Surface Science Division
Room 607 - Session SS2-MoA
Reactions on Metals

Moderator: F. Zaera, University of California, Riverside

2:00pm **SS2-MoA1 Surface Chemistry on Stepped Pt Surfaces - What Happens at the Steps?*, J.T. Yates, Jr.,*** *C.E. Tripa, T.S. Zubkov,* University of Pittsburgh*; M. Mavrikakis, J.K. Norskov,* Technical University of Denmark, Denmark **INVITED**

H.S. Taylor postulated in 1925 that step sites on metallic surfaces are active sites for catalytic reactions. This postulate has become one focus of surface science research since the 1970's. We have studied both photochemical processes and thermally driven processes which occur specifically at metallic step sites. The photodecomposition of adsorbed O@sub 2@ on Pt(335) and Pt(779) surfaces has been used to study the reaction of photogenerated O atoms with CO molecules on both step and terrace sites producing CO@sub 2@. A surface-aligned photochemical process is observed. In addition, the chemisorption of N@sub 2@ on the step sites of these two crystals has been investigated by infrared spectroscopy and by kinetic methods. Linear arrays of weakly-based N@sub 2@ molecules have been observed and their properties will be described. N@sub 2@ does not adsorb on the (111) terrace sites separating the steps.

2:40pm **SS2-MoA3 Investigations of the Role of Edges on the Reaction Kinetics on Nanometer-sized Catalyst Particles using Monte Carlo Simulations*, H. Persson*,** *P. Thormahlen,* Chalmers University, Sweden*; V.P. Zhdanov,* Boreskov Institute of Catalysis, Russia, Sweden*; B. Kasemo,* Chalmers University, Sweden

From basic research on single crystals of catalytic materials, it is today well established that the rate of a catalytic reaction may vary considerably from one crystal face to another@footnote 1@ and that defect sites such as steps, kinks, surface vacancies, adatoms etc, may have different catalytic activities than the perfect terrace sites.@footnote 2@ In addition, there are (for supported catalysts) additional types of sites located at the particle-support boundary. It is therefore not surprising that a wide variety of behaviours of catalytic activity versus particle size have been observed,@footnote 3@ sometimes differing considerably from single crystals. The collective set of such differences and the challenge to understand and explain them is referred to as the "structure gap" in catalysis. This presentation will be focussed on Monte Carlo simulations of the kinetics of supported nm catalyst particles, being large enough to have attained bulk-electronic properties.@footnote 4,5,6,7@ The basic underlying mechanisms for the phenomena we will analyse are: (i) the different catalytic activities on different facets of a small supported crystalline particle become coupled in a strongly non-linear fashion due to diffusion occuring over facet boundaries, (ii) different kinetic rate constants at the facet boundaries of a supported particle compared to those for the perfect facets give rise to new kinetics, (iii) and spillover by diffusion of reactants, between the particle and its support, also create new kinetics. The main focus will be on how edges may affect the reaction kinetics. @FootnoteText@ @footnote 1@ R. Imbihl and G. Ertl, Chem. Rev. 95 (1995) 697. @footnote 2@ J.T. Yates, J. Vac. Sci. Technol. A 13 (1995) 1359. @footnote 3@ P.L.J. Gunter et al Catal. Rev. Sci. Eng. 39 (1997)77 @footnote 4@ V.P. Zhdanov, B. Kasemo, Surf. Sci. 405 (1998) 27. @footnote 5@ V.P. Zhdanov, B. Kasemo, Phys. Rev. Lett. 81 (1998) 2482. @footnote 6@ H. Persson et al., J. Vac. Sci. Techn. A (1999), in press. @footnote 7@ H. Persson et al, Catal. Today (1999), in press.

3:00pm **SS2-MoA4 Dissociation and Desorption of NO and N@sub 2@ on Rh(100) and Rh(111), Effect of Surface Structure on Elementary Reaction Steps*, M.J.P. Hopstaken,*** *J.W. Niemantsverdriet,* Eindhoven University of Technology, The Netherlands

Removal of NO@sub x@ is an important issue in automotive exhaust catalysis. On the molecular level, dissociation of NO on rhodium is the crucial step in the reduction of NO by CO, H@sub 2@ or hydrocarbons. Here we use TPD/SIMS to study reactions of NO on Rh(100) and compare with similar results on Rh(111).@footnote 1@ On both surfaces the reaction rates of the different elementary steps depend highly on coverage. At low coverage, dissociation of NO is completed around 250 K and 340 K for the Rh(100) and the Rh(111) surface, respectively. When the surface is saturated with NO, dissociation only starts when NO desorbs i.e. when empty sites become available. However, inhibition of NO dissociation at higher coverages cannot be explained by site blocking alone. Monte Carlo simulations strongly indicate that the activation energy for dissociation of NO on Rh(111) increases when other adsorbates such as N, O, and NO are present. At low coverages we find an activation energy of 45 kJ/mole for dissociation of NO on Rh(100), which is 20 kJ/mole lower than on Rh(111). Desorption of NO from both surfaces proceeds at similar rates. However, formation of N@sub 2@ is slower on Rh(100). Apparently, bond breaking of NO is faster and formation of a N-N bond is slower on the more open Rh(100) surface. This can be explained on the basis of surface chemical reactivity theories.@footnote 2@ Unexpectedly, the oxidation of CO to CO@sub 2@ proceeds much faster on Rh(100) than on Rh(111). This, together with the higher rate of dissociation and lower rate of N@sub 2@ formation, has important consequences for the kinetics of the CO + NO reaction on the different rhodium surfaces. @FootnoteText@ @footnote 1@ H.J. Borg, J.P.C.-J.M. Reijerse, R.A. van Santen and J.W. Niemantsverdriet, J. Phys. Chem. 101 (1994) 10052. @footnote 2@ R.A. van Santen, J.W. Niemantsverdriet, Chemical Kinetics and Catalysis, Plenum Press, New York, 1995.

3:20pm **SS2-MoA5 Interactions between CO and NO on Rh Loaded Ceria Films*, D.R. Mullins*,** *Lj. Kundakovic, S.H. Overbury,* Oak Ridge National Laboratory

CO and NO were adsorbed sequentially on model catalysts composed of submonolayer amounts of Rh deposited on highly crystalline thin films of reduced cerium oxide. The chemical state of the adsorbed species was monitored by soft x-ray photoelectron spectroscopy (SXPS). It has previously been shown that a reduced ceria substrate promotes the dissociation of CO and NO on supported Rh, with essentially full dissociation occurring by 400 K or 500 K for adsorbed NO and CO, respectively. At a constant temperature of 200 K, a saturation coverage of CO blocks subsequent adsorption of NO, and vice versa. However, the reaction of CO or NO with the dissociation products of the other molecule leads to new states in the C 1s and N 1s SXPS spectra that do not occur if either gas is adsorbed separately. If NO is dosed first and then heated to decompose it into atomic N and O, subsequent CO exposure at 200 K leads to new high binding energy states in the C1s and O 1s spectra which appear after annealing to 400 K. The binding energies of these states are consistent with formation of CO@sub 2@ on Rh. Additional features occur in the C1s and N 1s spectra indicative of the formation of other forms of N and C, as yet unassigned. If CO is dosed and dissociated first, then CO@sub 2@ is not formed upon subsequent exposure to NO. However, the features associated with the unassigned, adsorbed species do appear upon annealing. The only products observed in thermal desorption are CO and N@sub 2@ and, in particular, no CO@sub 2@ is desorbed. Additional experiments are in progress to identify the unassigned species and to determine the mechanisms of their formation. * Research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. under contract number DE-AC05-96OR22464.

3:40pm **SS2-MoA6 Non-linear Behaviour in the NO-H@sub 2@ Reaction over Pt Group Metals: A Comparison*, C.A. de Wolf*,** Leiden University, The Netherlands*; M.Yu. Smirnov,* Boreskov Institute of Catalysis, Russia*; M.O. Hattink, B.E. Nieuwenhuys,* Leiden University, The Netherlands

Oscillations in the NO+H@sub2@ reaction have been observed over the single crystal surfaces of Rh(533), Rh(311), Rh(111) and Pt(100).@footnote 1@ The following N-containing products can be formed: N@sub2@, NH@sub3@ and N@sub2@O. Recently, we observed oscillations over Ir(110)@footnote 2,3@ and Ir(210). The rate of N@sub2@ formation oscillates out of phase with the rate of NH@sub3@ and H@sub2@O formation. No N@sub2@O is formed. By using synchrotron radiation we could perform fast XPS measurements during a heat and cool cycle in the reaction mixture.@footnote 4@ These measurements show that there is a strong repulsive interaction between adsorbed N and O and that N builds-up on the surface during the NH@sub3@ formation. This information was used to propose a model for the oscillations in which the surface oscillates between an N covered surface which blocks the hydrogen adsorption and an O covered surface, which is accessible to hydrogen. A comparable model was suggested for Rh. However, the H@sub2@/NO ratio, the period and the shape of the oscillations are different for these metals. This is probably caused by differences in the rate of the various reactions that take place. The NO+H@sub2@ reaction over Ru(0001) shows a different picture. In this case hardly any NH@sub3@ is formed during a heat and cool cycle even under H-rich conditions and instead of a build-up of N a build-up of O on the surface was obtained. No oscillations have been observed so far. A comparison of the non-linear behaviour in the NO+H@sub2@ reaction of these various metals will be made. @FootnoteText@@footnote 1@N.M.H. Janssen, P.D. Cobden, B.E. Nieuwenhuys, J. Phys.: Condens. Matter 9 (1997) 1889-1917 @footnote 2@C.A.de Wolf, B.E.Nieuwenhuys, A. Sasahara, K.Tanaka, M.M. Slinko, M.Yu. Smirnov, Surf. Sci. 411 (1998) L904-L909 @footnote 3@C.A. de Wolf, B.E. Nieuwenhuys, M.M. Slinko, M.Yu. Smirnov, accepted for publication in the Proc. of IVC-14 to be published in Surface Science @footnote 4@C.A. de Wolf, S. Lizzit, A. Baraldi, M. Kiskinova, B.E. Nieuwenhuys, in preparation.

4:00pm **SS2-MoA7 Chemical Diffusion, Percolation, and Order-Disorder Transitions in a Model for CO-Oxidation with c(2x2)-O Ordering**, ***D.-J. Liu,*** *E.W. James, J.W. Evans,* Iowa State University

Pattern formation during CO-oxidation on single crystal surfaces is mediated by the chemical diffusion of adsorbed CO in a disordered environment of coadsorbed relatively immobile oxygen. We analyze CO-diffusion in a lattice-gas models for this reaction which incorporates c(2x2) ordering of adsorbed oxygen,@footnote 1@ and thus preferential diffusion at higher oxygen coverages of CO along anti-phase boundaries between c(2x2)-O domains. This constitutes a novel type of problem involving transport in a disordered medium, where CO-diffusion is blocked by percolation of the c(2x2)-O domains. We further show that such percolation is strongly influenced by (but not necessarily coincident with) a c(2x2) order-disorder transition in the oxygen overlayer. The latter constitutes a non-equilibrium analogue of order-disorder transitions familiar in equilibrated adlayers with short-range repulsive interactions. Precise results characterizing diffusion, percolation, and the order-disorder transition are obtained from extensive Monte Carlo simulations. @FootnoteText@ @footnote 1@ Y. Suchorski, J. Beben, E.W. James, J.W. Evans, and R. Imbihl, Phys. Rev. Lett. 82 (1999) 1907.

4:20pm **SS2-MoA8 CO-oxidation Reaction as a Probe of Oxygen States at Oxygen-rich Ru(0001)**, ***A. Böttcher,*** Fritz-Haber-Institut der MPG, Germany

It has been demonstrated that the oxidation of a Ru(0001) surface proceeds via four well characterized stages:(a) chemisorption, (b) oxygen penetration, (c) interfacial growth, (d) lateral and scale growth. The physical properties of the resulting oxygen phases were determined by means of thermal desorption spectroscopy (TDS), ultraviolet photoionization spectroscopy (UPS(21.2eV)) and low energy electron diffraction (LEED). The CO-oxidation reaction as performed over oxygen-rich surfaces has been used as a sensitive probe of various oxygen states. The analysis of the integral yield and the reaction kinetics reveals four well distinguishable oxygen species which are characteristic for the consecutive oxidation stages. In the high temperature regime (T>550K) the very efficient reaction is limited only by the diffusion of oxygen atoms from the subsurface region toward the topmost layer. The activation energy for this limiting reaction step ranges from 0.1 to 0.3 eV. In the low temperature regime (T

4:40pm **SS2-MoA9 Metastable States of Nitrogen Atoms Adsorbed on Ru(0001)**, ***L. Diekhöner***, *H. Mortensen, A. Baurichter, A.C. Luntz,* Odense University, Denmark

There has been a tremendous amount of work in recent years in the study of nitrogen interacting with ruthenium, in part because of its possible role as an alternative ammonia catalyst. There is still considerable disagreement as to the maximum coverage of adsorbed N allowed on Ru surfaces. We report here a novel way to produce high coverage states of nitrogen atoms adsorbed on Ru(0001) using an atomic N atom beam for dosing. Low doses produces the well known low coverage overlayers. At higher atom beam doses, we find sequential fillings of several previously unknown higher coverage states on the surface, ultimately forming a maximum coverage of 1 ML N/Ru atom. A large decrease in Ru-N bond strength with N coverage is apparent in our results and is in good agreement with recent density functional calculations. A combination of these calculations and our experiments indicates that the higher coverage states are in fact metastable relative to associative desorption, stabilized only by an increase in the barrier between the gas phase and the adsorbed state with coverage as well. Independent confirmation of the higher barriers for the high coverage states was also obtained via laser induced thermal desorption (LITD). In these experiments the kinetic energy distribution of the N@sub 2@ formed in associative desorption was measured by time of flight (TOF) techniques. We find N@sub 2@ desorbing with high translational energy distributions, much higher than seen in earlier desorption experiments from low coverages. Preliminary analysis indicates barriers that are at least in excess of 1.5 eV.

5:00pm **SS2-MoA10 Atomic Scale Chemistry: Desorption of Ammonia from Cu(111) Induced by Tunneling Electrons**, ***L. Bartels,*** Columbia University; *M. Wolf,* Fritz-Haber-Insitut der Max-Planck-Gesellschaft, Germany; *T. Klamroth,* Freie Universität Berlin, Germany; *P. Saalfrank,* University College London, United Kingdom; *A. Kühnle, G. Meyer, K.-H. Rieder,* Freie Universität Berlin, Germany

Excitation experiments on individual ammonia molecules on Cu(111) were performed with a low-temperature scanning tunneling microscope (STM) at 15 K. It could be shown that multiple electronic excitation of ammonia molecules can lead to an excitation of their substrate bond sufficient to caues desorption of the molecules from the substrate. This frequently results in their transfer to the STM tip apex. Tunneling spectra acquired with bare metal tips at the adsorption site of ammonia are compared with spectra acquired with ammonia decorated tip apices. The dependence of the desorption yield on the tunneling current at different biases shows a change of the order of the desorption process which nicely correlates with the number of incomming electron energies necessary to make up the binding energy. Excitation with either polarity, i. e. electron and hole attachment, can cause desorption. The change of the net desorption yield at different biases can be related to the standard model of the tunnel junction. Hartree Fock calculations allow to deduce from spectroscopic data that the ammonia modified Cu 4s state near the Fermi edge is responsible for the desorption process.

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