

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. Electronic spectra in the UV-visible and overtone bands in the near-IR have been utilized in these studies. We have also recently begun using photoacoustic detection with a Nicolet 7199 FTIR system to obtain spectra in the mid-infrared range. All samples were run using a cell built in our laboratories that allows control of the gas composition in contact with the sample. The sample chamber can be sealed and detached, so that samples can be loaded in a dry box. Temperature control of the sample stage is also possible.

Ferrocene-centered reagents can be bound to the surface of high-surface-area ($400 \text{ m}^2/\text{g}$) silica powders by reaction of the silica with solutions of (1,1'-ferrocenediyl) dimethylsilane (DMP), or related reagents. PAS reveals a band-position shift from the unreacted reagent to the reacted product indicating ring opening of the strained C-Si-C linkage bridging the two cyclopentadienyl rings to yield a simple, monosubstituted ferrocene center attached to the surface. Reversible oxidation of the surface-bound ferrocene centers to ferricenium centers by washing with acidic solutions of benzoquinone is confirmed by photoacoustic spectra. The surface-confined ferricenium can be used to oxidize N,N,N',N'-tetramethyl-p-phenylenediamine

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(TMPD) to TMPD^+ in solution; this reaction allows an estimate of the surface coverage. This, in turn, provides a means to calibrate PAS signal response to surface for the powder used.

Similar use of PAS has been employed to monitor attachment chemistry using SiCl_4 with organic dyes on powders, flat surfaces, and silica microstructures. For this work, quantification of PAS signal response to surface coverage is obtained by comparing transmission and photoacoustic spectra for suitable samples. Photoacoustic spectra, however, can be conveniently obtained for a wider range of coverages and for coverages of nonuniform substrates such as microstructures.

The utility of PAS for investigations of heterogeneous catalyst systems is illustrated by a study of reactions of molybdenum hexacarbonyl, $\text{Mo}(\text{CO})_6$, on various support materials. On silica at -50°C , radiation-induced production of $\text{Mo}(\text{CO})_5$ on the surface can be followed. With further irradiation, more highly coordinately unsaturated molybdenum species are generated. The effects of support composition and preparation on these reactions have also been investigated in this study using PAS.

PAS can be used in the near-IR to examine vibrational overtone and combination bands. Silica samples derivatized with ferrocene using DMP illustrate the utility of this region. The DMP-derivatized silica shows both an aliphatic C,H-band at 1.7μ and an aromatic C,H-band at 1.63μ .

References

1. A.B. Fischer, J.B. Kinney, R.H. Staley, and M.J. Wrighton, "Derivatization of Surfaces via Reaction of Strained Silicon-Carbon Bonds. Characterization by Photoacoustic Spectroscopy," *J. Am. Chem. Soc.* 101, 6501-6506 (1979).