Surface Science Division
Room 607 - Session SS2-TuM

Model Catalysts

Moderator: A.G. Sault, Sandia National Laboratories

8:20am **SS2-TuM1 The Microscopic Mechanism of Methanol Synthesis over the Zn-promoted Cu(111)***, J. Nakamura,* University of Tsukuba, Japan*; I. Nakamura,* National Institute for Resources and Environment, Japan*; H. Nishimura, H. Nakano, M. Sano,* University of Tsukuba, Japan*; T. Fujitani,* National Institute for Resources and Environment, Japan

We had reported that the Zn-deposited Cu(111) could be regarded as a model of Cu/ZnO catalysts in terms of the turnover frequency of methanol formation and the activation energy. After establishing the catalyst model, we had further tried to look into the detailed mechanism on the promotional role of the Zn as well as the microkinetics using in-situ IRAS, XPS and STM apparatuses connected to a high pressure reactor. Very reactive formate species adsorbed in an inclined bidentate state was detected by IRAS, which was found to be responsible for the promotional effect of the Zn. Also the microkinetic picture was established for formate synthesis and formate decomposition. Interesting relationships between the ordered structure of formate observed by STM and the kinetics of decomposition were shown. That is, various ordered structures of formate intermediates synthesized from CO@sub 2@ and H@sub 2@ at 1 atm were very different from the structure of formate prepared by adsorption of formic acid, which cause a difference in the pre-exponential factor of the rate constant for the formate decomposition. This was explained by that a nearest neighbor formate species interfered with the OCO plane vibration of formate, which is probably necessary to overcome the transition state of the decomposition. The STM images of the Zn-deposited Cu(111) showed that Zn atoms were substituted for Cu atoms, leading to a Cu-Zn surface alloy. Upon the deposition of Zn, the alloying started at the step edges of the Cu(111) surface, and then the Zn atoms migrated toward the terrace. The migration rate was measured by time-resolved STM.

8:40am **SS2-TuM2 Vacuum and Electrochemical Characterization of a Model Pt(111) Catalyst Modified with Vapor-deposited Ru***, D.S.W. Lim, T.H. Madden, V.K. Medvedev, E.M. Stuve,* University of Washington*; T.J. Jarvi,* United Technologies Research Center

A practical liquid fuel cell anode catalyst must oxidize fuel in the presence of adsorbed carbon monoxide (CO), whether the actual fuel is methanol in the direct methanol fuel cell, or hydrogen from reformed hydrocarbons. While platinum (Pt) exhibits the greatest reactivity for fuel oxidation, it alone is unable to oxidize CO at potentials low enough to be practical. Pt modified with ruthenium (Ru) can however oxidize CO at lower potentials, although the details of the Ru enhancement have not yet been established. Also, the lack of reproducible performance of both model and industrial Pt / Ru fuel cell catalysts indicates that the preparation / processing effects on catalyst structure and performance have not been adequately assessed. In this work, a Pt(111) surface is modified with Ru via physical vapor deposition and characterized in ultra-high vacuum using AES, LEED, and TDS. The crystal is then transferred directly to an electrochemical cell where blank and methanol-oxidation voltammetry are performed. Early results using an industrial electron-beam Ru deposition source suggest simultaneous multi-layer growth of the Ru adlayer on Pt(111) at room temperature. Room temperature blank voltammetry indicates new features in the low-potential region due to Ru on Pt(111). Methanol-oxidation voltammetry indicates reduced peak currents due to lack of dissociative adsorption of methanol on surface Ru at room temperature. These electrochemical characteristics due to Ru on Pt(111) can largely be reversed by a mild 300 deg C anneal in vacuum. We recently developed a small electron-beam Ru deposition source in our lab which allows highly precise Ru deposition under good vacuum conditions. More detailed vacuum and electrochemical characterization using this source for the Ru / Pt(111) system will be discussed. This work was supported by the Office of Naval Research, the National Science Foundation, the Link Foundation, and the University of Washington.

9:00am **SS2-TuM3 Structurally Ordered Magnesium Vanadate Model Catalysts for Oxidative Dehydrogenation***, A.G. Sault, J.A. Ruffner,* Sandia National Laboratories

A fundamental understanding of the nature of the active sites in mixed metal oxide oxidation catalysts has proven elusive. The complex nature of these materials makes fundamental studies of active sites difficult. The use of single crystal surfaces to overcome this complexity is limited by the insulating nature of oxides, which restricts the use of many surface analytical probes. For simple oxides, some researchers have used ultrathin epitaxial oxide films to overcome these problems. Such films allow STM studies that provide unprecedented atomic detail regarding metal oxide surfaces. We are employing similar methods to study mixed metal oxide surfaces. Using RF sputter deposition, we have grown thin (<85 Å) films of Mg@sub 3@(VO@sub 4@)@sub 2@, a known selective oxidative catalyst. Bulk and surface analysis of films grown on Si wafers show the desired stoichiometry. By depositing Mg@sub 3@(VO@sub 4@)@sub 2@ on a 500 Å Au layer grown on an oxidized Si wafer, films strongly orientated in the (042) plane of Mg@sub 3@(VO@sub 4@)@sub 2@ can be grown. This plane consists of close packed oxygen layers, with Mg and V ions in octahedral and tetrahedral sites, respectively. Heating the films above 623 K in vacuum or 100 Torr propane results in partial reduction of V(V) to V(IV) and segregation of V to the surface. Treatment in oxygen reverses these changes. This reversible redox chemistry is consistent with the known mechanism for catalytic oxidation, which involves participation of lattice oxygen. We will report STM images of these surfaces, and detail the effects of heat treatments in reactive environments (e.g., oxygen/propane mixtures) on the structure and composition of these films. The formation of defects such as oxygen vacancies will be of special interest as lattice oxygen plays an important role in catalysis over mixed metal oxides. Through these studies we hope to provide the first detailed atomic scale view of active sites in this important class of catalysts.

9:20am **SS2-TuM4 The Atomic-scale Structure of MoS@sub 2@ Nano-cluster Catalysts Studied by STM***, S. Helveg, J.V. Lauritsen, E. Laegsgaard, I. Stensgaard,* University of Aarhus, Denmark*; B.S. Clausen, H. Topsoe,* Haldor Topsoe Research Laboratories, Denmark*; F. Besenbacher,* University of Aarhus, Denmark

Hydrodesulfurization (HDS) catalysis has recently attracted an increased interest partly augmented by the new severe environmental legislation. The activity of the industrial HDS catalysts has uniquely been related to the edge structure of MoS@sub 2@ nano-crystals. However, very little is known about the actual shape of the nano-crystalline MoS@sub 2@ particles and the exact edge structures. To obtain such structural insight, we have prepared a model system of 30 Å wide MoS@sub 2@ nano-clusters dispersed on the Au(111) model surface. High resolution Scanning Tunneling Microscopy (STM) studies unequivocally reveal that the MoS@sub 2@ nano-clusters are of triangular shape, and from atomically resolved STM images of the edge structures, we tentatively conclude that the edges are S restructured Mo terminated edges.

9:40am **SS2-TuM5 Linking Surface Science and Catalysis***, I. Chorkendorff,* Technical University of Denmark, DENMARK **INVITED**

Surface Science has in the past provided much of the framework and tools for understanding heterogeneous catalysis. Nevertheless, the pressure and structure gap still continues to provide unforeseen and interesting phenomena, which are necessary prerequisites in order that real catalytic processes under high-pressure conditions can be understood and modeled. It is therefore mandatory to identify which reaction pathways are prevailing and what structure and composition are present at increased pressure. In a number of examples it will be demonstrated how, by combining in situ high pressure experiments on well defined single crystals with DFT calculations, it is possible to gain a further insight in this direction. For example is it well known from UHV experiments that steps or defects may influence the surface reactivity substantially, but the influence on catalytic process have been of more speculative nature. It will be shown, how steps and/or defects increases the sticking of N@sub2@ on Ru(0001) by 8 to 9 orders of magnitude!! Since this is the rate-limiting step in the ammonia synthesis on Ru, it will naturally have a profound impact on the understanding of the ammonia synthesis, which was also studied. Turning to model system for alloy catalyst it will be demonstrated how the surface composition and availability for performing chemical reaction can be strongly dependent on gas induced segregation phenomena. A brief overview of the determining parameters will be given showing that the surface composition of alloys is dynamically dependent on temperature and the chemically potential of the gasses involved and cannot in many cases be determined from UHV experiments alone.

10:20am **SS2-TuM7 Flow Reactor Studies of Nanofabricated Model Catalysts; Activity and Reconstruction***, S. Johansson, E. Fridell, B. Kasemo,* Chalmers University of Technology, Sweden

Nanofabrication of model catalysts using the electron-beam lithography technique offers a way to produce geometrically well-defined model catalysts. Component interaction, particle separation and particle size (in the 10 nm range) can be controlled. Multi-layer structures can be obtained by repeating the fabrication-process. Furthermore, re-structuring can be accomplished by heat treatment afterwards in different gas mixtures. These nanofabricated catalysts are well suited to study, e.g., spillover effects in catalytic systems. A micro-reactor for catalytic evaluation of these nanofabricated model catalysts has been designed. It operates at atmospheric pressure and allows samples with a small total active surface area (below 1 mm@super 2@). This implies small gas-flows in the order of approx. 1-10 mm@super 3@/s. The small active surface-area comes from a limitation in the electron-beam lithography process to make large numbers of small structures in a reasonable time, due to the serial processing. The minimum Pt-surface-area needed for catalytic activity evaluation has not yet been determined for this system. Differences in the CO-reaction rate in the kinetically controlled region is measured as a function of interaction length between Pt and CeO@sub x@, where the total surface area of Pt has been kept constant. Morphology changes of nanofabricated Pt-discs with diameters up to 700 nm has been studied. Structural changes occur in reactant mixtures, e.g., CO+O@sub 2@ in Ar, at elevated temperatures (500Â°C). Disintegration of the larger Pt-discs into several smaller crystalline Pt-particles is observed.

10:40am **SS2-TuM8 Increasing the C-O Bond Anharmonicity of Methoxy on Cu(100) with Coadsorbates***, J.M. White,* ***H. Ihm****, K.C. Smith, H. Celio,* University of Texas, Austin

The C-O bond ahnarmonicity of methoxy induced by coadsorbates on Cu(100) has been studied using reflection absorption infrared spectroscopy (RAIRS). The analysis of the anharmonicity was carried out through the IR spectrum of a localized two-phonon bound state, the 2@nu@'@sub C-O@ excitation. For methoxy without coadsorbates, the vibrational frequencies of the C-O stretching mode and its overtone exhibit large coverage dependent shifts caused by dipole-dipole interactions. The anharmonicity of the C-O bond is @omega@@sub e@@chi@@sub e@=8.5 cm@sup -1@, which is 34% lower than that found for the gas phase methanol. Atomic oxygen markedly shifts the 2@nu@'@sub C-O@ band from 1951 cm@sup -1@ to 1940 cm@sup -1@, which consequently increases the anharmonicity by 11 cm@sup -1@. We have also compared results for methoxy from the thermal decomposition of methyl nitrite (CH@sub 3@ONO) on Cu(100) at different temperatures. We find that the 2@nu@'@sub C-O@ band can detect the presence of coadsorbed NO since the vibrational properties of the 2@nu@'@sub C-O@ band for both systems (methoxy-A-Cu(100) where A=O or NO) are quite similar. The definite correlation of the changes to the vibrational properties of methoxy induced by coadsorbates was achieved by using temperature programmed desorption (TPD) and Auger electron spectroscopy (AES).

11:00am **SS2-TuM9 Studies of the Oxidation Reactions of Methanol on a Heated Silver Membrane***,* ***R.J. Beuhler****, R.M. Rao, M.G. White,* Brookhaven National Laboratory

A polycrystalline Ag-membrane is being used as a model substrate for investigating the kinetics and dynamics of Ag-catalyzed oxidation reactions, such as the epoxidation (EO) of ethylene and the partial oxidation of methanol. These Ag-catalyzed reactions are carried out on a large-scale commercially, and despite considerable effort to understand the reaction mechanisms, much still remains uncertain. We have been attempting to study these oxidation reactions under collision free conditions (pressures less than 10@super -5@ torr), allowing both electron impact mass spectroscopy and state-selective laser ionization techniques to be used for product analysis. The main advantage of the membrane is that high surface coverages of adsorbed O@sub (a)@ can be prepared by diffusion of oxygen atoms produced by dissociative adsorption at the high pressure side of the heated Ag foil. The oxygenated Ag-foil is found to be very active in promoting the partial oxidation of methanol to formaldehyde. At a methanol pressure of 10@super -6@ torr, the reaction rate is on the order of 10@super 15@ molecules/cm sec@super 2@, with a measurable lower limit of about 5 x 10@super 13@ molecules/cm sec@super 2@. During the initial heating of the foil, activation of the surface is observed. In complementary studies, O 1s XPS measurements have been performed on the Ag-foil surface to identify the chemical state of the adsorbed oxygen, and (2+1) REMPI laser spectroscopy has been used to extract ro-vibronic and velocity distributions for desorbed molecular oxygen formed by the recombination reaction O@sub (a)@ + O@sub (a)@ = O@sub 2(g)@.

11:20am **SS2-TuM10 Improved Catalytic Activity and Selectivity by Photon Irradiation***, D. Chakarov,* Chalmers University of Technology and University of Göteborg, Sweden*; S. Ljungström,* Competence Centre for Catalysis, Sweden*; J. Bergeld, D. Ingert, V.P. Zhdanov,* ***B. Kasemo,*** Chalmers University of Technology and University of Göteborg, Sweden

Photo-catalysis is the enhancement of a chemical reaction by combined action of a catalyst and photons, on the reaction rate and/or selectivity. In heterogeneous photo-catalysis, the reaction occurs on a solid surface, with the reactants in gaseous or fluid state. The photons usually excite hot (photo) electrons that by transient attachment to one of the reactants enhance the reaction. In the present work, we explore the possibilities to increase the efficiency of catalytic emission cleaning by photo-catalysis. The approach includes both experimental and theoretical studies of the different parameters that may influence the photo-catalytic reactions, such as catalyst composition and wavelength dependence. The experiments are performed with conventional noble metal car exhaust catalysts at atmospheric pressure, nanofabricated model catalyst, and extended single crystals at UHV. Theoretical treatment includes studies of hot electron excitation-transport-attachment processes and Monte Carlo simulation. We present results concerning the reaction kinetics and light-off behavior for different CO + O2 and CO + NO mixtures on different catalysts. The main observations to date are: The light-off temperature can be reduced substantially (by up to 80 degrees) by photon irradiation at 365 nm. The single photon, non-thermal origin of this photocatalytic effect is confirmed by power- and wavelength- dependence measurements. The different characteristics of the photocatalysis on supported platinum, compared to single crystal Pt (111) in UHV, are discussed in terms of case specific adsorbate coverages, hot electron excitation, and reaction mechanisms.

11:40am **SS2-TuM11 Direct Observation of Propylene Transformation Chemistry on and in the Pores of Silver Exchanged Faujasite Catalyst***,* ***S. Sambasivan,*** Brookhaven National Laboratory*; D.A. Fischer,* National Institute of Standards and Technology*; A. Kuperman,* Dow Chemical Company*; B.M. DeKoven,* Intevac Inc.

For the first time Near-Edge Soft X-ray Absorption Spectroscopy Fine Structure (NEXAFS) electron yield (surface sensitive about 50 Å) and fluorescence yield (bulk sensitive) have been applied simultaneously to characterize the adsorbed state of propylene in the surface and the bulk of the silver exchanged faujasite (LZY-52) catalyst. This technique is non-destructive, element specific, and a direct probe of the bonding and concentration of the adsorbed species, and reactive intermediates on a highly complex zeolite catalyst. Propylene adsorption on Ag/LZY-52 faujasite at 125 K showed that a bulk adsorbed state was a weakly interacting gas-phase like species with a highly intense carbon 1s to @pi@ *intensity which begins to desorb upon heating from 150 K to 300 K. On the other hand the propylene adsorbed on the surface forms a strongly chemisorbed intermediate with a small of carbon 1s to @pi@ * intensity but a strong @sigma@ * intensity indicating a formation of a sigma complex which is stable up to 250 K. A very small adsorption of propylene was observed on a zeolite with similar cage structure, high Si/Al ratio and no silver loading. The difference in the nature propylene adsorption in the bulk and surface of Ag/LZY-52 is discussed with respect to the difference in acidity and the size of the Ag particles in the surface and bulk zeolite. The NEXAFS technique is demonstrated as a practical new probe of molecular level reaction chemistry in catalyst materials.

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