Wednesday Afternoon, October 17, 2007

Surface Science

Room: 608 - Session SS1-WeA

Reactions on Metal Surfaces

Moderator: A.J. Gellman, Carnegie Mellon University

1:40pm **SS1-WeA1 Thermally Induced Oxidation and Decomposition Products from NCO /Cu(001)**, ***E.Z. Ciftlikli***, *A.V. Ermakov, J. Lallo, S. Rangan, I.G. Shuttleworth, E.Y.-M. Lee, B.J. Hinch,* Rutgers, The State University of New Jersey, *S.D. Senanayake*, Oak Ridge National Laboratory

We report on high-resolution quantitative XPS studies, and complementary NEXAFS and TPD studies of adsorbed isocyanate (NCO) species on Cu(001). Adsorbed NCO can be prepared by room temperature dissociative adsorption of isocyanic acid (HNCO).[1] XPS and NEXAFS confirm that, following hydrogen desorption, solely NCO remains. This is stable to at least 473K. However this species is prone to oxidation from any coadsorbed atomic oxygen. At temperatures as low as 373K, quantitative XPS results indicate CO_2 desorption, while the surface N concentration is conserved. NCO oxidation to adsorbed nitrogen and CO_2, continues until the atomic oxygen is depleted. This chemistry, while observed over a wide range of initial O surface coverages, is however modified in the presence of CN coadsorbates. We have also prepared NCO containing surfaces, through room temperature O_2 and C_2N_2 exposures. Under these conditions, conversion of O and adsorbed CN, to NCO, is substantial though not complete, i.e. the resulting surface hosts NCO, CN and O species. These surfaces, on annealing to 373K again demonstrate N atom production but now also, in large part, CO desorption. This apparently direct NCO decomposition, to $N_{(a)}$ and CO, is observed only in the presence of coadsorbed $O_{(a)}$ and $CN_{(a)}$. At temperatures in excess of 573K, another thermally activated process is observed that is in common to both isocyanate containing surface types; i.e. those prepared with HNCO exposure or $O_2 + C_2N_2$ exposures. In this latter process any coadsorbed CN appears to be only a passive bystander. We discuss possible mechanisms for these thermally activated reactions, and implications of these chemistries on other more catalytic surfaces commonly used for NO_x reduction.

[1]H. Celio, K. Mudalige, P. Mills, M. Trenary, Surface Science 394 (1997) L168-L173.

2:00pm **SS1-WeA2 Nano-Structural Information Carried by Desorbing Products; Surface-Nitrogen Removal and Angular Distributions**, ***T. Matsushima***, Hokkaido University, Japan **INVITED**

Angle-resolved (AR) product desorption analysis assigns active surface species directly emitting products. Its application is limited to products with hyper-thermal energy. This paper delivers the analysis of surface-nitrogen removal processes in both the thermal decomposition of adsorbed N2O and steady-state NO reduction on Rh(100), Rh(110) and Pd(110), in which desorbing nitrogen holds high kinetic energy. In the thermal decomposition of N2O(a) on Rh(100), N2 desorption shows two peaks at around 85 K and 110 K. At low N2O coverage, the desorption at 85 K collimates at about 66 degrees off normal toward the [001] direction, whereas at high coverage, it sharply collimates along the surface normal. In the steady-state NO+D2 reaction on Rh(100), the N2 desorption preferentially collimates at around 71 degrees off normal toward the [001] direction at 550-700 K, whereas it collimates predominantly along the surface normal at higher temperatures. At lower temperatures, the surface nitrogen removal in the NO reduction is due to NO(a)+N(a) to N2O(a) to N2(g)+O(a), whereas, at higher temperatures, the associative desorption of nitrogen adatoms is predominant. This NO reduction mechanism is also operative on Rh(110) and Pd(110) with different contributions from the two pathways. The emission angle of nascent N2 is controlled by the orientation of adsorbed N2O and the collimation angle of desorbing N2 is also affected by co-adsorbed species. In the steady-state N2O+D2 reaction on Rh(110), the N2 desorption collimates closely along the [001] direction (close to the surface parallel) below 340 K and shifts to ca. 65 degrees off normal at higher temperatures. In the reduction with CO, the N2 desorption collimates along around 65 degrees off normal toward the [001] direction above 520 K, and shifts to 45 degrees at 445 K with decreasing surface temperature. In this temperature range, adsorbed CO increases and scatters the product N2.

2:40pm **SS1-WeA4 Reactivity of Atomic Oxygen on Gold Surfaces**, ***J.L. Gong****, *R.A. Ojifinni, J.M. White, C.B. Mullins*, University of Texas at Austin

The reactivity of atomic oxygen on Au(111) has been investigated by employing molecular beam scattering and temperature programmed desorption (TPD) techniques under ultrahigh vacuum (UHV) conditions.We demonstrate that ammonia does not dissociate on the clean Au(111) surface but adsorbed O atoms, O_{ad}, facilitate $NH_{3,ad}$ decomposition. The selectivity of the catalytic oxidation of ammonia to N_2 or to NO on Au(111) is tunable by the amount of atomic oxygen precovering the surface. Both N_2 and NO are likely formed via simple recombination reactions ($N_{ad} + N_{ad}$ and $N_{ad} + O_{ad}$). At low oxygen coverages ($\theta_O < 0.5$ ML) (1 ML of oxygen is defined as 1.387×10^{15} atoms/cm^2 and refers to a single atomic layer of close-packed gold), adsorbed ammonia is stripped to NH_x ad which decomposes to form gaseous N_2. At high O_{ad} coverages, NO is formed in a surface reaction between N_{ad} and O_{ad}, but most surface N species involved recombine to form N_2 which desorbs with a peak at ~ 460 K. Higher yields of N_2 can be obtained if the O_2/NH_3 mix is kept NH_3 rich. We also present results of low-temperature CO oxidation and the role of moisture on an atomic oxygen covered Au(111) surface. The effect of atomic oxygen precoverage on CO oxidation was examined at sample temperatures as low as 77 K. Prompt CO_2 production was observed when the CO beam impinges on the sample followed by a rapid decay of CO_2 production in all cases. At oxygen precoverages above 0.5 ML, the initial CO_2 production decreases with increasing oxygen precoverage primarily due to the decrease in CO uptake. CO oxidation at 77 K goes through a precursor mediated reaction mechanism, where CO is in a precursor or trapped state and oxygen atoms are in a chemisorbed state. The role of adsorbed water was studied by using isotopically labeled water [$H_2{}^{18}O$] to distinguish the oxygen species from that used in oxygen atom exposures [^{16}O]. Evidence is presented that shows activated water or OH groups formed from water can directly participate in oxidizing CO on an atomic oxygen covered Au(111) surface.

3:00pm **SS1-WeA5 Abstraction of ^{18}O Atoms Chemisorbed on Pd(111) by ^{16}O Atoms Incident from the Gas-Phase**, ***H.H. Kan***, *R.B. Shumbera, J.F. Weaver*, University of Florida

We investigated the reactions of gas-phase ^{16}O atoms with ^{18}O atoms initially chemisorbed on the Pd(111) surface using direct product monitoring and temperature programmed desorption. We find that $^{16}O^{18}O$ molecules desorb promptly at surface temperatures as low as 100 K during the atom-surface collisions, which suggests that ^{18}O abstraction occurs by a direct reaction with incident ^{16}O atoms. Only about 20% of the initially adsorbed ^{18}O evolves as $^{16}O^{18}O$ during the beam exposures, independent of the surface temperature from 100 K to 500 K. At all temperatures, the $^{16}O^{18}O$ desorption rate initially rises to a maximum and decays thereafter with increasing beam exposure. Above 200 K, a second maximum in the desorption rate also appears after longer exposures, with the intensity of this maximum increasing with increasing surface temperature. We find that the abstraction kinetics is primarily determined by the distribution of oxygen phases that develop on the surface during oxygen uptake from the beam. Specifically, the data suggests that the observed $^{16}O^{18}O$ desorption arises from direct reactions between gaseous ^{16}O atoms and ^{18}O atoms chemisorbed either on the bare metal or on top of a surface oxide, and that the abstraction of oxygen atoms incorporated within both surface and bulk oxides occurs with low probability. As a result, only a fraction of the ^{18}O atoms are abstracted before incorporating into oxide phases during the beam exposure. The second maximum in the $^{16}O^{18}O$ desorption rate is attributed to abstraction of ^{18}O atoms chemisorbed on top of a developing surface oxide. The increase in this rate maximum with increasing surface temperature will be discussed within the context of an exchange process between oxygen atoms within the surface oxide and oxygen atoms chemisorbed on top of the surface oxide, and a kinetic analysis of the exchange will be presented.

4:00pm **SS1-WeA8 An In Situ Investigation of Hyperactive States for CO Oxidation on Platinum Group Metal Catalysts**, ***Y. Cai***, *Z. Yan, K.K. Gath, M.S. Chen,* Texas A&M University, *D.W. Goodman*, Texas A&M Universtiy

The oxidation of carbon monoxide on platinum group metal catalysts has been studied for decades due to its technological importance in pollution control and fuel cells.[1-3] Ru catalysts were found to have dramatically different activities at ultrahigh vacuum compared with elevated pressure conditions. The formation of 1 monolayer (ML) surface oxide layer is

* Morton S. Traum Award Finalist

believed to give rise to the much higher activity of Ru catalysts under high pressure conditions.[4] On the other hand, at stoichiometric reaction conditions, similar activation energies and kinetic orders were found for supported Pd, Pt, Rh and Ir catalysts at high and low pressure conditions.[3] Recent studies have shown that there are hyperactive states on Pd, Pt and Rh catalysts, with the CO_2 formation rate per metal atom site per second (turnover frequency, TOF) reaching into the thousand's, two orders of magnitude higher than the rate measured at stoichiometric reaction conditions. This hyperactive state takes place on an oxygen-rich surface at a well-defined O_2/CO ratio and specific temperature for each metal. The oxygen adsorption energies for Pt, Pd, Rh and Ru correlate directly with the O_2/CO ratio required to achieve the hyperactive catalytic state. PM-IRAS is used to investigate in situ the surface species under reaction conditions. The thickness and chemical nature of the surface oxygen layer giving rise to the hyperactive state is explored with XPS.

[1]. T. Engel and G. Ertl, Adv. Catal. 28 (1979) 1
[2]. J.E. Turner, B.C. Sales, and M.B. Maple, Surf. Sci. 109 (1981) 591
[3]. P.J. Berlowitz, C.H.F. Peden and D.W. Goodman, J. Phys. Chem. 92 (1988) 5213
[4]. C.H.F. Peden and D.W. Goodman, J. Phys. Chem. 90 (1986) 1360.

4:20pm **SS1-WeA9 Imaging of Transition Metal Oxidation and Catalysis**, ***J.I. Flege***, *P. Sutter*, Brookhaven National Laboratory

Transition metals have attracted significant attention because of their high activity in oxidation catalysis. For several materials this activity is due to the formation of thin oxides under reaction conditions. The most prominent example of this type of activation is Ru(0001), which only turns into an excellent low-temperature oxidation catalyst at higher oxygen partial pressures.[1] Despite extensive efforts in characterizing this and other similar systems, a number of fundamental questions remain unanswered, e.g., regarding the initial oxidation mechanism, the nature of oxygen-rich near-surface structures, and their individual catalytic activities. Here we discuss major progress toward understanding both transition metal oxidation and the catalytic activity of the resulting oxygen-rich structures, made possible by a novel spectroscopic imaging technique: dynamic intensity-voltage low-energy electron microscopy (dIV-LEEM). In contrast to IV low-energy electron diffraction (IV-LEED), dIV-LEEM produces spectroscopic stacks of real-space images of a surface as a function of electron acceleration voltage. Hence, the technique combines the real-time nano-imaging capabilities of conventional LEEM with the structural sensitivity of IV-LEED, making it possible to obtain, for instance, local time-dependent IV-LEED characteristics at every image pixel. Combined with dynamic LEED theory, such data can be used to identify nanoscale surface phases, for real-time structural fingerprinting of complex structural transitions, and to explore cooperative effects in surface reactions. Specifically, we establish the pathway of initial oxidation of the 4d late transition metals. The initial oxidation of Ru(0001), for instance, was predicted to proceed via the formation of a thin surface oxide as a precursor to the RuO_2 bulk oxide.[2] Our dIV-LEEM movies show instead that bulk and surface oxides grow simultaneously without transforming into one another. This finding has far-reaching consequences for catalysis, which will be discussed on the basis of real-time dIV-LEEM movies during the catalytic cycle.[3] Strikingly, the coexistence of several nanoscale structures induces cooperative effects that may be visualized and quantified by dIV-LEEM analysis.

[1] H. Over et al., Science 287, 1474 (2000).
[2] K. Reuter et al., Chem. Phys. Lett. 352, 311 (2002).
[3] J. I. Flege and P. Sutter, submitted (2007).

4:40pm **SS1-WeA10 Multisite Lattice-Gas Modeling for Chemisorption and Reaction on Metal(100) Surfaces**, ***D.-J. Liu***, *J.W. Evans*, Iowa State University

A multisite lattice-gas model[1] has been developed to provide a realistic description of the chemisorption of single species (CO, O, etc) on the (100) surface of metals such as Rh, Pd, and Ir. In addition, the model describes more complicated chemisorption and reaction processes for mixed adlayers. Population of various adsorption sites must be incorporated for reliable modeling even for single species on a single surface at higher coverages. For reactions such as CO oxidation in mixed layers, distinct local reaction configurations or pathways can contribute to different peaks observed in the temperature-programmed-reaction (TPR) spectra. Thus, our general multisite lattice-gas model allows populations of different adsorption sites (e.g., bridge, top, and hollow sites) incorporating site-specific binding energy and interactions. Parameters are chosen based on comparison with experimental data and DFT results. In addition, it is necessaary to incorporate very rapid diffusion of the reacting species (with rates many order of magnitude above other rates). We utilize kinetic Monte Carlo simulations to analyze model behavior and to interpret a variety of experimental data (heat of adsorption, TPD, TPR, etc) for the above-mentioned metal surfaces.

[1] D.-J. Liu, J. Phys. Chem. C (2007); D.-J. Liu and J. W. Evans, J. Chem. Phys. 124 (2006) 154705.

5:00pm **SS1-WeA11 Adsorption and Oxidation of SiH_4 on Pd(111)**, ***D. Kershner***, *J.W. Medlin*, University of Colorado at Boulder

A better understanding of metal-silicon and metal-SiO_2 interfaces would be applicable in many areas of study. Due to the buried nature of these interfaces in applications, they have not been well studied. To study these interfaces, a model system consisting of sub-monolayer coverages of silicon containing molecules adsorbed on single crystal metal surfaces has been investigated, using the metal as the substrate rather than the silicon/silica. In this contribution, we report on a multi-technique surface science investigation of silane adsorption and reaction on clean and O-covered Pd(111). Silane adsorption on Pd(100) and other metals has been studied previously.[1-3] These studies found that silane desorbs dissociatively, producing H adatoms and SiH_X adsorbates at cold temperatures, followed by complete dissocation of the surface SiH_X and the formation of a metal silicide phase at higher temperatures. Studies were performed using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and auger electron spectroscopy (AES). SiH_4 adsorption resulted in the formation of SiH_X species on the Pd(111) surface stable to ca. 200K. Complete dissociation occurs upon heating, however it is unclear if a silicide is formed due to the lack of splitting in the Si LVV AES peak.[4] Coadsorption of SiH_4 and O_2 leads to low temperature oxidation of surface Si atoms, forming a layer of SiO_X. This is characterized by the presence of Si-O bonds in HREELS spectra and an AES feature at 84 eV.[5] CO adsorption has also been used to probe of the effect of the SiO_X layer on Pd surface chemistry. Density functional theory studies have also been performed to investigate the structures formed during surface silicon oxidation.

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[2] C.J. Ennis, S.A. Morton, L. Sun, S.P. Tear, E.M. McCash, Chemical Physics Letters 304 (1999) 217-224.
[3] E.M. Mccash, M.A. Chesters, P. Gardner, S.F. Parker, Surface Science 225 (1990) 273-280.
[4] G.Y. Robinson, Applied Physics Letters 25 (1974) 158-160.
[5] C.R. Helms, Y.E. Strausser, W.E. Spicer, Applied Physics Letters 33 (1978) 767-769.

Authors Index

Bold page numbers indicate the presenter

— C —

Cai, Y.: SS1-WeA8, **1**
Chen, M.S.: SS1-WeA8, 1
Ciftlikli, E.Z.: SS1-WeA1, **1**

— E —

Ermakov, A.V.: SS1-WeA1, 1
Evans, J.W.: SS1-WeA10, 2

— F —

Flege, J.I.: SS1-WeA9, **2**

— G —

Gath, K.K.: SS1-WeA8, 1
Gong, J.L.: SS1-WeA4, **1**
Goodman, D.W.: SS1-WeA8, 1

— H —

Hinch, B.J.: SS1-WeA1, 1

— K —

Kan, H.H.: SS1-WeA5, **1**
Kershner, D.: SS1-WeA11, **2**

— L —

Lallo, J.: SS1-WeA1, 1
Lee, E.Y.-M.: SS1-WeA1, 1
Liu, D.-J.: SS1-WeA10, **2**

— M —

Matsushima, T.: SS1-WeA2, **1**
Medlin, J.W.: SS1-WeA11, 2
Mullins, C.B.: SS1-WeA4, 1

— O —

Ojifinni, R.A.: SS1-WeA4, 1

— R —

Rangan, S.: SS1-WeA1, 1

— S —

Senanayake, S.D.: SS1-WeA1, 1
Shumbera, R.B.: SS1-WeA5, 1
Shuttleworth, I.G.: SS1-WeA1, 1
Sutter, P.: SS1-WeA9, 2

— W —

Weaver, J.F.: SS1-WeA5, 1
White, J.M.: SS1-WeA4, 1

— Y —

Yan, Z.: SS1-WeA8, 1