Thursday Afternoon, October 31, 2013

Applied Surface Science
Room: 204 - Session AS+BI+EM+NL+NS+SS-ThA

Nanoparticle Surface Chemistry II
Moderator: N. Kruse, Université libre de Bruxelles, Belgium

2:00pm AS+BI+EM+NL+NS+SS-ThA1 Fundamental Explorations of Chemical Bonding and Surface Chemistry at Graphene Interfaces, *B.J. Schultz, V. Lee, R. Dennis, J. Aldinger, S. Henderson,* **S. Banerjee**, University at Buffalo, The State University of New York **INVITED**
The distinctive 2D sp^2-hybridized structural framework of graphene gives rise to a unique electronic structure characterized by conical valence and conduction bands touching at the Dirac point with linear energy dispersion within ± 1 eV of the Fermi level. Given the entirely surficial geometric structure of graphene, the extent of manifestation of true Dirac physics in this material is substantially modulated by perturbations of the electronic structure as a result of interactions with charged impurities, coupling to the underlying substrate, orbital hybridization with deposited contacts, and buckling/corrugation of graphene sheets. I will focus on the results of our combined X-ray absorption spectroscopy, Raman microprobe analysis, and density functional theory studies of graphene/metal and graphene/dielectric interfaces. Depending on the nature of the transition metal and the proximity of the graphene surface, physisorption or covalent chemical bonding is observed. Studies of the hybridization of single-crystalline metal surfaces with graphene suggest clear facet selectivity. We further evidence the potential for anisotropically functionalizing only one surface of planar graphene. For dielectric interfaces, charge transfer is observed without formation of carbidic bonds. Next, I will discuss our recent results on nitrogen incorporation within graphene oxide achieved through chemical reduction or annealing under a NH_3 atmosphere. Using near-edge X-ray absorption fine structure spectroscopy in conjunction with electrical transport measurements, we have developed a detailed picture of the recovery of the electronic structure of graphene oxide upon chemical or thermal defunctionalization. I will further discuss the design of graphene—polyetherimide nanocomposites based on engineered graphene interfaces that endow remarkable corrosion protection to low alloy steel upon application as thin films.

2:40pm AS+BI+EM+NL+NS+SS-ThA3 Structure-dependent Trends in Adsorption of CO, O_2, and H_2 on Pd and Pt Nanoparticle Catalysts, *H. Mistry, F. Behafarid, B. Roldan Cuenya*, University of Central Florida
Many important catalytic reactions have shown striking dependence on particle size and shape. Therefore, understanding structure-dependent adsorption processes using model nanoparticles is key to designing highly active and selective catalysts. Temperature-programmed desorption and x-ray absorption fine structure spectroscopy were used to study the interaction of adsorbates with Pt and Pd nanocatalyts. The binding strength of oxygen and carbon monoxide adsorbed on Pd nanoparticles supported on $SiO_2/Si(111)$ was shown to increase with decreasing particle size. In addition, pressure-dependent changes in hydrogen coverage and structure of size- and shape- selected Pt/γ-Al_2O_3 nanoparticles were investigated.

3:00pm AS+BI+EM+NL+NS+SS-ThA4 CO-induced Scavenging of Oxide-Supported Platinum Nanoclusters, *N. Chaabane,* INSTN, CEA, France, *R. Lazzari,* **J. Jupille**, INSP, UPMC and CNRS, France, *G. Renaud,* INSC, CEA, France, *EA. Soares,* ICEx-IFMG, BeloHorizonte MG, Brazil
The efficiency of oxide-supported catalysts frequently relies on the dispersion of the metallic particles whereas the optimization of the proportion of active atoms of the often precious metals involved in catalysts is an economic issue. Beyond the achievement via synthesis processes of the optimum morphology that accounts for the combination of those constraints, a great attention is paid to the phenomena which drive changes in shape, size and structure of the clusters of catalysts in running conditions. Aside the capability to resist high temperature aging, a main concern is the sustainability of catalyst particles upon exposure to reactive atmospheres. A prototypical case is the effect of CO on transition metals catalysts, of which supported platinum is a thoroughly studied example because it combines a strong practical relevance with puzzling stability behavior in the presence of CO [1]. Under CO exposure, disruption and agglomeration of supported Pt clusters were simultaneously evidenced by extended x-ray absorption fine structures, scanning tunneling microscopy and infrared spectroscopy. However, those parallel phenomena are not explained yet.

In the present work, changes in size and shape of MgO(100)-supported Pt nanoclusters were tracked *in situ* by Grazing Incidence Small-Angle X-Ray scattering (GISAXS) at CO pressures ranging from 10^{-6} to 10^3 Pa [2]. MgO has been chosen as an archetype of non-reducible support giving rise to abrupt interfaces with platinum [3]. Between 300 K and 470 K, Pt particles smaller than a critical size of 1 nm were shown to disrupt at CO pressure as low as 10^{-1} Pa. Once formed, the disrupted particles - suggested to be carbonyl moieties - underwent scavenging by clusters larger than the critical size. Disruption and agglomeration are both consistent with a CO-driven ripening mechanism [4]. An additional agglomeration mechanism was evidenced. Upon annealing up to the desorption temperature of CO, CO-covered Pt clusters of size ranging between the critical value and 2 nm were seen to agglomerate by diffusion; this is discussed in terms of an adsorbate-induced weakening of the cluster-support bonding. Similar CO-induced mechanisms (ripening and cluster diffusion) are suggested to hold for other supported metal catalysts such as Ru, Rh and Ir.

[1] Y. Nagai et al., Catal. Today 175 (2011) 133.

[2] N. Chaâbane, R. Lazzari, J. Jupille, G. Renaud and E.A. Soares, J. Phys. Chem. C 116 (2012) 23362.

[3] J. Olander, R. Lazzari, J. Jupille, B. Mangili, J. Goniakowski and G. Renaud, Phys. Rev. B 76 (2007) 075409.

[4] R. Ouyang, J.-X. Liu and W.-X. Li, J. Am. Chem. Soc 135 (2013) 1760.

3:40pm AS+BI+EM+NL+NS+SS-ThA6 Adsorption Energies of Cu Nanoparticles on $CeO_{2-x}(111)$ Supports Studied by Microcalorimetry, *T.E. James, S.L. Hemmingson, C.T. Campbell*, University of Washington
The increasing demand for energy has accelerated the need to develop new and improved catalysts for existing and alternative technologies. Heterogeneous catalysts consisting of transition metal nanoparticles dispersed across oxide supports are found in solar cells, fuel cells, industrial chemical production and environmental cleanup. Fundamental understanding of these supported catalysts, such as the bond energies between the metal clusters and their supports, which is crucial to understand the sintering behavior and catalytic reactivity, is still largely missing. This work uses Cu clusters and a single-crystal ceria support as a well-defined model system to study the bond energies between metal clusters and the oxide support as a function of particle size. The adsorption energies and growth morphologies of Cu on $CeO_{2-x}(111)$ (where x= 0.05, 0.1 or 0.2) at 100 and 300 K were investigated using single crystal adsorption microcalorimetry together with x-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and sticking probability measurements. Ceria thin films (~4nm) were grown on Pt(111) single crystal. The initial heat of Cu adsorption decreased with the extent of reduction of the ceria surface. The measured heat of adsorption increases with additional Cu deposition until it reaches the Cu bulk heat of sublimation (ΔH_{sub} = 337 kJ/mol) at > 4 monolayers coverage. Interestingly, the Cu coverage required to reach ΔH_{sub} decreases as the ceria surface is reduced. These results indicate that Cu adsorbs more strongly to ceria terraces than to oxygen vacancy sites, since the primary defect for reduced ceria surfaces is oxygen vacancies, but weakens the Cu-Cu bond for particles nucleated at terraces. The growth modes of Cu on $CeO_{2-x}(111)$ was also studied by XPS, ISS and AES. It was found that Cu grows as three dimensional particles on ceria. At 100 K the Cu particle density increased compared to 300K with a similar initial heat of adsorption, but took longer to reach the Cu heat of sublimation. The sticking probability was near unity for Cu adsorption on all these surfaces.

4:40pm AS+BI+EM+NL+NS+SS-ThA9 Complimentary XPS and AES Analysis of MoS_3 Solid Lubricant Coatings, **J.R. Lince**, The Aerospace Corporation, *S.S. Alnabulsi, D.F. Paul, J.F. Moulder, J.S. Hammond*, Physical Electronics Inc.
Molybdenum disulfide (MoS_2) nanoparticles are an ideal additive in solid coating for lubricating mechanisms in vacuum environments, with widespread application in the spacecraft industry. The formation of these nanoparticles can be complex, and the use of MoS_3 nanoparticles, which are produced using a simple wet chemical synthesis is being explored as an alternate approach.[1] The use of MoS_3 as a tribological material has not been explored beyond its use as an oil additive.[2] There is new interest in investigating its potential for use in solid lubricant coatings.

To aid in the evaluation of the tribological performance of a MoS_3-formulated coating compared to MoS_2 based coatings, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) are utilized as complimentary techniques for the surface characterization of the contact wear regions created on the coating surface.

The unique scanning micro-focused monochromatic x-ray source was used to provide x-ray excited secondary electron images that help reveal

topographical and surface chemical information which aid in resolving and pinpointing the analysis area of interest within the contact region of the wear track that is 50 μm to 100 μm wide. The micro-XPS results provided quantitative chemical characterization that complement high spatial resolution imaging AES analysis of the sub 100 nm molybdenum sulfide particles.

Tribometer testing showed the MoS_3-formulated coating perform similar to the MoS_2-based coatings, with similar coefficients of friction and endurances in dry nitrogen. MoS_3 nanoparticles produced using simple wet chemical synthesis, and the tribology of resin-bonded MoS_3 nanoparticle coating is comparable to similarly prepared bonded coatings containing MoS_2. The surface analysis results show a lubricating effectiveness that is consistent with the production of a thin film of MoS_2 in the contact region, with an increase in the presence of sulfide relative to polysulfide in the wear track and surface segregation of lubricating species.

We will present results of micro-area XPS and AES surface analyses on worn coatings to reveal changes in composition and chemical state of the coating surface, which might explain the observed friction results of the mechanical testing.

References

P. Afanasiev, "Synthetic approaches to the molybdenum sulfide materials," Comptes Rendus Chimie, 11(1–2) (2008) 159–182.

O.P. Parenago, V.N. Bakunin, G.N. Kuz'mina, A.Yu. Suslov, and L.M. Vedeneeva, "Molybdenum Sulfide Nanoparticles as New-Type Additives to Hydrocarbon Lubricants," Doklady Chemistry, 383(1-3) (2002) 86-88.

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