In-Situ Spectroscopy and Microscopy Focus Topic
Room: 211C - Session IS+AS+SS-MoM

Fundamental Studies of Surface Chemistry of Single Crystal and Nanomaterials under Reaction Conditions
Moderator: Franklin (Feng) Tao, University of Kansas, Zili Wu, Oak Ridge National Laboratory

8:20am IS+AS+SS-MoM1 Hot Electron In-Situ Surface Chemistry at Oxide-Metal Interfaces. Foundations of Acid-Base Catalysis, *Gabor Somorjai*, University of California, Berkeley **INVITED**
The development of Catalytic Metal-Semiconductor Nanodiodes (CMSN) to measure the flow of electrons excited during exothermic catalytic reactions at the metal interface proved that oxidation on platinum generates a steady flux of hot electrons [1] Evidence is presented that the steady state of chemicurrent is correlated to the turnover frequency and that the exothermic hot electron production during reactions on transition metal particles may be widespread. The CO/O_2 and H_2/O_2 reactions were studied most frequently by this method and semiconductors included TiO_2, GaN, CoOx, NbOx and TaOx Charge transport between the metal and oxide interfaces also influences the product distribution of multipath reactions. These were shown in the hydrogenation of furfural and croton aldehyde at platinum/TiO_2 interfaces as compared to the platinum/silica interfaces [2]. The oxide-metal interfaces appear to produce ions, which carry out reactions that have long been called by the organic chemistry community as acid base catalysis. The typical catalytic structure is mesoporous oxide that is produced to hold the metal nanoparticles. The structures produce high surface area oxide metal interfaces and this is a catalytic architecture for acid base catalysis. Studies in changing the transition metal oxide using a single metal of platinum as nanoparticles, shows the tremendous amplification effect of the oxide metal interfaces in the reactions such as the carbon monoxide oxidation. Platinum alone produces on silica three orders of magnitude less CO_2 by the CO oxidation process than on cobalt oxide, that is the most active of these acid base oxide metal interface catalytic systems [3]. Nevertheless, not just cobalt oxide, but nickel oxide, manganese oxide, and iron oxide, produces much higher activity for this reaction than platinum alone. In other reactions, when n-hexane isomerization or cyclisation reactions studied, the pure oxides niobium or tantalum do not produce any reaction other than cracking two smaller molecular fragments. However, at the platinum-oxide interfaces with niobium oxide or tantalum oxide, almost 100% selectivity for isomerization could be achieved [4]. Thus it appears that charge catalysis plays a very important role, which is equal in importance to the role of pure metal covalent catalysis that produces molecules without any apparent charge flow. Generation of hot electron flows and the catalytic activity of two-dimensional arrays of colloidal Pt nanoparticles with different sizes are investigated using catalytic nanodiodes. Pt nanoparticles of smaller size lead to higher chemicurrent yield, which is associated with the shorter travel length for the hot electrons, compared with their inelastic mean free path [5]. In many oxide supports microporous sites are used, which are less than 1 nm in size and do not allow the larger platinum nanoparticles inside these pores. In that case, the metal that is used to create the catalysts are deposited on the outside surface of the microporous support. This sort of system, where the metal is outside, but the acidic microporous oxides are inside, can be active only by a spill over of the reaction intermediates from the metal to the oxide - and this is quite well known. However if the micropores are substituted by mesopores in the oxide phase the metal nanoparticles can go inside and then single site oxide-metal interface catalysis commences. These two different catalytic processes, where both the oxide and the metal are catalytically active, deserve attention and distinction.

9:00am IS+AS+SS-MoM3 In-situ GISAXS/GIXAS Characterization of $Co_{1-x}Pt_x$ Bimetallic Clusters under H_2 and CO + H_2 Mixture, *Bing Yang*, Material Science Division, Argonne National Laboratory, *G. Khadra, J. Tuaillon-Combes*, Institut Lumière Matière, University Lyon & CNRS, France, *E. Tyo*, Material Science Division, Argonne National Laboratory, *S. Seifert*, X-ray Science Division, Argonne National Laboratory, *X. Chen*, Department of Mechanical Engineering, Northwestern University, *V. Dupuis*, Institut Lumière Matière, University Lyon & CNRS, France, *S. Vajda*, Material Science Division, Argonne National Laboratory
CoPt alloy particles have recently attracted great interests for their excellent catalytic and magneticproperties. The alloy phase of cobalt and platinum may create dual-functional sites at the mixed interface which enables novel catalytic properties and synergic effect at nanometer scale. In-situ characterization is thus essential to probe the structure and composition of bimetallic clusters under reaction conditions in a catalytic process of interest.

$Co_{1-x}Pt_x$ bimetallic clusters with atomic-precise Pt/Co atomic ratio (x=0, 0.25, 0.5, 0.75, 1) were synthesized using mass-selected low energy clusters beam deposition (LECBD) technique and soft-landed onto the amorphous alumina thin film prepared by atomic layer deposition (ALD). The median diameter of size-selected $Co_{1-x}Pt_x$ alloy clusters is 3nm with size dispersion lower than 10 % according to transmission electron microscopy (TEM). Utilizing X-ray photoemission spectroscopy (XPS), the oxidation state of as-made clusters as well as the aged particles after extended exposure to air was characterized. After exposure to air, both cobalt and platinum species in the bimetallic clusters are found to be oxidized, while the shift of their covalent state exhibits a non-linear correlation with their atomic composition (Pt/Co).

Utilizing *in-situ* grazing incidence small-angle X-ray scattering and X-ray absorption spectroscopy (GISAXS/GIXAS), the evolution of particle size/shape and the oxidation state of the individual metals are monitored under atmosphere reaction conditions. The as-made $Co_{1-x}Pt_x$ clusters were first pretreated with hydrogen and further exposed to CO and H_2 mixture up to 225ºC. The change in the oxidation state of Co and Pt of the supported bimetallic clusters exhibited a non-linear dependency on the Pt/Co atomic ratio. For example, low Pt/Co ratio (x≤0.5) facilitates the formation of $Co(OH)_2$, whereas, high Pt/Co ratio (x=0.75) stabilizes Co_3O_4 composition instead, due to the formation of Co@Pt core-shell structure where the platinum shell inhibits the reduction of cobalt in the core of the $Co_{1-x}Pt_x$ alloy clusters.

In this work, we have demonstrated *in-situ* measurement of particle size/shape and the oxidation state of supported $Co_{1-x}Pt_x$ bimetallic clusters under operating conditions, and elucidated the different surface structure and chemical state with respect to their atomic ratio. The obtained results indicate ways for optimizing the composition of binary alloy clusters for catalysis.

9:20am IS+AS+SS-MoM4 Novel Surface Oxide on Pt(111) as the Active Phase for NO and CO Oxidation Studied with the ReactorSTM, *Matthijs van Spronsen**, *J.W.M. Frenken, I.M.N. Groot*, Leiden University, Netherlands
Platinum finds its main application as a car catalyst to control the emission of exhaust gases. Although automotive catalysis has been extensively investigated, challenges still exist. One of the challenges arises when increasing the oxygen/fuel ratio. Under oxygen-rich reaction conditions, much uncertainty exist about the structure of the active surface phase. This is even true for the Pt(111) surface, which is the facet lowest in energy and the simplest model catalysts available.

An early *operando* Scanning Tunneling Microscopy (STM) study [1] showed a stepwise increase in CO oxidation activity at oxygen-rich conditions. This increase concurred with a dramatic and instantaneous morphology change. From the STM images, the atomic structure could not be resolved, but roughening on a long length scale was observed. Under similar conditions, Surface X-ray Diffraction found the formation of thin, bulk-like α-PtO_2 [2]. Surprisingly, a theoretical study concluded that this oxide is inert to CO oxidation [3].

With the high-pressure, high-temperature ReactorSTM [4], we studied the oxidation of Pt(111) both by exposing to O_2 and to NO oxidation conditions.

Upon oxidation with O_2 (1.0 bar, 423-523 K), we found a stable surface oxide consisting of triangles assembled in a 'spoked-wheel' superstructure. In addition, we found a second structure consisting of a lifted-row pattern. The two structures were coexisting on different regions on the surface. The lifted-row structure was becoming more predominant at higher O_2 pressure. We propose that both oxides share the same building block, which are expanded Pt oxide rows.

After evacuation of the reactor, the ordered structures disappeared, although some remnants remained. The surface oxidation is a clear example of the pressure-gap effect. Furthermore, lower-temperature (291-323 K) experiments did not yield any ordered structure showing the dependence on atomic mobility.

Exposure of Pt(111) to NO and O_2 or exposure to NO_2 resulted in the formation of a mixture of small domains of both the spoked-wheel and the lifted-row structures.

The surface oxidation was accompanied with roughening of terraces. This is attributed to relaxation of adsorbate-induced stress on the surface. Identical roughness development was previously found under CO oxidation

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* Morton S. Traum Award Finalist

conditions [1]. Therefore, we argue that a surface oxide was also the relevant structure under CO oxidation conditions.

[1] Bobaru, PhD thesis, Leiden University, 2006

[2] Ackermann, PhD thesis, Leiden University, 2007

[3] Li & Hammer, Chem. Phys. Lettt., 409, 1, 2005

[4] Herbschleb, *et al.*, Rev. Sci. Instrum., 85, 083703, 2014

9:40am IS+AS+SS-MoM5 *In Operando* Study of Dimethyl Methylphosphonate Degradation Over Metallic and Oxidized Cu(111) Surfaces via Ambient-Pressure X-ray Photoelectron Spectroscopy, *Lena Trotochaud*, *A.R. Head*, Lawrence Berkeley National Laboratory (LBNL), *Y. Yu*, University of Maryland, *O. Karslioglu, M. Hartl*, LBNL, *B. Eichhorn*, University of Maryland, *H. Bluhm*, LBNL

Filtration systems for absorption and decomposition of chemical warfare agents (CWAs) are the first line of defense against exposure to these toxic compounds. Composite materials (such as ASZM-TEDA) commonly used in filtration systems consist of high-surface-area carbon supports impregnated with various metals and metal oxides. Despite decades of work to develop highly effective and versatile filtration materials with long-term usability, little is known about the mechanisms of CWA degradation by material surfaces and catalyst deactivation and poisoning, in part due to the challenges involved with spectroscopic characterization of catalyst surfaces under operating conditions. Enabling the rational design of more advanced filtration and decomposition materials for broad-spectrum protection against CWAs and other toxic industrial compounds requires a sophisticated understanding of the chemical mechanisms behind CWA sorption and degradation on the molecular scale.

We will present the surface spectroscopic study of metallic and oxidized Cu(111) single crystal surfaces for catalytic decomposition of dimethyl methylphosphonate (DMMP), a CWA simulant. Ambient-pressure X-ray photoelectron spectroscopy (APXPS) enables examination of these surfaces during DMMP adsorption and decomposition. Initial experiments indicate that adsorption of DMMP on Cu(111) is observed at pressures as low as 1×10^{-7} Torr, and degradation of DMMP is observed at this pressure and higher (60 mTorr) at room temperature. Possible mechanisms of DMMP degradation and deactivation of the surface will also be discussed.

10:00am IS+AS+SS-MoM6 Bridging the Pressure and Materials Gap between Surface Science and Catalysis: Probing the Surface of Metal Oxide Nanoparticles under Reaction Conditions, *Maria Kipreos, M. Foster*, University of Massachusetts, Boston

Traditionally, surface science employs ultra-high vacuum, cryogenic conditions and well defined crystal planes; however, heterogeneous catalysis and photocatalysis occur in ambient conditions with complex substrates composed of several crystal planes. Consequently, materials and pressure gaps exist that need to be bridged in order to better understand the surface chemistry of catalysts under reaction conditions. Metal oxide particles employed in catalysis contain a complex matrix of crystal planes, metal/oxygen bonds, metal/hydroxyl bonds, and oxide/water interactions. We utilize *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) to monitor reactions from ambient to high pressures between gaseous adsorbates (water, formic acid, and methanol) and metal oxide particles (TiO_2 and ZnO, semiconductors and ZrO_2, an insulator) commonly used as components of catalysts. The internal and external scattering of light that occurs in DRIFTS is well suited for analysis of reactions on the surface of metal oxide nanoparticles. Spectral shifts in frequency, peak area and width values, and absorbance values are used to interpret the structure and reactivity of the surface. Additionally, the use of Confocal Raman Spectroscopy aids in determining the structural variability in these substrates. The use of gaseous probes and these instrumental techniques provides a better understanding of the structure and reactivity of solid nanoparticles surfaces.

10:40am IS+AS+SS-MoM8 The Use of Integrated *Operando, In Situ* and DFT Techniques to Unravel the Steps of Heterogeneous Catalytic Reactions, *Fabio Ribeiro*, *W.N. Delgass, J. Greeeley, R. Gounder, J. Miller*, Purdue University, *W.F. Schneider*, University of Notre Dame **INVITED**

Our quest to understand catalysis is limited by our ability to observe the active site while it is turning over. To facilitate this task we developed model catalysts where the active sites are deposited on the external surface area of an appropriate support. Effective characterization, however, happens only with the simultaneous measurement of the rate of reaction while the catalyst is in operation, called operando measurements. The application of operando techniques is becoming a more common tool to help unravel catalytic functions. Our group has custom-built an operando reactor for the measurement of X-ray absorption spectroscopy. While operando measurements are a major improvement, they provide a static picture of a system that is actually dynamic. Dynamic techniques where the catalyst kinetic and structural properties can be followed simultaneously with a time resolution of a fraction of a turnover are the techniques of choice. We will show examples using a transmission FTIR cell we developed. The great advantage and sometimes necessity of performing experiments in the dynamic and operando modes will be discussed. The help from theory will also be illustrated.

11:20am IS+AS+SS-MoM10 In Situ XPS Of Graphene-Catalyst Interactions During Chemical Vapor Deposition, *Robert Weatherup*, Lawrence Berkeley National Laboratory

Critical to controlling the growth of graphene and carbon nanotubes during chemical vapor deposition (CVD) is a detailed understanding of the role of the catalyst, however this remains incomplete due the wide parameter space. Here we investigate the dynamics of graphene-catalyst interactions during CVD using time- and depth-resolved X-ray photoelectron spectroscopy[1-2], in situ scanning tunneling microscopy,[3] and grand canonical Monte Carlo simulations coupled to a tight-binding model[1]. We focus on Ni(111) as a model catalyst surface and probe in-operando a wide range of hydrocarbon exposure pressures (10^{-6}-10^{-1} mbar). The key atomistic mechanisms of graphene formation on Ni are thereby revealed and our data highlights an interdependency between the distribution of carbon close to the catalyst surface and the strength of the graphene-catalyst interaction.

The strong interaction of epitaxial graphene with Ni(111) causes a depletion of dissolved carbon close to the catalyst surface, which prevents additional layer formation leading to a self-limiting graphene growth behavior for low exposure pressures (10^{-6}-10^{-3} mbar). Increasing the hydrocarbon pressure further (to ~10^{-1} mbar) leads to weakening of the graphene-Ni(111) interaction accompanied by additional graphene layer formation, mediated by an increased concentration of near-surface dissolved carbon. We also reveal that the growth of more weakly adhered, rotated graphene on Ni(111) is linked to an initially higher level of near-surface carbon compared to the case of epitaxial graphene growth. We relate these results to the simple kinetic growth model that we have previously established,[6] and use them to consistently explain previous graphene CVD results in the literature. The key implications for graphene growth control and their relevance to carbon nanotube growth are thereby highlighted.

References

(1) Weatherup et al. J. Am. Chem. Soc. 2014, 136, 13698-13708

(2) Weatherup et al. Nano Lett. 2011, 11, 4154-4160

(3) Patera et al. ACS Nano 2013, 7, 7901-7912

(4) Weatherup et al. ACS Nano 2012, 6, 9996-10003

11:40am IS+AS+SS-MoM11 Mechanism Study for Salen Ligand Homogeneous Catalyst in a Heterogeneous Catalysis System, *Niclas Johansson*, *S. Chaudhary, A.R. Head, O. Snezhkova, J.N. Andersen, J. Knudsen, J. Schnadt*, Lund University, Sweden

Surface-immobilization of transition metal complexes otherwise used as homogeneous catalysts, i.e. in the same (solution) phase as the reactants and products, and their use as heterogeneous catalysts has been an active field of research for many years. The attractiveness of the idea of surface-immobilization lies in the potential to significantly increase the efficiency and selectivity of heterogeneous catalysts [1], the ease of catalyst and product separation [1], and the fact that the need for solvents and highly oxidizing agents might be eliminated in the heterogeneous system.

Here we direct our attention towards the transition metal Mn(III)-salen complex[R,R(-)N,N'Bis(3,5-di-t-butylsalicylidene, 1,2-cyclohexane diaminomanganese(III)chloride) which have been shown to be very effective homogeneous catalysts for enatioselective epoxidation of unfunctionalised olefins. Yet, while much research has been done to investigate the salen complexes' catalytic properties in the homogeneous phase, very few surface science studies have been performed [2,3].

Here we report a study starting from standard UHV conditions and bridging the pressure gap into more realistic conditions. Here, we will show UHV spectra coupled to Torr-range Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS).

We investigated propylene(C_2H_6) epoxidation reaction using surface-deposited Mn(III)-Salen on Au(111) as catalyst. With APXPS we were able to follow the electronic structure changes during reaction conditions in a gas mixture of propylene and oxygen. The spectra acquired show gas phase interactions and changes was found that were specific to the gas mixture. Surprisingly, O 1s spectra acquired at room temperature shows CO_2 which indicates complete oxidation of propylene. This result was further confirmed with a mass spectrometer in direct connection with the reaction chamber. Indeed, the complexes are active even in a heterogeneous system supporting the possibility of transferring homogeneous catalysts into heterogeneous catalytical systems.

References

[1] C. Copéret and J.-M. Basset, Adv. Synth. Catal. 349 , 78 (2007)

[2] K. Lämel et al, Nano Lett. 10, 2965 (2010)

[3] A. Schwartz et al., J. Phys. Chem. C 117, 1105 (2013)

Authors Index
Bold page numbers indicate the presenter