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ADSORPTION THERMODYNAMICS AND SURFACE
TRANSPORT OF METAL CATALYST POISONS

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The objective of our research is a fundamental understanding of the effect of surface structure and electronic properties of the metal substrate on the bonding type and binding energy of adspecies involved in catalyst deactivation. The transition metals under study include single crystals of different orientation and supported metal crystallites. The sorbates of interest comprise sulfur and halogen adatoms. These chemical species commonly cause catalyst deactivation ("poisoning") of many transition and non-transition metals of importance to industrial catalysis. The binding energies of the various adspecies are derived from adsorption-equilibrium studies over a range of temperatures. For the highly dispersed metal crystallite system a recirculating system is employed. The thermodynamic activity of sulfur or halogen (X), is determined as a function of the equilibrium surface coverage of S(a) or X(a). Since the concentrations of H₂S and HX used in the studies are very low (ppm range), quantitative analysis of these compounds require photo-ionization and electrolytic conductivity detectors. In single-crystal work, the surface coverage and structure of the adlayer is measured by means of LEED/AES*.

The results obtained demonstrate (1) significant differences in the binding energy of sulfur adatoms at low coverage ($\Theta < 0.2$) on different transition metals, (2) important variations in binding energy with degree of sulfur surface coverage, and (3) higher thermodynamic stability of the surface adlayer relative to the bulk sulfide. For group -VIII transition metals we observe a gradual weakening of the binding energy of sulfur with filling of the partially empty d-band. The participation of valence band electrons and local coordination are being examined in interpreting the results.

An important aspect of surface bonding is its influence on surface transport by diffusion. On Ni(111) the kinetics of surface diffusion of sulfur adatoms have been measured. The rate of diffusion increases with sulfur coverage. This effect is related to the decrease in binding energy of S(a) caused by repulsive interactions. In addition the diffusion data suggest the influence of local geometry and surface coordination of the adspecies on surface transport.

Current experimental studies deal with equilibrium adsorption of chlorine and bromine on different metal surfaces. The technique used is similar to that for the sulfur adsorption measurements except for the use of an electrolytic conductivity detector.

Future work will deal with the coadsorption of sulfur and carbon on single metal crystals using the LEED-Auger system. Previous measurements on Ni and Ru surfaces have indicated the existence of single surface carbon atoms (or small atom clusters) bound to metal atoms. These adspecies are highly reactive toward H₂, and represent the intermediates in methanation and Fischer-Tropsch synthesis from syngas. The effect of sulfur adatoms on the properties of the carbon species needs to be examined. Sulfur adsorption is known to cause surface reconstruction and faceting. As a result significant changes in the carbon adlayer may occur, such as the growth of carbon chains, the potential precursor reaction to "coking". In addition, better identification of the surface species during hydrocarbon synthesis and surface poisoning is planned with the aid of electron energy loss spectroscopy (EELS). As for the surface diffusion studies, we plan to extend our measurements to other single crystal metal surfaces of different orientation and to stepped surfaces. The recent acquisition of a scanning Auger electron spectrometer will be of special value for these studies.