In-Situ and Operando Spectroscopy and Microscopy for Catalysts, Surfaces, & Materials Focus Topic
Room 101C - Session IS+HC-WeA

Ambient Pressure XPS Studies of Surface and Chemistry of Catalysts

Moderators: Franklin (Feng) Tao, University of Kansas, Anatoly Frenkel, Yeshiva University

2:20pm **IS+HC-WeA1 The Electronic Structure of Electrochemically Active Interfaces***, V. Pfeifer,* Fritz-Haber-Institut der Max-Planck-Gesellschaft and Helmholtz-Zentrum Berlin, Germany*; J.J. Velasco-Velez,* Max-Planck-Institut für Chemische Energiekonversion, Germany*; R. Arrigo,* Diamond Light Source Ltd., UK*; T.E. Jones,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; M. Hävecker,* Max-Planck-Institut für Chemische Energiekonversion, Germany*; E. Stotz,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; R. Schlögl,* Fritz-Haber-Institut der Max-Planck-Gesellschaft and Max-Planck-Institut für chemische Energiekonversion, Germany*; **Axel Knop-Gericke**,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

In this presentation I will describe the application of near ambient pressure photoelectron spectroscopy (NAPXPS) to the investigation of electrochemically active gas-solid and liquid-solid interfaces during electrochemical processes. Understanding the oxygen evolution reaction (OER) on a molecular level has become increasingly important over the last few years, beacuse energy storage of renewables is becoming more relevant now that CO_2 emission has been identified as a source of climate change.

Nafion membrane based NAPXPS experiments performed on Pt electrodes during the OER demonstrate that Pt oxides are detrimental for the OER. An oxygen induced species characterized by an Pt4f binding energy 0.6 eV above the metallic Pt4f peak was observed. However, these experiments were done in water vapor and the relevance of the results for the OER in liquid water is questionable [1]. Therefore a new approach to study the liquid-solid interface during an electrochemical process in liquid water was developed.

In this new process the electrode material is deposited on a bilayer of graphene that is stabilized by a silicon nitride window with a pinhole structure. The electrode is exposed to the aqueous electrolyte and is irradiated at the same time by synchrotron light through the bilayer graphene membrane. The emitted photoelectrons have to pass the graphene membrane before being detected in the photoelectron analyzer [2]. Recent progress in the study of the electronic structure of noble metal electrodes used in OER reaction will be discussed [3,4].

References:

1. R. Arrigo et al., In Situ Study of the Gas-Phase Electrolysis of Water on Platinum by NAP-XPS, *Angew. Chem. Int. Ed.* **52**, 11660-11664 (2013)

2. J. J. Velasco-Velez et al., Photoelectron spectroscopy at the graphene-liquid interface reveals the electronic structure of an electrodeposited cobalt/graphene electrocatalyst, *Angew. Chem. Int. Ed.* **54**, 14554-14558 (2015)

3. V. Pfeifer et al., The electronic structure of iridium oxide electrodes active in water splitting, *PCCP*, **18**, 2292-2296 (2016)

4. V. Pfeifer et al., The electronic structure of iridium and its oxides, *Surf. Interface Anal.*, **48**, 261-273 (2016)

3:00pm **IS+HC-WeA3 In situ AP-XPS and NEXAFS Studies on CO Oxidation and CO_2 Dissociation on Copper Surfaces***, B. Eren, **Christian Heine**, G.A. Somorjai, M.B. Salmeron,* Lawrence Berkeley National Laboratory (LBNL)

This presentation contains three parts: 1- Surface science approach to CO oxidation reaction on the low-index Cu surfaces which shows at oxygen lean conditions where the Cu surface is not oxidized to Cu2O, (111) face of Cu is more active than more open (100) and (110) faces. This is due to high binding energy of atomic oxygen on Cu, i.e., poisoning of the lower coordinates sites of Cu. 2- Chemical state of the surface and subsurface, and adsorbate coverage on Cu(111) in steady state conditions. Here, we provide phase diagram of the surface under reaction conditions. Interestingly, no CuO phase occurs between 273K-413K when the CO:O2 ratio is chosen as 2:1 or above. Cu2O phase appears to be to more active phase, however it still unclean whether the reaction on Cu2O is a MvK or LH type. 3- Finally, we present the chemical state and the surface morphology of Cu during CO2 dissociation at ambient pressures, which appears to be different than in the presence of CO or O2 alone.

3:20pm **IS+HC-WeA4 Alcohol Adsorption and Reaction on $La_{0.7}Sr_{0.3}MnO_3$(100) by APXPS***, **David Mullins**, T.Z. Ward, S.H. Overbury,* Oak Ridge National Laboratory

Perovskite materials that are characterized by the composition ABO_3 can be formed by a wide variety of A and B cations. This enables the catalytic properties to be altered by selectively choosing the constituents while maintaining nominally the same structure. The adsorption and oxidation of simple alcohols such as methanol and ethanol have been identified as probe reactions to characterize and compare the catalytic properties of different oxide surfaces.

Methanol and ethanol oxidation on doped $La_{0.7}Sr_{0.3}MnO_3$(001) have been studied using ambient pressure x-ray photoelectron spectroscopy (APXPS). $La_{0.7}Sr_{0.3}MnO_3$(001) was grown on single crystal Nb-doped $SrTiO_3$(001) by pulse laser deposition. The growth of this film has been extensively characterized as a function of temperature, oxygen pressure and laser fluence in order to produce near ideal crystallinity and morphology in the film. The APXPS experiments were performed on the end station at the recently commissioned Beamline CSX-2 at NSLS II. In order to investigate the so-called "pressure gap" that may occur between reactions studied under vacuum conditions and at pressure approaching atmospheric pressure, experiments were conducted at nominally 10^{-5} torr and at 0.1 torr between 250° C and 350° C.

Methanol forms methoxy when adsorbed on the perovskite surface at 250° C. The surface coverage was four times greater at 0.1 torr compared to 10^{-5} torr. Methoxy was the only C-containing surface species observed at 10^{-5} torr with or without O_2. Methoxy was also the dominant surface species at 0.1 torr in the absence of O_2. However, small amounts of formate and atomic C were also evident. At the higher pressure the Mn 2p spectra indicated that the alcohol partially reduced Mn^{3+} to Mn^{2+}. There was also an indication in the O 1s spectra that O was removed from the surface.

When O was present at 0.1 torr formate became the dominant surface species with only trace amounts of methoxy and C also evident. Gas phase CO_2 and H_2O products were also detected in the C 1s and O 1s spectra.

Results using ethanol rather than methanol as the reactant were generally the same, i.e. only ethoxy on the surface at lower pressures, a mixture of ethoxy and acetate at higher pressure in the absence of O_2, and exclusively acetate on the surface when O_2 was present. The only significant difference between methanol and ethanol was a greater tendency for ethanol to form the carboxylate in the absence of O_2.

Operando experiments are planned to monitor the products with a mass spectrometer to determine whether the different pressures, and resulting surface species, lead to different products.

5:00pm **IS+HC-WeA9 *In situ* Spectroscopy for Catalyst Design***, **Rosa Arrigo**,* Diamond Light Source, Oxfordshire, UK **INVITED**

Observing structural dynamics of heterogeneous catalysts in action yields important mechanistic insights to guide the synthesis towards improved materials. Synchrotron-based ambient pressure X-ray photoemission spectroscopy (AP-XPS) has become very popular worldwide to serve this purpose.[1-3] One expanding field of application of this technique is electro-catalysis[2-3] due to its central role in a renewable energy scenario. In this contribution, I will present two examples of the application of this technique to study the gas/solid interface of electro-catalysts for a polymeric electrolyte membrane-based electrode assembly.[4] The first example is the oxygen evolution reaction (OER), which occurs at the anode side of an electrochemical cell for water electrolysis. Herein, the highly debated descriptions of the electronic structure of the oxygen evolving Pt[4] and Ir[5] surfaces are clarified. The second example is the CO_2 reduction reaction (CO_2RR) to fuel over Fe on N-functionalised carbon-based electro-catalysts. These catalysts proved to be active for the CO_2 reduction but the competing hydrogen evolution reaction (HER) from water reduction is favored. Results of this research will be presented which enable us to shine light onto the nature of the H evolving sites and CO_2 reducing sites on this type of catalyst.

[1] H. Bluhm, M. Hävecker, A. Knop-Gericke, M. Kiskinova, R. Schlögl, M. Salmeron, MRS Bulletin 32, 2007, 1022.

[2] J. J Velasco-Velez, V. Pfeifer, M. Hävecker, R. S Weatherup, R. Arrigo, C.-H. Chuang, E. Stotz, G. Weinberg, M. Salmeron, R. Schlögl, A. Knop-Gericke, Angewandte Chemie International Edition 54, 2015, DOI: 10.1002/anie.201506044.

[3] Z. Liu, H. Bluhm, Hard X-ray Photoelectron Spectroscopy (HAXPES), 447-466. DOI: 10.1007/978-3-319-24043-5_17.

[4] R. Arrigo, M. Haevecker, M. E. Schuster, C. Ranjan, E. Stotz, A. Knop-Gericke, R. Schloegl, Angewandte Chemie International Edition, 52, 2013, 11660-11664.

[5] V. Pfeifer, T. Jones, J.-J. Velesco-Velez, M. Greiner, C. Massué, R. Arrigo, D. Teschner, F. Girgsdies, M. Scherzer, J. Allan, M. Hashagen, G. Weinberg, S. Piccinin, M. Haevecker, A. Knop-Gericke, R. Schlögl, Physical Chemistry Chemical Physics 18, 2015, DOI: 10.1039/C5CP06997A.

5:40pm **IS+HC-WeA11 *In Situ* and *Operando* Characterization of Model Metal Nanoparticle Catalysts: Size, Shape, and Chemical State Effects*,* *Beatriz Roldan Cuenya,*** Ruhr-University Bochum, Germany **INVITED**

In order to comprehend the properties affecting the catalytic performance of metal nanoparticles (NPs), their dynamic nature and response to the environment must be taken into consideration. The working state of a NP catalyst might not be the state in which the catalyst was prepared, but a structural and/or chemical isomer that adapted to the particular reaction conditions. This talk provides examples of recent advances in the preparation and characterization of NP catalysts with well-defined sizes and shapes. It discusses how to resolve the shape of nm-sized Pt, Au, Pd, and Cu catalysts via a combination of *in situ* microscopy (AFM, STM, TEM), and *in situ* and *operando* spectroscopy (XAFS, GISAXS) and modeling, and how to follow its evolution under different gaseous or liquid chemical environments and in the course of a reaction. It will be highlighted that for structure-sensitive reactions, catalytic properties such as the reaction rates, onset reaction temperature, activity, selectivity and stability against sintering may be tuned through controlled synthesis.

Examples of catalytic processes which will be discussed include the gas-phase oxidation of alcohols (methanol, propanol, butanol), the oxidation and reduction of NO, the electrochemical oxidation of propanol and electrochemical reduction of CO_2. Emphasis will be given to elucidating the role of the NP size, shape and chemical state in the activity and selectivity of the former reactions.

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