[S-09]

Anomalous CO adsorption on surfactant-protected gold nanospheres

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Since the discovery of high catalytic activity of small gold nanoparticles dispersed on oxide surfaces in CO oxidation, numerous investigations have been made on the nature of CO adsorption. Yet the mechanism of CO oxidation is still not clearly understood. We have investigated CO adsorption by temperature-programmed desorption on the Langmuir-Blodgett monolayer of hexadecanethiol(HDT)-protected gold nanospheres(NS) on SiO_2/Si(100) wafer.

The CO adsorption was made at samole temperature of 90 K. The TPD spectra at low exposures(> 20L) showed a peak at 230K, which can be identified to be the chemisorbed CO on the gold NS surface. At higher exposures another low peak is observed, which starts to desorb at around 120 K. The desorption rate increases exponentially with increasing temperature followed by a sudden drop to zero, indicating a zeroth order desorption kinetics. Upon increasing the CO exposure, the peak temperature systematically shifted to a higher temperature to 160 K at the exposure of 5.0×10^7 L. By analyzing the peak shape we estimated the desorption energy of 13 kcal/mole. Comparison with the desorption signal for CO saturated Pt(111) surface reveals that **the total amount of adsorbed CO on gold NS monolayer amounts to 1.3×10^{17} molecules per cm^2 of the subtrate; This corresponds to 160 lalers of CO on Pt(111).** This is an astonishing result. The HDT surfactant chain is about 21 A long. Assuming a close packing of the HDT-gold NS's, one can estimate that the total surface area(neglecting HDT) of gold cores is comparable to that of Pt(111) surface. Thus, one can conclude that such a large amount of CO is due to CO condensation in the space between the HDT chains. The boiling point of CO is 81 K, only slightly higher than that of N_2 because of the smalldipole moment. Therefore, CO multilayer condensation of CO usually occurs below 77 K at low pressure. One can raise many interesting fundamental questions; how can CO molecules condense between

HDT chains at 150 K under UHV conditions? What force(s) responsible for CO condensation? Is the gold NS surface playing a role? These questions will be discussed.