Surface Science
Room: Picuris - Session SS1-MoM

Reactivity and Selectivity on Catalytic Surfaces
Moderator: C.T. Campbell, University of Washington

8:20am **SS1-MoM1 Structure and Reactivity of Alkyl Ethers Adsorbed on Hydroxylated CeOx(111) Model Catalysts**, ***F.C. Calaza***, Oak Ridge National Laboratory, *T.-L. Chen*, Brookhaven National Laboratory, *D.R. Mullins, S.H. Overbury*, Oak Ridge National Laboratory

The study of adsorption and reactivity of oxygenated molecules on model oxide catalysts is of great interest to gain a better understanding of the mechanism of industrial reactions. Cerium oxide is commonly used in three-way auto exhaust and WGS catalysts. Our experimental design is intended to find the conditions where UHV experiments could mimic the real catalytic processes and from these results explain the reaction pathway from the atomistic level.

From the surface science point of view, previous studies of alcohols, ketones and aldehydes adsorbed on the surface of cerium oxide model catalysts have shown a variety of pathways for decomposition and reactivity. In the present work we have examined these pathways for two ethers, diethyl ether (DEE) and dimethyl ether (DME). Both ethers adsorb on fully oxidized CeO$_2$(111) and highly reduced CeOx(111) under UHV conditions but only at low temperature (~150 K) and they do not decompose. If the catalyst surface is pre-covered by hydroxyls, by adsorbing water at room temperature on the reduced CeOx(111) surface, then the adsorption geometry of the ether on this hydroxylayted surface changes, indicating interaction with OH groups. Regarding their reactivity towards decomposition, the two ethers behave differently when exposed to hydroxylated CeOx(111) at 300-400 K. In the case of DEE, this molecule promptly reacts by breaking the C-O bond presenting a very interesting chemistry. By means of Reflection Absorption Infrared Spectroscopy (RAIRS) and soft X-Ray Photoelectron Spectroscopy (sXPS), we could detect ethoxide and possibly carboxylate species as adsorbed intermediates for the reaction. However, when the hydroxylated CeOx(111) is exposed to DME at same conditions, the ether shows no reactivity, indicating the importance of H on a carbon atom β to oxygen. Possible explanations for the role of hydroxyls in helping break the C-O bond of ether molecules will be given.

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8:40am **SS1-MoM2 Adsorption and Activation of n-alkanes on a PdO(101) Thin Film**, ***J.F. Weaver***, *C. Hakanoglu, J.A. Hinojosa, Jr., A. Antony, J.M. Hawkins, A. Asthagiri*, University of Florida

The formation of palladium oxide (PdO) is thought to be responsible for the exceptional activity of supported Pd catalysts toward the complete oxidation of alkanes under oxygen-rich conditions. In this talk, I will discuss our recent investigations of the adsorption and activation of n-alkanes on a PdO(101) thin film that is prepared by oxidizing Pd(111) in ultrahigh vacuum (UHV) using an oxygen atom beam. We find that alkanes adsorb relatively strongly on the PdO(101) surface by forming σ-complexes along the rows of coordinatively unsaturated Pd atoms. The formation of σ-complexes causes the alkane binding energies on PdO(101) to exceed those of alkanes physisorbed on Pd(111). We also find that the alkane σ-complexes on PdO(101) act as precursors for initial C-H bond cleavage; propane and n-butane undergo facile C-H bond cleavage below about 215 K in UHV. Finally, I will discuss density functional theory calculations which show that dative bonding between the alkane and cus-Pd atoms weakens the coordinated C-H bonds, thereby lowering energy barriers for C-H bond scission by as much as 100 kJ/mol. These findings provide insights for understanding the role of molecularly chemisorbed precursors in the initial activation of alkanes on PdO(101) and possibly other transition-metal oxide surfaces.

9:00am **SS1-MoM3 Stereo and Enantioselectivity in Surface Reactions**, ***F. Zaera***, University of California, Riverside **INVITED**

Achieving high selectivity is arguably the main upcoming challenge in heterogeneous catalysis for the 21st century. In complex reaction with competing parallel pathways, small changes in the relative values of the different activation energies are sufficient to switch the selectivity of those processes from one product to another. We in our laboratory have been carrying out mechanistic studies on the conversion of hydrocarbons on model metal surfaces to try to identify the key factors that control such selectivity. In this talk we will present a couple of examples of increasing subtlety from that work. In the first, we will discuss a reaction involving a C=C double bond isomerization, in particular cis-trans isomerization reactions. The second example will be focused on issues of bestowing enantioselectivity on solid surfaces by using cinchona alkaloid modifiers. In both case,s it will be shown how the mechanistic information obtained from surface-science studies can be extended to design more selective real catalysts.

9:40am **SS1-MoM5 Enantioselective Explosions on Chiral Surfaces**, ***A.J. Gellman***, *Y. Huang, F. Xu, V.V. Pushkarev*, Carnegie Mellon University

The high Miller index surfaces of single crystal metals have chiral structures and interact enantiospecifically with chiral adsorbates. The enantiospecificity of surface reaction kinetics is dictated by the enantiospecificity of surface reaction energetics but can also be influences by reaction order. Recently, it has been shown that tartaric acid decomposes with explosive reaction kinetics on Cu(110) surfaces. Tartaric acid is chiral and on naturally chiral Cu surfaces such as Cu(643), Cu(653), Cu(17,5,1), and Cu(531) the non-linear nature of the reaction kinetics leads to extremely high enantiospecificity. The explosive reaction kinetics originte with the need for empty surface sites for the decomposition process. At high coverages of tartaric acid the limited availablity of empty sites contrains the decomposition process. Once nucleated, however, the reaction proceeds autocatalytically and occurs over a very narrow temperature range during heating. The decomposition kinetics of R,R- and S,S-tartaric acid depend on the handedness of the Cu substrate and the decomposition features observed during temperature programmed reaction spectroscopy are completely resovled. Peak enantiospecificities in the decomposition reaction rates can reach a factor of fifty.

10:00am **SS1-MoM6 C-H Bond Activation of Light Alkanes on Pt(111): Dissociative Sticking Coefficients, Evans-Polanyi Relation, and Gas-Surface Energy Transfer**, *G. Cushing, J. Navin, S. Donald,* ***I. Harrison***, University of Virginia

Effusive molecular beam experiments were used to measure alkane dissociative sticking coefficients, S(T$_g$, T$_s$), for which the impinging gas temperature, T$_g$, and surface temperature, T$_s$, could be independently varied. The 500-1000 K temperature range primarily examined should be relevant to heterogeneously catalyzed industrial processes such as the steam reforming of alkanes. Methane, ethane, and propane all showed increasing dissociative sticking as either T$_g$ or T$_s$ was increased – indicative of activated dissociation reactions. Effusive beam experiments with gas impinging along the surface normal and T$_g$=T$_s$=T determined S$_n$(T), a close approximation and formal upper bound to the thermal dissociative sticking coefficient, S(T), appropriate to reaction with a thermal ambient gas. Activation energies determined from S$_n$(T) for methane, ethane, and propane are E$_a$= 58 kJ mol^{-1}, 43 kJ mol^{-1}, and 34 kJ mol^{-1}, respectively. An Evans-Polanyi plot of E$_a$ for alkane dissociative chemisorption versus the alkane thermal desorption energy, E$_d$, is linear with a slope of -0.94. Assuming that the alkane E$_d$ serves as a good approximation to the Van der Waals stabilization of the chemisorbed alkyl radical product of dissociative chemisorption, the slope of the Evans-Polanyi plot indicates a late transition state for alkane dissociative chemisorption on Pt(111). A microcanonical unimolecular rate theory model of dissociative chemisorption was used to model the effusive molecular beam experiments. Explicit accounting of the gas-surface energy transfer for the non-equilibrium experiments became increasingly important as the alkane size was increased. A simple exponential down model of the molecule/phonon collision step size distribution with a mean energy down parameter of α= 350 cm^{-1} for ethane, and α = 1400 cm^{-1} for propane, sufficed to provide a good description of the S$_n$(T$_g$, T$_s$) data.

10:40am **SS1-MoM8 Heat of Formation of Adsorbed Methoxy on Pt(111) by Adsorption Microcalorimetry**, ***E. Karp***, *M. Crowe, C.T. Campbell*, University of Washington

The heat of adsorption of methanol on clean and oxygen pre-covered Pt(111) surfaces was measured in the temperature range of 100 to 160 K using Single Crystal Adsorption Calorimetry (SCAC). Our ultrahigh vacuum calorimeter, which also includes capabilities for AES, LEED and ISS, routinely achieves pulse-to-pulse standard deviations in heat measurements of 0.5 kJ/mol using methanol pulses containing only 0.02 ML. Averaging 8 runs reduces this to below 0.2 kJ/mol. These measurements provide the heat of formation of methoxy, an important intermediate in several catalytic reactions, including methanol reforming for highly pure H2. Above 125K, methanol is known to react with pre adsorbed oxygen adatoms to form methoxy and co-adsorbed OH (Akhter et. al., Surf. Sci.,167, 1986, 101):

CH3OH(g)+Oads-->CH3Oads+OHads, at 125K< T <160 K.

Recently our group experimentally determined the heat of formation of OHads on Pt(111) to be -226.8 kJ/mol, using this value we have determined the heat of formation of adsorbed methoxy and compared this value to theoretical DFT work. Heats of adsorption of methanol were also measured on clean Pt(111) at 100K, as well as on the amorphous methanol multilayer, and compared to prior TPD measurements.

11:00am **SS1-MoM9 Interaction of Ethylene and Nitrogen Atoms on the Pt (111) Surface**, ***J. Yin***, *R. Meyer, M. Trenary*, University of Illinois at Chicago

The selective catalytic reduction (SCR) of NO_x by hydrocarbons on noble metals is critically important to the implementation of leaner burning more fuel efficient processes. Understanding the reaction mechanisms and pathways is essential for designing an effective catalytic system. As one small part of this effort, we focus on the interaction of nitrogen atoms and simple alkenes such as ethylene on the Pt(111) surface under UHV conditions in an effort to understand the potential intermediates in NO_x reduction. The adsorption of ethylene on a nitrogen pre-covered Pt(111) surface has been investigated using reflection absorption infrared spectroscopy (RAIRS) and thermal desorption spectroscopy (TDS) as well as density functional theory calculations. Three interesting observations have been made. First, we observed the presence of π-bonded ethylene below 220 K, indicating a switch in the preferred binding site for ethylene on N-Pt (111) as compared to the clean surface. Second, above 500 K, CN coupling occurs as indicated by the desorption of HCN and the identification of CNH_2 with RAIRS. Third, the formation of ammonia is observed through NH_3 desorption as well as by observation of the d_s (NH_3) mode of NH_3 at ~1170 cm^{-1} with RAIRS. The appearance of ammonia is believed to be the result of a reaction between N atoms (or NH) with coadsorbed ethylidyne.

11:20am **SS1-MoM10 Probing the Reaction Intermediates for the Water–gas Shift Over Inverse CeO_x/Au(1 1 1) Catalysts**, ***D.J. Stacchiola***, *S.D. Senanayake, J. Hrbek, J.A. Rodriguez*, Brookhaven National Laboratory

The water–gas shift (WGS) is an important reaction for the production of molecular H_2 from CO and H_2O. An inverse CeO_x/Au(1 1 1) catalyst exhibits a very good WGS activity, better than that of copper surfaces or Cu nanoparticles dispersed on a ZnO substrate which model current WGS industrial catalysts. In this work we report on intermediates likely to arise during the CO + H_2O reaction over CeO_x/Au(1 1 1) using soft X-ray photoemission (sXPS) and near-edge X-ray absorption fine structure (NEXAFS). Several potential intermediates including formates (HCOO), carbonates (CO_3) and carboxylates (HOCO) are considered. Adsorption of HCOOH and CO_2 is used to create both HCOO and CO_3 on the CeO_x/Au(1 1 1) surface, respectively. HCOO appears to have greater stability with desorption temperatures up to 600 K while CO_3 only survives on the surface up to 300 K. On the CeO_x/Au(1 1 1) catalysts, the presence of Ce^{3+} leads to the dissociation of H_2O to give OH groups. We demonstrate experimentally that the OH species are stable on the surface up to 600 K and interact with CO to yield weakly bound intermediates. When there is an abundance of Ce^{4+}, the OH concentration is diminished and the likely intermediates are carbonates. As the surface defects are increased and the Ce^{3+}/Ce^{4+} ratio grows, the OH concentration also grows and both carbonate and formate species are observed on the surface after dosing CO to H_2O/CeO_x/Au(1 1 1). The addition of ceria nanoparticles to Au(1 1 1) is essential to generate an active WGS catalyst and to increase the production and stability of key reaction intermediates (OH, HCOO and CO_3).

11:40am **SS1-MoM11 Reactivity of CO towards Nanocrystals and Continuous Films of α-Fe_2O_3 on Au(111) at Ambient Pressure: Implications for the Water-Gas Shift Reaction**, ***X. Deng***, *J. Lee, C. Wang, C. Matranga,* National Energy Technology Laboratory (NETL), *F. Aksoy, Z. Liu*, Lawrence Berkeley National Laboratory

The reactivity of CO towards nanocrystals and continuous films of α-Fe_2O_3 grown on Au(111) was investigated using in-situ X-ray photoelectron spectroscopy (XPS) at near ambient pressure (hundreds of mTorr). On Au(111) decorated with α-Fe_2O_3 nanocrystals (6-7nm), adsorbed CO was detected by XPS at room temperature when exposed to 200 mTorr of CO. At the same time, surface hydroxyl groups (adsorbed OH) were also observed as a result of H_2O dissociation. Upon heating the surface to 373 K, adsorbed formate (HCOO-) was detected on the surface and believed to originate from the reaction of CO with the OH groups. The adsorbed formate desorbed or decomposed above 473 K. Continuous α-Fe_2O_3 thin films on Au(111) were inert towards CO under the same conditions studied for nanocrystalline α-Fe_2O_3. Specifically, adsorbed CO was *not* observed on this surface when it was exposed to 200 mTorr of CO at room temperature. This reactivity difference can be explained by the presence of α-Fe_2O_3 crystal edges and the interfaces between α-Fe_2O_3 and Au. These edges and interfaces are present for the nanocrystalline α-Fe_2O_3/Au(111) system, but are not present in significant amounts for the continuous films of α-Fe_2O_3. Implications of these experimental results for the water-gas shift reaction will be also discussed.

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