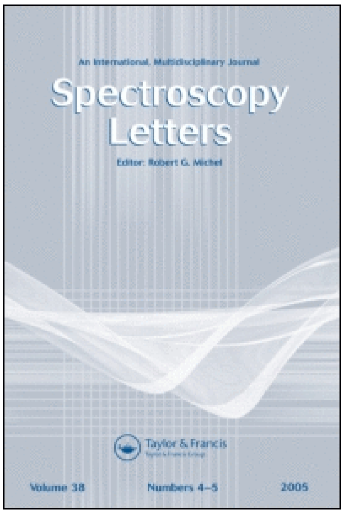

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Infrared Photothermal Deflection Spectroscopy of Carbon-Supported Metal Catalysts

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INFRARED PHOTOTHERMAL DEFLECTION SPECTROSCOPY OF CARBON-SUPPORTED METAL CATALYSTS

Key Words: Surfaces, Adsorbed Species, Infrared, Photoacoustic Spectroscopy, Photothermal Deflection Spectroscopy, Catalysts, Carbon, Carbon-dispersed Metals

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INTRODUCTION

The infrared (IR) study of surface species and reactions occurring on solids has contributed markedly to our understanding of surface chemistry and heterogeneous catalysis, and a wide variety of solids has been examined. However, an entire class of catalysts consisting of metal dispersed on carbon has never been studied because the carbon catalyst support absorbs IR radiation so strongly in even the thinnest practical layers that conventional IR techniques fail. As IR data would be helpful in understanding how such catalysts function, we have explored the feasibility of examining carbon-supported catalysts with photothermal beam deflection spectroscopy (PDS) and describe the first IR spectra of surface species on a Ni-on-carbon catalyst.

EXPERIMENTAL

The samples were 50 wt.% Ni-on-carbon (Ni-C) prepared by the controlled charring of $Ni(NO_3)_2$-impregnated cellulose, followed by reduction with H_2 and exposure to CO. A sample remained under controlled conditions within a cell at all times. The high vacuum and other techniques conventional to surface studies were employed. Prior to PDS study, the sample cell pressure was raised to 1 atmosphere with purified N_2, at room temperature.

The PDS techniques[1] and the spectrometer[2] employed are described in detail elsewhere. Spectra were recorded at a resolution of 8 cm^{-1} using 800 scans. The ordinates of single-beam, uncorrected spectra were marked S. Correction and compensation was done by ratioing a sample spectrum against the spectrum S_o of a reference carbon. The ordinates S/S_o of compensated spectra are arbitrary.

RESULTS

It is instructive to examine single-beam spectra such as those shown in the largely self-explanatory Fig. 1 as well as compensated spectra such as those of Fig. 2 to obtain an over-view of the data obtainable. The signals observed with the Ni-C samples were appreciably weaker and therefore noisier than those obtained with the reference carbon, attributable in part to the presence of the large quantity of nickel and in part to the texture of the samples. The Ni-C samples were roughly rectangular pieces about 15 x 10 mm weighing about 20 mg, with uneven surfaces so that the interaction of the laser probe beam with the surface was not as efficient as with that of the carbon reference, which was a smooth bed of powder. Comparison of the spectra of Ni-C catalyst with that of the reference carbon shows that the material on which the Ni was dispersed was indeed a fully-formed carbon. Variations in the spectra of the carbon support material after various surface treatments are significant but not pertinent to the present report and will be described elsewhere.

When a Ni-C sample was exposed to CO at room temperature, the negative absorption of gaseous CO within the sample cell was observed and, significantly, a band appeared centered near 2040 cm^{-1}. The insert is a scale-expanded segment and

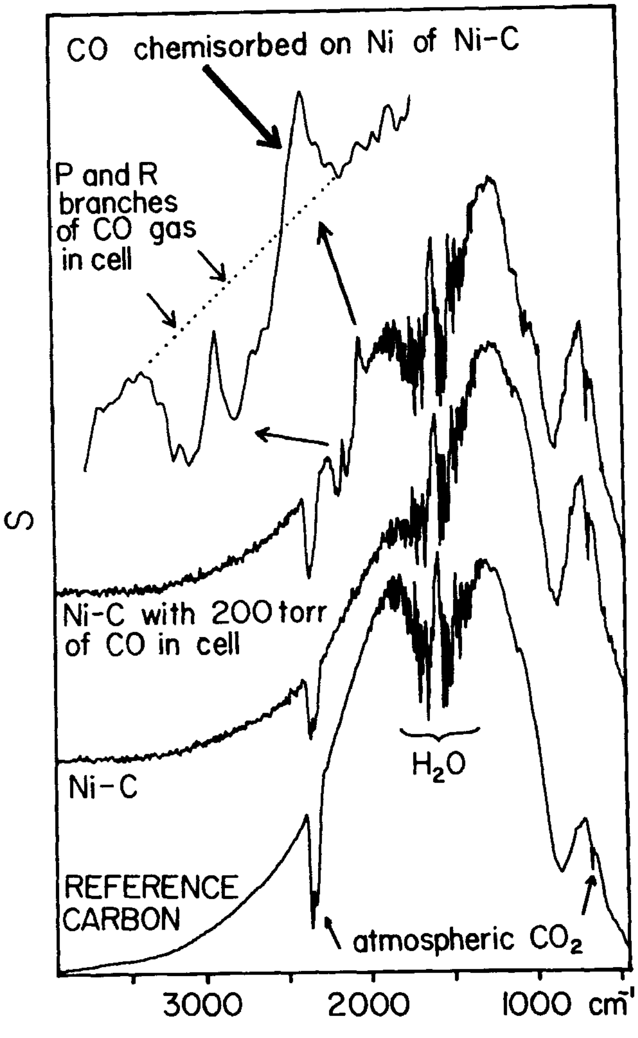

Fig. 1 IR-PDS spectra; see text.

shows the bands more clearly. The 2040 cm^{-1} band is unequivocably attributable[3] to "linear" chemisorbed CO, i.e., surface Ni-C-O species on the Ni portion of the catalyst. Segments of compensated

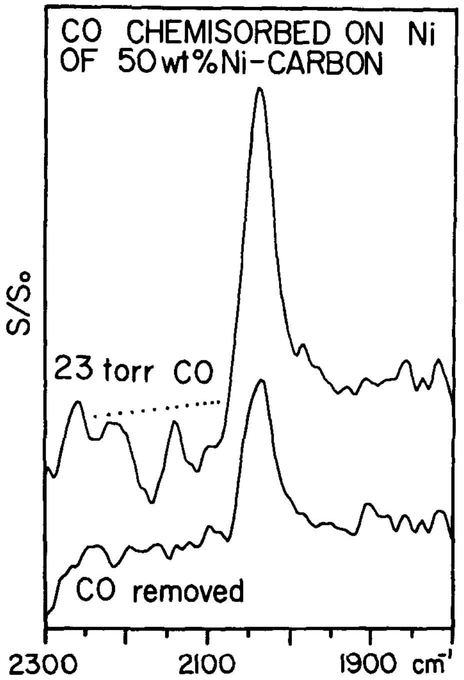

Fig. 2 IR-PDS spectra of CO chemisorbed on Ni-C.

spectra are shown in Fig. 2. The CO chemisorption is known to be slowly reversible so that when the CO pressure was reduced, the band of the surface species decreased slightly in intensity. When the cell was evacuated briefly to 10^{-4} torr to remove residual gaseous CO, the resulting spectrum did not show the absorption of gaseous CO and the Ni-C-O band was diminished because some CO had been desorbed.

DISCUSSION

The data shown and others not presented prove that it is possible to observe CO chemisorbed on the Ni-C catalysts; we have also made analogous observations with Fe-C, Pt-C and Cu-C catalysts. It is worth mentioning that the present Ni-C material is a particularly difficult sample from the spectroscopic point of view because of the simultaneous presence of the carbon support and of the large amount of nickel. It must also be noted that the absorption of the chemisorbed CO is a very intense one, and that the observation of other surface species will present greater difficulties. Also, specular reflection affects PDS and photoacoustic spectra in a totally negative way so that some band distortions will occur with highly reflective samples.[4] However, it seems feasible to apply PDS techniques to other systems so that an entire class of catalyst, which IR studies have so far been forced to neglect, can now be examined. It should be possible to examine graphite intercalates as well as other carbon-supported catalysts such as $HgCl_2$, and to study "spill-over" effects during adsorption and catalysis. Also, our exploratory experiments on the interaction of gases with Fe-C indicate that the presence of the iron exerts a marked effect on the reactions occurring on the carbon, suggesting that a particularly interesting and rewarding area will be the meatl-catalyzed conversion of coal.

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