

Tuesday Afternoon, October 20, 2015

Surface Science

Room: 113 - Session SS+AS+EN-TuA

Mechanistic Insight of Surface Reactions: Catalysis, ALD, etc. - II

Moderator: Bruce D. Kay, Pacific Northwest National Laboratory

2:20pm **SS+AS+EN-TuA1 How does Absorbed Hydrogen Drive Olefin Hydrogenation on Pd?**, *Satoshi Ohno, M. Wilde, K. Fukutani*, The University of Tokyo, Japan

Pd-dissolved hydrogen is an essential ingredient in the highly selective hydrogenation of olefinic C=C double bonds catalyzed by Pd, yet the particular role played by H below the surface has long been debated controversially. Some proposed that absorbed H atoms become directly involved in hydrogenation reactions after they emerge from the metal interior onto the catalyst surface in an energetic state. Others considered that sizeable populations of subsurface sites by absorbed hydrogen indirectly activate surface-adsorbed hydrogen by altering the electronic structure of the catalyst.

To resolve this dispute we have studied the hydrogenation reaction of cis-2-butene to butane on a Pd(110) model catalyst surface with temperature-programmed desorption (TPD) and ^1H (^{15}N , ag) ^{12}C nuclear reaction analysis (NRA) that reveals the hydrogen distribution on and beneath the surface. TPD demonstrates that the catalytic hydrogenation reaction proceeds efficiently between 160 and 250 K. NRA under the hydrogenation reaction condition, on the other hand, shows that the H concentration in the Pd subsurface region is as small as 0.5 at. %. Thus, the scenario of indirect surface-hydrogen activation through large quantities of H in the subsurface sites appears rather unrealistic for our experimental conditions. We furthermore elucidate that the butane reaction yield scales linearly with the number of Pd-dissolved H atoms that reach the surface after diffusion from the Pd bulk. This observation clarifies that the Pd-catalyzed olefin hydrogenation is triggered by the emergence of bulk-dissolved hydrogen onto the Pd surface. Our NRA H profiles also demonstrate that the catalytic reaction proceeds on the Pd surface fully saturated with chemisorbed hydrogen. This surface hydrogen is considered important, as it possibly prevents deactivation of reactive surface hydrogen species in vacant chemisorption sites.

Finally, the TPD spectrum of butene shows four peaks at 140, 165, 190, and 225 K, suggesting multiple butene-adsorption modes onto Pd(110) surfaces. Reactive TPD experiments in presence of absorbed hydrogen exhibit a significant decrease in the 165 K peak, identifying this feature as the reactive butene species in the catalytic hydrogenation reaction.

2:40pm **SS+AS+EN-TuA2 CO Oxidation over Pd Catalysts Supported on Different Low-Index Surfaces of CeO₂: A Combined Experimental and Computational Study**, *Xiao Liu, Y.W. Wen, Z.Z. Chen, B. Shan, R. Chen*, Huazhong University of Science and Technology, China

Pd/CeO₂ has attracted much attention on the low temperature CO oxidation due to the strong metal-support interactions. In this study, we have systematically investigated the interface properties and CO oxidation activities of Pd catalysts supported on different low-index surfaces of CeO₂. The Pd/CeO₂ nanorods have been prepared by incipient wetness impregnation method and the exposed surfaces of CeO₂ nanorods have been controlled by changing the calcination temperature after their successful synthesis by hydrothermal method. Their catalytic activities in CO oxidation have been tested and the results show that Pd catalysts supported on CeO₂ nanorods exposed by (100) and (110) (calcined at 500 °C) are more activated than that exposed by (111) (calcined at 700 °C), which is related to the surface oxygen vacancies concentration and the strength of interface interaction. By performing density functional calculations, the surface oxygen activities and the binding strength of Pd clusters on these low-index surfaces of CeO₂ have been investigated. The results show that the oxygen vacancy formation energies of (100) and (110) are smaller than that of (111). The binding strength of Pd clusters on these surfaces follows the sequence: (100) > (110) > (111). Furthermore, CO oxidation routes on these surfaces proceeding through the LH, ER and MvK mechanism have been studied. Our studies not only reveal that the catalytic performance of Pd/CeO₂ can be tuned by controlling the exposed surface of oxide but also shed light on the interface structures and CO oxidation mechanism of Pd/CeO₂ system.

3:00pm **SS+AS+EN-TuA3 In Situ Adsorption and Decomposition Studies of Dimethyl Methyl Phosphonate on Molybdenum Oxide Surfaces and Nanoparticles**, *Ashley Head, L. Trotochaud, Y. Yu, Lawrence Berkeley National Laboratory (LBNL), Z. Hicks, X. Tang, K. Bowen, Johns Hopkins University, B. Eichhorn, University of Maryland, College Park, H. Blum, LBNL*

There is great interest in understanding the interaction between the nerve agent simulant dimethyl methyl phosphonate (DMMP) and metal oxide surfaces to further nerve agent filtration technology and decomposition methods. To this end, we have studied the room temperature adsorption of DMMP on MoO₂ and MoO₃ surfaces up to 30 mTorr using ambient pressure x-ray photoelectron spectroscopy (APXPS). On both surfaces, the majority of DMMP adsorbs intact, but differences in the behavior of DMMP on the two substrates are found upon heating. Two phosphorus species are seen on the MoO₂ surface and three are seen on the MoO₃; these species remain on both surfaces up to 450 °C. Additionally, carbon remains on the MoO₂ at high temperatures but is removed from MoO₃ by 420 °C. The APXPS data were correlated with TPD measurements of DMMP adsorbed on MoO₃ clusters on HOPG, a model system closer to real filtration materials. Methanol was found as the major decomposition product in addition to trace amounts of dimethyl ether. The easily reducible MoO₃ is likely responsible for an oxidative cleavage of the P-CH₃ bond on both the surface and nanoparticles. These studies highlight how APXPS coupled with TPD yields chemical information relevant to real-world applications.

3:20pm **SS+AS+EN-TuA4 Adsorption of Sterically Hindered Sulfur Containing Molecules on a Heterogeneous Model Catalyst**, *Signe Sørensen, J.V. Lauritsen*, Aarhus University, Denmark

Cobalt promoted MoS₂ nanoclusters (CoMoS) are the active phase of the hydrodesulfurization catalyst which enables sulfur removal from crude oil. New legislations on sulfur impurity levels in diesel in EU and US demands still lower sulfur content which increases the requirements for even more effective catalysts.

Previously catalysts were improved by costly trial-and-error experiments. To target the improvements attempts, understanding of the catalytic mechanism is crucial. In the hydrodesulfurization catalysis the main source to residual sulfur content is the sterically hindered sulfur containing molecules, as the reactivity towards these is very low. To targeted enhance the catalytic activity, atomic scale understanding of this catalytic mechanism is essential.

Scanning tunneling microscopy (STM) is an outstanding tool for real space, atomic-scale imaging of supported nano-scale systems. This makes it the optimal tool for investigating the interaction between the sulfur containing molecules and metal-supported CoMoS, as it offers the unique and powerful ability to directly observe the catalytic active site by imaging single molecules adsorbing on the nanoparticles.

In this study STM is used on a model system of Co-promoted MoS₂ on a gold substrate under ultrahigh vacuum conditions. To study the adsorption of the strongly steric hindered sulfur containing molecule 4,6-dimethyl-dibenzothiophene the molecule is dosed directly onto the nanoparticles which means that their location, orientation and the dynamics of single molecules can successfully be revealed through atom-resolved STM images and films. All observed adsorption modes are either associated with a sulfur vacancy on the corner site of the nanoclusters or with the one-dimensional metallic edge state associate with the edge of the Co-promoted MoS₂ nanoclusters. These observations strongly indicate that these sites are important active sites of the catalyst and enable targeting the attempts for enhanced activity to optimization of the number of these apparent active sites in the industrial catalyst.

4:20pm **SS+AS+EN-TuA7 Metal Nanoparticles on Thin Film Oxide Supports: Interaction and Reaction of Metals with Hydroxyls**, *Martin Sterrer*, University of Graz, Austria **INVITED**

Water-oxide interaction is of great importance in a number of technologically relevant fields, among them heterogeneous catalysis. Several studies report on the promoting effect of water in catalytic reactions, the participation of surface hydroxyls in catalytic reactions, and the influence of hydroxylation on the binding of metals to oxide surfaces. Achieving a fundamental atomic scale understanding of water-oxide interaction at environmentally and catalytically relevant conditions (e.g. ambient pressure) represents, therefore, a challenge for surface science studies related to heterogeneous catalysis. In this contribution, I will present results of our recent studies related to the interaction of water with thin, single crystalline oxide films (Fe-oxides, alkaline earth oxides) carried out

in a wide range of water chemical potential (from UHV to mbar water pressures). Topics that will be discussed are the characterization of ordered water monolayers, the dewetting of ice on oxide surfaces, hydroxylation of oxide surfaces at elevated pressure, the influence of hydroxyls on metal nucleation and sintering, and metal deposition onto oxide surfaces from aqueous solutions.

5:00pm **SS+AS+EN-TuA9 Dynamics of Isolated Surface Complexes Formed Between a Chemisorbed Chiral Molecule and a Prochiral Reactant**, *Jean-Christian Lemay, Y. Dong, P.H. McBreen*, Laval University, Canada

Adsorbed chiral molecules (chiral modifiers) can interact stereoselectively with prochiral co-adsorbates on reactive metal surfaces (1). This is used in one of the most common methods to perform asymmetric heterogeneous catalysis. The chiral modifier provides stereoselection through non-covalent assembly with a substrate, forming isolated complexes with well-defined geometries. We will present a variable temperature STM study of individual bimolecular complexes formed by enantiopure 1-(1-naphthyl)ethylamine and three representative prochiral substrates on Pt(111). The results reveal sub-molecularly resolved and time-resolved stereospecific data for competing complexation geometries. Time-lapsed STM measurements of individual substrate molecules sampling a set of interaction geometries provide new insight on the dynamics of stereocontrol. The results reveal that a single prochiral substrate can probe various sites on the surface due to diffusion and prochiral switching. This shows the importance of considering interconversion between complexation geometries to fully understand the stereocontrol operated by the chiral modifier. The results will be discussed in the context of proposed mechanisms for enantioselective hydrogenation.

5:20pm **SS+AS+EN-TuA10 Density Functional Theory Study of CO Assisted Water Dissociation**, *Liney Arnadottir, L. Halberstadt*, Oregon State University

Previous computational studies of methanol oxidation reaction intermediates (H-C=O and C-OH) have shown significant effects of water on both adsorbate adsorption energy as well as activation energies of interconversion between the two. On a clean Pt(111) surface the interconversion between the two forms goes through a very stable COads and Hads intermediates and the activation barriers of CO + H to form HCO or COH are high or 1.3 and 1.8 eV respectively. In the presence of a single coadsorbed water molecule the activation barrier for this interconversion from HCO to COH was found to be much lower or 0.62 eV. These studies were motivated by experimental studies of methanol oxidation on Pt which found CO₂ formation at potentials lower than typically required for CO oxidation. Here we investigate Pt-water interactions and the effects of co-adsorbate CO on water dissociation as a possible CO assisted water dissection as an alternative reaction pathway on Pt surfaces.

6:00pm **SS+AS+EN-TuA12 Crystalline Growth of Ice - Studying the Transition from the First Wetting Layer to Multilayers with Scanning Tunneling Microscopy**, *Barbara Lechner, S. Maier, M.B. Salmeron*, Lawrence Berkeley National Laboratory

The growth of water layers on model substrates has been studied intensively, yet many questions still remain [1,2]. After many years of research, the structure of the first wetting layer on metal surfaces has been determined in comprehensive experimental and theoretical studies [3-5]. A surprisingly complex behavior was revealed, showing that the strain caused by the mismatch of the hexagonal planes in the ice crystal structure and the lattice of the substrate is released by forming structures that include rotated hexagons, pentagons and heptagons of molecules, in addition to strongly bound hexagonal rings commensurate with the substrate. A range of experimental and theoretical investigations showed that, on many substrates, the water monolayer does not expose any dangling hydrogen bonds as all water molecules adsorb either flat-lying or with a hydrogen atom pointing towards the surface [1,6]. Growth of multilayer water films that preserve the "down-pointing" average dipole orientation of water has been proposed to occur in some cases, resulting in the formation of "ferroelectric ice" [7]. However, the growth of the entropically more favorable, proton-disordered ice requires flipping some of the molecules in the first layer to expose dangling hydrogen bonds. Such molecular reorientation may be kinetically hindered, and has been invoked to be the reason for the hydrophobic character of many water monolayer films at low temperatures [6].

Here, we present high-resolution scanning tunneling microscopy (STM) measurements of water layers adsorbed on Pt(111) and Ru(0001) to study the transition from the first layer to multilayers. We observe that a second water layer initially grows in an amorphous structure when grown on the crystalline monolayer containing pentagons, hexagons and heptagons of water molecules. To facilitate the growth of ice in a bulk-like hexagonal

arrangement, the first wetting layer needs to rearrange into a hexagonal structure commensurate with the surface.

[1] Hodgson, A.; Haq, S. *Surf. Sci. Rep.* **2009**, *64*, 381–451.

[2] Carrasco, J.; Hodgson, A.; Michaelides, A. *Nat. Mater.* **2012**, *11*, 667–674.

[3] Maier, S.; Stass, I.; Cerdá, J. I.; Salmeron, M. *Phys. Rev. Lett.* **2014**, *112*, 126101.

[4] Tatarikhonov, M.; Ogletree, D. F.; Rose, F.; Mitsui, T.; Fomin, E.; Maier, S.; Rose, M.; Cerdá, J. I. *J. Am. Chem. Soc.* **2009**, *131*, 18425–18434.

[5] Nie, S.; Feibelman, P. J.; Bartelt, N. C.; Thürmer, K. *Phys. Rev. Lett.* **2010**, *105*, 026102.

[6] Kimmel, G. A.; Petrik, N. G.; Dohnálek, Z.; Kay, B. D.; Kimmel, G. A.; Petrik, N. G.; Dohnálek, Z.; Kay, B. D. *J. Chem. Phys.* **2007**, *126*, 114702.

[7] Su, X.; Lianos, L.; Shen, Y. R.; Somorjai, G. A. **1998**, 1533–1536.

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