

Wednesday Afternoon, October 21, 2015

Surface Science

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

Metals, Alloys & Oxides: Reactivity and Catalysis

Moderator: Daniel Killelea, Loyola University Chicago

2:20pm **SS+AS+EN-WeA1 Understanding Chemical Activity in Pt-Re Bimetallic Systems**, Donna Chen, R.P. Galhenage, K. Xie, A.S. Duke, University of South Carolina, H. Yan, Brookhaven National Laboratory
INVITED

The nucleation, growth and chemical activity of bimetallic Pt-Re clusters on titania have been investigated as model systems for understanding Pt-Re catalysts for oxidation reactions. Scanning tunneling microscopy studies demonstrate that exclusively bimetallic clusters can be grown from the sequential deposition of Pt on Re or Re on Pt, provided that the deposition of the first metal creates a high enough cluster density for the nucleation of the second metal. Low energy ion scattering experiments indicate that the bimetallic clusters are Pt-rich regardless of the order of deposition. However, X-ray photoelectron spectroscopy (XPS) suggest that a Pt-Re alloy is formed from deposition of Re on Pt but not from Pt on Re. Furthermore, Re interacts more strongly with the titania support than Pt, resulting in reduction of titania. Temperature programmed desorption studies for CO desorption and methanol reaction confirm that the Re clusters have lower activity than Pt despite their higher surface area, and this behavior is attributed to oxidation of Re by the titania support. The alloyed clusters exhibit new activity for CO and H₂ evolution that is not observed for the pure or unalloyed clusters. Methanol oxidation activity of these model surfaces are studied in a microreactor attached to an ultrahigh vacuum chamber so that the surfaces can be characterized by XPS before and after reaction. Specifically, changes in the oxidation states of Re in the bimetallic and pure Re clusters are investigated.

3:00pm **SS+AS+EN-WeA3 Removal of Surface Carbon from Pt(111) by Hydrogenation via an Ethylidyne Intermediate**, J.D. Krooswyk, C.M. Kruppe, Michael Trenary, University of Illinois at Chicago

Transition metals that are used to catalyze reactions of hydrocarbons are often deactivated by the deposition of unreactive carbon on the catalyst surface. The structure and properties of the deposited carbon are often poorly defined. We have investigated the reactivity of carbon deposited onto a Pt(111) surface through exposure to acetylene at 750 K. At this temperature the acetylene is completely dehydrogenated leaving only carbon on the surface. Earlier work had shown that the carbon deposited in this way largely consists of C₂ molecules. We have used reflection absorption infrared spectroscopy (RAIRS) to characterize the reactivity of the deposited carbon under ambient pressures of H₂(g) up to 10 torr. The results show that C₂ can be hydrogenated to ethylidyne (CCH₃) and that the ethylidyne is slowly hydrogenated to ethane, which desorbs thus removing carbon from the surface. The maximum coverage of the C₂ molecules can be deduced from comparison with the peak areas measured with RAIRS for ethylidyne formed from ethylene exposure, which is known to give an ethylidyne coverage of 0.25 monolayer. Auger electron spectroscopy confirms that surface carbon is removed by hydrogenation under these conditions. In separate experiments based on comparisons of s- and p-polarized RAIR spectra in which both surface and gas phase species can be simultaneously monitored, we have shown that surface ethylidyne is a spectator species as gas phase acetylene is converted first to gas phase ethylene and then to gas phase ethane. Although ethylidyne is a spectator species in the hydrogenation of ethylene and acetylene to ethane over Pt(111), in the case of C₂ hydrogenation, ethylidyne plays the role of a reaction intermediate.

3:20pm **SS+AS+EN-WeA4 Density Functional Study of the Oxygen Chemistry and NO Oxidation Mechanism on Low-index Surfaces of SmMn₂O₅ mullite**, X. Liu, Z.Z. Chen, Huazhong University of Science and Technology, China, K.J. Cho, The University of Texas at Dallas, R. Chen, Bin Shan, Huazhong University of Science and Technology, China

SmMn₂O₅ mullite has recently been reported to be a promising alternative to traditional Pt-based catalysts for environmental and energy applications. By performing density functional calculations, we systematically investigated lattice oxygen reactivity and oxygen adsorption/dissociation/migration behaviors on low index surfaces of SmMn₂O₅ mullite with different terminations. The (001), (010) and (100) surfaces have lowest barriers against exchanging O species with environments and thus are expected to be active surfaces. Furthermore, we have calculated the reaction routes along different channels on these three

surfaces. Our results show that both ER and MvK mechanisms co-exist in NO oxidation by SmMn₂O₅. The most active surface is the (010) facet with Mn⁴⁺ ions in the surface layer where oxidation can be realized by a synergetic mechanism involving ER processes along bridge-MnO channels. The (001) surface with Mn⁴⁺ ions in the surface layer is also expected to be active for oxidation via the MvK mechanism. On the other hand, despite the low oxygen vacancy formation energy, the (110) surface could easily undergo surface reconstruction and quickly lose active sites. Our calculations also suggest that the rate determining step of oxidation reaction on SmMn₂O₅ surfaces is the desorption of NO₂ on both (010) and (001) facets. Our study presents systematic pictures on catalytic activities of SmMn₂O₅, which are important to the full understanding and improvement of SmMn₂O₅ performance. The comprehensive micro-kinetic model on the reaction dynamics of SmMn₂O₅ is under construction.

4:20pm **SS+AS+EN-WeA7 Medard W. Welch Award Lecture - Thermodynamics and Kinetics of Elementary Reaction Steps on Late Transition Metal Catalysts**, Charles Campbell*, University of Washington
INVITED

Experimental and theoretical results concerning the thermodynamics and kinetics of surface chemical reactions of importance in late transition metal catalysis will be reviewed. Topics include: (1) calorimetric measurements of the adsorption energies of small molecules and molecular fragments on single crystal surfaces, and their comparison to different DFT methods; (2) measurements of the entropies of adsorbates and their trends, (3) using these together with elementary-step rate measurements to build microkinetic models for multi-step catalytic reactions, and a method for analyzing these that quantifies the extent to which each elementary step and intermediate controls the net rate; and, (4) measurements of the energies of transition metal atoms in nanoparticle catalysts as a function of particle size and support, which correlate with catalytic activity and sintering rates.

* Work supported by NSF and DOE-OBES Chemical Sciences Division.

5:00pm **SS+AS+EN-WeA9 Bridging Hydroxyl Formation from Water on Reduced TiO₂(110)**, Nikolay Petrik, G.A. Kimmel, Pacific Northwest National Laboratory

TiO₂ is an important photocatalyst with many practical applications. It is also a good model system for fundamental studies of thermal and non-thermal reactions, including photocatalytic water splitting. Our understanding of water's reactions on TiO₂ surface is limited. In this paper, we have investigated temperature-dependent reaction of water molecules with bridging oxygen vacancy (V_O) on rutile TiO₂(110) surface using three independent methods: i) infrared reflection absorption spectroscopy (IRAS) to monitor the bridging hydroxyl (OH_B or OD_B) formation, ii) electron-stimulated desorption (ESD) of molecular water to monitor the water coverage,¹ and iii) photon-stimulated desorption (PSD) of CO₂ – which is a product of CO photooxidation – to monitor the unoccupied V_O coverage.² Narrow, distinct peaks for isolated OD_B and OH_B at ~2736.5 cm⁻¹ and ~3711.5 cm⁻¹ are detected in P-polarized mode for the samples exposed to D₂O and H₂O, respectively. If water is dosed at low temperature and annealed, bridging hydroxyl peaks appear above 150 K, growing with temperature until ~250 K, then saturate. In the same temperature range, molecular water and V_O coverages from the ESD and PSD data decrease in correlated fashion according to the reaction H₂O_{Ti} + V_O → 2OH_B. The temperature range for this conversion appears to be too broad to be fitted with a single Arrhenius term and a reasonable pre-factor. On the other hand, the data can be fitted well using a “normal” prefactor (ν = 10¹² s⁻¹) and a distribution of activation energy (E_a) centered at 0.545 eV with ΔE_a(FWHM) = 0.125 eV. These parameters are close to those obtained from STM data³ and theory⁴ for the water monomer diffusivity on Ti sites, which most likely controls the water – vacancy reaction. This work was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences.

(1) Zhang, Z.; Du, Y.; Petrik, N. G.; Kimmel, G. A.; Lyubintsky, I.; Dohnalek, Z. Water as a Catalyst: Imaging Reactions of O₂ with Partially and Fully Hydroxylated TiO₂(110) Surfaces. *J. Phys. Chem. C* 2009,113, 1908-1916.

(2) Petrik, N. G.; Kimmel, G. A. Off-Normal CO₂ Desorption from the Photooxidation of CO on Reduced TiO₂(110). *J. Phys. Chem. Lett.* 2010,1, 2508-2513.

* Medard W. Welch Award Winner

(3) Matthiesen, J.; Hansen, J. O.; Wendt, S.; Lira, E.; Schaub, R.; Laegsgaard, E.; Besenbacher, F.; Hammer, B. Formation and Diffusion of Water Dimers on Rutile TiO₂(110). *Phys. Rev. Lett.* 2009, 102, 226101.

(4) Hammer, B.; Wendt, S.; Besenbacher, F. Water Adsorption on TiO₂. *Top. Catal.* 2010, 53, 423–430.

5:20pm **SS+AS+EN-WeA10 The Adsorption and Desorption of Small Hydrocarbons on Rutile TiO₂(110), Long Chen, R.S. Smith, B.D. Kay, Z. Dohnalek, Pacific Northwest National Laboratory**

The interaction of small hydrocarbons with metal and metal oxide surfaces is important for a wide range of applications including heterogeneous catalysis, atmospheric chemistry, geochemistry and chemical sensing. In this work, temperature programmed desorption (TPD) and molecular beam techniques are used to study the adsorption and desorption kinetics of small hydrocarbons (C₁ - C₄) on rutile TiO₂(110) surface. In addition to n-alkanes, 1-alkenes (ethylene, propylene and 1-butylene) and 1-alkynes (acetylene, propyne and 1-butyne) were included to follow the effect of the nature of the carbon-carbon bond on hydrocarbon binding. We show that the sticking coefficients for all the hydrocarbons studied here are close to unity (> 0.95) at an adsorption temperature of 60 K. Similar to previous studies on metal and metal oxide surfaces, for n-alkanes on TiO₂(110) we find a linear increase in desorption energy with chain length. In contrast, for 1-alkenes and 1-alkynes, a roughly linear relationship between desorption energy and chain length is also observed at low coverages, but with a much smaller slope, suggesting that the additional CH₂ segments either interact less efficiently with the substrate or destabilize the bonding of the unsaturated carbon-carbon bond. Further, we also determined the absolute saturation coverages of each hydrocarbon on the five-fold coordinated titanium sites (Ti_{5c}). We show that except for CH₄, the saturation coverages of the same type of hydrocarbons on Ti_{5c} sites are nearly independent of the chain length, and that the saturation coverages of 1-alkynes consistently exceed those of n-alkanes and 1-alkenes, contrary to what one would expect based on their sizes.

5:40pm **SS+AS+EN-WeA11 Pd-Au Single Atom Alloys for the Activation of Diatomic Molecules, Felicia Lucci, E.C.H. Sykes, Tufts University Department of Chemistry**

Pd-Au alloys are known to catalyze a wide range of hydrogenation and oxidation reactions; however, the size of Pd ensembles in Au required for small molecule activation is not well understood. On the atomic scale, we investigate size effects of Pd atoms in Au for the catalytic activation of H₂ and O₂. We show that isolated Pd atoms are capable of catalyzing the dissociative adsorption of H₂, a process which was previously thought to require contiguous Pd sites. H spillover from active Pd sites to the Au surface can be induced the adsorption of CO. Conversely, single Pd atoms are not capable of O₂ dissociation. Small Pd clusters on Au enable O₂ activation and adsorption at Pd-Au interface sites. Since weakly bound H and O atoms are capable of enhancing reaction selectivity on Au substrates, this Pd-Au system serves as an ideal model system with which to probe selective hydrogenation and oxidation reactions at both single and ensemble active sites.

6:00pm **SS+AS+EN-WeA12 Pt/Cu Single Atom Alloys for Highly Selective Formic Acid Dehydrogenation, Matthew Marcinkowski, C.J. Murphy, M.L. Liriano, N.A. Wasio, F.R. Lucci, E.C.H. Sykes, Tufts University Department of Chemistry**

Selective decomposition on metal catalysts is a critical step in formic acid's application as a hydrogen storage molecule and for its use in direct formic acid fuel cells. Depending on the metal, formic acid can decompose via a dehydrogenation pathway to produce CO₂ and H₂, or a dehydration pathway to produce CO and H₂O. For most applications, very high selectivity to dehydrogenation is preferred as reactively formed CO from dehydration can poison the catalyst. The Cu(110) surface is known to selectively decompose formic acid via dehydrogenation, however, despite being the most dominant facet of nanoparticles, Cu(111) has received little study. Pt surfaces exhibit greater reactivity to decomposition, but are not as selective resulting in increased catalyst poisoning. We report that formic acid on Cu(111) and Pt/Cu(111) selectively decomposes via dehydrogenation. We find the bare Cu(111) surface to be 100% selective towards dehydrogenation, but not very active. Substitution of 1% of a monolayer of Pt into the Cu(111) surface results in a single atom alloy (SAA) that maintains this high selectivity and is ~six times more reactive than Cu(111). Higher coverages of Pt improve reactivity further, but beyond the single atom regime the selectivity towards dehydrogenation decreases and dehydration is observed. Our results show that Pt/Cu SAAs significantly improve the reactivity of Cu, while also maintaining high selectivity towards dehydrogenation, therefore avoiding catalyst poisoning by CO. Based on our results, real nanoparticle catalysts designed on the SAA principle are expected to be promising candidates for formic acid dehydrogenation.

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