub 3@, and CCl@sub 4@ on Ir(110) and Ir(111) has been examined at surface temperatures from 77-1200 K using molecular beam methods. From our ongoing studies two particularly exciting results have emerged. (1) We have identified the reactive site for methyl chloride on Ir(110). An examination of CH@sub 3@Cl on hydrogen precovered Ir(110) indicates that the reaction pathway for dissociative chemisorption can be shut off by filling the high temperature desorption state. This result implies that methyl chloride chemisorbs in the hollow site of the rows of the (110) surface. (2) The production of phosgene was observed when a CCl@sub 4@ beam was impinged on an oxygen modified Ir (111) surface. We propose that phosgene forms via a Langmuir-Hinshelwood mechanism from the reaction of absorbed oxygen with CCl@sub 2@ surface species formed during the decomposition of carbon tetrachloride. Competing reactions involving the oxidation of completely dissociated carbon tetrachloride become significant as the surface temperature increases. COCl@sub 2@ formation was maximized at an

oxygen surface coverage of approximately 0.3 ML. At higher oxygen coverages, the production of phosgene decreases due to a diminished reactive adsorption of carbon tetrachloride but the efficiency of COCl@sub 2@ formation per dissociatively chemisorbed CCl@sub 4@ increases dramatically.

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