In Situ Spectroscopy and Microscopy Focus Topic
Room: 106 - Session IS+AS+SS-MoM

In Situ Studies of Catalysis and Gas-Solid Reactions
Moderator: G. Rijnders, University of Twente, the Netherlands

8:20am IS+AS+SS-MoM1 In Situ X-ray Studies of Model and Real Catalysts: Bridging the Complexity Gap, *A.I. Frenkel*, Yeshiva University **INVITED**
In the last decade, there was a surge in advanced characterization methods to study catalytic materials at work. Most notable innovations in synchrotron-based techniques include the coupling of in situ/operando x-ray absorption and scattering methods to vibrational spectroscopies, empowered by improved time and energy resolutions. For example, in situ XAFS-XRD combination enables complementary studies of short and long range order in the same system, a great tool when multiple spatial dimensions evolve in a certain process, such as: modifications of both the catalyst and the support during catalytic reaction, the nucleation and growth of a nano-catalyst, oxidation/reduction of a bulk oxide. Combining in situ XAS or XRD with infrared or Raman spectroscopy is critical for understanding how the structural and electronic properties of a catalyst relate to its reactivity.

Although these are important new improvements in the way we currently study, and understand, processes in nanomaterials, they are done by methods that are not sensitive to local fluctuations in size, shape, structure of nanomaterials, that are present even in well-defined, model catalysts. Thus, in addition to the ensemble averaging that these and other commonly used methods provide, local information, such as one provided by electron microscopy, is needed. In this talk, I will focus on the new efforts in combining the local and average information by coupling the in situ x-ray absorption spectroscopy to in situ environmental transmission electron microscopy (E-TEM) for in situ investigations. Such experiments, done in two separate facilities (NSLS and CFN) at Brookhaven National Laboratory, revealed anomalous, mesoscopic phenomena in the electronic, structural and thermal properties of supported Pt nanoparticles. These systems have long been excellent model systems in catalysis research, yet, at a closer look, as our in situ measurements demonstrated, they turned out to be much more unstable and complex then previously perceived. These clusters exhibited unique physical properties, such as negative thermal expansion, increase in the Debye tempeature, broad amorphous-to-crystalline transition zone, large surface strain, as well as charge exchange with support and adsorbates.

I will review recent works showing how such complex behaviors can be, in the case of Pt on g-alumina and carbon supports, theoretically understood by separately studying the effects of their size, shape, support and adsorbates.

9:00am IS+AS+SS-MoM3 Communicating Nanostructures: Spillover Processes Studied on Ceria-supported Platinum Nanoparticles, *M. Happel*, Friedrich-Alexander-Univ. , Germany, *Y. Lykhach, T. Staudt*, Friedrich-Alexander-Univ., Germany, *N. Tsud*, Charles Univ., Czech Republic, *T. Skála, K.C. Prince*, Sincrotrone Trieste, Italy, *V. Matolín*, Charles Univ., Czech Republic, *A. Migani*, Univ. de Barcelona, Spain, *G.P. Petrova*, Univ. of Sofia, Bulgaria, *A. Bruix, F. Illas, K.M. Neyman*, Univ. de Barcelona, Spain, *G.N. Vayssilov*, Univ. of Sofia, Bulgaria, *J. Libuda*, Friedrich-Alexander-Univ. Erlangen-Nuremberg, Germany
Ceria-based catalysts are technologically important for various applications, including automotive catalysis, SO_x scrubbers, and hydrocarbon transformation reactions. The complex surface chemistry and reaction kinetics in these systems are assumed to be strongly influenced by so-called metal-oxide (MO) interactions. We use a surface science-based model approach to obtain detailed insight into the origins of such effects at the microscopic level.

The model catalysts are based on ordered $CeO_2(111)$ films on Cu(111), on which noble metal nanoparticles (e.g. Pt) are grown by PVD under UHV conditions. The growth and geometric structure of the model catalysts are characterized by STM. Adsorption and reaction are followed by XPS, synchrotron radiation photoelectron spectroscopy (SR-PES), IRAS, and molecular beam (MB) methods, in combination with DFT calculations. Resonant PES (RPES) is used to monitor the changes in the cerium oxidation state with high sensitivity.

Two types of MO interaction are identified, electron transfer from the Pt nanoparticle to the support, and oxygen transfer (spillover) from ceria to Pt. Whereas electron transfer occurs on ceria supports irrespective of their morphology, oxygen transfer shows a pronounced structure dependency, i.e. it requires the presence of nanostructured ceria aggregates in close contact with Pt.[1]

Not only oxygen spillover, which is a key step in oxidative-self cleaning of carbon-poisoned catalysts, but also spillover and reverse-spillover of hydrogen and hydrocarbon fragments can be followed in detail by RPES. A particularly complex behavior is expected for SO_x, for which strong MO effects and spillover have been suggested in previous studies on powder catalysts. On the Pt-free model support we identify different sulfur species forming upon SO_2 exposure even at 150 K (sulfites, atomic sulfur, and potentially sulfates), formed via different adsorption, decomposition and disproportionation pathways. At higher temperature, these species transform into a bulk-like cerium oxysulfide. For interpretation of the sulfur-chemistry on Pt/CeO_2, reference experiments on Pt(111) were performed and numerous SO_x species were identified by IRAS and SR-PES. RPES for SO_2 adsorption on Pt/CeO_2 provides direct evidence for spillover of SO_x to the Pt nanoparticles above 300 K. Between 300 K and 600 K Pt acts as a "sulfur-collector", before at even higher temperatures sulfur is finally transformed into a cerium oxysulfide species.

[1] G. Vaysillov, Y. Lykhach, A. Migani, T. Staudt, G.P. Petrova, N. Tsud, T. Skála, A. Bruix, F. Illas, K.C. Prince, V. Matolín, K.M. Neyman, J. Libuda, *Nat. Mater.* **2011**, *10*, 310.

9:20am IS+AS+SS-MoM4 HPXPS Study of the Oxidation of 10 nm PdAg Nanoparticles, *S. Blomberg*, *J. Gustafson, N.M. Martin, M.E. Messing, K. Deppert, J.N. Andersen,* Lund University, Sweden, *L.E. Walle, A. Borg,* Norwegian University of Science and Technology, Norway, *H. Grönbeck,* Chalmers University of Technology, Sweden, *M.E. Grass, Z. Liu,* Lawrence Berkeley National Laboratory, *E. Lundgren*, Lund University, Sweden
Due to the economic and environmental rewards, one goal in catalysis related research is to create cheaper catalysts. One way to realize this is to dilute the more expensive active catalyst material with a less costly one. This requires that the active material stays at the surface. This could be achieved by using a material which is less prone to interact with the reactant gases, such as a noble metal. In most catalysts, the active material is dispersed in a high area complex oxide support as nanoparticles. In order to maintain the high activity, it would be necessary to ensure that the active material is at the surface of the nanoparticle.

In the present contribution we report on our initial findings from attempts to produce PdAg alloy particles using an aerosol deposition technique [1]. The particles have a diameter of 10 nm distributed over a SiO_x wafer. The samples was characterized by high pressure XPS, SEM and TEM as was done previously for aerosol Pd particles [2,3]. By comparing to XPS data from a single crystal $Pd_{75}Ag_{25}(100)$ and from The X-ray Energy Dispersive Spectroscopy (XEDS) analysis we show that the PdAg particles have a similar alloy composition.

The *in-situ* high pressure XPS data from the 10 nm PdAg particles demonstrates that the Pd segregates to the surface in an oxygen rich environment and that the core of the particles are rich in Ag. Although a thin PdOx shell is formed, bulk oxidation is inhibited. The limited oxide formation is promising for the full oxidation of methane, since recent investigations [4] suggest that the PdO is less active for methane oxidation than the metallic Pd.

[1] M. E. Messing, K. A. Dick, L. R. Wallenberg, K. Deppert, Gold Bull. **42** (2009) 20.

[2] M. E. Messing *et al*, J. Phys. Chem. C. **114** (2010) 9257 .

[3] R. Westerström *et al*, Phys. Rev. B. **83**, (2011) 115440.

[4]A. Hellman *et al.,* submitted.

9:40am IS+AS+SS-MoM5 New Assignment for Ag(III) from *In Situ* XPS of Highly Oxidized Silver Films, *T.C. Kaspar*, *T. Droubay, S.A. Chambers,* Pacific Northwest National Laboratory, *P.S. Bagus*, University of North Texas
For decades, it has been a goal to elucidate the mechanisms behind the unique chemistry of both oxygen-exposed silver metal and silver oxides. Silver compounds in bulk, thin film, and nanoparticle form are widely investigated for applications including industrially-relevant catalysis, electrochemistry, transparent conducting oxides, and antimicrobial coatings. Determining the chemical state of both silver and oxygen is critical to developing a mechanistic understanding of the remarkable properties of these materials. *Ex situ* x-ray photoelectron spectroscopy (XPS) has been applied, starting in the 1970's, to determine the chemical state of Ag in various silver metal and silver oxide compounds. In contrast to most elements, Ag^{x+} (x>0) cations exhibit a negative binding energy (BE) shift

relative to metallic Ag(0); thus, the lowest XPS core level binding energy observed for the Ag 3d peak, 367.3 eV, has been assigned to Ag(III) in AgO [Ag(I)Ag(III)O_2]. However, the XPS analysis has been hindered by the ease with which silver oxides form carbonate species upon atmospheric exposure, as well as the instability of silver oxides in vacuum. In this work, silver oxide films have been formed under very oxidizing conditions, by molecular beam epitaxy (MBE) deposition of silver metal in the presence of activated oxygen. *In situ* XPS was then collected in an appended chamber. For the most highly oxidizing deposition conditions, a substantially lower BE, 366.8 eV, was found for the Ag 3d peak, with an associated satellite located at 368.2 eV. This oxide species proved unstable in vacuum over several days, but could be recovered by further exposure to activated oxygen. Based on the decomposition behavior of the Ag 3d and O 1s spectra, the low BE species was assigned as Ag(III), while the previous peak position for Ag(III) was re-assigned as Ag(I). These assignments are supported in part by electronic structure calculations predicting the photoemission spectra of Ag(III). The combination of highly oxidizing deposition conditions and *in situ* characterization allowed identification of the true Ag(III) XPS spectrum for the first time.[1]

[1] T.C. Kaspar, T. Droubay, S.A. Chambers, and P.S. Bagus. *J. Phys. Chem. C* **114** 21562 (2010).

10:00am **IS+AS+SS-MoM6 The Oxidation of Methane Over Pd**, *A. Hellman,* Chalmers Univ. of Tech., Sweden, *A. Resta,* European Synch. Rad. Fac., France, *J. Gustafson*, *N.M. Martin,* Lund Univ., Sweden, *A. Trinchero, P.-A. Carlsson,* Chalmers Univ. of Tech., Sweden, *O. Balmes,* European Synch. Rad. Fac., France, *J.N. Andersen,* Lund Univ., Sweden, *R. Feici,* European Synch. Rad. Fac., France, *E. Lundgren,* Lund Univ., Sweden, *H. Grönbeck,* Chalmers Univ. of Tech., Sweden

An important goal in surface science is to provide fundamental information on gas-surface interactions for the design of cheaper and more efficient catalysts. For this purpose, the required minimum knowledge is the composition of a catalyst for a certain reaction under realistic reaction conditions. Although this information seems trivial it is surprisingly difficult to obtain due to the complex structural nature of a real catalyst and the sometimes high temperatures and pressures under reaction conditions.

In the case of the complete oxidation of methane using Pd as the catalyst**,** pure Pd metal, Pd surface oxides and bulk PdO have all been reported to be most efficient to convert CH4 into CO2 and H2O [1-5]. This highlights the complexity of catalysis even for a relatively simple catalytic reaction.

In order to shed some light on the state of Pd during complete methane oxidation, we have performed in-situ Surface X-Ray Diffraction (SXRD) over a Pd(100) surface in a realistic reaction environment combined with DFT calculations. Our study demonstrates that significant roughening of the surface occur during the reaction, which increases the active surface area and thus affects the overall reactivity. Nevertheless, our study strongly suggests that the Pd metal is the most active phase for the full oxidation of methane.

[1] R. Burch, P. K. Loader, and F. J. Urbano, Catalysis Today **27** (1996) 243.

[2] R. F. Hicks, H. H. Qi, M. L. Young, and R. G. Lee, J. Catal. **122** (1990) 280.

[3] M. Lyubovsky and L. Pfefferle, Catalysis Today **47** (1999) 29.

[4] S. Oh, P. J. Mitchell, and R. Siewert, J. Catal. **123** (1991) 287.

[5] J. G. McCarthy, Catalysis Today **26** (1995) 283.

11:00am **IS+AS+SS-MoM9 The New Ambient Pressure X-ray Photoelectron Spectroscopy Instrument at MAX-lab - An Instrument also for Ultrahigh Vacuum Studies**, *J. Schnadt*, *J. Knudsen, A,. Pietzsch, N. Johansson, A. Olsson, F. Hennies,* Lund University, Sweden, *N. Mårtensson, H. Siegbahn,* Uppsala University, Sweden, *J.N. Andersen*, Lund University, Sweden

Ambient pressure x-ray photoelectron spectroscopy (APXPS) is a technique, which dates back to the 1970s and 1980s, but which only during the past ten years has developed a very significant impact, driven forward especially by groups at the Advanced Light Source and BESSY. APXPS makes possible x-ray photoelectron spectroscopy (XPS) measurements under realistic or close-to realistic conditions, while conventional XPS is limited to vacuum conditions of 10^{-6} mbar or better. APXPS thus contributes to closing the "pressure gap" of surface science, which has inhibited the understanding of processes and chemical reactions, for which the chemical potential of the gas atmosphere plays a decisive role. It also renders possible experiments on samples with a large vapour pressure, such as liquids or solid samples with a high degasing rate. Today, there exist a

number of APXPS instruments around the world, including a small number of systems at synchrotrons. Common to these instruments is that they perform well at elevated pressures, but none of them is specifically designed to also allow studies under ultrahigh vacuum conditions. This complicates the connection to results from ultrahigh vacuum studies.

A new instrument for APXPS has just been installed at beamline I511 of the Swedish Synchrotron Radiation Facility MAX-lab. This instrument, which has been delivered by SPECS GmbH, Berlin, Germany, and which makes use of a PHOIBOS 150 NAP analyser, has been developed with the particular aim of building a strong link between ultrahigh vacuum and ambient pressure experiments and science. The instrument is capable of performing XPS measurements on the same sample in both types of environment. This is made possible by a unique design, which is based on the use of a retractable ambient pressure cell. For ambient pressure measurements at pressures of around 0.1 to 10 mbar the cell is docked to the electron energy analyser. Once the sample is loaded the cell is locked, and the only leak to the vacuum is through the nozzle of the analyser's lens system. Hence, even during ambient pressure measurements the vacuum remains intact in the analysis chamber. For UHV measurements the cell together with the nozzle is retracted into a separate chamber, and UHV XPS measurements can be performed normally. This entails also another attractive feature of the instrument, namely, that the high pressure cell easily can be replaced by dedicated cells for other sample environments.

In this contribution the design and concept of the APXPS instrument at MAX-lab will be discussed and first results shown. Also plans for an upgraded and dedicated new beamline at MAX-lab will be presented.

11:20am **IS+AS+SS-MoM10 In Situ XPS and STM Studies of Ge$_2$H$_6$ Interactions with the Si(100) Surface**, *S. McDonnell*, *J.F. Veyan,* University of Texas at Dallas, *J. Ballard, J.H.G. Owen, J.N. Randall,* Zyvex Labs, *Y.J. Chabal, R.M. Wallace*, University of Texas at Dallas

We present a study of the reactions between Ge2H6 and Si(100) surfaces. Ge2H6 is a potential precursor that could allow atomic layer epitaxy (ALE) on Ge(100) and Si(100) surface [1,2] which will be a vital component for atomically precise manufacturing (APM). We investigate the effects of various growth conditions such as substrate temperature, dosing pressure and post deposition annealing. We study the formation of seed layers for ALE along with the reactions on both the atomically clean and the hydrogen passivated surfaces, were we see evidence of Ge2H6 reacting with the dangling bonds.

To facilitate these studies, we utilize a UHV deposition/characterization tool. Chemical analysis of the surfaces is achieved using *in-situ* x-ray and ultraviolet photoelectron spectroscopy. Differences in the chemical states of germanium present on the surface under the various growth conditions are indentified. This analysis is supplemented by *in-situ* scanning tunneling microscopy, which allows us to monitor the growth of germanium on silicon and confirm 2D or 3D growth. Comparisons a made with similar experiments carried out in a different UHV chamber where the surface is characterized with Fourier transform infrared spectroscopy (FTIR) and shows evidence of the digermane reacting with the surface at 173K as Ge2H5 rather than GeH3.

This material is based upon work supported by the Defense Advanced Research Project Agency (DARPA) and Space and Naval Warfare Center, San Diego (SPAWARSYSCEN-SD) under contract N66001-08-C-2040. It is also supported by a grant from the Emerging Technology Fund of the State of Texas to the Atomically Precise Manufacturing Consortium.

[1] D.-S. Lin, K.-H.Huang, T.-W. Pi, and R.-T. Wu. Phys. Rev. B, 54 16 (1996) 958

[2] K.-H.Huang, T.-S. Ku, and D.-S. Lin Phys. Rev. B, 56 8 (1997) 4878

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