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

Surface Reactions: CO and NO
Moderator: G. Fisher, Delphi Research Labs

2:00pm **SS1-MoA1 Bridging the Pressure Gap at the Atomic Level: CO/Pt(110) and CO/Pt(111)**, ***E.K. Vestergaard***, *P. Thostrup, T. An, B. Hammer, F. Besenbacher*, University of Aarhus, Denmark

We have studied the adsorption of CO on Pt(111)[1] and Pt(110)[2] over 12 orders of magnitude, up to 1 bar, using high-resolution scanning tunneling microscopy.[3] Here we demonstrate the possibility of bridging the pressure gap for these systems at the atomic level. For both surfaces, our new high-pressure STM results show that the adsorbate structures formed at high CO pressures are identical to high-coverage structures observed at low temperatures under vacuum conditions. Our findings are at variance with previous STM results where it was concluded that new structures develop at the platinum surfaces at high CO pressures. From these and other pertinent cases we attempt to extract general directions for making conjectures as to the high-pressure response of chemisorption systems.

[1] E. Kruse Vestergaard, P. Thostup et al., submitted to Phys. Rev. Lett.

[2] P. Thostrup et al., Phys. Rev. Lett. 87, 126102 (2001)

[3] E. Laegsgaard, P. Thostrup et al., Rev. Sci. Instr. 72, 3537 (2001).

2:20pm **SS1-MoA2 Fluctuations and Bistability in CO Oxidation on Nanoscale Facets**, ***D.-J. Liu***, *J.W. Evans*, Iowa State University

Recent experiments of catalytic surface reactions, especially CO oxidation on nanoscale Pt field-emitter-tips,[1] provides tremendous new possibilities for modeling of surface reactions and for comparison with stochastic theories of chemical reactions. Particularly, in a chemical reaction with bistability, fluctuations can induce transitions between the two stable states for sufficiently small systems. We analyze a "hybrid" atomistic model mimicking CO oxidation on nanoscale facets of metal(100) catalyst surfaces. The model, which incorporate infinite CO diffusion and superlattice ordering of immobile O, display bistability for an infinite system. We focus on the probability distribution for the populations of adsorbed species, as well as dynamics of the fluctuations-induced transitions. An effective potential picture emerges from our analyses of kinetic Monte Carlo simulations. Qualitative behavior can be approximated by traditional master equation and Fokker-Planck equations, where the system size dependence and the approach to the critical point can be characterized by the mean-field behavior. Analysis of a generalized model with finite CO diffusion reveals the role of CO diffusion in the crossover from the mean-field to the equilibrium Ising-like behavior.

[1] Y. Suchorski et al., Phys. Rev. Lett. vol. 82, 1907 (1999).

3:00pm **SS1-MoA4 In situ Monitoring of the Catalytic CO + NO Reaction on Pd(111) at 240 mbar: The Formation of Isocyanate**, ***Ch. Hess***, *E. Ozenzoy, D.W. Goodman*, Texas A&M University

The CO + NO reaction to form CO_2, N_2O and N_2 has been studied on a Pd(111) surface at pressures up to 240 mbar by using in situ polarization modulation infrared reflection absorption spectroscopy (PM-IRAS). At a pressure ratio of $P_{CO}/P_{NO} = 1.5$ and temperatures above 500 K, i.e., under reaction conditions, besides CO and NO, isocyanate is adsorbed on the surface as evidenced by isotope experiments. Below 0.1 mbar total pressure, however, no isocyanate formation was observed. The role of the isocyanate in the CO + NO on Pd(111) is discussed by comparison of the spectroscopic and kinetic results. In addition, kinetic measurements of the CO + NO reaction between 590 and 650 K showed an increase in the N_2O selectivity, a result of temperature-dependent changes of the ratio $[NO]_a/[CO]_a$. Within this temperature range, the apparent activation energy of the reaction was determined to be 54 ± 21 kJ/mol.

3:20pm **SS1-MoA5 Fundamental Studies of Function and Deactivation of NOx Storage Catalysts**, ***E. Fridell***, *A. Amberntsson, P. Broqvist, J. Dawody, A.W. Grant, L. Olsson, M. Skoglundh*, Chalmers University of Technology, Sweden **INVITED**

We have investigated the function of the different components in so called NOx storage catalysts regarding both the storage/reduction of NOx and deactivation by sulphur. These types of catalysts are used in lean burn applications for trapping NOx as nitrates, which in turn are reduced during lean conditions We have investigated model samples containing Ba compounds for storage of NOx and Pt and Rh as catalysts for oxidation and reduction reactions. We find that NO2 plays an important role in the storage mechanism as an oxidising agent. Two different mechanisms for this are discussed: The formation of surface peroxides and the oxidation of nitrites to nitrates. FTIR studies show that NOx is stored as surface nitrates. The stability of these species is also confirmed by first principle calculations. The sulphur deactivation is found to be more severe when SO2 is added during the rich phase than when SO2 is added during the lean period. This observation is found to be connected to the interaction between Pt and SO2. FTIR shows the formation of bulk sulphates both under lean and rich conditions. The influence of the choice of noble metals for the deactivation and regeneration was also investigated. It is found that Rh plays an important role for the regeneration after sulphur deactivation. Further, XPS studies show that the formation of platinum oxides is significant in the presence of NO2, especially for the Ba-containing samples. This has strong implications for the reactions.

4:00pm **SS1-MoA7 Nitrite and Nitrate Formation from NO and NO2 Adsorption on Alkaline Earth Metal Oxide Surfaces**, ***M. Miletic***, University of Michigan, *P.J. Schmitz, W.F. Schneider*, Ford Research Laboratory, *J.L. Gland*, University of Michigan

Alkaline earth oxides surfaces are currently being explored as a means of trapping NOx species under excess oxygen conditions typical of lean burn (e.g. diesel) engine exhaust. These metal oxides have been proposed as active components in automotive NOx abatement strategies because of their role in effectively storing and releasing NOx under lean/rich exhaust cycling. However, molecular understanding of the adsorption and reactions of NO, and NO2 on alkaline earth oxide surfaces remains incomplete. A series of temperature programmed studies of NO and NO2 on alkaline earth oxide surfaces are reported here. These experiments, coupled with XPS and ab-initio studies, indicate that reactive chemisorption plays a unique, adsorbate-specific role for both low and high temperature desorption. The effect of coverage on the molecular species is unexpected both in reactive adsorption and desorption on these oxide surfaces. Experimental and computational Density Functional Theory results are coupled, highlighting the importance of reactive configurations, charge transfer, surface-adsorbate Lewis acidity/basicity, and surface oxidation/reduction processes. Together, these approaches are used to form an integrated understanding of the driving forces behind nitrite and nitrate formation on alkaline earth oxide surfaces.

4:20pm **SS1-MoA8 Adsorption and Reaction of NO on $SrTiO_3$ Surfaces**, ***S. Azad***, *L.-Q. Wang, M.H. Engelhard, J. Szanyi, C.H.F. Peden*, Pacific Northwest National Laboratory

The adsorption and reaction of NO on metal oxide surfaces has recently received considerable attention in relation to the efficient removal of toxic pollutants from automobile exhaust. In this study, the reactivity of NO on $SrTiO_3$ surfaces has been investigated using temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS). On oxidized surfaces containing predominantly Ti^{4+} cations NO was found to be much less reactive and desorbed mainly as molecular NO around 250 K. Similar TPD spectra obtained for NO adsorption on $SrTiO_3$ prepared by sputtering or annealing the surface to 750 K, 850 K and 900 K in vacuum and in O_2 suggested that thermal annealing of this surface did not affect the reactivity of NO with Ti^{4+} cation sites. However, a significant number of defects containing mainly Ti^{3+} (observed by XPS) that was created by Ar^+ ion bombardment greatly increased the reactivity of the surface towards the adsorbed NO molecules. NO is reduced by the Ti^{3+} sites on these defected surfaces and the major decomposition products are N_2 and N_2O. Co-adsorption of NO with CO on both reduced and oxidized surfaces has also been examined. The results of NO on $SrTiO_3$ surfaces will be compared with the results of ongoing studies of NO adsorption on $Ce_{1-x}Zr_xO_2$/YSZ(111).

4:40pm **SS1-MoA9 Structural and Chemical Properties of Ti/Pt(100)-c(2x2) Second Layer Alloy - Evidence for Strong Ligand Effects**, *S. Hsieh, T. Matsumoto*, University of Southern California, *M. Batzill*, Tulane University, ***B.E. Koel***, University of Southern California

We have investigated the structure and chemisorption properties of a Ti/Pt(100) surface alloy using AES, XPS, LEED, STM, XPD, ALISS, and TPD of CO and H_2. Samples were prepared by evaporating Ti onto a clean Pt(100)-hex reconstructed surface at 300 K. After annealing the sample to 800 K, a c(2x2) ordered LEED pattern was observed that sharpened as the temperature was increased to 920 K. Further annealing to 1000 K caused the LEED pattern to become diffuse, due to onset of disorder in the surface layers resulting from Ti diffusion into the bulk. Using XPD and ALISS, we have determined that Ti atoms in the Ti/Pt(100)-c(2x2) surface alloy are not present in the topmost layer, but instead, in the second layer. Thus, the surface layer is pure Pt. XPS results showed that the Ti $2p_{3/2}$ peak from the surface alloy is shifted about 1.4 eV from a thick Ti film, and the Pt 4f peak is shifted 0.1 eV, consistent with the formation of strong intermetallic bonds upon alloying. CO adsorbed reversibly on the alloy, desorbing in a broad peak with a maximum at 376 K, showing a strong downward shift of 132 K compared to CO desorption from clean Pt(100). Thermal desorption of H_2 was also studied and a similar peak shift toward lower temperatures was observed. In addition, much less H_2 adsorbed on the Ti/Pt(100)-c(2x2) surface than on Pt(100). These results show that the second-layer Ti atoms exert a strong "ligand effect" on the Pt atoms at the surface, and this is a good model system for studying pure ligand effects at alloy surfaces.

5:00pm **SS1-MoA10 Dissociation/Dehydrogenation of Hydrocarbons on NiAl(100)**, *K.A. Layman*, ***Y. Jiang***, *J.C. Hemminger*, University of California, Irvine

HREELS has been used to study the reactivity of CO, CO_2, acetone, and pyridine on NiAl(100) as a function of surface coverage and temperature following adsorption at 140 K. While CO adsorbs primarily associatively at low CO exposures, we observe that CO begins to dissociate on the NiAl(100) substrate after very high CO exposures (100-1000 L), as indicated by the formation of a predissociation CO stretch at ~1366 cm^{-1}. In addition, CO_2 interacts very strongly with the NiAl(100) surface, as indicated by the shifting of the asymmetric CO_2 stretch to ~2027 cm^{-1}. This shift is observed for CO_2 exposures as small as 0.1 L. In contrast, the adsorption of acetone and pyridine on the NiAl(100) substrate is non-dissociative. Upon annealing the NiAl(100) surface after exposing the NiAl(100) single crystal to CO_2, acetone, or pyridine, the adsorbate begins to dissociate and/or dehydrogenate. After annealing the surface to approximately 260 K, the hydrocarbons begin to dehydrogenate. Further annealing to approximately 500 K results in the cleavage of the C-O or the C-N bond, forming Al_2O_3 or Al_xN_y thin films. The thin films of Al_2O_3 follow the phase temporal regimes exhibited for Al_2O_3 thin films grown by exposing the NiAl(100) single crystal to oxygen. Further annealing of the Al_xN_y thin films results in a similar ordering/phase change as observed for the Al_2O_3 thin films.

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