Surface Science
Room 210B - Session SS1-TuM

Catalytic Reactions: The Role of Surface Steps and Structure

Moderator: G.B. Fisher, Delphi Research Labs

8:20am **SS1-TuM1 Surface Reactions and Catalysis***, **G.A. Somorjai,*** Lawrece Berkeley National Laboratory and University of California, Berkeley **INVITED**

New techniques developed over the past ten years permit the monitoring of surface structure and surface composition at high pressures and at solid-liquid interfaces. Among them sum frequency generation (SFG) vibrational spectroscopy and high pressure scanning tunneling microscopy high pressure (STM) have been used in my laboratory to monitor catalyst surfaces during reaction. C-H bond activation was studied using C6 hydrocarbons, and reaction intermediates that produce branched isomers or benzene on platinum (111) surfaces (both components of high-octane gasoline) were detected by SFG. High pressure STM reveals surface mobility of adsorbates during catalytic hydrogenation and active metal surfaces. Poisoning the reaction by the coadsorption of carbon monoxide also produces ordered surface structures. These studies indicate that diffusional mobility of adsorbates correlates with catalytic activity.

9:00am **SS1-TuM3 The CO-oxidation Reaction on Pt(111) and Pt(553): The Role of Steps***, **J.N. Andersen,** J. Gustafson, M. Borg, A. Mikkelsen, J. Weissenrieder, E. Lundgren,* Lund University, Sweden*; W.X. Li, B. Hammer,* Aarhus University, Denmark

Catalytic materials often consist of small metallic particles dispersed on a support. The large proportion of undercoordinated (edge) atoms on such small particles may substantially influence the catalytic activity. Experimentally, the influence of undercoordinated atoms may be scrutinized by studying vicinal surfaces using methods that allow separate monitoring of what happens at the steps. Theoretically, the effects may be simulated using density functional theory (DFT) based total energy calculations. We present experimental and theoretical results for the adsorption of O and CO as well as for the CO-oxidation on Pt(111) and Pt(553) surfaces using high resolution core level spectroscopy and DFT based slab calculations. The results directly demonstrate that Pt(553) is more efficient in oxidizing CO than Pt(111), and allow us to obtain a very detailed picture of the microscopic processes responsible for this increased reactivity. A crucial result is the experimental and theoretical demonstration that CO molecules adsorbed at steps and on terraces, respectively, can be distinguished via their C 1s binding energies. These C1s fingerprints allow us to follow in a very detailed manner where CO molecules adsorb and react with preadsorbed oxygen. We study the CO oxidation by preadsorbing oxygen at 310K followed either by exposure to CO at the chosen reaction temperature or by annealing at the chosen reaction temperature of a CO overlayer adsorbed at low temperature. The results show that the CO2 production is more efficient on Pt(553) than on Pt(111). By utilizing the mentioned core level fingerprints, we show directly that the increased oxidation rate on Pt(553) is due to that the oxygen adsorbed in the proximity of steps is more reactive than oxygen adsorbed on the terraces. Comparison to theoretical results from DFT proves vital in fully understanding these experimental results and constructing the detailed microscopic model.

9:20am **SS1-TuM4 Controlling the Catalytic Reactivity and Selectivity of Ni Surfaces by Step Blocking**, ***R.T. Vang,*** University of Aarhus, Denmark*; K. Honkala,* Technical University of Denmark*; S. Dahl,* Haldor Topsøe A/S, Denmark*; E.K. Vestergaard, J. Schnadt, E. Lægsgaard,* University of Aarhus, Denmark*; B.S. Clausen,* Haldor Topsøe A/S, Denmark*; J.K. Nørskov,* Technical University of Denmark*; F. Besenbacher,* University of Aarhus, Denmark

Step or defect sites have been shown to dominate the reactivity of catalytic surfaces for the dissociation of a number of diatomic molecules, but so far no studies have addressed the influence of steps in the decomposition of more complex molecules. In most catalytic processes involving hydrocarbon molecules, selectivity (between, e. g., C-H and C-C bond breaking) is crucial for the overall efficiency of the catalyst. In this study we have used STM and DFT calculations to investigate the dissociative adsorption of a simple molecule, CO, as well as a more complex molecule, ethylene (C@sub 2@H@sub 4@), on Ni(111). The STM studies reveal that both molecules decompose at the step edges at a much higher rate than on the (111) facets. These observations are supported by DFT calculations showing a much lower activation barrier for decomposition at a step site compared to a terrace site. Furthermore, the steps are shown to have a crucial influence on the selectivity of the Ni(111) surface towards ethylene decomposition, in the sense that the step effect is much more pronounced for C-C bond breaking than for C-H bond breaking. We also demonstrate how we can control the number of active step sites and thus the reactivity by depositing small amounts of Ag, which from STM studies are shown to block all the step sites on the Ni(111) surface. Finally we exploit this new principle of step control by synthesizing a new high-surface area supported NiAg alloy catalyst. We show in flow reactor tests that the NiAg catalyst has a much lower activity for ethane hydrogenolysis than a similar Ni catalyst, thus confirming that we can block C-C bond breaking by step control.

9:40am **SS1-TuM5 High Pressure Scanning Tunneling Microscopy Study on CO Poisoning of Ethylene Hydrogenation on Metal Single Crystals***, G.A. Somorjai,* University of California, Berkeley*; **D.C. Tang**[1], M. Salmeron,* Lawrence Berkeley National Laboratory*; K.S. Hwang,* University of California, Berkeley

The nature of catalyst poisoning under reaction conditions is an important question in catalysis science@footnote 1@@super ,@@footnote 2@. During a reaction the catalyst surface is covered with a dense layer of adsorbates in equilibrium with the gas phase. This layer consists of reactants, inactive spectator molecules, and active poisoning adsorbates@footnote 3@. For the reaction to occur the surface should remain flexible, atomic rearrangements should be possible, and adsorbate mobility should be high enough so that favorable adsorption sites can be accessed. Using a high pressure scanning tunneling microscope we monitored the co-adsorption of hydrogen, ethylene and carbon dioxide on rhodium (111) and platinum(111) crystal faces in the mTorr pressure range at 300 K in equilibrium with the gas phase. We show that poisoning occurs when surface mobility is suppressed and the adsorbate species become locked into static ordered structures. During the catalytic hydrogenation of ethylene to ethane in the absence of CO the metal surfaces are covered by an adsorbate layer that is very mobile on the time scale of STM imaging. We found that the addition of CO poisons the hydrogenation reaction and induces ordered structures on the single crystal surfaces. Several ordered structures were observed upon CO addition to the surfaces pre-covered with hydrogen and ethylene: domains of c(4 x 2)-CO+C@sub 2@H@sub 3@, previously unobserved (4 x 2)-CO+3C@sub 2@H@sub 3@, and (2 x 2)-3CO on Rh(111), and a (@sr@19 x @sr@19)R23.4° on Pt(111). A mechanism for CO poisoning of ethylene hydrogenation on the metal single crystals was proposed, in which CO blocks surface metal sites and reduces adsorbate mobility to limit adsorption and reaction rate of ethylene and hydrogen. @FootnoteText@ @footnote 1@ Bartholomew, C. H. App. Catal. A 212, 17-60 (2001).@footnote 2@ Kumbilieva, K., Kiperman, S. L. & Petrov, L. Kinet. Catal. 36, 73-79 (1995).@footnote 3@ Zaera, F. Prog. Surf. Sci. 69, 1-98 (2001).

10:00am **SS1-TuM6 Iridium (210): Nanoscale Faceting and Structure-sensitivity of Surface Reactions***, **I. Ermanoski,** W. Chen, T.E. Madey,* Rutgers University

The stability of the atomically rough fcc Ir(210) surface depends on its cleanliness. The clean surface is planar and unreconstructed after heating in UHV up to 2100K. The oxygen-covered surface is, however, structurally unstable, and undergoes a dramatic faceting transformation: Nanometer-sized pyramids exposing {311} and (110) faces are formed upon deposition of more than 0.5 monolayers of oxygen and annealing to 600K, completely replacing the original planar surface. The oxygen-covered faceted surface reversibly reverts to planar at ~ 900K. LEED and STM experiments show that pyramid sizes increase with annealing temperature, and can reach ~25nm. This growth does not have an effect on the orientation of the facets. The complete thermal desorption of oxygen from iridium requires a temperature of ~1400K, and causes a complete destruction of the faceted structure. Nevertheless, by using catalytic CO oxidation (at ~550K) and reaction of H2 to form H2O (at ~400K), we have been able to routinely prepare a clean faceted surface in situ. Owing to the ability to prepare clean surfaces of different nano-scale structure (planar, faceted, varying facet sizes) from Ir(210), we have found it to be an excellent substrate for studying the kinetics of surface chemical reactions that depend on the surface structure. Our temperature programmed desorption (TPD) experiments show that thermal decomposition of acetylene, hydrogen recombinative desorption and ammonia decomposition all exhibit structure sensitivity, and proceed differently on the planar and faceted surfaces. Furthermore, differences are observed in reactions on clean

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faceted surfaces with different average facet sizes, showing that particle-size effects also play an important role in these reactions.

10:20am **SS1-TuM7 Kinetics of Co Oxidation Catalyzed by Supported Iridium Particles in a Wide Pressure Range**, ***M.M. Sushchikh**, E.W. McFarland,* University of California, Santa Barbara

Recent work in ultra-high vacuum (UHV) has demonstrated kinetic hysteresis in the CO oxidation reaction on single crystal iridium surfaces@footnote 1@,@footnote 2@; the reaction rate variation in CO and O@sub 2@ partial pressures varied depending upon the initial partial pressure. The phenomena observed were explained using a Langmuir-Hinshelwood mechanism. We have investigated the phenomena at elevated pressures on a supported Ir catalyst to test the validity of the model scaled more than 9 orders of magnitude in pressure. It is expected that sticking coefficients at the high surface coverages are not equal to those at lower coverages and as the pressure approaches atmospheric, kinetic phase transitions are affected by changes in the gas composition. Furthermore, on the supported metal particulate catalyst heat transfer effects are more complex. The rate of CO@sub 2@ formation on Ir as a function of reactant pressures (up to 1 atm) was monitored and excellent agreement was found with the UHV experiments. @FootnoteText@ @footnote 1@ S.Wehner, F.Baumann, M.Ruckdeschel, J.Küppers, J.Chem.Phys., 119(13)(2003)6823.@footnote 2@ S.Wehner, F.Baumann, J.Küppers, Chem.Phys.Lett., 370(2003)126.

10:40am **SS1-TuM8 High Pressure Methane Activation on Platinum Single Crystal Surfaces**, ***A.L. Marsh**, R.M. Rioux, J.S. Gaughn,* University of California, Berkeley; *G.A. Somorjai,* University of California, Berkeley and Lawrence Berkeley National Laboratory

The interest in alternative sources of energy has generated research on the conversion of hydrocarbons such as methane into hydrogen for both stationary and mobile fuel cell applications. To optimize the processes for the conversion of methane into hydrogen using platinum catalysts, reaction mechanisms must be characterized at a molecular-level. For that reason, we have characterized the high-pressure (up to 40 Torr) activation of methane on platinum single crystal surfaces using infrared-visible sum frequency generation (IR-VIS SFG) spectroscopy and Auger electron spectroscopy (AES). At low temperatures (300 K) and high pressures (1 Torr), methane is activated to form a number of different dehydrogenated intermediates on the Pt(111) surface. The extent of dehydrogenation increases with increasing temperature and pressure. In addition, the amount of carbon deposited on the surface increases with increasing temperature and pressure. Comparisons are made with molecular beam and high pressure experiments on other metal single crystal surfaces to develop a detailed mechanistic picture of the activation of methane at high pressures on platinum catalyst surfaces.

11:00am **SS1-TuM9 Nanoporous Pd Films Grown Via Ballistic Deposition: Structural And Catalytic Properties**, ***J. Kim**, Z. Dohnálek, B.D. Kay,* Pacific Northwest National Laboratory

Hydrogenation of ethylene was studied on dense and nanoporous Pd films using molecular beams and temperature programmed desorption (TPD). Porous films were deposited on a Mo(100) substrate at temperatures ranging from 22 to 300 K. Due to limited surface mobility at such low temperatures, the growth is dictated by a ballistic deposition mechanism. The adsorption properties of the films were characterized as a function of Pd deposition angle as well as growth and post-annealing temperatures using N@sub 2@ physisorption. The highest surface area of ~ 80 m@super 2@/g was observed for films grown at 85° and 22 K. Upon annealing to 300 K, the films lose ~40 % of their area, further annealing to 500 K leads to complete densification. Reactivity studies show that nanoporous Pd, covered with H and subsequently saturated with ethylene at 22 K, is highly efficient catalyst for ethylene hydrogenation. This is in sharp contrast with dense Pd films where only trace amounts of ethane were observed. As seen from the reaction yields on films preannealed to various temperatures, the number of catalytically active sites decreases faster than the area of the films. Additionally, cycling of the ethylene hydrogenation reaction also leads to a decrease of ethane production due to poisoning of the active sites.

11:20am **SS1-TuM10 Novel NO Adsorption States on Pd (111) at Elevated Pressures: Irreversibility of the Effects of Temperature and Pressure on Heterogeneous Catalytic Systems**, ***E. Ozensoy**[1],* Texas A&M University; *Ch. Hess,* Fritz-Haber-Institut der Max-Planck-Gesellschaft,Germany; *C. Yi,* Texas A&M University; *D. Loffreda,* Institut de Recherches sur la Catalyse, Centre National de la Recherche Scientifique, France; *D.W. Goodman,* Texas A&M Univeristy

NO adsorption states on Pd (111) single crystal model catalyst surface were investigated using in-situ polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) and density functional theory (DFT) calculations within 10@super -9@ - 400 mbar and 25-600 K. Vibrational spectroscopic data and DFT calculations indicate that besides the well-known monomeric NO adsorption states, a novel high-coverage monomeric adsorption state was observed at elevated pressures which was identified to have a (3x3)-7NO structure. NO-dimer states were also determined to exist under both ultra high vacuum (UHV) and elevated pressure conditions, however the nature of the NO-dimers that are formed at low and high pressures were found to be different in terms of their surface coverage, the strength of their interaction with the Pd (111) surface and the intrinsic N-N bond strength. In addition, the formation of dinitrosyls at @theta@@sub NO@ > 0.778 ML was also observed and found to take place only at elevated pressure and temperature conditions suggesting that not all of the thermodynamic equilibrium states at elevated temperatures and pressures are kinetically available at low temperatures and pressures for NO/Pd (111), emphasizing the danger of extrapolating the results of traditional surface scientific experiments performed under to UHV conditions to elevated pressure and temperature cases where the behavior of the system can show remarkable deviations from the expectations.

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