

Tuesday Afternoon, October 20, 2015

In-Situ Spectroscopy and Microscopy Focus Topic

Room: 211C - Session IS+AS+SS-TuA

Environmental TEM Studies for Catalytic and Energy Materials

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

2:20pm **IS+AS+SS-TuA1 In Situ and Operando TEM of Thermal and Photocatalysts**, Peter Crozier, B.K. Miller, L. Zhang, Q. Liu, Arizona State University **INVITED**

Heterogeneous catalysts play a vital role in the development of energy technologies. Understanding the fundamental relationships between catalyst activity and structure at the nanoscale will enable the improved design of catalyst nanostructures. *In-situ* and *operando* environmental transmission electron microscopy (ETEM) is a powerful technique for the investigation of structure-reactivity relationships in high surface area catalysts under reaction conditions. With current instruments, atomic resolution imaging and spectroscopy can be carried out in the presence of gas, liquid, light and thermal stimuli. The combination of mass spectrometry and electron energy-loss spectroscopy allow catalytic products to be detected and quantified directly in the electron microscope. Several specific applications of ETEM instrumentation and experiments to several heterogeneous catalysts will be presented.

Photocatalytic water splitting can be accomplished by a heterostructure of several materials, including a light absorbing semiconductor and one or more co-catalysts. Our group has focused on Ni-NiO co-catalysts on both TiO₂ and Ta₂O₅. In the Ni-NiO/TiO₂ system, deactivation occurs due to this Ni dissolution into water during illumination and H₂ is only produced by the oxidation of Ni metal[1]. For the Ta₂O₅ supported catalyst, H₂ was produced predominantly by a catalytic reaction [2] and the deactivation rate was found to be inversely proportional to the initial thickness of the NiO shell. In both systems, deactivation is observed only during light illumination, so that this deactivation is properly called photocorrosion.

Our group has also been pioneering the use of operando TEM to study CO oxidation over supported Ru nanoparticles [3]. There is uncertainty and debate in the literature regarding the most active form of this catalyst. Images of the Ru nanoparticles after reduction *in-situ* show a clean metal surface, but after only 0.5% O₂ is introduced into the cell, a thin oxide layer forms on the surface. Similar experiments are currently being performed under operando conditions.

References:

- [1] L. Zhang, et al. The Journal of Physical Chemistry C, **119**, (2015), p. 7207–7214.
- [2] Q. Liu, et al. Applied Catalysis B: Environmental, **172–173**, (2015), p. 58–64.
- [3] B.K. Miller, P.A. Crozier Microscopy and Microanalysis **20**, (2014), p. 815–824.
- [4] The support from the U.S. Department of Energy (DESC0004954), and the National Science Foundation (CBET-1134464), and the use of ETEM at John M. Cowley Center for HR Microscopy at Arizona State University is gratefully acknowledged.

3:00pm **IS+AS+SS-TuA3 Environmental TEM Study of Gold and Platinum Nanoparticulate Catalysts**, H. Yoshida, Y. Kuwauchi, H. Omote, Seiji Takeda, Osaka University, Japan **INVITED**

The catalytic activity of metal nanoparticles depends on their size, shape, and surface structure. It is well-known that the adsorption of gases induces changes in the shape and surface structure of metal nanoparticles. Thus, it is important to obtain structural information about metal nanoparticles under reaction conditions to elucidate the correlation between the catalytic activity and the morphology of the nanoparticles. Environmental transmission electron microscopy (ETEM) is one of the powerful methods for the study of catalytic materials under reaction conditions at atomic scale [1]. In this study, we have investigated the shape and surface structure of Au and Pt nanoparticles that are supported on CeO₂ in reactant gases by a Cs-corrected ETEM.

We have found that the surface structure of a Au nanoparticle was reconstructed during CO oxidation at room temperature [2]. The {100} facets remain unreconstructed in vacuum. Under CO oxidation reaction conditions, the Au atomic columns on the topmost and second topmost {100} layers shift to peculiar positions. In the reconstructed surface the Au

atoms on the topmost surface layer form an undulating hexagonal lattice, while those on the second topmost surface layer form a normal square lattice with slight distortion. This atomic-scale *in-situ* visualizing method provides us with insights into reaction mechanisms in heterogeneous catalysis.

We have observed the oxidation and reduction processes of the surface of Pt nanoparticles by ETEM. Atomic layers of Pt oxide were formed gradually in O₂ at room temperature during ETEM observations. In situ atomic resolution ETEM, combined with in situ electron energy-loss spectroscopy, showed that atomic layers of Pt oxides, including α -PtO₂ and Pt oxides of other forms, first started forming on the preferential facets of Pt nanoparticles at the early stage, entire oxidization on the whole surface of Pt nanoparticles then followed. The oxides were reduced promptly to Pt by adding a small amount of CO or H₂O vapor to the dominant O₂ gas. It is concluded that electron irradiation during ETEM observation activates the gases non-thermally, therefore promoting or suppressing the processes at room temperature [3].

[1] S. Takeda, Y. Kuwauchi, H. Yoshida, *Ultramicroscopy*, **151** (2015) 178.

[2] H. Yoshida, Y. Kuwauchi, J. R. Jinschek, K. Sun, S. Tanaka, M. Kohyama, S. Shimada, M. Haruta, S. Takeda, *Science***335** (2012) 317.

[3] H. Yoshida, H. Omote, S. Takeda, *Nanoscale*, **6** (2014) 13113.

4:40pm **IS+AS+SS-TuA8 Environmental Study of the Reaction-driven Restructuring of Ni-Co Bimetallic Nanoparticles**, C.S. Bonifacio, University of Pittsburgh, H.L. Xin, Brookhaven National Laboratory, Sophie Carenco, M.B. Salmeron, Lawrence Berkeley National Laboratory, E. Stach, Brookhaven National Laboratory, J.C. Yang, University of Pittsburgh

Bimetallic nanoparticles (NPs) possess novel catalytic, optical, and electronic properties compared to their monometallic counterparts. These catalytic properties can be controlled by fine-tuning the NP structure and dimension, surface oxidation, and chemical composition. For instance, bimetallic NPs with a core-shell structure can allow for fine tuning of reactivity, averting sintering issues in the core, and even increase tolerance to high temperature exposure. Above all, elemental segregation in the core-shell structure has been demonstrated as a potential route of modifying the NPs catalytic properties through *in situ* gas reaction studies. To confirm this hypothesis, we have used *in situ* imaging and spectroscopy techniques to study Ni-Co core-shell NPs under environmental conditions to provide direct evidence of elemental redistribution during reaction. Two pairs of oxidation and reduction reactions were performed in an environmental transmission electron microscope (ETEM) at 0.3 Torr in O₂ and H₂ gas at 220°C and 270°C, respectively. Electron diffraction patterns and electron energy loss spectroscopy (EELS) maps showed a reaction-driven restructuring of the core-shell NPs with Ni species migrating to the NP surface by the 2nd reduction cycle. These results are in agreement with previous ambient-pressure x-ray photoelectron spectroscopy (AP-XPS) studies of the same NPs under identical reaction conditions. Furthermore, the ETEM results confirm the NP structure without erroneous interpretations that may result from post-mortem analysis of the samples. Quantitative analysis of the EELS results is underway to identify the valence states during the oxidation-reduction reactions. Correlation of the reaction-driven restructuring of NPs with the electronic structure changes from ETEM and AP-XPS will provide insight into the optimum reaction conditions, i.e., catalytic properties, of the Ni-Co core-shell NPs in challenging reactions such as selective CO₂ reduction.

5:00pm **IS+AS+SS-TuA9 In situ Vibrational Spectroscopy Investigation of the Surface Dependent Redox and Acid-base Properties of Ceria Nanocrystals**, Zili Wu, Oak Ridge National Laboratory **INVITED**

Ceria is best known for its excellent redox property that makes it an important component in the three-way catalyst for auto exhaust cleanup. This is a result of its high oxygen storage capacity associated with the rich oxygen vacancy and low redox potential between Ce³⁺ and Ce⁴⁺ cations. Equally interesting yet less is known about ceria is its versatile acid-base properties. Either as a standalone catalyst, a modifier or a support, ceria and ceria-based catalysts can catalyze the transformation of a variety of organic molecules that makes use of the acid-base as well as the redox properties of ceria.

Recent advances in nanomaterials synthesis make it possible to achieve nanocrystals with crystallographically defined surface facets and high surface area, which can be considered as ideal model systems for catalytic studies under realistic conditions. In this work, I will showcase how we can make use of ceria nanoshapes as model systems to gain molecular level understanding of the shape effect on both redox and acid-base properties

and catalysis of ceria nanocrystals *via in situ* IR and Raman spectroscopy. Insights have been gained into how the surface structure of ceria catalyst affects profoundly its redox and acid-base properties and consequently the catalytic behaviors. It is suggested that the surface structure of ceria controls the catalytic performance through the combination of various factors including structure-dependent surface sites geometry, lattice oxygen reactivity, surface vacancy formation energy, defect sites, and acid-base property on ceria.

Acknowledgements: This work was supported by Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy. A portion of the work was supported by the Center for Understanding & Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE-ME), an Energy Frontier Research Center funded by DOE, Office of Science, Basic Energy Sciences. The IR and Raman work were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

5:40pm **IS+AS+SS-TuA11 Direct Writing of sub-10 nm Structures from Liquid with Helium Ions.** *V. Iberi, R.R. Unocic, Nathan Phillip, A. Belianinov, A.J. Rondinone, D.C. Joy, O.S. Ovchinnikova,* Oak Ridge National Laboratory

In-situ direct writing by electron beam from solutions opens a pathway for resistless fabrication of nanostructures at high throughput. However, when using electrons to direct write in solution the minimal size of the created structures is limited to the micron scale due to fundamental physics of the interactions between the electron beam and the liquid, including the lateral transport of solvated electrons and ionic species. Use of the helium beam with the opposite charge and shorter mean free path offers the potential for the localization of the reaction zone on the single digit nanometer scale. Here we will present our results demonstrating writing of platinum structures from liquid (beam induced electroplating) in a platinum chloride solution using helium ions with sub-10 nm resolution. Using data analytics on acquired in-situ growth movies we are able to elucidate the main statistical descriptors for helium ion beam initiated platinum structure growth. The possible mechanisms of beam induced growth and ultrahigh localization of reaction zone are discussed. Furthermore, we will discuss optimization of solution chemistry and instrumental parameters as they relate to the quality and thickness of structures and the extension to device fabrication on a single digit nanometer level.

This work was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility.

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