Surface Science
Room 121 - Session SS2-WeM
Surface Reactions on Metals

Moderator: D.R. Mullins, Oak Ridge National Laboratory

8:20am **SS2-WeM1 CO Oxidation on Au Crystals: Studies on the Nanoscale***, T. Bär, T. Visart de Bocarmé,* Free University of Brussels, Belgium*; B.E. Nieuwenhuys,* Leiden University, The Netherlands*; **N. Kruse**,* Free University of Brussels, Belgium

Until recently gold was regarded as a metal of little interest for applications in heterogeneous catalysis. The discovery that supported gold catalysts are among the most active ones in CO oxidation has completely changed this picture. The mechanism of the reaction is, however, still under debate. In particular, the question for the role of the support material and for possible impurity effects must be asked. With this background we have studied oxygen activation and reaction with CO on pure Au single crystal specimens, in the absence of any oxidic support material, using Field Ion Microscopy (FIM) and atom-probe techniques. FIM-images (using H@sub 2@ and Ne as imaging gas at 55 K and at field strengths of up to 35 V/nm) indicated clean, nearly hemispherically shaped Au crystals of (111) orientation. Exposure of such a specimen to O@sub 2@ gas at 100 mbar and temperatures between 300 and 450 K, in the absence of an electric field, led to oxygen chemisorption and formation of a "surface oxide". In particular, layer edges of (111) and (100) planes were decorated by oxygen atoms. In situ studies of surface oxide formation performed in an O@sub 2@ gas atmosphere of 1,0*10@super -4@ mbar showed that the presence of an electric field of 12-15 V/nm significantly enhances oxygen adsorption. Exposure to CO gas at 300 K led to the removal of the surface oxide, i.e. CO@sub 2@ formation. This was associated with the occurrence of a reaction front which started in the apex centre, i.e. the (111) pole, and extended in nearly concentric circles to the outskirts of the Au specimen. Using video-FIM several cycles of oxide build-up and titration with carbon monoxide were performed to demonstrate the reversibility of the surface processes. Using atom-probe techniques during the ongoing reaction AuO and AuCO ionic species could be observed in variable amounts. We conclude that pure gold crystals are active catalysts for the CO oxidation at 300 K.

8:40am **SS2-WeM2 Surface Phase Transitions of Pt(110) Studied by Desorption Dynamics of Product CO@sub 2@ in Steady-state CO Oxidation***, **I. Rzeznicka**, M.G. Moula, T. Matsushima,* Hokkaido University, Japan

This paper reports the first confirmation of the transition from (1x2) to (1x1) through angular distribution analysis of desorbing product CO@sub 2@. Clear distribution changes were observed in the inhibited region where CO retards its oxidation. The surface phase transition of Pt(110)from (1x1)to(1x2) yields differently-oriented adsorption sites of oxygen. The CO oxidation on these sites induces differently-collimated CO@sub 2@ desorption, since this desorption mostly collimates along the local normal of the site. Both the angular and velocity distributions of desorbing CO@sub 2@ will switch sharply around the transition condition. This phenomenon was examined in steady-state CO oxidation on Pt(110) in a wide range of surface temperature and reactant pressures by means of cross-correlation time-of-flight techniques. In the active region where the surface is covered by O(a), desorbing CO@sub 2@ mostly collimated in a two-directional way along +25° or -25° off the surface normal in the (001) plane. This indicates CO@sub 2@ formation on the declining (111) terraces of the (1x2) form. On the other hand, in the inhibited region where the surface is mostly covered by CO(a), the normally directed desorption was sharply enhanced at a critical CO pressure where the two-directional components were suppressed. Below 3x10@super -4@ Torr of fixed O@sub 2@, this critical pressure shifted from the kinetic transition pressure (where the inhibition by CO starts) to higher values with increasing surface temperature. This critical point was confirmed to indicate the completion of the phase transition from LEED and CO adsorption measurements.

9:00am **SS2-WeM3 Dynamic Spatial Patterns in a Surface Reaction - The Microscopic and Mesoscopic Scales***, **J. Wintterlin**, C. Sachs, M. Hildebrand, S. Voelkening, G. Ertl,* Fritz-Haber-Institut, Germany **INVITED**

One of the most spectacular observations in surface catalytic reactions is the formation of dynamic spatial patterns that are connected with non-linear terms in the reaction kinetics. We have investigated such phenomena, both on the atomic and the mesoscopic scales, for the catalytic water formation from adsorbed oxygen and hydrogen on a Pt(111) surface. By means of scanning tunneling microscopy (STM) propagating reaction fronts were observed on a 10 to 1000 nm scale. Simulations were performed with a reaction diffusion model that contains an autocatalytic reaction sequence. The model predicts reaction fronts, formed by travelling interfaces between adsorbed oxygen and water. The fronts contain the reaction intermediate OH, in full qualitative agreement with the experiment. However, quantitative simulations reveal deviations from the experiment, demonstrating the limitations of this description. The atomic scale processes in the fronts, which were resolved by STM, indicate that the reasons for these deviations lie in the simplifications of standard reaction-diffusion models, namely the assumptions of a random occupation of adsorption sites and of spatially independent kinetic constants.

9:40am **SS2-WeM5 Hydrogenation of Oxygen on Pd(111)***, **T. Mitsui**,* Lawrence Berkeley National Laboratory*; M.K. Rose, E. Fomine,* University of California, Berkeley*; F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

The reaction of hydrogen with (2x2) oxygen islands on Pd(111) has been studied with scanning tunneling microscopy under UHV conditions. Hydrogenation of oxygen, to form OH, was observed at 25 K. The reaction destabilizes the (2x2) ordering of oxygen and results in the formation of new (@sr@3x@sr@3) islands above 120 K. The OH islands remain stable up to 210 K even after the H@sub 2@ gas phase has been removed. Above this temperature, however the OH species decompose back to oxygen which reorganizes into (2x2) structures. The (@sr@3x@sr@3) OH islands can be formed again by additional hydrogen. If H@sub 2@ gas phase (10@super -8@ torr) is maintained during heating at 220 K, the (2x2) oxygen islands disappear completely from the surface by forming of H@sub 2@O that desorbs. Based on these results, the mechanisms of the formation of H@sub 2@O on Pd(111) from oxygen and hydrogen will be discussed.

10:00am **SS2-WeM6 Abstraction of Si and SiH@sub x@ (x=1,2,3) Adsorbed on Cu(100) Surfaces with Gaseous D towards Silane***, **D. Kolovos-Vellianitis**,* EPIII, University of Bayreuth, Germany*; Th. Kammler,* Focus GmbH, Germany*; Th. Zecho, J. Kueppers,* University of Bayreuth, Germany

The study of metal-silicide interfaces is of significant imterest because of their important technological applications. In particular, a better understanding of the formation of silicon structures on metal surfaces using chemical vapor deposition (CVD) of silane and disilane can provide valuable information about the elementary processes of adsorption, dissociation and reaction with other gaseous atoms. The interaction of silane and disilane with Cu(100) surfaces was studied in the temperature range 77 K to 650 K with thermal desorption and Auger electron spectroscopies. Silane admission to Cu(100) at low temperatures initially leads to a complete decomposition of the silanes into adsorbed Si and H. Close to saturation of the surface with H, SiH@sub x@ species remain intact on the surface. They were identified as SiH@sub 3@ and to a smaller extent SiH@sub 2@ by monitoring the silane abstraction products and their kinetics during admitting gaseous D to the surface between 77 K and 200 K. Silane desorption through recombination of SiH@sub 3@ and SiH@sub 2@ with adsorbed H occurs around 157 K and 224 K, respectively. After hydrogen desorption around 300 K a Si covered surface remains, which can be converted to a clean Cu(100) surface by activating Si bulk diffusion around 700 K. Adsorbed Si is abstracted from the surface below 200 K by gaseous H via formation of silane through a sequence of 4 hydrogenation steps. The first hydrogenation reaction is rate determining and is significantly accelerated by increasing the temperature between 77 K and 200 K. Above 200 K a thermally unstable SiH@sub x@ species blocks the abstraction reaction. The reaction kinetics phenomenology is in accordance with an Eley-Rideal scenario.

10:20am **SS2-WeM7 Catalytic Reactions on Alkali-modified Vicinal Cu(100) Surfaces***, **J Onsgaard**,* Aalborg University, Denmark*; J.P. Godowski,* University of Wroclaw, Poland*; S.V. Hoffmann,* Aarhus University, Denmark*; L. Bech,* Odense University, Denmark

Coadsorption of atoms and molecules with alkali-metal(AM) atoms on single crystal metal surfaces is of importance in heterogenous catalysis. The roles of AM (K or Cs) coverage and steps on vicinal Cu(100) surfaces - Cu(115) and Cu(117) - have been studied with respect to reactivity with low-molecular gases. It is demonstrated that the presence of steps and AM in the submonolayer coverage regime enhances the reactive properties of these surfaces. The Cu(115) surface, particularly, but also the Cu(117) surface modified with AM exhibit a high surface reactivity. The processes studied include dissociation of CO and synthesis of formate from coadsorption of H and CO@sub 2@. The C and O 1s core level shifts and the changes in the intensities of the satellite peaks are discussed in terms of the CO-substrate and/or the interatomic C-O interactions. A series of techniques, including photoelectron spectroscopy based on synchrotron radiation, thermally programmed desorption, work function measurements and LEED has been used.

11:00am **SS2-WeM9 Formation of Methylaminomethylidyne(>CNH(CH@sub 3@)) by Hydrogenation of Methyl Isocyanide and by Dehydrogenation of Dimethylamine on Pt(111)***, **D.H. Kang**, M.W, Trenary,* University of Illinois at Chicago

Fourier transform-reflection absorption infrared spectroscopy(FT-RAIRS) and temperature programmed desorption (TPD) have been used to study the adsorption and the surface reaction of methyl isocyanide (CNCH@sub3@) and dimethylamine ((CH@sub3@)@sub2@NH)) on the Pt(111)surface. Our previous studies have shown that the CN containing molecules, like azomethane (CH@sub3@N=NCH@sub3@), methylamine (CH@sub3@NH@sub2@) and hydrogen cyanide (HCN), have a common highly stable intermediate, aminomethylidyne (>CNH@sub2@), which is an aminocarbyne (>CNR@aa R@) species. An aminocarbyne species is a likely surface intermediate that could be formed by hydrogenation of the isocyanides and by dehydrogenation of amines.It is, therefore, of great interest to understand the adsorption and surface reaction of isocyanides and amines on metal surfaces. At low coverage and 85 K, methyl isocyanide adsorbs at on-top sites with an upright structure and then adsorbs on bridge sites at higher coverage. The RAIR spectra show new peaks by exposing hydrogen to the sample at or above 200 K, indicating a new surface species formed by hydrogenation. This species is identified as methylaminomethylidyne (MAM),(>CNH(CH@sub3@)),and exists as a stable species up to 350 K. Dimethylamine (DMA) adsorbs molecularly at 85K and the RAIR spectra show the same characteristic peaks as the hydrogenation of methyl isocyanide after annealing the sample to 350 K. This MAM species could be formed by the dehydrogenation of DMA as shown by TPD. At 400 K, the MAM species changes to a (>CNCH@sub3@) species, by dehydrogenation of the N-H bond and part of the (>CNCH@sub3@) species rearranges to the on-top site methyl isocyanide. When coadsorbing hydrogen at 300 K following annealing the sample to 400 K, part of the (>CNCH@sub3@) species changes to MAM by hydrogenation. The RAIR spectra also show peaks corresponding to aminomethylidyne (>CNH@sub2@), suggesting the existence of CN on the surface at 400 K.

11:20am **SS2-WeM10 Experimental and Theoretical Imaging of the Decomposition of Furan on Pd(111)***, **A. Loui,*** University of California, Davis*; D.N. Futaba,* Hokkaido University, Japan*; S. Chiang,* University of California, Davis

Experimental and theoretical studies have been performed on the decomposition of furan, C@sub4@H@sub4@O, adsorbed on Pd(111). The reaction of furan on this substrate has been previously studied using LITD/FTMS.@footnote 1@ In that study, furan was observed to decompose to H, CO, and C@sub3@H@sub3@ in the temperature range of 280-320 K; the latter species can then dimerize to form benzene above 350 K. Using scanning tunneling microscopy, our observations of the pre-reaction surface at 126 K show features adsorbed along the upper step edges, which match theoretical images of furan@footnote 2@ (generated using Extended Hückel Theory) in overall shape, size and internal structure. Comparison of the calculated and experimental furan features show that these molecules seem to preferentially orient with the oxygen atom facing away from or towards the step edge. Data obtained in the temperature range of 280-320 K show evidence of decomposition, which is consistent with the previous desorption studies. We have observed two distinct types of features that are discernible based on size, location and internal detail. The larger features populate the upper step edge region and are consistent with the data obtained at 126 K for unreacted furan. The smaller features appear to be clumped along the lower step edges. Based on the size and the known reaction products, we attribute these features to C@sub3@H@sub3@. In some reaction data, this species is resolved as an oblong feature with a bisecting node, agreeing well with the calculated images for flat-lying C@sub3@H@sub3@ molecules in shape, size and internal structure. These experiments indicate that there is a fundamental difference in the properties of the upper step edge versus the terrace with respect to this decomposition reaction. @FootnoteText@ @footnote 1@ Caldwell, T. E. and Land, D. P., Polyhedron, 16(18), 3197 (1997). @footnote 2@ Futaba, D. N. and Chiang, S., J. Vac. Sci. Technol. A, 15(3), 1295 (1997).

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