

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 313 - Session IS+AS+MC+SS-TuM

Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS)

Moderator: Franklin (Feng) Tao, University of Notre Dame

8:00am **IS+AS+MC+SS-TuM1 The ISS Facility at BESSY II and Beyond: The Application of Near Ambient Pressure X-ray Electron Spectroscopy in the Surface Characterization of Technical Catalysts, Michael Hävecker**, Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherung BESSY II, Germany, *Ch. Heine, M. Eichelbaum, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, F. Rosowski, BasCat, UniCat-BASF JointLab, Germany, A. Trunschke, R. Schlögl, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*

INVITED

The surface of functional materials like catalysts responds to the ambient conditions. Surface sensitive in-situ spectroscopy, i.e. in the presence of a reactive gas allows studying the formation of the gas/solid interface of a catalyst. The ISS facility operated by the FHI at the synchrotron radiation source BESSY II of the HZB is dedicated to this kind of in situ studies [1 - 3]. Online gas analytics allows correlating the electronic surface structure with the catalytic performance. Examples for the dynamic formation of the electronic surface structure by interaction with the ambient gas under equilibrium will be presented focusing on technical catalysts like multi-element mixed oxide powders. The direct catalytic oxidation of alkanes to olefins and oxygenates is becoming increasingly important for the chemical industry due to the up-coming shortage of crude oil resources. Vanadyl pyrophosphate is the industrially used catalyst in the selective oxidation of n-butane to maleic anhydride. We characterized the surface of this catalyst material with NAP-XPS in the mbar pressure range and with NAP-soft XAS in the electron yield mode at pressures up to 1000mbar at various gas mixtures. In addition to the determination of composition and vanadium oxidation state also semiconductor properties like work function changes and Fermi level pinning have been studied [4].

Finally, an outlook on future activities at HZB/BESSY to develop further synchrotron based ambient pressure characterization methodologies will be given. The Energy Materials In-Situ Laboratory Berlin (EMIL) is a research alliance of the HZB and FHI that will include a NAP-high kinetic energy XPS endstation capable to operate at kinetic energy of photoelectrons up to 7000eV that allows studying buried layers and liquid/solid interfaces.

References

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Bluhm, H., Hävecker, M. et al., In situ x-ray photoelectron spectroscopy studies of gas-solid interfaces at near ambient conditions, *MRS BULLETIN.*, 63, 169 (2007).

Bluhm, H. et al., Investigation of solid/vapor interfaces using ambient pressure X-ray photoelectron spectroscopy. *Chem. Soc. Rev.*, 42, 5833 (2013).

Heine, Ch. et al., Work function, band bending, and microwave conductivity studies... *J. Phys. Chem. C*, 117, 26988 (2013).

8:40am **IS+AS+MC+SS-TuM3 Recent Trends and Instrument Development in Ambient Pressure Photoelectron Spectroscopy, Henrik Bergersen, J. Åhlund**, VG Scienta AB, Sweden

The field of Ambient Pressure Photoelectron Spectroscopy (APPEs) has gone through rapid development in recent years. Although the field was pioneered in the 1970's, most instrument as well as application development has happened in the last decade. In this contribution we will discuss some recent trends in APPEs and present state-of-the-art work within the different applications areas.

Experiments done under normal surface science conditions (Ultra High Vacuum) are of limited use in some applications, e.g. catalysis, due to the pressure gap problem. This motivates the study of systems at ambient pressures. While the presence of a gas atmosphere surrounding the sample enables new types of studies, it also poses instrumentation difficulties. The most notable of these is signal decrease due to inelastic scattering of the photoelectrons in the surrounding gas. We will show state-of-the-art solutions to limit this scattering together with recent results.

Photoelectron spectroscopy went through a revolution in the 1990's, with the development of parallel angular detection using 2D detectors, a

development that VG Scienta is proud to have contributed to. The possibility of simultaneous recording of Angular Resolved PES (ARPES) spectra enables not only band structure measurements, but also x-ray photoelectron diffraction (XPD), depth profiling and standing wave spectroscopy. Recent examples within APPEs will be given.

The use of 2D detectors to record parallel spatially resolved spectra is a related technique. Here we will show experimental results as well as very recent instrument development to obtain world leading spatial resolution at ambient conditions.

The combination of APPEs and Hard X-ray Photoelectron Spectroscopy (HAXPES) has recently become an established technique. We will show results of the use of this combination to decrease inelastic scattering of the photoelectrons as well as to tailor the probing depth of advanced systems.

In APPEs, more than in UHV PES, instrument usability and sample handling is a key to successful measurements. VG Scienta has developed several complete system offerings to maximize productivity in the lab. These will be discussed on a conceptual level, as well as in some detail.

9:00am **IS+AS+MC+SS-TuM4 In Situ Studies of Exceptionally Active Catalyst of Earth Abundant Elements for Complete Combustion of Methane at a Relatively Low Temperature, F. Tao, J. Shan, L.T. Nguyen, S. Zhang, Weixin Huang**, University of Notre Dame

It is critical to develop a catalyst made of earth-abundant elements highly active for a complete combustion of CH₄ at a relatively low temperature for catalytically transforming CH₄ to electrical energy in power plant. The currently available catalysts with high activity consist of precious metal nanoparticles supported on rare earth oxides. Their high cost limits the application of these catalysts at industrial scale. Here we report a new catalyst, early transition metal oxide-based mixed oxide only consisting of earth-abundant elements which can completely combust CH₄ at 350°C at a gas hourly space velocity of 240,000 ml 0.5% CH₄ on 1 gram in one hour. This comparable or even higher catalytic activity results from the integration of Ni cations and surface lattice oxygen atoms at the atomic scale. With such an integration, the carbon atom dissociated from CH₄ can bond with its neighboring surface oxygen atoms to form an intermediate of CO₂ and then desorb.

In-situ studies of catalyst surface using AP-XPS and monitoring of products formed from isotope-labeled catalysts show that (1) molecules O₂ dissociates on surface oxygen vacancies, (2) half of the dissociated oxygen atoms stay in oxygen vacancies, (3) the other half of dissociated oxygen atoms directly bond with hydrogen atoms dissociated from CH₄ to form OH and then H₂O molecules, (4) CH₄ progressively dissociates on Ni cations to form CH_n (n=3, 2, 1, 0), (5) carbon atoms bind to two surface lattice oxygen atoms nearby to form a carboxylate species, O-C-O intermediate, and then desorb. The mixed cations and surface lattice oxygen atoms in this mixed oxide at atomic level makes the formation of an -O-C-O- intermediate at a mild temperature since a spillover of dissociated species is not necessary.

9:20am **IS+AS+MC+SS-TuM5 Ambient Pressure XPS Studies of Fuel Cell and Electrolysis Catalysis, Hirohito Ogasawara**, SLAC National Accelerator Laboratory

INVITED

Fuel cell and electrochemical reactions were studied by ambient pressure X-ray photoemission spectroscopy at Stanford Synchrotron Radiation Lightsource (SSRL) [1]. We will present our recent studies: platinum catalyst under different operating conditions of oxygen reduction fuel cell reaction, iridium oxide catalyst during the oxygen evolution reaction and molybdenum sulfides catalyst during the hydrogen evolution reaction. Surface changes under these electrochemical reactions, which are keys to understanding activity and durability will be shown [2,3].

[1] Ambient-pressure photoelectron spectroscopy for heterogeneous catalysis and electrochemistry, *CatalysisToday* 205 (2013) 101.

[2] Direct observation of the oxygenated species during oxygen reduction on a platinum fuel cell cathode, *Nature Communications* 4 (2014) 2817

[3] In situ observation of surface species on iridium oxide nanoparticles during the oxygen evolution reaction, submitted

11:00am **IS+AS+MC+SS-TuM10 Environmental Cells with 2D Electron Transparent Windows for Ambient Pressure Photoelectron Imaging and Spectroscopy, Andrei Kolmakov**, National Institute of Standards and Technology (NIST)

We have designed and characterized electron transparent windows for environmental cells dedicated for ambient pressure XPS spectroscopy and electron microscopy of liquid and gaseous samples. These windows made of single or multi-layered graphene have thicknesses comparable to the effective attenuation length of 200-1000 eV electrons what allow to conduct

interfacial spectroscopy of fully hydrated samples without differential pumping setup. In addition, these membranes are thermally and chemically stable, gas impermeable and mechanically robust. Based on this unique combination of properties and on recent developments in graphene fabrication and transfer protocols we demonstrate the capability to perform in situ XPS and electron microscopy studies of the electrochemical processes taking place at liquid electrolyte-solid interface.

11:20am **IS+AS+MC+SS-TuM11 The Effect of Interfacial Ethanol on Ionic Distributions in Aqueous Solution**, *Marijke Van Spyk, K.A. Perrine, M.J. Makowski*, University of California Irvine, *H. Bluhm*, Lawrence Berkeley National Laboratory, *J.C. Hemminger*, University of California Irvine

In this study, liquid microjet X-ray photoelectron spectroscopy (LJ-XPS), carried out at beam line 11.0.2 of the ALS synchrotron at LBNL, was used to probe the interfacial behavior of aqueous magnesium or sodium chloride solutions with the addition of organics including ethanol under one torr of water vapor. Our results address fundamental issues of solvation at the surface and in the bulk of ternary solutions. For these studies, aqueous ethanol solutions were generated, and salt was added to produce an ionic solution. The ternary solution is pumped continuously through a temperature-controlled quartz capillary to produce a micron-sized laminar jet within 0.5 mm of the PES analyzer aperture. Synchrotron radiation ionizes the solution, and ejected photoelectrons are detected using differentially pumped electron optics. Tunable photon energy, together with the inelastic scattering attenuation of photoelectrons in solution, provide a variable probe depth. Here, photoelectrons with low kinetic energies (200 eV) are detected from the surface of solution, and those with high kinetic energies (600 eV) are detected from deeper into solution, where chemistry is consistent with bulk solution. The high kinetic energy photoelectrons have sufficiently large inelastic mean free paths so that a percentage are not attenuated by inelastic scattering.

Carbon (C1s), oxygen (O1s), sodium (Na2s), magnesium (Mg2s), and chloride (Cl2p) photoelectron spectra were collected at two photoelectron kinetic energies to investigate the relative concentration of species at the surface and in the bulk for various ethanol concentrations. The C1s spectra were deconvoluted into two gas phase and two solution phase peaks corresponding to the carbon groups in ethanol. Surface adsorption was evident for aqueous ethanol without ions, and was diminished in the presence of ions. The relative ionic propensities at the surface change with ethanol concentration. In particular, the solvation of magnesium was impacted by dehydration. Understanding the interfacial solute distribution of these ternary solutions is important for predicting reactivity at aqueous surfaces.

11:40am **IS+AS+MC+SS-TuM12 Studying Zeolites and Clays with the Tools of Surface Science from UHV to Near-Ambient Pressures**, *Jorge Boscoboinik*, Brookhaven National Laboratory **INVITED**

While Surface Science provided useful insights into a variety of materials of interest for catalysis, its contribution to the understanding of zeolites and clays has been limited. This was mainly due to the lack of suitable well-defined surfaces that successfully mimic the properties of these important materials while allowing its analysis using the vast toolkit of surface science. This talk will describe an aluminosilicate ultra-thin (~ 0.5 nm) film that was recently synthesized, which provides a good model system for zeolites and clays. It consists of a bilayer structure, as shown in the figure, and it counts with bridging hydroxyl groups. The latter are the active sites in zeolite catalysts, of great importance for energy transformations such as the cracking of crude oil and the methanol to gasoline conversion. This model system allows then to study the interaction of molecules involved in these catalytic processes and potentially contribute to the understanding of these chemical transformations. I will provide first a description of the system itself as characterized in ultra-high vacuum (UHV) conditions and then move on to analyze the interaction of these aluminosilicate films with different molecules of interest from UHV to near-ambient pressures.

References

- [1] J.A. Boscoboinik, X. Yu, B. Yang, F.D. Fischer, R. Włodarczyk, M. Sierka, S. Shaikhutdinov, J. Sauer, H.-J. Freund, *Angew. Chem. Int. Ed.* 51 (2012) 24, 6005-6008. *Angew. Chem.* 124 (2012) 6107-6111.
- [2] J.A. Boscoboinik, X. Yu, B. Yang, S. Shaikhutdinov, H.-J. Freund. *Micropor. Mesopor. Mater.* (2013) 165, 158-162.
- [3] J.A. Boscoboinik, X. Yu, E. Emmez, B. Yang, S. Shaikhutdinov, F. Fischer, J. Sauer, H.-J. Freund. *J. Phys. Chem. C* (2013) 117, 13547-13556.

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