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**Exploring Particle Size Dependent Chemistry on Ni Particles Supported on TiO<sub>2</sub>(110)**

D. Chen, B. Long (U. South Carolina) and Gang Liu, Z. Chang, J. Rodriguez and J. Hrbek (Brookhaven National Laboratory)

Beamline: U7A

**Introduction:** Although the reactivity of metals on oxides is important for heterogeneous catalysis applications, relatively little is known about metal-on-oxide chemistry at the atomic level or about the influence of surface morphology on chemical activity. The goal of this project is to understand how the surface chemistry of oxide-supported metal nanoparticles is affected by particle size and structure and metal-oxide interactions.

**Methods and Materials:** We have examined the growth and surface chemistry of catalytically active metals such as Ni deposited on a single-crystal TiO<sub>2</sub>(110) surface under ultrahigh vacuum conditions. The size and structure of these particles were characterized by scanning tunneling microscopy in D. A. Chen's laboratory at the University of South Carolina. By varying the deposition and annealing conditions for growth, the particle sizes are systematically controlled while maintaining a narrow size distribution. The surface chemistry of these nanoparticles were probed using temperature programmed desorption and high-resolution X-ray photoelectron spectroscopy at the beamline.

**Results:** Three model reactions were carried out on Ni particles of three different sizes in order to probe possible particle size effects. STM studies at U. South Carolina showed that a Ni deposition rate of 0.5 ML/min is sufficiently high to naturally produce a narrow size distribution upon deposition at room temperature. The average Ni particle size at room temperature was 34 Å diameter, 9 Å height. Subsequent annealing to 800 K and 900 K produced particles with average dimensions of 42 Å diameter, 10 Å height, and 50 Å diameter, 15 Å height, respectively. The Ni particles were oxidized by exposure to O<sub>2</sub>, and the changes in the valence band and Ni(3p) signals were monitored by XPS as a function of annealing temperature. The particles were also oxidized by exposure to CO, and changes in the C(1s), Ni(3p) and valence band were again studied as the surface was heated. The smallest Ni particles appeared to dissociate CO more readily than the larger ones. Methanethiol adsorption and reaction on the Ni particles indicated that methyl thiolate may be bound at different Ni sites on the different sized particles. Due to problems with equipment and the limited beamtime, we did not complete this project. However, plans have been made to conduct additional experiments at U7A next year.

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