

Surface Science

Room 2002 - Session SS1-WeM

Reactions on Metal & Bimetallic Surfaces

Moderator: B.E. Koel, Lehigh University

8:00am **SS1-WeM1 Modes of Alloy Crystal Growth Dominated by Sub-Surface Defect Dynamics**, *J.P. Pierce, N.C. Bartelt, K.F. McCarty*, Sandia National Laboratories

INVITED

We show that the evolution of an alloy's surface during film deposition can be controlled by phenomena typically thought of as bulk or sub-surface processes. The response of a two-element compound, NiAl, is observed in real time with low-energy electron microscopy as one element, Al, is deposited on its surface. At low temperature (<600 K), this is a conventional heteroepitaxial system; the NiAl is a template on which increasingly Al-rich film phases grow. At higher temperatures, however, the substrate actively participates in the crystal growth by supplying a flux of Ni atoms to the surface. New layers of NiAl alloy form on the substrate even though only Al is deposited. As more Al is deposited, initially immobile bulk dislocations dissociate and move, and new atomic layers nucleate along their tracks. This behavior is unlike typical epitaxial growth in two ways. First, the compositions of the deposited and growing materials differ - Al is deposited but NiAl grows. Second, localized changes in the surface's topography and composition accompany the dislocation motion. These dynamics relate simply to the type and abundance of point defects in the near-surface region. Quantitative analysis shows that exactly half of the deposited Al atoms replace Ni in the bulk and the other half incorporate into new NiAl on the surface, establishing that Ni antisites are the point defects that initially supply Ni to the surface for NiAl growth. Analysis also shows that dislocations begin to move when the near-surface concentration of these defects is depleted to the critical composition below which Ni vacancies form. We find that the crystallographic direction of dislocation motion changes with composition. Finally, we describe how the motion of dissociated (partial) dislocations both locally enhances the crystal growth rate and changes the local composition. This work supported by U. S. DOE, OBES, Division of Materials Sciences under contract DE-AC04-94AL8500.

8:40am **SS1-WeM3 CO Adsorption on a Transition Metal Quantum Well System: fcc Co/Cu(100)***, *L. Tskipuri, H. Yao, R.A. Bartynski*, Rutgers University

Nanoscale metal thin films can exhibit quantum size effects (QSE) whereby their electronic, structural, magnetic and chemical properties may differ greatly from those of the bulk. The quantum confinement of electrons forms so-called metallic quantum well (MQW) states which give rise to many of these interesting phenomena. In previous studies we found that MQW states the strength of CO bonding to Cu MQW overlayers on the pseudomorphic fcc-Co/Cu(100) and fcc-Fe/Cu(100) systems. Here we report on the adsorption properties of the pseudomorphic transition metal layers themselves. These systems have partially filled d-bands may be grown in a metastable structure. We have examined the unoccupied electronic structure and CO bonding strength on the n-ML fccCo/Cu(100) system using inverse photoemission (IPE) and temperature programmed desorption (TPD), respectively. As-grown Co films exhibit well-defined MQW states that disperse upward with increasing film thickness, but are less pronounced than on other similar systems owing to partial overlap of exchange split states. Upon CO adsorption a well-defined structure centered about 3.8 eV above the Fermi level appears and is assigned to the unoccupied CO 2 π * orbital. CO adsorbs molecularly at room temperature and in TPD measurements we find a desorption temperature of approximately 375 K, which is about 30 K lower than what is observed for CO adsorbed on the hcp Co surfaces. When Co films are dosed at low temperatures (~ 120K), we find a second CO desorption peak around 230 K, once again similar to what is seen for hcp Co, but as a markedly lower temperature. We have observed similar desorption peak temperature shifts when CO desorption from the Ni/Cu(100) system is compared to single crystal Ni(100). The CO desorption temperature varies with Co layer thickness and the possible role of quantum size effects on the molecule-surface bond will be discussed. * funded by the Petroleum Research Fund.

9:00am **SS1-WeM4 Interaction of O₂, CO, and Methanol with Bimetallic Model Catalysts**, *T. Nowitzki, B. Juergens, H. Borchert*, University of Bremen, Germany; *S. Giorgio*, CRMCN-CNRS, France; *T. Risse*, Fritz-Haber-Institut, Germany; *V. Zielasek*, University of Bremen, Germany; *C. Henry*, CRMCN-CNRS, France; *H.-J. Freund*, Fritz-Haber-Institut, Germany; *M. Baeumer*, University of Bremen, Germany

Bimetallic particles may exhibit catalytic activities which reach far beyond those of the monometallic components. For the Co/Pd combination which is, e.g., of technological relevance for the hydrogenation of CO on the route from natural gas to liquid fuel, we have studied the interaction with CO, O₂ and methanol on the molecular scale. As a model system, mono- and bimetallic nanoparticles were prepared under UHV conditions by physical vapour deposition on a thin alumina film grown on a NiAl(110) single crystal. Bimetallic particles were obtained by sequential deposition of the two metals. The composition of these particles depends on the succession of metal depositions: depositing Co first leads to Co-core Pd-shell particles, whereas depositing Pd first results in separated Pd crystallites with a Co shell and Co nanoparticles in between. Upon O₂ deposition at room temperature, monometallic Co clusters completely oxidize as revealed by XPS and TPD. Yet, the particles can be reduced by heating to temperatures above 550K. While XPS indicates mostly metallic Co, both, metallic and oxidic components are detected in TPD, pointing to a thin persistent surface oxide layer. Upon CO deposition on metallic Co particles we find significant CO dissociation above room temperature, which may be relevant for the CO hydrogenation. Methanol, which is known to dissociate at Pd nanoparticles, was exposed to monometallic Co and bimetallic Co-Pd particles to determine if and how the composition of the particles influences methanol decomposition and oxidation. In order to relate the investigation of the UHV model systems to technologically relevant catalytic processes, we have performed turn-over experiments for CO oxidation and methanol decomposition in ambient conditions at bimetallic particles of well-defined atomic structure. Surface adsorbate species were analyzed by IR spectroscopy.

9:20am **SS1-WeM5 Bimetallics - From Theory to Catalysis of Olefin Oxidation**, *M.A. Barteau*, University of Delaware

INVITED

The overall strategy of our research is to utilize first principles approaches: Density Functional Theory (DFT) calculations and surface science experiments, to understand surface reaction mechanisms and to design new and improved heterogeneous catalysts. This has led to the demonstration of new bimetallic catalysts for the oxidation of ethylene to ethylene oxide. The key has been the demonstration, utilizing experimental and theoretical tools in concert, of surface oxametallacycle intermediates as the species that control the selectivity of this reaction. This discovery permits the influence of catalyst promoters on selectivity to be probed, and new catalyst formulations to be developed. We have proposed a new mechanism of catalyst promotion for this system by alkalis based on surface ion-dipole interactions. We have predicted, using DFT, that Cu-Ag bimetallic catalysts should offer improved performance over silver alone, and have confirmed this prediction by experiment. This represents one of the first examples of catalyst design for improved selectivity based on first principles approaches.

10:40am **SS1-WeM9 'Live' Observations of Working Catalysts with STM and X-rays at High Pressures**, *J.W.M. Frenken*, Leiden University, The Netherlands, Netherlands; *B.L.M. Hendriksen*, Lawrence Berkeley National Laboratory; *S.C. Bobaru, M.D. Ackermann*, Leiden University, The Netherlands

INVITED

We employ scanning tunneling microscopy (STM) and surface X-ray diffraction (SXRD) to obtain direct information on the structure and the atomic and molecular processes that occur on the surface of a catalyst while it is active in a chemical reaction under the high-temperatures and high-pressures conditions typical in catalysis. STM-movies obtained during the oxidation of CO on Pt and Pd surfaces, demonstrate that at high O₂ pressures the surface oxidizes and the reaction changes from a Langmuir-Hinshelwood to a Mars-Van-Krevelen mechanism.^{1,2} We resolve various ultrathin oxide structures, which only appear under high partial pressures of oxygen.³ Finally, we introduce a new explanation for self-sustained oscillations in the reaction rate², which involves a novel role for atomic steps in catalysis.⁴ ¹ B.L.M. Hendriksen and J.W.M. Frenken, Phys.Rev.Lett. 89, 046101 (2002). ² B.L.M. Hendriksen et al., Surf.Sci. 552, 229 (2004). ³ M.D. Ackermann et al., Phys.Rev.Lett. 95, 255505 (2005). ⁴ B.L.M. Hendriksen et al., to be published. .

Wednesday Morning, November 15, 2006

11:20am **SS1-WeM11 Pinpointing where CO Molecules Reside and React on Stepped Surfaces**, *J.N. Andersen, A. Resta, E. Lundgren, A. Mikkelsen*, Lund University, Sweden

The geometrical as well as the electronic structure in the vicinity of steps differs from that on the flat parts of the surface. These differences often significantly influence the adsorption of and reactions amongst adsorbate molecules and atoms. As small particles used for instance in catalysis has a high concentration of steps, step induced reactions may be dominant for such particles. In the present contribution we demonstrate that the C1s binding energy as measured by high resolution core level spectroscopy (HRCLS) can be used to pinpoint if CO molecules are adsorbed at steps on a number of vicinal surfaces and discuss why this is so. We give a number of examples of how this can be utilized for obtaining information related to the CO adsorption and to oxidation reactions of the CO molecules. We demonstrate how HRCLS measurements on a Pt(332) surface in thermodynamic equilibrium with an in-situ CO background pressure directly demonstrate a higher CO adsorption energy at the steps. Measurements from different vicinal Rh surfaces show that the specific facet present at the steps has a significant influence on the adsorption sites taken by CO molecules on the terraces at higher CO coverage. Finally, we show that this methodology allows pinpointing that oxidation of CO on a vicinal Pt(332) surface proceeds via the reaction with a 1D oxide exclusively found at the steps.

11:40am **SS1-WeM12 Adsorption of Gas-Phase Oxygen Atoms on Pt(100)-hex-R0.7°**, *R.B. Shumbara, H.H. Kan, J.F. Weaver*, University of Florida

We investigated the adsorption of gaseous oxygen atoms on Pt(100)-hex-R0.7° at surface temperatures of 450 and 573 K using temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (ELS), and low energy electron diffraction (LEED). Differences in the O@sub2@ TPD spectra reveal that the types and relative populations of the oxygen phases that develop on Pt(100) are strongly dependent on the surface temperature during adsorption. At 573 K, oxygen atoms initially adsorb into disordered (3x1) domains up to a coverage of about 0.32 ML (monolayers), and then arrange into a complex, ordered phase until the surface saturates at a coverage of 0.63 ML. In contrast, chemisorption at 450 K results in the simultaneous growth of the disordered (3x1) phase as well as a "high-concentration" phase that populates at the expense of the complex, ordered phase up to a coverage of about 0.50 ML. The temperature dependence of the oxygen phase distribution suggests that slow kinetics hinders formation of the complex, ordered phase, and forces oxygen atoms to become trapped in the high-concentration phase at 450 K. Further atomic oxygen uptake at 450 K produces an additional disordered phase that acts as a precursor to the growth of three-dimensional Pt oxide particles that saturate at approximately 3.6 ML for the incident fluxes employed. Finally, thermal decomposition of the Pt oxide is characterized by an explosive O@sub2@ desorption peak that shifts to higher temperature and intensifies dramatically as the initial oxygen coverage is increased, similar to prior observations on Pt(111).

12:00pm **SS1-WeM13 Fluctuation Effects in Nanoscale Surface Reaction Systems: Influence of Reactant Phase Separation during CO Oxidation**, *D.-J. Liu, J.W. Evans*, Ames Laboratory (USDOE)

For catalytic surface reactions on supported metal nanoclusters@footnote 1@ or on the nanofacets of metal field-emitter tips,@footnote 2@ strong fluctuation effects can significantly impact behavior. A realistic atomistic multi-site lattice-gas model@footnote 3@ is used to assess such behavior in nanoscale CO-oxidation systems at lower temperatures (or higher pressures). Here, adspecies interactions and the availability of various adsorption sites play an important role due to higher reactant adlayer coverages. Time-series for coverages and related quantities reveal fluctuation-induced transitions between distinct states associated with phase separation of reactant adspecies (in addition to transitions between stable reactive and inactive states associated with the Langmuir-Hinshelwood reaction mechanism). The former are plausibly observed in field-emission-microscopy studies.@footnote 2@ We also characterize unusual features of hysteresis analyses in this regime, and assess the role played by defects in enhancing transitions. @FootnoteText@ @footnote 1@ V. Johaneck et al., Science 304 (2004) 1639.@footnote 2@ Y. Suchorski et al., Phys. Rev. Lett. 82 (1999) 1907.@footnote 3@ D.-J. Liu and J.W. Evans, J. Chem. Phys. 124 (2006) 154705.

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