Surface Science
Room: C-108 - Session SS1-TuM

Hydrocarbon Catalysis
Moderator: J.L. Gland, University of Michigan

8:20am **SS1-TuM1 The Role of Defects in Surface Resistivity: The Unusual Case of Sulfur on Cu(100)**, ***R.G. Tobin***, Tufts University

Adsorbate-induced surface resistivity -- the change in electrical resistivity of a metal film when a gas adsorbs on its surface -- provides a simple but powerful probe of the dynamical interaction between conduction electrons and adsorbates.[1] The dominant mechanism is generally diffuse scattering of the electrons from the adsorbate, and the scattering cross section per adsorbate is usually nearly independent of adsorbate coverage. For sulfur on Cu(100), however, the resistivity increases rapidly with coverage up to a threshold, and then remains constant as the coverage increases further. This effect was first observed by Xu and Hirschmugl using infrared reflectance and a single crystal sample.[2] They attributed the rapid increase at low coverage to a large scattering cross section for S adsorbed on defect sites, with a near-zero cross section for S on terrace sites. In the present study the same behavior is seen in both the dc resistivity and the infrared reflectance of epitaxial Cu(100) thin films. The transition between the two scattering regimes, however, occurs at a higher coverage (~0.2 ML) than in the single-crystal measurements (0.04 ML). The role of defects is investigated by quantitatively estimating the defect density from CO adsorption measurements, and by sputtering the surface before adsorption to increase the defect density.

[1] R.G. Tobin, Surf. Sci., in press.

[2] X.F. Xu and C.J. Hirschmugl, Surf. Sci. 490 (2001) 69.

8:40am **SS1-TuM2 Chemistry of One-dimensional Metallic Edge States in MoS_2 Nanoclusters**, ***J.V. Lauritsen***, University of Aarhus, Denmark, *B.S. Clausen, H. Topsoe*, Haldor Topsoe A/S, Denmark, *F. Besenbacher*, University of Aarhus, Denmark

We report on interesting chemistry of MoS_2 nanoclusters, which we show to be able to hydrogenate and break up thiophene (C_4H_4S) molecules at unusual sites on the cluster edges. We associate this behavior with one-dimensional metallic electron states located at the perimeter of the otherwise insulating nanoclusters. Since MoS_2 nanoclusters constitute the basis of hydrotreating catalysts used to remove sulfur from oil products through the hydrodesulfurization (HDS) process, the kind of chemistry identified in this work has significant implications. Our approach exploits recent progress in the synthesis of a relevant catalyst model system, i.e. we can synthesize MoS_2 nanoclusters image them on the atomic-scale with STM.[1] With STM prominent electronic features are observed near the edges of triangular MoS_2 clusters, which are associated with 1D metallic edge states.[2] By adsorbing hydrogen and thiophene, we pin-point, in the STM studies, active sites on these metallic edge states and reveal signatures of thiophene reaction intermediates adsorbed onto the metallic edge state. At the cluster edges, we find that S-H groups form, which are involved in a hydrogenation reaction and subsequent C-S cleavage of thiophene. In an interplay with density functional theory we elucidate the reaction pathway and classify the adsorbed species as ring-opened thiolates. We have thus identified a new route for activating a relatively inert, sulfur containing molecule like thiophene. Unexpectedly, this process does not take place through direct interaction with the Mo atoms. Instead, metallic states on the fully sulfided edges have the ability to donate and accept electrons and thus act as catalytic sites just like ordinary metal surfaces.

[1] S. Helveg, J. V. Lauritsen et al. Phys. Rev. Lett. 84, 951 (2000).

[2] M. Bollinger, J. V. Lauritsen et al., Phys. Rev. Lett. 87, 196803 (2001).

9:00am **SS1-TuM3 Electron-Induced Dissociation and Reactions of Methyl Groups Adsorbed on Cu(110)**, *Y.L. Chan, P. Chuang*, National Taiwan University, Republic of China, *R. Klauser*, Synchrotron Radiation Research Center, Taiwan, Republic of China, *S-H. Chien*, ***T.J. Chuang***, National Taiwan University, Republic of China

Methylene was suggested in some prior studies to be the key species responsible for the propagation of long chain hydrocarbons from methyl groups on catalyst surfaces. So far, direct evidence to show the presence of such reaction intermediate remains elusive, particularly under UHV condition. With the combination of HREELS vibrational spectroscopy, TPD and LEED techniques, we have observed that CH_3(ads) groups adsorbed on Cu(110) can be dissociated by low energy electrons to form CH_2(ads). In subsequent thermal process, CH_2(ads) can react with coadsorbed CH_3(ads) to produce C_2H_4, C_3H_6 and C_4H_8 molecules desorbed from surface. The desorption peaks for the various alkenes center at the same temperature independent of the CH_2(ads) average surface concentration and exhibiting the first-order reaction kinetics. Furthermore, the product ratio of C_3H_6/C_2H_4 is found to be linearly proportional to the ratio of CH_2(ads)/CH_3(ads) concentrations. The results show that aggregation of the adsorbates and close proximity of the reactants in the form of two-dimensional islands may be essential for the chain propagation reactions. In this study, the e-beam irradiation effects on molecular dissociation and desorption are investigated in the electron energy range of 5-70 eV. Preliminary report of these effects was given recently,[1] and a detailed account will be presented in this paper.

[1] P. Chuang, Y.L. Chan, S.-H. Chien, R. Klauser and T.J. Chuang, Chem. Phys. Lett. 354,179 (2002).

9:20am **SS1-TuM4 Oxidative Coupling of Methane to Higher Hydrocarbons Using Li_2O/MgO Catalysts**, *J. Langohr, R. Heinisch*, ***F. Behrendt***, Technische Universität Berlin, Germany

Oxidative coupling of methane represents an important pathway to produce higher hydrocarbons especially those with two carbon atoms, i. e, ethane and ethane, representing a key component for chemical industry. The reaction scheme - which still is not completely understood -involves a number of steps with the heterogeneous formation of methyl radicals and the homogeneous recombination of methyl radicals to ethane as key parts. The second of these reactions is in competition with reactions leading to the total oxidation products carbon dioxide and water - a pathway occurring both homogeneously and heterogeneously. With respect to the concentration of methyl radicals the reaction order is one for the total oxidation but two for the formation of ethane. An increase of the concentration of methyl radicals should promote an increased production of the C_2 hydrocarbons. For the example of a set of Li_2O/MgO catalysts it is shown that an increase of the BET surface area - resulting in a higher number of active sites at the catalyst¹s surface - results in an increased yield of C_2 hydrocarbons. By variation of the preparation technique (aqueous mixtures of various Li and Mg salts are dried and then calcinated at different temperatures and periods of time) catalysts are produced which indeed show an increase in methane turn-over - without losing selectivity for C_2 hydrocarbons - with increasing surface area. The BET surface area is varied between 0.3 and 4.2 m^2/g. Ongoing experiments aim at further increasing this surface area. Modifications of the preparation technique will include calcination under low-pressure conditions and on carrier materials having high surface areas themselves, e. g., polyurethane foams or activated carbon.

9:40am **SS1-TuM5 The Dynamics of Alkane Adsorption on Pt(111), Pd(111) and Ni(111): Prediction from One Metal to Another?**, *C.-L. Kao*, Stanford University, *J.F. Weaver*, University of Florida, ***R.J. Madix***, Stanford University **INVITED**

The adsorption and reaction of alkanes on metal surfaces is fundamental to hydrocarbon catalysis. In order to adsorb the kinetic energy of the incident molecule must be dissipated in the gas-surface collision. To develop a predictive capability for the adsorption probabilities of alkanes on surfaces we have combined molecular beam methods with molecular dynamics simulations. The objective is to determine simple empirical potential parameters that govern the alkane-metal interaction from experimental measurements for a single alkane-surface combination and to use these parameters to predict trapping probabilities for other alkanes on other surfaces. A single set of potential parameters, determined from measurements of the trapping probabilities of ethane on Pt(111) can be used to predict the trapping probabilities of C3-C5 alkanes on Pt(111) and ethane and propane on Pt(110). More recently, these predictions have been extended to C1 - C5 alkane trapping on Pd(111). Palladium and platinum have similar lattice constants and Debye temperatures, differing primarily in their atomic mass, and thereby offer a good first order test of the predictive capability of the molecular dynamics simulations. Indeed, the trapping probabilities for Pd(111) are accurately predicted. Generally, the trapping probabilities for a given alkane are higher on Pd(111) due to the lower mass of the palladium atoms. The simulations show the importance of both the excitation of lattice vibrations and cartwheel rotational motion in affecting trapping. Predictions for Ni(111) are potentially more challenging, since the Ni-Ni force constants are much higher and both the mass and lattice parameter differ significantly from those of platinum. The theory correctly predicts that the adsorption probabilities on Ni(111) are lower than those for both Pt(111) and Pd(111). In general trapping probabilities are predicted to within about 50%.

10:20am **SS1-TuM7 Molecular Mechanisms of Propylene Adsorption and Oxidation on the Stepped Pt(411) Surface**, ***H.D. Lewis***, *D.J. Burnett, A.M. Gabelnick*, University of Michigan, *D.A. Fischer,* National Institute of Standards and Technology, *J.L. Gland,* University of Michigan

The influence of surface defects on the chemistry of propylene adsorption and oxidation was investigated using temperature-programmed reaction spectroscopy (TPRS) and in-situ fluorescence yield soft x-ray techniques on the stepped Pt(411) surface. Mass spectrometer based TPRS studies show that propylene adsorbed on Pt(411) at 100 K undergoes disproportionation and decomposition to propylene, propane, hydrogen and surface carbon. Reacting coadsorbed propylene with excess oxygen, complete oxidation occurs with oxydehyrdogenation to water preceding skeletal oxidation to carbon dioxide. Based on the qualitative mechanistic understanding from TPRS, in-situ oxidation experiments were performed in oxygen pressures up to 0.02 Torr. The mechanism is the same in flowing oxygen, and preadsorbed propylene is completely oxidized by 475 K. The 280 K initiation temperature for oxydehydrogenation is independent of oxygen pressure, while the initiation temperature for skeletal oxidation is oxygen pressure dependent beginning at 370 K in 1 x 10^{-5} Torr oxygen and decreasing to 300 K in 0.02 Torr oxygen. A stable intermediate is observed after oxydehydrogenation is complete. The molecular mechanism for propylene oxidation on Pt(411) with both propylene and oxygen in the gas phase was also studied. With increasing oxygen pressure less propylene is adsorbed and the onset temperature for deep oxidation decreases. Taken together, results indicate that the inhibition of oxygen adsorption is important in limiting this complex oxidation reaction. Results for propylene oxidation on this stepped surface are compared to studies on Pt(111) to delineate the role of surface defects in this interesting surface reaction network.

10:40am **SS1-TuM8 Catalytic Arene Oxidation on Supported Platinum Nanoparticles**, ***A.L. Marsh***, University of Michigan, *G.E. Mitchell,* The Dow Chemical Company, *D.A. Fischer,* National Institute of Standards and Technology, *J.L. Gland,* University of Michigan

The cleanup of volatile organic compounds from industrial emissions is a current environmental issue that requires knowledge of molecular-level mechanisms for catalytic processes. Aromatics such as benzene, toluene, and chlorobenzene are often present in emissions because of their stability. However, these molecules can be removed by oxidation over nanoparticulate-supported catalysts. In order to better understand the mechanisms of catalytic oxidation, the reactions of benzene, toluene, and chlorobenzene on a commercial alumina-supported platinum catalyst have been characterized both in vacuum and in the presence of oxygen. Molecular-level mechanisms for both decomposition and oxidation have been determined using Temperature-Programmed Reaction Spectroscopy. The structures of intermediates present during oxidation or decomposition have been identified using Fluorescence Yield Near-Edge Spectroscopy. Comparisons will be made to the chemistry on the Pt(111) surface in an effort to show the effects of particle size and of the support. Substantial substituent effects on the chemistry of the aromatic ring are also observed. This molecular-level understanding of these reactions will aid in tailoring catalysts for the efficient cleanup of industrial emissions.

11:00am **SS1-TuM9 In situ XPS Investigation of the Methanol Oxidation Over Copper**, ***H. Bluhm***, *M. Hävecker, A. Knop-Gericke,* Fritz Haber Institute of the Max Planck Society, Germany, *V.I. Bukhtiyarov,* Boreskov Institute of Catalysis, Russia, *D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory, *R. Schlögl*, Fritz Haber Institute of the Max Planck Society, Germany

We have used in situ X-ray photoelectron spectroscopy (XPS)[1] in combination with mass spectrometry to investigate the partial oxidation of methanol to formaldehyde over a polycrystalline copper sample. The experiments were performed at a methanol to oxygen flow ratio of 3:1 (total pressure 0.4 torr) in the temperature range from 300 K to 750 K. The correlation of in-situ XPS spectra of the copper surface and the simultaneously obtained mass spectrometer data (which show the catalytic activity) allow us to draw conclusions about the electronic state of the catalyst under reaction conditions. Valence band and Oxygen 1s spectra show that after the onset of the catalytic reaction at T>550 K the copper surface has a metallic character. The Oxygen 1s spectra reveal that at least two different oxygen species with binding energies (BE) of 529.7 eV and 531.4 eV, respectively, are present at the catalytically active Cu surface. The O 1s peak at 529.7 eV is assigned to chemisorbed oxygen at the Cu surface. The integrated intensity of the chemisorbed oxygen peak is proportional to the amount of formaldehyde that is produced in the catalytic reaction. The peak at 531.4 eV is assigned to subsurface oxygen. The formaldehyde yield increases linearly with the integrated intensity of the subsurface oxygen peak, up to a concentration of the equivalent of about one monolayer of subsurface oxygen. A further increase of the amount of subsurface oxygen does not lead to an increase of the formaldehyde yield.

[1] D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, submitted to Rev. Sci. Instrum.

11:20am **SS1-TuM10 Determination of the Adsorption Site of a Polyatomic Adsorbate Using Vibrational Spectroscopy and ab initio Calculations: Methoxy and Ethoxy on Cu(100)**, ***P. Uvdal***, *M.P. Andersson*, Lund University, Sweden

Using infrared vibrational spectroscopy and ab initio electronic structure calculations of small metal cluster models we have determined the adsorption site of methoxy and ethoxy on Cu(100). The experimental intramolecular vibrational frequencies are very well reproduced by the model cluster representing the four-fold hollow adsorption site. In contrast calculated frequencies for intermolecular modes modeled by clusters representing bridge and on-top adsorption is not not reproduce as well.

11:40am **SS1-TuM11 A Model Catalyst with Selectivity Controllable Functions: The Effects of Frequency in Thickness Extension Mode Resonance Oscillation on Ethanol Decomposition Over a Thin Ag Film Deposited on a Ferroelectric z-cut $LiNbO_3$ Single Crystal**, ***N. Saito***, *Y. Yukawa, H. Nishiyama, Y. Inoue*, Nagaoka University of Technology, Japan

The resonance oscillation of acoustic waves is generated on a poled ferroelectric crystal by a piezoelectric effect. We have shown that the thickness extension mode resonance oscillation (TERO) has the ability to remarkably change the reaction selectivity over thin metal catalysts deposited on a z-cut $LiNbO_3$ (z-LN) crystal.[1] The TERO has a series of resonance frequencies (the first, the second, the third and so on) determined by the crystal constants. A z-LN crystal shows 3.5(first), 10.8 (second) and 17.9 (third) MHz. It is interesting to see the frequency effects on TERO-induced selectivity changes. In the present work, the TERO of 10.8 and 17.9MHz were employed for ethanol decomposition on a thin Ag film catalyst deposited, and the results were compared with those reported previously for 3.5MHz. The TERO of 10.8 and 17.9 MHz at 1.5W caused the enhancement of ethylene production without significant changes in acetaldehyde production. The selectivity for ethylene production, S_e, increased from 62% without the TERO to 96% for 3.5MHz, 85% for 10.8MHz and 75% for 17.9MHz. The selectivity increases became small with increasing resonance frequency. Laser Doppler measurements showed that the TERO generated randomly distributed standing waves vertical to the surface. With increasing frequency, the magnitude of the waves, corresponding to lattice displacement, decreased (98 nm for 3.5 MHz, 28 nm for 10.8 MHz and 15 nm for 17.9MHz at 1W), whereas the number of the standing waves per unit area increased remarkably. In photoelectron emission spectroscopy, the TERO shifted the threshold energy of photoelectron emission from Ag surface by 0.08-0.25eV. The present results indicate that the magnitude and the density of standing waves strongly related to activity enhancement and selectivity changes. A mechanism of the frequency-dependent TERO effects is discussed.

[1] N.Saito and Y.Inoue, J.Chem. Phys. 133,469(2000).

Authors Index

Bold page numbers indicate the presenter