Thursday Morning, November 10, 2016

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

In-situ and Operando Spectroscopy and Microscopy with Infrared Absorption Spectroscopy

Moderators: Franklin (Feng) Tao, University of Kansas, Judith Yang, University of Pittsburgh

8:00am **IS-ThM1 In-situ and Operando Characterization of Catalytic Reactions with Infrared Absorption Spectroscopy*, Francisco Zaera,*** University of California, Riverside **INVITED**

Infrared absorption spectroscopy has been used in our laboratory to study a number of catalytic systems, from model flat surfaces to catalysts with novel nanostructures, under in situ and operando conditions, and in both gas and liquid-solid interfaces. Examples of these applications will be discussed in this presentation, including adsorption on flat metal surfaces probed by reflection-absorption infrared spectroscopy (RAIRS) under ultrahigh vacuum, in operando conditions at atmospheric pressures, and in situ at liquid/solid interfaces. The liquid-solid interface has been characterized in total attenuated reflection (ATR) mode as well. In transmission mode, IR has been used to probe diffusion through different nanostructures, including dendrimers and silica and titania shells. Finally, diffuse-reflectance (DRIFT) IR absorption spectroscopy has been employed to follow reactions on yolk-shell nanocatalysts.

8:40am **IS-ThM3 Studying Birth, Life and Death of Catalytic Solids with In-situ and Operando Spectroscopy*, Bert Weckhuysen,*** Utrecht University, Netherlands **INVITED**

The search for new or more effective catalysts would benefit from a multiscale science approach bridging the molecular world with the macroscopic world. Recent breakthroughs in chemical imaging techniques, based on optical, electron and X-ray methods, demonstrate that such approach is within reach.

This lecture discusses the advances in spectro-microscopy of catalytic solids at different length scales, starting from single molecules and single atoms up to the level of individual catalyst particles. Special emphasis will be devoted to the exploration of mesoscale effects in heterogeneous catalysis.

9:20am **IS-ThM5 Direct Observation of CVD Graphene Growth and the Dynamics of Active Catalysts by *In situ* Scanning and Transmission Electron Microscopy***, Z-J. Wang, J. Cao, R. Farra, R. Schlögl,* ***Marc Georg Willinger,*** Fritz Haber Institute of the Max Planck Society, Germany **INVITED**

During the last three years, we have modified the set-up of a conventional scanning electron microscope in order to enable the observation of catalyst surface dynamics under controlled atmosphere and temperature. Using this instrument, we investigate chemical vapor deposition (CVD) growth of graphene on different metal catalysts. Since the experiments are performed in the chamber of a microscope, it is possible to observe a complete CVD process from substrate annealing through graphene nucleation and growth and, finally, substrate cooling in real time at nanometer-scale resolution without the need of sample transfer. The nucleation and growth of single layer graphene can be investigated at temperatures of up to 1000°C, while at the same time, surface dynamics of the active metal catalyst can be imaged and directly related to the catalytic activity [1]. Due to the high sensitivity of the secondary electron signal to changes in the work function and charge transfer at the surface, we are able to visualize different degrees of graphene-substrate coupling [2] as well as the stacking sequence of few layer graphene. In addition, the *in situ* SEM images of edge misalignment between mutual layers and individual sheets provide real-time information on the evolution of the rotation angle between growing layers and formation of the stacking order. The growth behavior of graphene on nickel, copper and platinum substrates shows characteristic differences that are related to the catalytic activity and carbon solubility of the respective catalysts. In the case of Cu and Pt substrates, we observe grain orientation dependent growth dynamics. Real-time imaging during growth thus allows us to directly visualize and study the catalytic activity of differently oriented surfaces. ESEM observations during graphene growth highlight the dynamic nature of catalysts and reveal the sensitive response of the surface to changes in the chemical potential of the gas phase. *In situ* scanning electron microscopy furthermore covers the spatial resolution of complementary *in situ* techniques that provide spectroscopic information, such as ambient pressure X-ray and Raman spectroscopy. It completes the spectroscopic data with visual information and spatially resolved chemical dynamics. Finally, in combination with *in situ* TEM, it allows to correlate locally observed phenomena with collective dynamics of active catalysts.

References:

[1] Zhu-Jun Wang et al., ACS Nano, **2015**, 9 (2), 1506-1519

[2] Piran R. Kidambi et al., Nano Lett., **2013**, 13 (10), 4769-4778

11:00am **IS-ThM10 Characterizing Working Catalysts with Correlated Electron and Photon Probes*, Eric Stach,*** Brookhaven National Laboratory*; Y. Li,* Yeshiva University*; S. Zhao,* University of Illinois at Urbana Champaign*; A. Gamalski,* Brookhaven National Laboratory*; D. Liu, R. Nuzzo,* University of Illinois at Urbana Champaign*; J.G. Chen,* Columbia University/Brookhaven National Laboratory*; A.I. Frenkel,* Yeshiva University **INVITED**

Heterogeneous catalysts often undergo dramatic changes in their structure as the mediate a chemical reaction. Multiple experimental approaches have been developed to understand these changes, but each has its particular limitations. Electron microscopy can provide analytical characterization with exquisite spatial resolution, but generally requires that the sample be imaged both ex situ and ex post facto. Photon probes have superior depth penetration and thus can be used to characterize samples in operando (i.e when they are actively working). But they generally lack spatial resolution and thus give only ensemble average information.

We have taken advantage of the recent developments in closed-cell microscopy methods to develop an approach that allows us to successfully combine electron, x-ray and optical probes to characterize supported nanoparticle catalysts in operando. By measuring the reaction products at each stage of the reaction, we can directly correlate the information that can be obtained from each approach, and thus gain a deep insight into the structural dynamics of the system.

In this work, we will show how a combination of x-ray absorption near edge (XANES) and scanning transmission electron microscopy (STEM) can be used to characterize the changes that occur in a model NiPt bimetallic catalyst during oxidation and reduction. Bimetallics are of broad interest in heterogeneous catalysis as the provide the opportunity to selectively tune reactivity and selectivity. However, the characterization of their structure by averaged probes such as x-ray absorption spectroscopy is comprised by the heterogeneity that such systems may proscribe.

The presentation will focus on the development and application of experimental methods used to describe the morphological changes that occur in this model bimetallic system. These will include high temperature atmospheric pressure electron microscopy, the direct measurement of reaction products using gas chromatography-mass spectrometry and the ability of a newly developed electron microscope for operando microscopy (based on the FEI Talos platform) to characterize bimetallic nanoparticles through energy dispersive x-ray spectroscopy.

11:40am **IS-ThM12 Tracking Atoms and Charges in Metal Catalysts under Reaction Conditions*, Anatoly Frenkel,*** Yeshiva University

In the last decade, complexity of catalytic nanoparticles attracted much attention as a major factor in catalytic processes. Atomic and electronic structure and dynamics of particles, as well as their interactions with support and adsorbates, are important descriptors of their catalytic activity. The main challenge is how to investigate these factors in a working catalyst, at high temperature and pressure, and how to do so without breaking the correlations between components of this complex system. I will give a brief overview of new methods developed recently to enable such combined studies under realistic reaction conditions. Our approach is to single out electronic charge of metal atoms in a cluster as an “observable” quantity and develop methods to “observe” it experimentally under realistic reaction conditions, and model theoretically. In this framework, complex interactions between metal and adsorbates, metal and support, and support and adsorbates can be all accounted for in terms of their effects on the cluster charge. I will review recent results utilizing this approach for a prototypical catalyst, 1nm Pt nanoparticles supported on silica. Using high energy resolution methods of X-ray absorption and emission spectroscopies (HERFD and RIXS), as well as in situ IR spectroscopy (DRIFTS) and electron microscopy, aided with first-principles (DFT) modeling, we deduced that the structure of atoms and charges in the catalyst is strongly heterogeneous and that it changes dynamically with the change in temperature and pressure of adsorbates (H_2 or CO).

12:00pm **IS-ThM13 STEM Imaging of Catalysts to the Single-Atom Level, via Closed-Cell *In Situ* Gas Reaction Technology*, Lawrence Allard,*** Oak Ridge National Laboratory*; S. Duan, J. Liu,* Arizona State University

In recent years, catalysis by single-atom species dispersed on supports has been shown to be an exciting and viable possibility, for catalytic reactions in many systems [e.g. ref. 1]. The stability of single metal atoms on a support during elevated temperatures typically seen in "real" reaction processes is a critical issue, and is necessary to characterize appropriately in order to develop robust single-atom catalysts (SACs). Imaging single heavy atoms on lower Z supports via aberration-corrected high-angle annular dark-field (HAADF) imaging techniques in modern electron microscopy has become routine over the past decade, and extending this imaging capability into the realm of *in situ* gas-reaction technology is a natural goal for the catalytic scientist to better understand dynamical movement and the anchoring of noble metal atoms on specific support sites. This understanding will allow the ability to synthesize SACs with significant loadings of catalytic species while maintaining the full dispersion at the single-atom level.

Novel *in situ* gas-reaction technologies that utilize MEMS-based heater devices retained in a "closed-cell" reactor specimen holder for use in aberration-corrected (S)TEM instruments have shown the remarkable ability for imaging atomic columns in a crystal structure even at elevated temperatures and at pressures up to a full atmosphere [e.g. ref 2]. The possibility to extend this imaging capability to SACs has been a goal of our work, and will be demonstrated in this talk. The effects of the electron beam on the sample, and the effects of electron scattering processes within the gas and window materials that comprise the gas-cell are problematical questions that are being addressed. An "ideal" SAC catalyst comprising Pt atoms on NiO nanocrystals has been used as the model sample for HAADF images to demonstrate cases from material on a standard TEM grid to material in the full geometry of the closed gas-cell reactor.

References:

1. B. Qiao, A. Wang, X. Yang, L.F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li and T. Zhang, "Single-atom catalysis of CO oxidation using Pt1/FeOx," *NatureChemistry***3** August 2011, pp. 634-641.

2. L.F. Allard, S.H. Overbury, W.C. Bigelow, M.B. Katz, D.P. Nackashi and John Damiano; "Novel MEMS-Based Gas-Cell/Heating Specimen Holder Provides Advanced Imaging Capabilities for *In Situ* Reaction Studies," *Microsc. Microanal.***18**, 2012, pp. 656–666.

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