

Surface Science

Room 327 - Session SS2-MoM

Catalysis I: Adsorption and Reactions of Small Molecules at Surfaces

Moderator: J.E. Reutt-Robey, University of Maryland

8:20am **SS2-MoM1 Atomic Level Explanation of the Compensation Effect in Heterogeneous Catalysis**, *T. Bligaard, K. Honkala, A. Logadottir*, Center for Atomic-scale Materials Physics, Denmark; *J.K. Norskov*, Technical University of Denmark, Denmark; *S. Dahl, C.J.H. Jacobsen*, Haldor Topsoe A/S, Denmark

For a class of heterogeneously catalyzed reactions, we explain the compensation effect in terms of a switching of kinetic regimes leading to a concomitant change in the apparent activation energy and in the prefactor for the overall rate of the reaction. We first use the ammonia synthesis to illustrate the effect. Both experiments and a detailed kinetic model show a compensation effect. Secondly, we use density functional theory calculations to show that the compensation effect is not only due to changes in the activation barrier and prefactor of the rate-determining step, N_2 dissociation. We compare N_2 dissociation on Ru and Pd. The barrier for dissociation differs by more than 2 eV (200 kJ/mol), but calculations of the prefactor based on harmonic transition state theory shows a difference of less than 10%. In order to analyze the origin of the compensation effect we construct a general kinetic model for a surface catalyzed reaction, and show that the effect can be related to a shift in kinetic regime, from one dominated by the rate of activation of the reactants to a regime where the stability of the reaction products on the surface becomes increasingly important. Finally, we present arguments, why this should be a general effect for a broad class of reactions. We will show that the compensation effect in the rate is intimately linked to the underlying linear relationships between activation energy and stability of intermediates, which have been found to hold for a number of surface reactions.

9:00am **SS2-MoM3 Formation of Surface Cyanide through Carbon-Nitrogen Coupling Reactions on Pt(111)**, *E. Herceg, M. Trenary*, University of Illinois at Chicago

The C-N coupling reaction to form CN on the Pt(111) surface has been studied with temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). This reaction underlies the industrially important synthesis of HCN from NH_3 and CH_4 over platinum catalysts. In the absence of oxygen, the catalytic reaction is endothermic and occurs at 1200 °C. In previous kinetic studies using model reactors, it has been inferred that the C-N coupling reaction occurs through surface C and N atoms. The surface CN formed is then hydrogenated to HCN. However, direct support for this mechanism has been lacking. Alternatively, surface CH_x and NH_y with $x = 1, 2, \text{ or } 3$ and $y = 1 \text{ or } 2$, may react to form a CNH_z species with $z \geq 2$, which is then dehydrogenated to HCN. Therefore characterization of the possible CH_x and NH_y surface species is important. Although NH_3 and CH_4 do not react on Pt(111) under ultrahigh vacuum conditions, the present study shows that the C-N coupling reaction is readily achieved in UHV in various ways, such as from coadsorbed CH_3 , produced from thermal decomposition of CH_3I , and NH , produced from electron beam induced dissociation of adsorbed NH_3 . The conversion of adsorbed NH_3 to NH_2 , NH , and N was monitored with RAIRS and TPD. The surface N atoms readily react with hydrogen to reform surface NH , which is identified by its intense NH stretch peak at 3317 cm^{-1} . The presence of surface CN is detected through its reaction with hydrogen to form a surface CNH_2 (aminocarbonyl) species, which has characteristic RAIRS peaks, as well as by HCN desorption. From the fact that C-N bond formation occurs at a temperature above where all CH_x and NH_y species have dehydrogenated indicates that the reacting species are in fact surface C and N atoms. ¹ D. Hassenberg and L. D. Schmidt, *J. Catal.* 97, 156 (1986).

9:20am **SS2-MoM4 The Effect of Atomic Steps on the Adsorption and Desorption of CO on Ru(109)**, *G.A. Morgan, Jr., T. Zubkov, J.T. Yates, Jr.*, University of Pittsburgh; *O. Kühler, M. Lisowski, R. Schillinger, D. Fick, H.J. Jänsch*, Philipps University, Germany

Ru is well known as an effective catalyst for the hydrogenation of CO to produce hydrocarbons. CO hydrogenation likely occurs after CO dissociation on Ru. We have shown that the dissociation of CO occurs preferentially on the atomic step sites of the Ru(109) surface, which exposes 9-atom wide terraces of (001) orientation, separated by double-atom height steps. This was demonstrated by isotopic mixing studies where ^{12}C and ^{13}C were shown to extensively mix above 480 K, a temperature where the C-O bond has just disappeared in the reflection IR spectrum. The isotopically mixed CO desorbs in a distinct recombination process at about 500 K, a kinetic process which is absent on the planar Ru(001) surface. Carbon atoms deposited from the decomposition of ethylene can poison the step sites, which are responsible for CO dissociation. Thus the well known activity of Ru as a Fischer-Tropsch catalyst may be due to the special activity of defect sites with low Ru-Ru coordination numbers compared to Ru(001) sites. ¹ Work Supported by DOE-BES.

9:40am **SS2-MoM5 Medard W. Welch Award Address: Get Real ! --- The Importance of Complexity for Understanding the Function of Surfaces**, *M. Scheffler*¹, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

INVITED

Knowledge of the surface composition and atomic geometry is a prerequisite for understanding the physical and chemical properties of (most) modern materials as for example hardness, electronic and magnetic properties, and chemical activity. In this talk I will emphasize that to understand the function of surfaces it is important to "get real!", i.e. to go out of the vacuum and to take into account the influence of environmental gas and liquid phases at finite (possibly high) temperature and pressure. ¹ We employ ab initio, atomistic thermodynamics to construct a phase diagram of surface structures in the (T, p)-space from ultra-high vacuum to technically-relevant pressures and temperatures. ²⁻⁴ The value of such phase diagrams as well as the importance of the reaction kinetics that may be crucial e.g. close to phase boundaries will be emphasized. -- We also calculated reaction pathways and energy barriers and use this information for a long time-scale modeling of surface diffusion, island nucleation, crystal growth, and oxidation catalysis. Examples in this talk are: semiconductor quantum-dot formation, ⁵ the function of transition metals and transition-metal oxides, and heterogeneous catalysis. ⁶ ¹ C. Stampfl, et al., *Catalysis and Corrosion: The Theoretical Surface-Science Context*, *Surf. Sci.* 500, 368 (2002). ² X.-G. Wang, et al., *Phys. Rev. Lett.* 81, 1038 (1998). ³ K. Reuter and M. Scheffler, *Phys. Rev. Lett.* 90, 046193 (2003); and *Phys. Rev. B*, in print. ⁴ W. X. Li, C. Stampfl, and M. Scheffler, *Phys. Rev. Lett.*, in print (June 2003); and *Phys. Rev. B*, in print. ⁵ P. Kratzer and M. Scheffler, *Surface Knowledge: Toward a Predictive Theory of Materials, Computing in Science & Engineering* 3, 16 (2001); and *Phys. Rev. Lett.* 88, 036102 (2002). ⁶ K. Reuter and M. Scheffler, to be published.

10:20am **SS2-MoM7 CO and Ethylene Dissociation on Ni(111): Influence of Steps**, *R.T. Vang, E.K. Vestergaard, F. Besenbacher*, University of Aarhus, Denmark

Steps on metal surfaces are well known to be more reactive than terraces and often provide the important active sites for catalytic processes. From high-resolution STM experiments we have found direct atomic-scale evidence that CO and C_2H_4 (ethylene) dissociate on the step edges of Ni(111) with a much higher rate than on the terraces. When CO is dosed at 400 K onto a clean Ni(111) surface small carbon islands are nucleated at the step edges. The coverage of these carbon islands saturates as soon as a thin brim of carbon is formed along the steps, indicating that adsorbed carbon prevents further CO dissociation, thus blocking the step sites. Concerning ethylene adsorption we observe the same mechanism of carbon growth at steps saturating after the formation of a thin carbon brim, when the dosing is performed at room temperature (RT). At higher temperatures (above 350 K), however, ethylene dosing leads to a continuous growth of carbon islands, which is interpreted as dissociation on terrace sites. When the step sites are blocked by small amounts of Ag,

¹ Medard W. Welch Award Winner

Monday Morning, November 3, 2003

Au or S, we find that the dissociation rate of the two molecules is dramatically changed. No carbon is seen along the modified step edges after exposure to CO at 400 K or ethylene at RT. It is, however, still possible to form carbon islands by dosing ethylene at elevated temperatures owing to dissociation at terrace sites. These findings exemplify the concept of active sites in catalytic reactions and provide new directions for designing selective catalysts from fundamental surface science studies.

10:40am **SS2-MoM8 From Atomic Scale Reactant Ordering to Mesoscale Pattern Formation: CO Oxidation on Pd(100)**, *D.-J. Liu, J.W. Evans*, Iowa State University

We successfully connect-the-length-scales from the realistic modeling of reactant ordering in CO+O/Pd(100) to the prediction of mesoscale reaction front propagation. Description of ordering of CO on bridges sites, and O on four-fold hollow sites requires atomistic lattice-gas modeling. Repulsive CO-CO and O-O interactions beyond nearest-neighbor in range must be carefully selected to match experimentally observed ordering. Precise description of reaction-diffusion fronts also requires sophisticated analysis of chemical diffusion of CO which reflects CO-CO interactions and the presence of the coadsorbate. Numerical techniques are developed to analyse both reaction kinetics and diffusion under inhomogenous conditions using realistic lattice gas modeling. The results are then incorporated into a continuous reaction-diffusion equation. Pattern formation problems on the mesoscale, e.g., chemical wave profiles, can then be studied efficiently.

11:00am **SS2-MoM9 The Correlation between the Electronic Structure and the Energetics of CO Chemisorption on Pd/Re (0001) Surfaces**, *B.S. Mun, C.M. Lee, V. Stamenkovic, N.M. Markovic, P.N. Ross*, Lawrence Berkeley National Laboratory

We explored the nature of CO chemisorption on a Pd thin film electrode by utilizing ex-situ x-ray photoelectron spectroscopy (XPS) and in-situ Fourier transform infrared (FTIR) spectroscopy. The Pd film was deposited on Re (0001) single crystal by evaporation in UHV. Upon the deposition of the Pd thin film, the valence band (VB) photoemission spectrum shows a significant change from the bulk Re VB spectrum, yet also unlike the VB of bulk Pd(111). The morphology of the Pd thin film on the Re surface is discussed from LEED measurements. Careful analysis and comparison of lineshape and peak positions of the VB spectrum of the monolayer Pd film revealed a valence band spectrum similar to that of Ag(111), implying a filling of the Pd d-band from the intermetallic bonding with the Re substrate. Analysis of FTIR spectrum on this same sample transferred from UHV to the in-situ electrochemical cell indicated direct evidence of a modified (unlike Pd) CO bonding state consistent with reduced back-bonding from the Pd d-band to the CO π^* antibonding orbitals. It is also found that this "weakly bonded" CO is oxidized to CO₂ at a much lower (ca. 0.2 V) electrode potential than on the Pd multilayer film.

11:20am **SS2-MoM10 Chemisorption Bond Weakening on Finite Size Terraces: CO on the Stepped Ru(109) Surface Compared to Ru(001)**, *T. Zubkov, G.A. Morgan, Jr., J.T. Yates, Jr.*, University of Pittsburgh

We have compared the bonding energy, compressional LEED structures, and vibrational frequency of chemisorbed CO on the 10 atom wide (001) oriented terrace sites of Ru(109) with chemisorbed CO on the Ru(001) surface as a function of CO coverage. The measurements indicate that the Ru-CO bond energy is significantly smaller on the 22 Å wide (001) terrace sites than on the Ru(001) surface, except at the zero coverage limit where equal bond energies are observed. This results in lower saturation coverage and in a less dense saturated CO overlayer on the terraced surface with finite-width (001) planes. The results are explained by compressive relaxation of the (001) Ru terrace sites, leading to a decrease of the average d-band energy and to weaker chemical bonding of the CO. The implication of a finite-size substrate effect on chemical bonding to transition metal catalyst crystallites is important since, within the framework of this finding, smaller facets will exhibit weaker chemisorptive bonding than larger facets. *Work supported by DOE-BES.

11:40am **SS2-MoM11 Orientation of N₂O on Pd (110) and Rh(110) at Low Temperatures**, *H. Harino, I. Rzeznicka, K. Imamura, T. Matsushima*, Hokkaido University, Japan; *K. Takahashi, E. Nakamura*, Institute for Molecular Science, Japan

Catalytic N₂O decomposition on Pd(110) and Rh(110) has attracted much attention because N₂O is a major by-product in catalytic NO decomposition and also the intermediate emitting N₂ in an inclined way along the [001] direction. To understand this peculiar

desorption, the orientation of adsorbed N₂O was examined at 60 K on Pd(110) and Rh(110) by near-edge X-ray absorption fine structure (NEXAFS). On Pd(110), N₂O adsorbs in a molecular form. Remarkable anisotropy was found in the X-ray incidence angle dependence of two π resonance NEXAFS peaks at 401 and 405 eV of the photon energy, i.e., with increasing shift of the x-ray incidence from the surface normal up to grazing angles, their intensities increased about 70% when the x-ray polarization was in a plane along the [001] direction, and for the polarization in a plane along the [11-0] direction, the intensities decreased about 25%. It is derived that major N₂O is lying along the [001] direction and minor species is standing. This is consistent with DFT calculations. On Rh(110), at small exposures, only one π resonance at 401 eV was observed and its polarization dependence was very similar to that of N₂O (a), indicating dissociation of N₂O. N₂O (a) stands on the surface. At saturation, N₂O is partly standing, and lying either along the [001] or the [11-0] direction with similar populations, since with increasing shift of the x-ray incidence from the surface normal, the π resonance at 405 eV decreased only slightly when the polarization was in a plane in either the [001] or [11-0] direction. No anisotropy was found in NEXAFS peaks. The signal at 401 eV is affected by the contribution from co-adsorbed N₂O (a).

Author Index

Bold page numbers indicate presenter

— B —

Besenbacher, F.: SS2-MoM7, **1**

Bligaard, T.: SS2-MoM1, **1**

— D —

Dahl, S.: SS2-MoM1, **1**

— E —

Evans, J.W.: SS2-MoM8, **2**

— F —

Fick, D.: SS2-MoM4, **1**

— H —

Herceg, E.: SS2-MoM3, **1**

Honkala, K.: SS2-MoM1, **1**

Horino, H.: SS2-MoM11, **2**

— I —

Imamura, K.: SS2-MoM11, **2**

— J —

Jacobsen, C.J.H.: SS2-MoM1, **1**

Jänsch, H.J.: SS2-MoM4, **1**

— K —

Kühlert, O.: SS2-MoM4, **1**

— L —

Lee, C.M.: SS2-MoM9, **2**

Lisowski, M.: SS2-MoM4, **1**

Liu, D.-J.: SS2-MoM8, **2**

Logadottir, A.: SS2-MoM1, **1**

— M —

Markovic, N.M.: SS2-MoM9, **2**

Matsushima, T.: SS2-MoM11, **2**

Morgan, Jr., G.A.: SS2-MoM10, **2**; SS2-

MoM4, **1**

Mun, B.S.: SS2-MoM9, **2**

— N —

Nakamura, E.: SS2-MoM11, **2**

Norskov, J.K.: SS2-MoM1, **1**

— R —

Ross, P.N.: SS2-MoM9, **2**

Rzeznicka, I.: SS2-MoM11, **2**

— S —

Scheffler, M.: SS2-MoM5, **1**

Schillinger, R.: SS2-MoM4, **1**

Stamenkovic, V.: SS2-MoM9, **2**

— T —

Takahashi, K.: SS2-MoM11, **2**

Trenary, M.: SS2-MoM3, **1**

— V —

Vang, R.T.: SS2-MoM7, **1**

Vestergaard, E.K.: SS2-MoM7, **1**

— Y —

Yates, Jr., J.T.: SS2-MoM10, **2**; SS2-MoM4, **1**

— Z —

Zubkov, T.: SS2-MoM10, **2**; SS2-MoM4, **1**