

VI. INTERFACIAL CHEMISTRY

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1. PHOTOACOUSTIC SPECTROSCOPY AND CHEMICALLY MODIFIED SURFACES

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Work has focused on using photoacoustic spectroscopy (PAS) to characterize the results of chemical attachment reactions of molecules to surfaces and to study heterogeneous catalyst systems and their reactions. PAS is being developed as a tool for the study of molecules adsorbed on surfaces. With the use of a Nicolet 7199 Fourier-transform infrared spectrometer, PAS can be applied in the mid-infrared region to obtain vibrational information about the surface species. The PA cell used is of our own design which allows the cell to be separated from the microphone and loaded in an inert-atmosphere box or attached to a vacuum line for sample preparation or reaction. The technique works best for studying surface species when the support is a high-surface-area powder ($>10 \text{ m}^2/\text{g}$). This technique has been used to study a variety of systems.

A study of the adsorption of $(\text{COD})\text{Pt}(\text{Me})_2$ on silica shows that the complex is only slightly perturbed by the silica. However, upon hydrogen exposure, the methyl groups are eliminated, presumably as methane, and the COD ligand is reduced to some form of saturated hydrocarbon that does not readily pump off. The platinum is in the zero-valent state and is an active catalyst at this point, as is seen by the adsorption of carbon monoxide. Preliminary work on $(\text{COD})\text{Pt}(\text{Me})_2$ on alumina has shown that the complex reacts with the alumina, liberating methane.

In another study, reactions of gases with supported metals have been examined. These include the reactions of carbon monoxide and nitric oxide on platinum

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supported on silica and alumina. Results are comparable to those obtained by other techniques. Reactions of hydrogen cyanide with platinum on silica and alumina, and silver on alumina, have also been studied. The carbon-hydrogen bond is cleaved and the surface is left covered with CN groups. Positions of the CN bands can be associated with different site structures for the CN groups on the surface. This study is being expanded to include supported nickel, rhodium, and ruthenium.

Cobalt carbonyls attached to surfaces via silicone functionalities are also under study. The photochemistry of these systems is of particular interest.