

## Surface Science

### Room 327 - Session SS2-ThM

#### Catalysis III: High vs. Low Pressures

**Moderator:** J.N. Russell, Naval Research Laboratory

8:20am **SS2-ThM1 Oxide Nucleation Kinetics on Al(111): The Role of Short-range and Long-range Interactions between Chemisorbed O Atoms**, D.E. Oner, B. Kasemo, I. Zori@aa c@, Chalmers University of Technology and Göteborgs University, Sweden

Experimental work indicates that oxide nucleation on Al(111) takes place in a heterogeneous surface phase, at an average coverage of chemisorbed O atoms of about 0.15ML, specifically at the edges of chemisorbed O islands containing 10-15 O atoms. The former observation was based on spectroscopic evidence while the latter was directly observed in STM experiments. In this contribution we suggest that the rate for oxide nucleation is strongly influenced by a combination of a long-range repulsive (elastic) interaction in competition with a short-range (nearest neighbor) attractive interaction between O adatoms. The model used to describe oxide formation is an extension of an earlier kinetic model that in addition to the oxide nucleation step also includes adsorption/chemisorption step. In the pure chemisorption phase O@sub 2@ dissociative adsorption takes place that leads to an O island size distribution in agreement with the STM observations. Chemisorbed O atoms interact via superimposed short-range attractive and long-range repulsive interactions. The oxide nucleation is simulated via a place exchange step. The latter step is the rate-limiting step for oxide nucleation. The short-range interaction stabilizes the chemisorbed phase, while the repulsive long-range interaction promotes oxide formation, i.e. it enhances the place exchange jump rate. Our Monte Carlo simulations, based on the transition theory approach, can account for: a) the observed threshold in O island size needed for oxide nucleation to occur, b) the total oxygen uptake kinetics and c) the oxide formation kinetics, reported in recent STM-surface spectroscopic experiments. The two important parameters in the model are the strengths of the long-range and short-range interactions, respectively. Agreement between simulation predictions and experimental data is achieved for a unique and reasonable choice of model parameters.

8:40am **SS2-ThM2 Chemical Inhibition of Aluminum Surface Oxidation**, V.J. Bellitto, Naval Surface Warfare Center; J.N. Russell, Jr., Naval Research Laboratory

Aluminum powders are used to tailor the energetic content of propulsion and explosive systems. As the size of aluminum particles approach the nano-scale, the performance of the energetic materials may be enhanced by providing greater surface to volume ratios, but not if the nano-particle is largely comprised of aluminum oxide. Therefore, we are examining chemical methods for passivating aluminum surfaces and inhibiting oxidation. We report the surface chemistry of a series of perfluoro- and perhydro- carboxylic acid compounds on an Al(111) surface and their ability to inhibit aluminum surface oxidation. Using x-ray photoelectron spectroscopy and infrared reflection absorption spectroscopy we established the compounds chemisorb on the atomically clean Al(111) surface through scission of the O-H bond and formation of carboxylate species. We monitored the temperature dependent chemistry of the adsorbates, demonstrating the greater thermal stability of the fluorinated surface species. The oxidation rates of the clean, partially functionalized (0.5 ML) and fully functionalized (1ML) Al(111) surfaces were compared. The fully functionalized surface did not exhibit spectroscopic features characteristic of O@sub 2@ chemisorption or Al@sub 2@O@sub 3@ formation even after being exposed to  $> 1 \times 10^5$  L of O@sub 2@ at room temperature. The thermal dependence of the oxidation inhibition is under investigation.

9:00am **SS2-ThM3 Methane Dissociative Chemisorption on Ni(100): Closing the Non-equilibrium Gap between Surface Science and Catalysis**, H.1 Abbott, Unaffiliated; A. Bukoski, D. Kavulak, I. Harrison, University of Virginia

A simple, 3-parameter microcanonical unimolecular rate theory of gas-surface reactivity is shown to predict experimental dissociative sticking probabilities for methane dissociative chemisorption on the Ni(100) surface over roughly 10 orders of magnitude variation in both pressure and sticking - even at quantum state resolved levels of detail. Facile energy randomization within the transiently formed gas-surface collision complexes is postulated to make the pooled energy from 15 local degrees

of freedom statistically available to surmount the barrier to dissociation. The apparent threshold energy for C-H bond cleavage of CH@sub 4@ incident on Ni(100) is 65 kJ/mol, down from 432 kJ/mol in the gas phase. Interestingly, this threshold energy is in quantitative accord with ab initio quantum chemistry calculations, but 15-45% smaller than calculations based on generalized gradient approximation density functional theory. More generally, some of the difficulties faced when interpreting non-equilibrium surface science experiments and comparing them with equilibrium catalysis experiments will be discussed.

9:20am **SS2-ThM4 High Pressure STM Studies of Metal and Alloy Surfaces: Adsorption Induced Phase Separation**, E.K. Vestergaard, R.T. Vang, F. Besenbacher, University of Aarhus, Denmark

A major issue in the catalytic community concerns the validity of applying surface science data obtained under Ultra-High Vacuum (UHV) conditions to "real" catalytic processes occurring at atmospheric pressure and above. Using high-pressure scanning tunneling microscopy (HP-STM) we have studied the adsorption structures on Pt(111) and Ni(111) at 1 bar of CO, and for these simple systems we demonstrate that the CO adsorption structures at high pressures are similar to structures formed under low pressure and low temperature conditions. Furthermore, we present results concerning the influence of high CO pressures on the stability of a Au/Ni surface alloy. Exposing the Au/Ni(111) surface alloy to 1 bar of CO results in a Ni(111) surface covered with small Au clusters, showing that high CO pressures induce a phase separation of the alloy. When scrutinizing this process at slightly lower pressures (10-20 torr), we have been able to follow the phase separation in real time. STM movies show that the Au cluster formation starts at the step edges of the Ni surface. Ni atoms are removed from the steps, and as the steps thus move over the surface Au clusters are nucleated and left behind in the wake of the moving steps. We propose that the removal of Ni-atoms is caused by Ni-carbonyl formation; CO is known to react with Ni surfaces at elevated pressures to form Ni-carbonyls, which are volatile at room temperature and therefore leave the surface. This latter study provides an example of a pressure gap, where model systems studied under UHV conditions certainly lack important aspects of the processes found at more realistic conditions.

9:40am **SS2-ThM5 STM Observation of Model Catalysts in Action: from Vacuum to High Pressures**, J.W.M. Frenken, B.L.M. Hendriksen, M. Ackermann, S. Bobaru, Leiden University, The Netherlands **INVITED**

Surface-science research in the field of catalysis is plagued by the presence of a large disparity between the gas pressures acceptable in most surface-sensitive instruments and the pressures used in practical catalysis. This so-called 'pressure gap' can easily be as large as ten orders of magnitude. One may expect that there are several phenomena that behave non-linearly over this enormous pressure range, which makes it difficult, and in some cases even impossible to simply extrapolate the results of low-pressure experiments to the high-pressure reality of catalysis. In order to bridge the pressure gap, we have recently constructed a special-purpose STM, which is integrated with a tiny flow reactor cell. Only the tip of the STM is inside the reactor. With this new instrument, we have obtained a first atomic-scale look at 'live' (model) catalysts, while they were active under semi-realistic conditions, namely high pressures and elevated temperatures. Simultaneously with the STM-observation, the instrument can analyze the composition of the gas leaving the reactor. Results will be shown for CO-oxidation on Pt(110), Pt(111), and Pd(001). These results reveal a new reaction mechanism, the so-called 'Mars-van-Krevelen'-mechanism, which is only active at high pressures. On each of these surfaces, the surface structure and the chemical reactivity are observed to switch simultaneously at a specific pressure ratio between O@sub 2@ and CO. In each case, the most active structure is identified as a thin surface oxide, which takes part in the reaction with CO. @FootnoteText@ @footnote 1@ B.L.M. Hendriksen and J.W.M. Frenken, Phys.Rev. Lett. 89 (2002) 046101. @footnote 2@ STM movies of catalysts in action can be viewed on our website: <http://www.physics.leidenuniv.nl/sections/cm/ip>.

10:20am **SS2-ThM7 Universality in Heterogeneous Catalysis**, J.K. Nørskov, Technical University of Denmark, Denmark **INVITED**

Electronic structure methods based on density functional theory have reached a level of sophistication where they can be used to describe complete catalytic reactions on transition metal surfaces. This gives an unprecedented insight into these processes, and it allows us to pinpoint the origin of the catalytic activity of a metal in terms of its electronic structure. The ammonia synthesis is used to exemplify the approach. It will be shown that by combining density functional calculations with kinetic modelling we can now predict relative catalytic activities of different

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metals. The generality of the approach is illustrated by including a number of other catalytic reactions into a universal property-activity scheme, which identifies the surface properties that determine the catalytic activity for a whole class of reactions.

11:00am **SS2-ThM9 Lateral Interactions in the Kinetics of Surface Reactions**, *D.L.S. Nieskens, D. Curulla Ferre, A.P. van Bavel, J.W. Niemantsverdriet*, Eindhoven University of Technology, The Netherlands

The rate of a chemical reaction on a surface depends strongly on the presence of neighboring adsorbate species. As lateral interactions between adsorbates are predominantly repulsive, their effect becomes notable at highly covered surfaces. Lateral interactions can change the kinetic parameters (the activation energy and the pre-exponential factor) of a reaction. A change in these kinetic parameters can cause a reaction to occur at a different temperature or pressure. Lateral interactions can even enable a certain reaction pathway which otherwise would be inaccessible. Our goal is first to quantitate these lateral interactions, and second to make good use of them in enabling new reaction pathways. For this we do experiments on single crystal surfaces. We use a combination of techniques: Temperature Programmed Desorption (TPD), Static Secondary Ion Mass Spectrometry (SSIMS), Low Energy Electron Diffraction (LEED) and High Resolution Electron Energy Loss Spectroscopy (HREELS). Using this combination of techniques we obtain a complete picture of the concentration of species, both in the gas phase as well as on the surface. Furthermore we can detect any ordering that occurs on the surface. In addition to the experimental work we also performed Density Functional Theory (DFT) calculations on the same kind of systems. Our strategy for determining lateral interactions is to find ordered structures of an adsorbate A on the surface, then co-adsorb a species B and determine the effect of A on the desorption of this species B. By using an ordered structure of adsorbate A, we are able to "count" the number of "A-neighbors" of the desorbing species B and thus assign the total interaction energy to a known number of neighbors. This enables us to quantify the lateral interaction energy between adsorbate A and B. The energies acquired by the experiments are quite consistent with the ones determined by the computational approach.

11:20am **SS2-ThM10 Strategies for the Study of Methanol and CO Electrocatalysis on Nanometer-Scale Catalysts**, *C. Korzeniewski*, Texas Tech University

The electrochemical oxidation of methanol and related small molecules has been of special interest in relation to fuel cell research. The development of fuel cells that operate below 100 °C on methanol, or H<sub>2</sub> has stimulated interest in the reaction steps involved in methanol and carbon monoxide oxidation at metal electrodes. In addition to being a by-product of methanol oxidation, carbon monoxide can also be present as an impurity in H<sub>2</sub>. Adsorption of carbon monoxide on the anode catalyst generally degrades its performance. We have approached the study of methanol and carbon monoxide oxidation with the use of electrochemical techniques in combination with in situ infrared spectroscopy and wet-analytical methods. This presentation will focus on the surface electrochemistry of methanol and carbon monoxide at nanometer scale Pt and bimetallic Pt materials. Catalysts are adsorbed onto smooth gold and highly ordered pyrolytic graphite (HOPG) electrodes. Gold enables infrared sampling in a standard reflectance geometry, while HOPG allows particle characterization with respect to size distribution and spatial arrangement by atomic force microscopy. Properties of nanometer-scale metal particles in relation to CO oxidation and methanol oxidation pathways will be discussed.

11:40am **SS2-ThM11 The Water Formation Reaction on a Palladium and Platinum Catalysts, Studied with Laser-induced Fluorescence and Kinetic Modelling**, *A. Johansson, M. Forsth, A. Rosen*, Goteborg University and Chalmers University of Technology, Sweden

The noble metals palladium and platinum are widely used as catalysts where the most important application is said to be the cleaning of exhaust gases. In addition, high-temperature data, especially for palladium are very scarce. In this study we have studied water formation on the palladium metal at high temperatures (1300 K) and moderate pressures (13-26 Pa). The OH desorption was studied with laser-induced fluorescence and the water production with microcalorimetry as a function of the hydrogen mixing ratio,  $\alpha_{H_2}$ . With basis on the experimental data a theoretical model was also obtained using Chemkin. The result was compared with similar experiments for platinum. The following differences were observed. The maximum in OH desorption occurs at the same  $\alpha_{H_2}$  for both platinum and palladium, however the maximum in water production is measured to be at different

$\alpha_{H_2}$ ; at 20% for platinum and 40% for palladium. From the model the initial sticking coefficients for hydrogen and oxygen are found to be about a factor of ten larger on Pd than for Pt. The OH desorption was also seen to have a first order coverage dependence on palladium, no such behaviour was found for platinum. The main route for water formation on a platinum surface is the hydrogen addition reaction however, the main water forming reaction on palladium is not straightforward to determine because of the coverage dependent OH desorption. The reverse of the hydrogen addition reaction was found to be more important for the OH formation on Pd than on Pt. The apparent desorption energy as a function of  $\alpha_{H_2}$  was also measured for palladium. It was seen that it is increasing with  $\alpha_{H_2}$  to a maximum and then stays constant. It is interesting to note that the maximum in apparent desorption energy occurs at the same  $\alpha_{H_2}$  as the maximum in water production. The same phenomenon is also observed on platinum, but at a different  $\alpha_{H_2}$ .

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