

Wednesday Afternoon, October 22, 2008

In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference
Room: 310 - Session IS+NS+TR-WeA

In Situ Microscopy and Spectroscopy – Interfacial Science and Catalysis

Moderator: I. Petrov, University of Illinois at Urbana-Champaign

1:40pm **IS+NS+TR-WeA1 Large Sample Volume, Constant Flow, High Temperature MAS Probe for Catalytic Systems**, *J.J. Ford, J.Z. Hu, J.A. Sears, J.H. Kwak, D.W. Hoyt*, Pacific Northwest National Laboratory

We have recently finished construction of a new NMR probe to study catalytic systems under conditions where the reactions actually occur. The probe uses a 9.5 mm commercially available MAS rotor system and is built to operate in a 500 MHz wide bore magnet. An integrated heater assembly is able to raise the sample temperature to 400°C while the sample is spinning up to 3.5kHz. The rotor and stator assembly have been modified to allow a continuous flow of reactants through the rotor while it is spinning and at temperature. The carrier gas of either N₂ or He can carry reactants into the probe and move products out of the probe. Inserts for the rotor diffuse the gas stream over the catalyst bed and collect it on the other side. This allows steady state NMR measurements to be made under conditions comparable to those in typical catalytic environment – high temperatures and a steady influx of reactants and exhaust of products. The high sensitivity from this larger sample volume probe allows 13C observation at natural abundance. Performance test results will be presented, including an investigation of the reaction mechanisms of the carbonylation of dimethyl ether to methyl acetate on mordenite. This work has been supported by an intramural capability grant from EMSL and a DOE-Catalyst grant.

2:00pm **IS+NS+TR-WeA2 Photoelectron Emission Microscopy during CO Oxidation on Non Reconstructing Noble Metal Surfaces**, *S. Wehner, S. Karpitschka*, Universität Bayreuth, Germany, *P. Hoffmann*, Hahn-Meitner-Institut Berlin, Germany, *Y. Burkov, D. Schmeißer*, Technische Universität Cottbus, Germany, *H.R. Brand, J. Küppers*, Universität Bayreuth, Germany

The catalytic CO oxidation on Iridium(111) and Palladium(111) surfaces was investigated experimentally under ultrahigh vacuum (UHV) conditions using photoelectron emission microscopy (PEEM) to visualize surface species. The underlying reaction-diffusion system based on the Langmuir-Hinshelwood mechanism was analyzed numerically. The effect of noise on this bistable surface reaction was examined for both surfaces. In a surface science experiment the effects on product formation detected by mass spectroscopy and the development of spatio-temporal patterns on the surface were explored. The influence of noise on the reaction rates and the formation of spatio-temporal patterns on the surface was analyzed by superposing noise of Gaussian white type on the feed gas composition, characterized by the molar fraction of CO Y (variance $(\Delta Y)^2$), which represents multiplicative and additive noise. CO- and oxygen-covered regions are visible in PEEM images on both surfaces as brighter resp. darker areas as a consequence of their work function contrast. In the Iridium case islands of the adsorbate, corresponding to the globally stable branch, are formed in a background of the other adsorbate. The long transient times are the result of the extremely slow domain wall motion of these islands (around 0.05 $\mu\text{m s}^{-1}$). For small noise only a few islands nucleate and grow until they merge and finally fill the whole surface. With increasing noise the number of islands increases and their maximum size decreases. At constant ΔY the island wall velocity and the number of islands increases when Y approaches the hysteresis boundary. The island density increases with noise, but the wall velocity is independent of applied ΔY . In the Palladium case quasi-periodic breakdowns of the CO₂ with an interval of some thousands of seconds are recorded. These breakdowns are connected with very large patterns on the surface. Their domain wall motion is very fast (about 10 $\mu\text{m s}^{-1}$). This long quasi-periodic behavior vanishes, already when small noise is superposed. For larger noise the CO oxidation reaction on both surfaces shows bursts and switching in the product CO₂ rate and the recorded PEEM images.

2:20pm **IS+NS+TR-WeA3 Catalytic Raman Spectroscopy: Structure and Activity during Reaction**, *M.A. Bañares, S.J. Khatib, O. Guerrero-Pérez, M.V. Martínez-Huerta, A.E. Lewandowska*, Catalytic Spectroscopy Laboratory, CSIC, Spain

INVITED

Catalysts with large surfaces are much more complex than the model single crystals. To single out the active site under real working conditions of the catalyst is an enormous task. It requires a combination of techniques and the development or adaptation of techniques, which allow measurements under catalytic conditions (high temperatures and high pressures). This is the field of in situ spectroscopy. We have recently developed a new methodology that combines the determination of catalyst activity/selectivity and its molecular structure in a single experiment.^{1,2} We have named this methodology “operando” (Latin for “working”). The presentation will cover Raman studies to assess structure-activity relationships on supported oxides (namely V, Cr, Mo) during alkane and ammonia activation (ammoxidation). In addition, a combination of in situ Raman, XANES, and EPR spectroscopies is used to study the nature of the interaction between V and oxides supports. On most oxide supports, the redox cycle involves reversible reduction of supported vanadia sites. Ceria support behaves differently, though. Surface V⁵⁺ species strongly interact with ceria support promoting a reduction of surface Ce⁴⁺ to Ce³⁺. Upon heating or during reaction surface vanadia reacts with ceria support forming a CeVO₄ phase. The active site appears to be V⁵⁺-O-Ce³⁺ for both systems. The redox cycle for oxidative dehydrogenation appears to be associated with Ce, rather than with V sites.³

ACKNOWLEDGMENT. The support of the Spanish Ministry of Education and Science (CTQ2005-02802/PPQ)

¹ “Operando Raman study of alumina-supported Sb-V-O catalyst during propane ammoxidation to acrylonitrile with on line activity measurement”, M. O. Guerrero-Pérez and M. A. Bañares, Chem. Commun. 12, 1292 (2002).

² Miguel A. Bañares, Catal. Today 100, 71 (2005) (SPECIAL ISSUE NUMBER 100)

³ M.V. Martínez-Huerta, J. M. Coronado, M. Fernández-García, A. Iglesias-Juez, G. Deo, J.L.G. Fierro, M.A. Bañares, J. Catal. 225 (2004) 240-248

3:00pm **IS+NS+TR-WeA5 Understanding Nanoparticle Behavior in Solution: Combining Real-Time In Situ with Selective Ex-Situ Measurements to Study Transformations of Nanoparticulate Iron, D.R. Baer**, Pacific Northwest National Laboratory, *P.G. Tratnyek, J.T. Nurmi*, Oregon Health & Science University, *J.E. Amonette, P. Nachimuthu, C.M. Wang, M.H. Engelhard*, Pacific Northwest National Laboratory, *A. Sharma, Y. Qiang*, University of Idaho

In many circumstances nanoparticles are transformed by their environment. These transformations may impact particle structure, involve the formation of surface or contamination layers or alter important particle chemical or physical properties critical for specific applications. In our studies of nanoparticulate iron in aqueous solution related to contaminant transport in the environment, we need to understand the nature of the transformations and the time frame over which they occur. We are also working to develop methods to control (increase or decrease) the rate of these changes. We find that real-time in situ measurements are essential in addition to some batch ex-situ measurements to fully characterize the transformation. Determining minimum combination of in-situ and ex-situ measurements that provides the essential information is a challenge. We have used electrochemical potential and gas production (hydrogen production) to observe the real-time dependence of particle reaction properties. These have been correlated with batch ex-situ measurements, often involving anaerobic sample handling, of surface composition (XPS), particle phase composition and structure (XRD and TEM) and reaction rates with probe molecules (carbon tetrachloride). Real time in situ measurements are increasingly important as we develop ways to alter the particles with the intent of controlling the transformation rate of particles in aqueous solution. Initial data indicates that sulfur and transition metal doping of the particles significantly alters the overall reactivity and the interaction with contaminants. We are currently examining the impact of sulfur and transition metal additions as well as changes in oxide shell thickness on the reaction lifetime of core-shell iron nanoparticles. Because of a need to provide additional types of time-dependent information we are applying microbeam XRD and TEM in closed cells to examine these particles as they change in solution. This work is supported by the US Department of Energy Offices of Basic Energy Science and Biological and Environmental Research. A portion of the work has been conducted the EMSL, a US DOE national user facility.

4:00pm **IS+NS+TR-WeA8 Dynamics of Catalytic Nanoparticles**, *A. Dadye*, *A. Delariva*, *J. Gabaldon*, *L.M. Sanders*, *R. Goeke*, *Q. Xu*, University of New Mexico, *T. Hansen*, University of New Mexico and Haldor Topsøe A/S, Denmark, *S. Helveg*, *P. Hansen*, *B.S. Clausen*, Haldor Topsøe A/S, Denmark **INVITED**

Nanometer sized particles constitute the active phase in heterogeneous catalysts, such as those used in automotive exhaust pollution control, in energy conversion and for synthesis of chemicals. The unique properties of heterogeneous catalysts, their activity and selectivity, depend on the size and composition of nanoparticles. Since catalysts are used at elevated temperatures, these nanoparticles undergo coalescence and ripening leading to particle growth. Understanding and controlling these growth processes is critical since supplies of precious metals (such as Platinum, or Gold) are limited and demand keeps increasing, for example in fuel cells. Fundamental understanding of catalyst deactivation via sintering requires careful experimental work using a combination of ex-situ and in-situ studies. Ex-situ studies allow us to map out global rates and kinetics of particle size evolution. For this purpose, we have used a combination of TEM, STEM, XRD, chemisorption and reactivity measurements. In-situ observations can reveal nanoparticle dynamics and are crucial to bridge the gaps in our understanding, often revealing unexpected events. In this presentation, we will highlight our current state of understanding of sintering phenomena in heterogeneous catalysts. This research is supported by the National Science Foundation.

4:40pm **IS+NS+TR-WeA10 In-situ Transmission Electron Microscopy of Solid-Liquid Interfaces**, *H. Saka*, Nagoya University, Japan **INVITED**

Most of the industrially important inorganic materials are manufactured from liquid phase. This is true for metallic materials and semiconductors (e.g. Si). Even in the case of ceramic materials, the liquid phase plays an important role in the process of sintering. The performances of the final products of these materials are controlled during the transformation from liquid to solid states. Needless to say, the reaction front of the liquid-to-solid transformation is the interface between the solid, being solidified, and the liquid phases. Thus, in order to manufacture final products with high performance, it is of great necessity to control the solidification process, and this necessitates, in turn, a detailed knowledge of the solid-liquid (S-L) interface, which controls the solidification process. Recently it has become possible to observe S-L interface by an in-situ heating experiment in a transmission electron microscope (TEM), some of which will be presented in this presentation.

Authors Index

Bold page numbers indicate the presenter

— A —

Amonette, J.E.: IS+NS+TR-WeA5, 1

— B —

Baer, D.R.: IS+NS+TR-WeA5, **1**

Bañares, M.A.: IS+NS+TR-WeA3, **1**

Brand, H.R.: IS+NS+TR-WeA2, 1

Burkov, Y.: IS+NS+TR-WeA2, 1

— C —

Clausen, B.S.: IS+NS+TR-WeA8, 2

— D —

Datye, A.: IS+NS+TR-WeA8, **2**

Delariva, A.: IS+NS+TR-WeA8, 2

— E —

Engelhard, M.H.: IS+NS+TR-WeA5, 1

— F —

Ford, J.J.: IS+NS+TR-WeA1, **1**

— G —

Gabaldon, J.: IS+NS+TR-WeA8, 2

Goeke, R.: IS+NS+TR-WeA8, 2

Guerrero-Pérez, O.: IS+NS+TR-WeA3, 1

— H —

Hansen, P.: IS+NS+TR-WeA8, 2

Hansen, T.: IS+NS+TR-WeA8, 2

Helveg, S.: IS+NS+TR-WeA8, 2

Hoffmann, P.: IS+NS+TR-WeA2, 1

Hoyt, D.W.: IS+NS+TR-WeA1, 1

Hu, J.Z.: IS+NS+TR-WeA1, 1

— K —

Karpitschka, S.: IS+NS+TR-WeA2, 1

Khatib, S.J.: IS+NS+TR-WeA3, 1

Küppers, J.: IS+NS+TR-WeA2, 1

Kwak, J.H.: IS+NS+TR-WeA1, 1

— L —

Lewandowska, A.E.: IS+NS+TR-WeA3, 1

— M —

Martínez-Huerta, M.V.: IS+NS+TR-WeA3, 1

— N —

Nachimuthu, P.: IS+NS+TR-WeA5, 1

Nurmi, J.T.: IS+NS+TR-WeA5, 1

— Q —

Qiang, Y.: IS+NS+TR-WeA5, 1

— S —

Saka, H.: IS+NS+TR-WeA10, **2**

Sanders, L.M.: IS+NS+TR-WeA8, 2

Schmeißer, D.: IS+NS+TR-WeA2, 1

Sears, J.A.: IS+NS+TR-WeA1, 1

Sharma, A.: IS+NS+TR-WeA5, 1

— T —

Tratnyek, P.G.: IS+NS+TR-WeA5, 1

— W —

Wang, C.M.: IS+NS+TR-WeA5, 1

Wehner, S.: IS+NS+TR-WeA2, **1**

— X —

Xu, Q.: IS+NS+TR-WeA8, 2