

Surface Science Division

Room 203C - Session SS+AS+HC-FrM

Near/Ambient Pressure and Bridging Gaps between Surface Science and Catalysis

Moderators: Donna Chen, University of South Carolina, Janice Reutt-Robey, University of Maryland

8:20am **SS+AS+HC-FrM-1 Ambient Pressure Electron Spectroscopy (XPS, XAS) and Electron Microscopy Studies of the Structure and Chemistry of Nanostructured Model Catalysts, John Hemminger**, University of California Irvine **INVITED**

We use physical vapor deposition to create a high density of metal oxide nanoparticles on highly oriented pyrolytic graphite (HOPG). Photoelectrochemical methods are then utilized to selectively decorate the metal oxide nanoparticles with transition metal nanoparticles. This talk will describe our studies of the Pt/TiO₂/HOPG ; Cu/ZnO/HOPG systems. The nanostructured surfaces are characterized by SEM, TEM, XPS, and synchrotron based XAS. Lab-based and synchrotron based ambient pressure XPS experiments have been used to study the CO oxidation reaction on Pt/TiO₂/HOPG and the CO₂ reduction reaction on CuO_x/TiO₂/HOPG. In addition, the catalytic activity of CuO_x/TiO₂/HOPG for electrochemical CO₂ reduction has been studied using differential electrochemical mass spectrometry (DEMS).

9:00am **SS+AS+HC-FrM-3 In-operando Investigation of the Initial Oxidation Stages for NiCr-(W) Alloys with X-ray Photoelectron Spectroscopy, Cameron Volders, V Angelici Avincola, P Reinke**, University of Virginia

Ni-Cr alloys are of technical interest as they exhibit superior corrosion resistance due to the formation of a passive chromia film which helps protect the underlying alloy from degradation, and limits catastrophic events such as pitting and crevice corrosion. A wide range of Ni-Cr alloys have been developed to satisfy industrial needs and the properties for each alloy differ slightly based on its application. The properties are controlled by manipulating Cr content as well as adding minor alloying elements such as Mo or W, which have been shown to enhance corrosion resistance. The ideal composition for these alloys has been optimized over many decades but the mechanistic understanding of the role of Mo or W additions is not fully developed.

The current work presents an *in-operando* ambient pressure – X-ray photoelectron spectroscopy (AP-XPS) study which investigated the early stages of oxidation for four alloy concentrations; (1) Ni-5% Cr, (2) Ni-15% Cr, (3) Ni-30% Cr, and (4) Ni-15% Cr-6% W by weight percent between 573 and 773 K and p(O₂) < 0.1mbar. The primary objectives were to elucidate how varying Cr content in the alloys and the addition of W impacts the nucleation and growth of different oxide phases. The modulation of alloy and oxide composition and bonding was observed over an extended time period delivering a detailed view of the reaction pathways.

A key result from this work is the Cr surface segregation in the alloys prior to oxidation, which contributes to the rapid nucleation of Cr-oxides in the first reaction step with O₂. The surface enrichment of Cr influences the initial nucleation of the different oxide species and prejudices the progression of oxide growth. The main portion of this work will focus on the time evolution of the different oxide phases and the kinetics of Ni-oxide and Cr-oxide formation for all alloys, which allows to build a detailed model of the reaction. An additional component accounts for a substantial portion of the oxide signal, and is interpreted as the combination of spinel and non-stoichiometric oxide. The addition of W in the alloy resulted in a near complete suppression in the formation of Ni oxide species, and different models to interpret the impact of W on the progression of the oxidation reaction will be discussed.

9:20am **SS+AS+HC-FrM-4 Surface Hydroxylation of Polar (000-1) and Non-polar (11-20) ZnO Probed with AP-XPS, Sana Rani, A Broderick, J Newberg**, University of Delaware

The interaction of ZnO with water vapor has been an important topic of research due to the relevance for numerous catalytic processes including water-gas shift reaction, methanol synthesis, olefin hydrogenation, and gas sensor applications. ZnO based humidity nanosensors were found to have high sensitivity towards humidity and fast response time in heterogeneous catalysis. The presence of water strongly modifies the surface properties depending on the substrate and coverage. The adsorbed water can catalyze

heterogeneous reactions and corrosion by proton transfer and solvating products. Dissociation of adsorbed water is of particular interest for catalysis, as this may be the first step in the activation of water molecules for chemical reactions. In this work, surface thermodynamic calculations were applied to synchrotron based ambient pressure X-ray photoelectron spectroscopy (AP-XPS) data to investigate the interface between water vapor and the low index polar (000-1) and non-polar (11-20) ZnO surfaces. Three isobaric experiments were performed over a range of temperatures from 10 to 500°C. It is hypothesized that observed hydroxyl groups, adsorbed water and carbonates on the ZnO surface can significantly influence heterogeneous catalytic reactions under ambient conditions.

9:40am **SS+AS+HC-FrM-5 Reason of High Stability and Reactivity of Ni/silicalite-1 Catalyst for Dry Reforming of Methane, Evgeny Vovk, X Zhou, Z Liu, C Guan, Y Yang**, ShanghaiTech University, China; *W Kong*, Shanghai Advanced Research Institute, China; *R Si*, Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, China

Dry reforming of methane (DRM) is an environmentally favored process transferring two greenhouse gases (CH₄ and CO₂) into syn-gas (H₂+CO). Ni-based catalysts demonstrate good potential in this application because of comparable reactivity and low cost. DRM is highly endothermic reaction which requires high operating temperatures. At high temperatures sintering is a common issue of catalyst deactivation. Deactivation of Ni catalyst in DRM process is also accompanied by carbon deposition (coking) induced by methane decomposition and CO disproportionation (Boudouard reaction).

In the current work we investigated catalyst obtained by encapsulating Ni clusters (2.5±0.2 nm) into microporous silicalite-1 (aluminum free zeolite with MFI structure). No deactivation and coking under a wide range of conditions where carbon formation is thermodynamically favorable were observed for this sample. This atom-economical Ni/silicalite-1 catalyst was compared with Ni/SiO₂ catalyst prepared by impregnation method. XPS study has been performed in ThermoFischer ESCALAB 250X photoelectron spectrometer. The gas treatments of catalysts (up to 1 bar) was performed in high pressure gas cell (Model HPGC 300, Fermi Instruments) connected to the spectrometer.

XPS analysis of Ni/silicalite-1 demonstrates the presence of a peak with binding energy (BE) 856.2 eV in Ni 2p_{3/2} region. Nickel silicate has a similar spectrum shape with close BE. The presence of this peak in Ni/silicalite-1 sample suggests of the Ni-O-Si species and strong metal-support interaction. After oxidation of this sample at 400°C there are no changes of the Ni-O-Si species. At the same time nickel in Ni/SiO₂ catalyst which has shown mostly metallic Ni⁰ state with minor content of Ni-O-Si upon oxidation transforms into NiO. Reduction of Ni/silicalite-1 catalyst in hydrogen at 650°C leads to partial reduction of nickel into Ni⁰ while a significant portion of Ni-O-Si still remains. The behavior of Ni-O-Si feature in both oxidizing and reducing conditions clearly indicates its very high stability. We attribute this feature to the Ni-O-Si formed at the interface between Ni nanoparticles and the silicalite support. The Ni/silicalite-1 novel oxygen-philic interfacial catalyst system consists of very small metallic Ni clusters intercalated into silicalite framework and surrounded by Ni-O-Si species. Ni-O-Si provides high stability of Ni nanoparticles and prevents sintering and carbon deposition making this catalyst also very interesting for commercial application.

10:00am **SS+AS+HC-FrM-6 Recent Development in XPS and Ambient Pressure XPS Techniques, Lukasz Walczak**, PREVAC sp. z o.o., Poland

Many important processes such as energy conversion, electrochemical, corrosion and biological processes take place at solid-gas and solid-liquid interfaces [1-3]. X-ray photoelectron spectroscopy (XPS) is the most powerful technique for understanding of these processes at the atomic level and it is the key to improving the performance of novel battery generation or renewable energy sources such as solar, wind or hydropower energy conversion devices. We would like to promote the latest equipment, technology solutions and innovations for the photoelectron spectroscopies field. Here it will be presented an innovative and compact spectrometers for the routine X-ray photoemission spectroscopy and ambient pressure photoemission spectroscopy for study of important phenomena in the current research. The design, construction, and technical parameters of new analyser will be presented. We will report the research results of XPS measurements conducted on the photovoltaic [4], catalytical [5] or bio-materials. Moreover, it will be demonstrated the analyser operation in ambient pressure. Also the results of interaction of oxygen and surface alloy will be presented, in order to permit complete characterization for the different pressure and temperature conditions.

Friday Morning, October 26, 2018

References

- [1] B. Lassalle-Kaiser et al. J. Electron Spectrosc. Relat. Phenom. 221, 18-27 (2017).
- [2] Y. Takagi et al. Phys.Chem.Chem.Phys. 19, 6013 (2017).
- [3] Z. Y. Ong et al. Appl. Mater. Interfaces 9, 39259–39270 (2017)
- [4] L. K. Preethi et al. Energy Technol., 5, 1-10 (2017)
- [5] Urszula Filek et al. Appl. Catal. A – submitted

10:20am **SS+AS+HC-FrM-7 Quantum Mechanics and Reaction Kinetics Study on SiO₂ and SiN Dry Isotropic Chemical Etching Process**, *Taiki Kato, M Matsukuma, K Matsuzaki, L Chen*, Tokyo Electron Technology Solutions Limited, Japan

Dry isotropic chemical etching processes are important for semiconductor manufacturing, but such processes often require subtle process tuning to achieve high etching rates and the desired etching selectivity between SiO₂ and SiN. For example, the dry chemical etching solely with HF gas (Process 1) requires fine tuning of conditions for SiN etching rate because it has a peaky dependence on the process temperature; whereas dry chemical etching with NH₃/HF binary gas mixtures (Process 2) requires subtle tuning to simultaneously maximize etching rate and SiO₂:SiN selectivity. Notably, in Process 2, SiN etching rate increases with the etching time while SiO₂ etching rate slows down with the etching time. This slowdown is attributed to the formation of an etchant diffusion barrier from the solid byproduct, AFS (Ammonium fluorosilicate). Because of these contradictions, it has been difficult to achieve highly selective and rapid SiO₂ etching, thus a better understanding of the etching mechanisms is important to further develop the high selectivity required for the formation of scaled multicomponent semiconductor device structures. This study therefore focuses on revealing these mechanisms by using the quantum mechanics and by the analysis of reaction kinetics.

Firstly, Process 1 was studied with a quantum mechanical analysis by using the GRRM (Global Reaction Route Mapping) program. For this study, GRRM searched possible etching reaction paths automatically. From this reaction path search, it was revealed that SiN etching by HF gas, when used by itself, is much more rapid than SiO₂ etching. Further analysis was conducted by the reaction kinetics analysis. The kinetics parameters comprised HF adsorption, desorption and etching reactions. This model shows good agreement with the experimental SiN etching behavior.

Moreover, Process 2 was studied with similar quantum mechanics and kinetics analyses. Quantum mechanics analysis revealed that NH₃ combined with HF enhances both SiO₂ and SiN etching reactions. An NH₄F etching model was then added to the kinetics model. Because the etching byproduct, AFS, may be both an SiN etching accelerator and an SiO₂ etching decelerator, we could model the SiN etching kinetics initiated by NH₄F and propagated by NH₄F + AFS. This model quantitatively agrees with the experimental SiN etching data. Likewise, the SiO₂ kinetics model is composed of NH₄F etching, the diffusion resistance through solid AFS and the sublimation of AFS. This model also shows good agreement with experiment.

These analyses reveal the chemical etching mechanisms and enable process optimization. Further discussion will be presented on AVS 65th.

10:40am **SS+AS+HC-FrM-8 Viscosity and Surface Tension Effects on Metal Sputtered onto Low Vapor Pressure Liquids**, *Mark De Luna, M Gupta*, University of Southern California

Sputtering onto low vapor pressure liquids has garnered a lot of attention due to the ease of creating metal thin films and nanoparticles. However, the effects of the liquid viscosity and surface tension on the resulting morphologies has been neglected. In this work, we studied DC magnetron sputtering of gold and silver onto liquid substrates of varying viscosities and surface tensions. We were able to decouple the effects of viscosity from surface tension by depositing the metals onto silicone oils with a range of viscosities. The effects of surface tension were studied by depositing the metals onto squalene, poly(ethylene glycol), and glycerol. It was found that dispersed nanoparticles formed on liquids with low surface tension and low viscosity whereas dense films formed on liquids with low surface tension and high viscosity. We also observed that nanoparticles formed on both the liquid surface and within the bulk liquid for high surface tension liquids. Our results can be used to tailor the metal and liquid interaction to facilitate the fabrication particles and films for various applications.

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