

# Wednesday Morning, October 31, 2012

## Nanometer-scale Science and Technology

Room: 12 - Session NS+AS+SS+SP-WeM

## Nanoscale Catalysis and Surface Chemistry

Moderator: U.D. Schwarz, Yale University

8:20am **NS+AS+SS+SP-WeM2 Preparation and Performance of Solid Rocket Propellant Containing *In Situ*-Synthesized Nanoparticle Catalysts and Fuels**, *D. Reid, R. Draper*, University of Central Florida, *M. Johnson, T. Allen, A. Demko, E. Petersen*, Texas A&M University, *S.S. Seal*, University of Central Florida

Energetic nanocomposites have the potential to substantially increase the performance of rocket propulsion systems, but adoption outside the laboratory has been slow, largely due to manufacturing difficulties, safety challenges, and performance that falls short of theoretical potentials. In this study, we explore some novel synthesis methods to significantly improve performance and alleviate the difficulties of incorporating nanoparticles into energetic materials. Solid rocket propellants containing in-situ synthesized catalytic TiO<sub>2</sub> and energetic aluminum nanoparticles were prepared. These propellants exhibited significant performance improvements over those containing conventionally prepared nanoparticles. The performance gains are attributed to the small particle sizes, high degree of dispersion, and surface property control afforded by the in-situ synthesis methods.

9:00am **NS+AS+SS+SP-WeM4 Synthesis and Catalytic Activity of WS<sub>2</sub> Nanotube Supported Cobalt and Nickel Catalysts Towards Thiophene Hydrodesulfurization**, *M. Komarneni, Z. Yu, A. Chakradhar, U. Burghaus*, North Dakota State University, *Y. Tsvetin, R. Popovitz-Biro, Y. Feldman, R. Tenne*, Weizmann Institute of Science, Israel

Inorganic nanotubes (INT) including WS<sub>2</sub> INT are promising materials for heterogeneous catalysis due to their intriguing properties like enhanced surface area, defects, and confinement effects. The promotion effects of Co and Ni combined with novel nanomaterials such as INT-WS<sub>2</sub> may create the next generation hydrodesulfurization (HDS) catalysts. To verify this, M/INT-WS<sub>2</sub> (M = Co or Ni) catalysts were synthesized and their catalytic activity towards HDS of thiophene was characterized by gas chromatography/ambient pressure catalytic tests and ultra-high vacuum (UHV) thermal desorption spectroscopy (TDS) experiments. Synthesis of M/INT-WS<sub>2</sub> involved two steps: Surface activation of INT-WS<sub>2</sub> by palladium seeding process and electroless plating method to coat nanoparticles of M. The deposited nanoparticles of M formed non-uniform layer on the INT surface. Nanoparticles of size 10-20 nm for Co (*hcp* structure) and 10-20 nm for Ni (*fcc* structure) were coated on INT-WS<sub>2</sub>. Next, the catalytic activity of M/INT-WS<sub>2</sub> towards thiophene HDS was characterized using an atmospheric flow reactor. M/INT-WS<sub>2</sub> catalysts exhibited enhanced HDS activity when compared to pristine INT-WS<sub>2</sub> mainly due to the promotion effects of Co and Ni. Hydrogen sulfide and hydrocarbons such as 1,3-butadiene, butane, cis-2-butene, and trans-2-butene were formed as HDS products by both pristine and M/INT-WS<sub>2</sub>. Commercial HDS catalysts, CoMo and NiMo from Haldor Topsoe were found to show ~ 4 times higher activity than M/INT-WS<sub>2</sub> synthesized in this study. These results are promising and show that further optimization of the nanofabrication process yields better HDS nanocatalysts. Furthermore, the adsorption kinetics of thiophene on M/INT-WS<sub>2</sub> was studied by TDS at UHV conditions. Thiophene adsorbed on internal, external, and groove sites of the M/INT-WS<sub>2</sub> bundles. Binding energies of thiophene on Ni/INT-WS<sub>2</sub> are ~ 10 kJ/mol smaller than that of pristine INT-WS<sub>2</sub>. Thiophene also decomposed on M/WS<sub>2</sub> NT at UHV conditions. In addition, catalytic screening of nanocatalysts such as Au and Co-Ni coated INT-WS<sub>2</sub>, pristine MoS<sub>2</sub> nanoparticles with fullerene-like structure (IF), and Re-doped IF-MoS<sub>2</sub> for HDS was also performed. Overall, M/INT-WS<sub>2</sub> catalysts were the best HDS catalysts among the new nanocatalysts studied. The results also reflected the promotion effects of Co and Ni on the M/INT-WS<sub>2</sub> catalysts for higher thiophene conversion rates.

11:20am **NS+AS+SS+SP-WeM11 Charge Exchange and Molecule/Metal Coupling in Fulvalene Surface Chemistry**, *G. Rojas, B.G. Sumpter*, Oak Ridge National Laboratory, *J.A. Schlueter*, Argonne National Laboratory, *P. Maksymovych*, Oak Ridge National Laboratory

Understanding the epitaxy of organic semiconductors on the surface, and the ensuing processes of charge transfer and band-alignment is vitally important for the deterministic design of energy harvesting and light-emitting devices based on molecular heterojunctions. While most of the attention so far has been directed to pi-conjugated aromatic compounds, little is known about the properties of the fulvalene family in contact with

metal surface. Here we will present a spectroscopic study of bis(ethylenedithio)tetrathiafulvalene (ET) on Ag(111) in the sub-monolayer to monolayer coverage. Varying coverages of ET adsorption show the molecules dimerize in parallel, bonding to the Ag surface along the long-axis of the molecule. The dimers remain mobile after adsorption, resulting in the formation of a two-phase surface material: unidimensional loosely stacked nanoclusters and finely packed, two-dimensional domains of interlocked molecules. These structures are an intermediate kinetic state, as the molecules further chemically react with the underlying Ag surface following annealing to temperatures as low as 40 C. It is thought based on these data that the dimers form chemical bonds with a single, shared Ag adatom upon adsorption, as observed for other pi orbital dominated aromatic molecules such as PTCDA. Formation of a reactive layer has significant implications for the orbital alignment at the interface. We have therefore probed the properties of the 2D ordered layer and the reacted layers using a combination of current-distance and image-potential state spectroscopy. The interpretation of these results will be presented in conjunction with the first-principles calculations of the respective structures, and correlated with the induced density of interface states (IDIS) model for orbital alignment at metal-molecule interface.

This research was conducted at the Center for Nanophase Materials Sciences, sponsored at the Oak Ridge National Laboratory by the Division of User Facilities, U.S. Department of Energy.

11:40am **NS+AS+SS+SP-WeM12 Subpicosecond-pulse Photoinduced Chemistry on Nanoscale Palladium Model Catalyst Surfaces**, *A. Bhattacharya*, Brookhaven National Laboratory, *R. Palomino, J.C. Lofaro*, Stony Brook University, *H. Park, M.G. White, N. Camillone*, Brookhaven National Laboratory

To date, time-resolved investigations of surface chemical reaction dynamics have almost exclusively been conducted on metal single crystals. However, current and proposed catalysts and photocatalysts generally consist of nanometer-scale metal particles supported on metal oxides. To conduct time-resolved investigations of the surface chemical dynamics of such systems we have synthesized and characterized arrays of palladium nanoparticles (approximately 4 to 10 nm in diameter) supported on clean rutile TiO<sub>2</sub>(110). We will present our synthetic approach and the results of chemical and morphological characterization and thermal chemistry experiments on these arrays. We will also discuss the results of subpicosecond-pulse photoinduced desorption of molecular oxygen and carbon monoxide, as well as the photoinduced bimolecular reaction between adsorbed atomic oxygen and carbon monoxide. Comparisons to the same reactions on single crystal Pd(111) surfaces will be made, and the unique features of the chemistry and dynamics at the nanoscale highlighted.

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