

VIBRATIONAL SPECTROSCOPIC STUDIES OF COAL CONVERSION CATALYSTS

John M. Stencel
and
Leo E. Makovsky

Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, Pennsylvania 15236

Objective

The objective of this Raman spectroscopic investigation is to determine structural characteristics of oxide supported catalysts as a function of synthesis procedures, activation, and use, and as a consequence, to describe surface species that may be important in catalytic activity, selectivity, and stability.

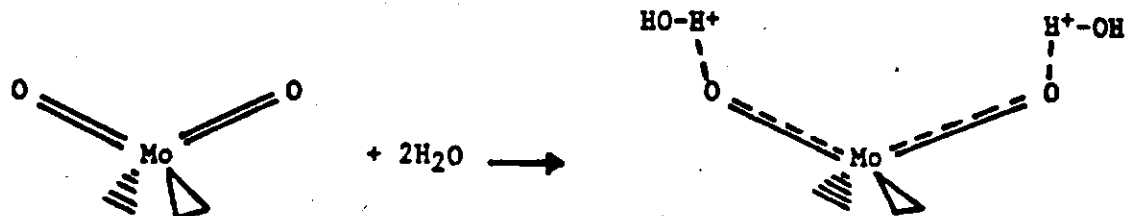
Research Description

This research employs Raman spectroscopy as the primary technique to investigate the vibrational spectra of oxide supported catalysts. Catalysts that have been investigated are $\text{MoO}_3/\text{Al}_2\text{O}_3$, $\text{WO}_3/\text{Al}_2\text{O}_3$, $\text{NiO-MoO}_3/\text{Al}_2\text{O}_3$, $\text{NiO-WO}_3/\text{Al}_2\text{O}_3$, and $\text{CoO-MoO}_3/\text{Al}_2\text{O}_3$. The concentration of the active metal and of the promoter have been systematically varied, the order of metal impregnation reversed, and the treatment of the support prior to metals impregnation altered to obtain a maximum amount of structural information from the spectroscopic results as a function of these variables. Other experimental techniques such as ISS, XPS, and XRD have also been used to provide information complementary to the Raman data.

To accomplish the acquisition of Raman data as a function of activation of the catalysts, e.g. calcination in O_2 , H_2 reduction, or $\text{H}_2\text{S}/\text{H}_2$ sulfidation, a sample cell and associated gas sampling/UHV vacuum system was constructed. In the first experiments using this cell, a series of catalysts containing (3-25) wt % MoO_3 dispersed on $200 \text{ m}^2/\text{g } \gamma\text{-Al}_2\text{O}_3$ were investigated during O_2 calcination and subsequent H_2O exposure. An impetus for these investigations was the discrepancies found in the literature for frequencies of the Mo=O stretching mode in $\text{MoO}_3/\text{Al}_2\text{O}_3$; in addition, experiments performed in our lab showed that the Mo=O symmetric stretching frequency changed by as much as 20 cm^{-1} as a result of long-term exposure of the catalysts to atmospheric conditions. A 500°C O_2 calcination of an air-exposed 15 $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst was found to increase the Mo=O stretching frequency from 950 cm^{-1} to 1006 cm^{-1} . Subsequent exposure of this calcined catalyst to H_2O or D_2O at 25°C decreased the Mo=O stretching frequency to 950 cm^{-1} . This 60 cm^{-1} frequency shift was reversible with further $\text{O}_2\text{-H}_2\text{O}$ exposure cycles; NH_3 exposure to the calcined catalyst also caused a decrease in the Mo=O stretching frequency. In catalysts containing less than 10 wt % MoO_3 the reaction of H_2O or D_2O with the surface molybdate was

at least an order of magnitude slower than with the surface molybdate in the 15 MoO₃/Al₂O₃ catalyst.

These results can be explained by an attack of the molybdate surface species by H₂O. For example, the following reaction could occur:



The result is a weakening of the Mo=O bond during H₂O exposure of the calcined catalyst. Hence, discrepancies between the frequencies reported for the Mo=O stretching mode can be explained by the fact that the molybdate monolayer is very reactive to H₂O and that Raman spectra have traditionally been acquired while the catalysts were exposed to atmospheric conditions.

Besides the shift in the Mo=O stretching frequency, the appearance of bands in the 100-700 cm⁻¹ region is also dependent on the amount of H₂O exposure the catalyst has experienced. This dependency will be addressed in on-going work to determine whether these low frequency bands are dependent on a surface polymerization caused by hydrogen bonding or whether they are related directly to the symmetry of the surface Mo species. In addition, in the calcined state the Mo=O stretching frequency is dependent on the amount of molybdenum on the Al₂O₃ support and, at a specific molybdenum concentration, is dependent on the amount of promoter. These changes will be addressed more thoroughly to define metal-support and metal-metal interactions in these oxide supported catalysts.