

## HETEROGENEOUS CATALYSIS RELATED TO ENERGY SYSTEMS\*

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### Research Scope and Objectives

The major objective of this program has been to analyze the interaction of adsorbates on metal surfaces using energy and angle resolved alkali and inert gas ion scattering in combination with LEED and Auger. This entails two simultaneous research efforts. The first is to develop the techniques, both experimental and computational, necessary for exploiting the potential of ion scattering as a structure sensitive surface probe. The second is to apply the technique to determine the bonding geometry of adsorbates on single crystal surfaces and their effect upon the structure of the underlying substrate.

The objective of a second project, which is still in a very preliminary phase, is to characterize reaction mechanisms, reactivity, and selectivity of hydrodesulfurization reactions on metal sulfide or sulfided single crystal metal surfaces.

### Description of Research Effort

Recent work has focused on the interaction of CO, C<sub>2</sub>H<sub>4</sub>, N<sub>2</sub> and especially O<sub>2</sub> on the Mo(001) surface. The reactivity of this surface is strongly affected by the presence of the atomic overlayers which result from the dissociative adsorption of these molecules on clean Mo(001). A complete understanding of this behavior requires information about the location of the adatoms and their effect upon the structure of the underlying Mo substrate. A combination of K<sup>+</sup>, Li<sup>+</sup> and He<sup>+</sup> scattering results, for the clean and adsorbate covered surface, have been obtained and correlated with LEED/AES data. Data has been obtained for each adsorbate as a function of coverage and adsorption temperature. The ion scattering data has been analyzed by applying qualitative arguments based upon fundamental concepts of ion scattering, and also by detailed comparison between experimental and computer simulated energy and angular distributions.

Coverages in the range of 0.7 to 1.0 ML of oxygen, carbon, or of both oxygen and carbon are all found to yield virtually identical K<sup>+</sup> scattering spectra indicating that in each case the surface structure is the same. Analysis of the K<sup>+</sup> energy distributions indicate that the C and O adatoms are located at four-fold adsorption sites. Analysis of the dependence of Li<sup>+</sup> ion scattering upon angle of incidence shows that the oxygen atoms are located at a perpendicular height of 0.3 ± 0.1 Å above the plane of the first layer Mo atoms and that carbon atoms also are at about this height. These results apply to oxygen adsorption at 1000 K. Adsorption near room temperature gives reproducibly different K<sup>+</sup> energy distributions indicating structural differences which may be associated with early oxide formation at sub-monolayer coverages. Nitrogen adsorption, which is believed

to saturate at about 0.5 ML coverage, gives energy and angular distributions which differ from those obtained from higher coverage C and O. However, similar distributions are obtained for 0.5 ML C indicating that perhaps a different bonding site or substrate structure applies for 1/2 ML of C and N. Oxygen adsorption has not been found to yield this bonding state.

Comparison of  $K^+$ ,  $Li^+$  and  $He^+$  scattering from Mo has led to interesting new conclusions about the process of ion neutralization. The scattered ion intensity was monitored for each ion under identical scattering conditions as a function of oxygen induced work function change. From these measurements it was concluded that the ion neutralization probability for  $He^+$  ion is a strong function of oxygen coverage. This result has important implications for surface analysis based on  $He^+$  ISS. The  $Li^+$  and  $K^+$  neutralization behavior was found to be consistent with resonant neutralization processes, although the neutralization probability for  $K^+$  is low for all oxygen coverages.

#### Future Research

Ion scattering studies planned for the immediate future will continue to be based upon studies of bonding geometry of atomic overlayers and their effect on substrate structure. The particular systems chosen will be largely those for which there is evidence of possible strong interaction between adatom and substrate, including C on W(100) and O on Pd(100). Structural studies of surfaces of binary systems such as  $MoO_3$  and  $MoS_2$  are also planned as are studies of the microscopic surface structure of glassy metals. Ultimately, studies of adsorbed molecular species are planned.

The effort to study hydrodesulfurization reactions on well characterized sulfide surfaces will be expanded in the next few years. A high pressure/UHV system will be designed, built and put into operation and studies initiated. The adsorption, desorption, co-adsorption and reaction of  $H_2$ ,  $H_2S$ , thiophene and other adsorbates will be studied as a function of various surface and gas phase parameters. The surfaces will be characterized in UHV by a combination of techniques including XPS, AES, TDS and HREELS.

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