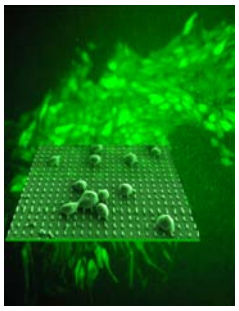
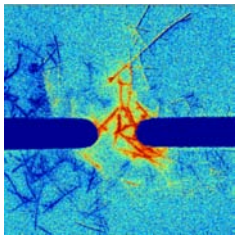
CNMS DISCOVERY SEMINAR SERIES

Thursday, February 9, 2012
4:00 pm
Iran Thomas Auditorium, 8600

Determination of CO, H_2 and H_2O Coverage by XANES on Pt and Au During Water Gas Shift Reaction: Experiment and DFT Modeling





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Abstract:
Water Gas Shift Reaction: The turn-over-rate (TOR) for the water gas shift (WGS) reaction of 1.4 nm Au/Al_2O_3 is approximately 20 times higher than that of 1.6 nm Pt/Al_2O_3. In addition, Au has high activity at lower reaction temperature than Pt. Operando XAFS experiments at both the Au and Pt L_3 edges reveal that under reaction conditions, the catalysts are fully metallic. Adsorption of CO, H_2 and H_2O leads to changes in the XANES spectra that can be used to determine the surface coverage of each adsorbate under reaction conditions. During WGS, the coverage of CO, H_2O, and H_2 are obtained by the linear combination fitting of the difference XANES, or ΔXANES, spectra. Pt catalysts adsorb CO, H_2, and H_2O more strongly than the Au, in agreement with the lower CO reaction order. At low reaction temperature, the low rate of Pt is due to saturation of the metallic surface by adsorbed CO, while on Au there is little CO coverage and higher rates.

Density Functional Theory of XANES Spectra: In order to better understand these changes in XANES spectra with adsorbates and particle size, Pt nano-particles from about 1 to 10 nm have been prepared on different supports. The EXAFS spectra of the reduced catalysts in He show a contraction of the Pt-Pt bond distance as particle size is decreased below 3 nm. The bond length decreased as much as 0.13 Å for 1 nm Pt particles. Adsorption of CO and H_2 lead to a increase in Pt-Pt bond distance to that near Pt foil, e.g., 2.77 Å. In addition to changes in the Pt bond distance with size, as the particle size decreases below about 5 nm there is a shift in the XANES to higher energy at the L_3 edge, a decrease in intensity near the edge and an increase in intensity beyond the edge. At the L_2 edge, there are only small shifts to higher energy at the edge. However, beyond the edge, there are large increases in intensity with decreasing particle size. At the L_1 edge there are no changes in position or shape of the XANES spectra. Adsorption of CO and H_2 also lead to changes in the L_3 and L_2 edges, however, no changes are observed at the L_1 edge. Density Functional Theory and XANES calculations show that the trends in the experimental XANES can be explained in terms of the d electron density of states available near the Fermi level.

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