

Monday Morning, November 10, 2014

Surface Science

Room: 309 - Session SS+AS+EN-MoM

Mechanistic Insights into Surface Reactions: Catalysis, ALD, etc.

Moderator: Falko Netzer, University of Graz, Junseok Lee, National Energy Technology Laboratory

8:20am **SS+AS+EN-MoM1 Electron Trap or Atomic Hydrogen Recombination Catalyst? The Role of Metals in Photocatalysis Revisited**, *J.-B. Joo, R.J. Dillon, I. Lee, C.J. Bardeen, Francisco Zaera*, University of California - Riverside **INVITED**

The production of hydrogen from water with semiconductor photocatalysts is often promoted by the addition of a small amount of a metal to their surfaces. It is commonly believed that the resulting enhancement in catalytic activity is due to a fast transfer of the excited electrons generated by photon absorption from the semiconductor to the metal, a step that prevents de-excitation back to the ground electronic state. Here we provide several pieces of evidence to argue against this mechanism. An alternative explanation is advanced where the metal acts as a catalyst for the recombination of the hydrogen atoms made via the reduction of protons on the surface of the semiconductor instead. New metal@TiO₂ yolk-shell nanomaterials were conceived to test our hypothesis, and the preparation and characterization of those will be discussed in this presentation as well.

9:00am **SS+AS+EN-MoM3 Atomically Resolved Observation of Defects Catalysing Phase Transitions in an Adsorbate System**, *M. Cordin, B.A.J. Lechner, S. Duerrbeck, A. Menzel, Erminald Bertel*, University of Innsbruck, Austria, *J. Redinger*, Vienna University of Technology, Austria, *C. Franchini*, University of Vienna, Austria

First order phase transitions exhibit a nucleation barrier. Normally, the barrier is lowered by heterogeneous nucleation at interfaces or extrinsic defects. Homogeneous nucleation, in contrast, is strongly activated and results in a significant hysteresis. Molecular dynamics calculations have suggested that an important step in homogeneous nucleation involves the formation and subsequent separation of defect pairs^{1,2}.

Here we report a (2x1)→c(2x2) order-order phase transition in a two-dimensional (2D) adsorbate system (Br/Pt(110) at 0.5 monolayer coverage) as a function of temperature³. Although an order-order phase transition is first-order according to Landau rules, the present system exhibits strong fluctuations within a wide temperature range (50K-250K). At 50 K the fluctuations are sluggish enough to allow atomically resolved observation of the phase conversion mechanism by temperature-variable Scanning Tunneling Microscopy. The transition is heralded by local density fluctuations in the adsorbate. The density variation consists of a compression (soliton) and a dilution (anti-soliton). At the transition temperature the two defect moieties are able to separate and travel independently through the system, thereby converting one phase into the other. Away from the transition temperature, separation of the defect pair would create the "wrong" phase, thus increasing the free energy of the system. This is equivalent to an effective attractive interaction between soliton and anti-soliton, in close analogy to the string interaction in spin systems⁴. The one-to-one correspondence can be made transparent by introducing a pseudo-spin variable, i.e. an occupation number +/-1 assigned to every bonding site. The defect-pair separation mechanism partially circumvents the nucleation barrier and thus promotes fluctuations, particularly in low-dimensional systems.

Defect-pair separation as a key step in phase transitions is a concept which arose from the analysis of molecular dynamics calculations. To our knowledge, the present study represents the first direct experimental observation with atomic resolution of such a mechanism. Furthermore, it illustrates the important role of the string interaction in suppressing fluctuations, which is very efficient in 3D systems, weaker in 2D systems and totally absent in 1D.

¹ K. Mochizuki, M. Matsumoto, and I. Ohmine, *Nature* **498**, 350 (2013).

² M. Forsblom and G. Grimvall, *Nat Mater* **4**, 388 (2005).

³ M. Cordin, B. A. J. Lechner, S. Duerrbeck, et al., *Sci. Rep.* **4** (2014).

⁴ T. Giamarchi, *Quantum Physics in One Dimension* (Oxford University Press, New York, 2004).

9:20am **SS+AS+EN-MoM4 The Co-adsorption of Water and ammonia on Pt(111)**, *B.A.J. Lechner*, Lawrence Berkeley National Laboratory, *Y. Kim, H. Kang*, Seoul National University, Korea, *Miquel Salmeron*, Lawrence Berkeley National Laboratory

Water (H₂O) and ammonia (NH₃) are arguably the most important inorganic molecules in the chemical industry. Both have the ability to form hydrogen bonds and mix readily in the liquid form. However, upon adsorption onto a metal surface, the molecules can form fewer yet more directional hydrogen bonds. To investigate the interaction between these two species at the molecular level we present a scanning tunneling microscopy (STM) study of the co-adsorption of water and ammonia on Pt(111), a substrate which bonds both molecules strongly but does not promote their decomposition.

Prior investigations have suggested the formation of the ammonium ion, NH₄⁺, upon adsorption of ammonia onto a water monolayer on Ru(0001) [1], implying that the two molecules react readily when adsorbed on transition metal surfaces. Furthermore, a theoretical study of the co-adsorption of ammonia and water on Cu(110) proposed an intimately mixed layer of ammonia and water as the energetically most favorable structure [2].

Here, we present the first microscopic investigation of co-adsorbed water and ammonia species. Upon adsorption at 4 K, ammonia and water form disordered structures, yet as the temperature is increased the two species segregate on the substrate. Indeed, at temperatures above 77 K, ammonia invariably prefers to bond to the Pt surface and only adsorbs on a water film once the monolayer is complete and no active sites remain on the substrate. When adsorbed on the water layer, we find that ammonia bonds to the water molecules that are lifted off the substrate due to a lattice mismatch of the water monolayer and the Pt(111) geometry, which we believe is due to their ability to provide a hydrogen atom for the hydrogen bond more readily than the molecules bonded more strongly to the substrate.

[1] Y. Kim, E. Moon, S. Shin, H. Kang, *Angew. Chem. Int. Ed.* **51**, 12806 (2012).

[2] G. Jones, S. J. Jenkins, *Phys. Chem. Chem. Phys.* **15**, 4785 (2013).

9:40am **SS+AS+EN-MoM5 Thermal Decomposition of Ethylene on Ru(001)**, *Yuan Ren, I. Waluyo, M. Trenary*, University of Illinois at Chicago

Ruthenium is an important catalyst in the Fischer-Tropsch process which deals with the conversion of syngas (CO and H₂) into hydrocarbons. One of the most important aspects in the Fischer-Tropsch reaction is the chain growth from a C₁ species to longer chain hydrocarbons. It is, therefore, important to study the chemistry of various C_xH_y hydrocarbon fragments on transition metal surfaces as building blocks in the chain growth mechanism. Ethylidyne (CCH₃) is an interesting hydrocarbon fragment that has been studied on many surfaces as the decomposition product of ethylene. Although the formation of ethylidyne on Ru(001) from the dehydrogenation of ethylene has been studied using high resolution electron energy loss spectroscopy (HREELS) and reflection absorption infrared spectroscopy (RAIRS) in the past, there is a lack of agreement in the literature about the mechanism of ethylene decomposition.

In this study, reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) were used to characterize and identify the surface intermediates formed in the thermal decomposition of ethylene (C₂H₄) on Ru(001). Ethylene is found to adsorb to the surface in a di-σ bonded complex at 95 K and dehydrogenates to form ethylidyne (CCH₃) above 150 K. Upon further annealing the crystal to above 300 K, ethylidyne dehydrogenates to ethynyl (CCH). Annealing to higher than 450 K causes ethynyl to decompose to methylidyne (CH). The characterization of surface intermediates provides us with more insights into the thermal decomposition of ethylene on Ru(001), which is essential to reveal the reaction mechanism.

10:00am **SS+AS+EN-MoM6 Kinetics of Alkyl Species on Pt(111)**, *Yifeng Song, I.A. Harrison*, University of Virginia **Kinetics of Alkyl Species on Pt(111)**

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A heated effusive molecular beam was used to dose hot alkanes on to a relatively cold Pt(111) surface to overcome the initial activation barrier for dissociative chemisorption and to trap reactive intermediate species on the surface for subsequent spectroscopic and kinetic studies. Both reflection absorption infrared spectroscopy (RAIRS) and temperature programmed

reaction (TPR) techniques were employed, in a complimentary way, to investigate the kinetics of alkyl fragments. Particular attention was paid to methylidyne (-CH) decomposition kinetics, which have been proposed to be potentially rate-limiting in catalytic steam reforming of methane according to recent DFT calculations. Comparison between reforming kinetics of single crystal surfaces and nanocatalysts are made. Elementary steps including the cleavage and formation of C-H and C-C bonds within other C1, C2 and C3 reactive intermediates were also studied. The experimental findings, together with some theoretical work, provide molecularly resolved information relevant to catalytic reforming of light alkanes.

10:40am **SS+AS+EN-MoM8 C₂ Hydrogenation at Ambient Pressure on Pt(111)**, *Joel Krooswyk, M. Trenary*, University of Illinois at Chicago

Carbon has been shown to be the decomposition product from catalytic reactions involving hydrocarbons adsorbed on metal catalysts. Its presence reduces the amount of active surface sites available during a reaction. The decomposition products from adsorbed acetylene and ethylene on Pt(111) are C₂ and C₁ species, respectively. A previous UHV study showed that C₂H₂ adsorbed on Pt(111) at 750 K immediately decomposes to mostly C₂ species. H₂ was then coadsorbed with C₂ at 85 K and annealed to 400 K, which produced ethylidyne (CCH₃), ethynyl (CCH), and methylidyne (CH) species. None of the species were hydrogenated to ethylene or ethane, and after annealing to 750 K, a percentage of the carbon on the surface could be rehydrogenated after cooling the crystal to 300 K and coadsorbing H₂.

In this study, the hydrogenation of C₂ species in 1 × 10⁻² to 1 Torr of H₂ was monitored with RAIRS. The species was created on Pt(111) with C₂H₂ adsorption at 750 K as done previously and the crystal was cooled to 300 K. The crystal was then annealed in an ambient pressure of H₂. The C₂ species are hydrogenated to ethylidyne at 400 K and then to ethane at approximately 450-500 K. This reaction is shown to be dependent on the pressure of H₂. The results show that ethylidyne will be hydrogenated at 450 and 500 K at 1.0 and 1 × 10⁻² Torr H₂, respectively. To show that the C₂ species are fully hydrogenated and desorbed as ethane, which indicates that the surface is clean, CO was leaked into the cell with H₂. We observe after the 500 K anneal that the peak assigned to the CO species is similar in intensity to one from CO adsorbed on a clean surface. This indicates that there are no C₂ species remaining on the surface. Also, the peak positions of the terminal and bridge sites are shifted, which indicates that there is a high coverage of H atoms adsorbed on the surface.

11:00am **SS+AS+EN-MoM9 Reaction Kinetics and Mechanism between Nitrate Radicals and Functionalized Organic Surfaces**, *Yafen Zhang, J.R. Morris*, Virginia Tech

Interfacial reactions of nitrate radicals (NO₃) with organic surfaces play an important role in atmospheric chemistry. To gain insight into the kinetic and mechanistic details, reactions between gas-phase nitrate radicals and model organic surfaces have been investigated. The experimental approach employs *in situ* reflection-absorption infrared spectroscopy (RAIRS) to monitor bond rupture and formation while a well-characterized effusive flux of NO₃ impinges on the organic surface. Model surfaces are created by the spontaneous adsorption of either vinyl-terminated alkanethiols (HS(CH₂)₁₆CHCH₂) or hydroxyl-terminated alkanethiols (HS(CH₂)₁₆OH) onto a polycrystalline gold substrate. The H₂C=CH-terminated self-assembled monolayers (SAMs) provide a well-defined surface with the double bond positioned precisely at the gas-surface interface. The surface reaction kinetics obtained from RAIRS revealed that the consumption rate of the terminal vinyl groups is nearly identical to the formation rate of a surface-bound nitrate species and implies that the mechanism is one of direct addition to the vinyl group rather than hydrogen abstraction. Upon nitrate radical collisions with the surface, the initial reaction probability for consumption of carbon-carbon double bonds was determined to be (2.3 ± 0.5) × 10⁻³. This rate is approximately two orders of magnitude greater than the rate of ozone reactions on the same surface, which suggests that oxidation of surface-bound vinyl groups by nighttime nitrate radicals may play an important role in atmospheric chemistry despite their relatively low concentration. In addition to studies involving the H₂C=CH-terminated SAMs, we have probed the reaction dynamics of NO₃ on HO-terminated SAMs. These experiments have revealed that the polarity of the terminal group has a large effect on the interfacial reaction rates. For the HO-terminated SAMs, the initial reaction probability was determined to be (5.5 ± 0.6) × 10⁻³ and the reaction mechanism appears to involve efficient hydrogen abstraction at the methylene group adjacent to hydroxyl terminus.

11:20am **SS+AS+EN-MoM10 Oxide Growth Kinetics at SiO₂/Si(001) Interfaces Induced by Rapid Temperature Raising**, *Shuichi Ogawa, J. Tang*, Tohoku University, Japan, *A. Yoshigoe*, JAEA, Japan, *K. Nishimoto*, Tohoku University, Japan, *S. Ishidzuka*, Akita Nat. Col. Technol., Japan, *Y. Teraoka*, JAEA, Japan, *Y. Takakuwa*, Tohoku University, Japan

Thermal oxidation of Si is widely used in the fabrication of electric devices and MEMS. In the recent process, rapid thermal annealing (RTA) is used in a thermal oxidation process. In the RTA process, the temperature changes during the oxidation, but the temperature changing effects in the oxidation rate have not been cleared yet. In this study, the dependence of interface oxidation kinetics on the temperature was investigated by real-time RHEED combined with AES to measure the oxide growth rate. Based on the activation energy and pre-exponential factor of the interface oxidation at SiO₂/Si(001) interface, the rate-limiting reaction of the interface oxidation is discussed.

The oxidation experiments were performed with an apparatus equipped with facilities of RHEED combined with AES (Tohoku Univ.), and chemical bonding states including not only suboxide components but also strained Si atoms were investigated XPS at BL23SU, SPring-8. The clean Si(001) surfaces were oxidized by dry O₂ gas at initial temperature T₁. When the clean surfaces were completely oxidized, the temperature was raised from T₁ to T₂. T₁ was changed between room temperature (RT) and 561 °C.

When temperature was raised from T₁ to T₂, the interface oxidation is enhanced. The initial oxidation rate after rising temperature k₂ is discussed in this study. The k₂ strongly correlates to the difference of T₁ and T₂. The Arrhenius equations between k₂ and T₂ are obtained in various T₁. As the result, activation energy is obtained as 0.27 eV in good agreement with the previous experimental result[1] and theoretical study[2]. In addition, it is found that activation energy is independent from T₁. On the other hand, pre-exponential factor decreases with increasing T₁, decreasing by about one order when T₁ increases from RT to 561 °C. In the XPS results, the Si⁴⁺ component increases and suboxide components and strained Si components (Siⁱⁱ and Si^β)[3] decrease with temperature elevation from 300 to 600 °C.

Based on these results, we propose the reaction between point defects (emitted Si atoms and its vacancies) generated by the oxidation-induced strain and O₂ molecules as the rate-limiting reaction of the interface oxidation.

[1] H. Watanabe et al., Phys. Rev. Lett. **80** (1998) 345.

[2] H. Kageshima et al, Jpn. J. Appl. Phys. **45** (2006) 7672.

[3] S. Ogawa et al., Jpn. J. Appl. Phys. **52** (2013) 110128.

11:40am **SS+AS+EN-MoM11 Electron Beam Induced Surface Reactions of Adsorbed π-allyl Ruthenium Tricarbonyl Bromide: Towards the Design of Precursors Specifically for Electron Beam Induced Deposition**, *Julie Spencer*, Johns Hopkins University, *R.G. Thorman*, University of Iceland, *M.S. Barclay*, Johns Hopkins University, *J.A. Brannaka*, University of Florida, *O. Ingólfsson*, University of Iceland, *L. McElwee-White*, University of Florida, *D.H. Fairbrother*, Johns Hopkins University

This surface science study focuses on elucidating the electron stimulated elementary reactions involved in Electron Beam Induced Deposition (EBID) of π-allyl ruthenium tricarbonyl bromide (π-C₃H₅Ru(CO)₃Br), an organometallic precursor synthesized specifically to test its suitability as an EBID precursor. EBID is a minimally invasive, resistless lithographic process which uses the electron stimulated decomposition of volatile organometallics under low vacuum conditions to fabricate and prototype three-dimensional metallic nanostructures. To date, EBID of nanostructures has used precursors designed for thermal processes, such as chemical vapor deposition (CVD). However, precursors that yield pure metal deposits in CVD often create EBID deposits with high levels of organic contamination which severely limits the range of potential applications for EBID nanostructures, highlighting the need to better understand how the structure of organometallics influences their electron stimulated reactions. To address this knowledge gap we have conducted ultra-high vacuum (UHV) surface science studies to probe the effects of 500eV electrons on nanometer scale films of organometallics adsorbed on inert substrates at low temperatures using X-ray Photoelectron Spectrometry and Mass spectrometry. Recently, we have collaborated with synthetic organometallic chemists to study organometallic complexes not designed for CVD to test specific hypotheses about how the EBID process occurs; the first example of this new collaboration is π-allyl ruthenium tricarbonyl bromide (π-C₃H₅Ru(CO)₃Br). Experimental results indicate that electron stimulated decomposition of π-C₃H₅Ru(CO)₃Br causes the central Ru atom to become reduced and in the process causes the vast majority of the carbonyl ligands to be ejected into the gas phase, with no loss of Br or the carbon atoms in the π-allyl ligand. A parallel study of π-C₃H₅Ru(CO)₃Cl indicated that the identity of the halogen does not affect the decomposition process. However, although halogen atoms are not labile in the initial decomposition step, they can be removed by a slower electron stimulated desorption process at higher electron fluxes

more representative of those encountered in typical EBID experiments which are conducted in electron microscopes. Collectively, these results suggest that organometallic precursors whose ligand architecture contains a combination of carbonyl and halogen ligands could be used to create EBID deposits with higher metal contents than are currently possible. To test this hypothesis we will also present results on the behavior of cis-dicarbonyldichloro platinum(II), *cis*-PtCl₂(CO)₂.

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