(Co)MoS$_2$/Alumina Hydrotreating Catalysts: An EXAFS Study of the Chemisorption and Partial Oxidation with O$_2$

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Introduction

Alumina-supported Mo and W sulfide catalysts are widely used in petroleum refining for removal of S and N heteroatoms.[1] The activity of MoS$_2$ catalysts is promoted by addition of Co or Ni, and the structure of the active site has been extensively studied by numerous techniques.[1,2] Mössbauer and EXAFS analysis have provided the most detailed and complete information about the local structure of the active phase. The catalytic site in (Co)MoS$_2$ is composed of isolated, five to six S-coordinate Co ions located at the edge of small MoS$_2$ crystallites bridging two Mo atoms.[3-6] While several research groups have proposed that the catalyst has four bridging Co–S–Mo bonds and one or two terminal Co–S bonds, only one Co–S distance at 2.20 Å has been resolved using standard EXAFS analysis.[7-9]

This paper describes the changes that occur at the Co and Mo atoms of MoS$_2$/alumina and (Co)MoS$_2$/alumina catalysts after chemisorption and partial oxidation with O$_2$. Since the changes that occur to the catalytic surface are relatively small, a modified EXAFS analysis procedure has been adopted. Based on this analysis, two Co–S distances have now been resolved. Furthermore, it is observed that only the long, nonbridging Co–S bond is reactive to O$_2$. By contrast, at the Mo ions, oxidation with O$_2$ leads to replacement of a portion of the bridging S by O ions.

Methods and Materials

Prior to the EXAFS measurements, presulfided catalysts (KF-756 from Akzo Nobel) were heated to 350ºC for 1 h at atmospheric pressure in a flow of 5% H$_2$ in He (150 cc/min). The EXAFS data were collected at room temperature in 5% H$_2$/He. Following reduction and purging with He, the catalyst was treated in 5% O$_2$/He at room temperature and at 100ºC. After each oxidative treatment, EXAFS data were collected at room temperature in 5% O$_2$/He.

The EXAFS signal is composed of a linear combination of the absorption fine structure of each scattering path in the sample.[10] To a first approximation (ignoring electronic changes), removing one coordinating atom from the environment of one absorbing atom will eliminate the scattering path from that pair of atoms, resulting in an immeasurably small change in the EXAFS. The difference method extends this idea to larger changes. In the case of MoS$_2$, if oxygen is adsorbed to the edge of the MoS$_2$ particles at the exposed Mo sites, then additional scattering paths will contribute to the signal. In small enough particles with a large fraction of surface-exposed Mo atoms, the adsorption of oxygen will have a measurable effect. If two scans of the same sample differ by a small amount, subtracting one spectrum from another will result in a data set that describes the difference between the state of the sample in the two scans. Furthermore, the difference may be analyzed by standard analysis methods, with just one variation. Instead of positive-definite coordination numbers, the coordination number for a path may now be positive or negative, indicating whether that path has been added or removed. This procedure has been verified for the one set of conditions in which it was possible to fit each data set individually as well as to use the difference technique, namely, the difference between the reduced MoS$_2$ catalyst and the same sample oxidized at 100°C.[11]

Results and Discussion

At 100°C, the Mo–O coordination number, $N_{\text{Mo–O}}$, is 1.3 at a distance of 1.66 Å, which is significantly shorter than the 1.77 Å in Na$_2$MoO$_4$, i.e., Mo$^{(6+)}$–O.[12] Also, there are decreases of about 0.7 and 0.4 in $N_{\text{Mo–S}}$ and $N_{\text{Mo–Mo}}$, respectively. The replacement of Mo–S by Mo–O disrupts the MoS$_2$ structure, as evidenced by the smaller Mo–Mo coordination; however, much of the MoS$_2$ structure remains unchanged.

While the EXAFS spectrum of catalyst oxidized at 100°C could be fit by standard analysis procedures, the spectrum for MoS$_2$/alumina exposed to oxygen at 20°C could not, because of the large, overlapping Mo–S path, which dominated the fit. The small changes, however, could be fit by analysis of the difference spectrum between the sulfided catalyst and the catalyst with oxygen. These measurements revealed formation of 0.3 Mo–O bonds per Mo atom and the elimination of 0.2 Mo–S bonds per Mo atom. Figure 1 shows the EXAFS spectrum for the reduced MoS$_2$/alumina catalyst and two difference spectra.

At the Co edge the results are more striking. Exposure to O$_2$ at 20°C leads to the formation of 0.9 Co–O bonds per Co atoms, at a distance of 1.98 Å, which is considerably shorter than the 2.13 Å in CoO.[13] At the same time, the Co–S coordination number decreases by 0.6 at a distance of 2.29 Å. The Co–S bond,

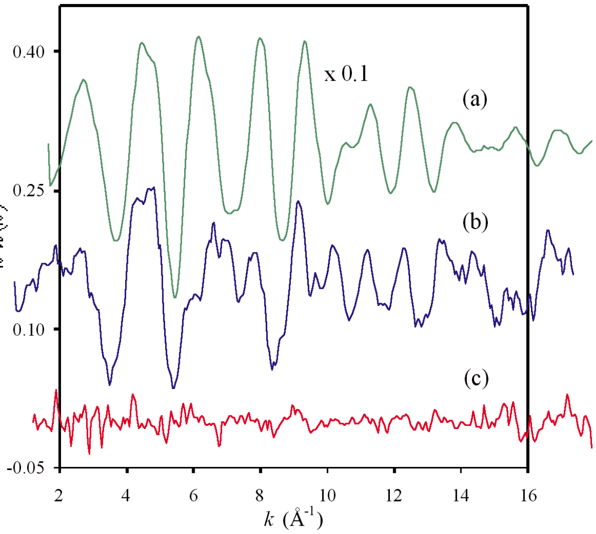

FIG. 1. Molybdenum-edge EXAFS for (a) the reduced MoS$_2$/alumina catalyst, (b) the difference between the reduced catalyst and the catalyst exposed to O$_2$ at 20°C, and (c) the difference between two consecutive scans of the reduced catalyst.[11]

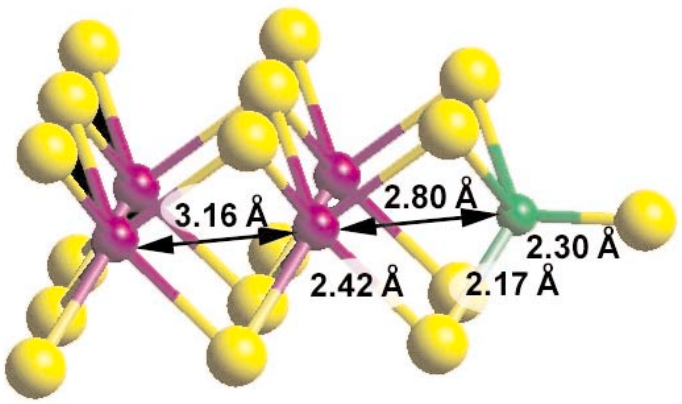

FIG. 2. Molecular model of the local structure of (Co)MoS_2/alumina. Sulfur atoms are represented by the yellow balls, molybdenum by purple balls, and cobalt by the green ball.

which has been displaced by oxygen, is significantly longer than the average Co–S distance in the sulfided catalyst, which is 2.20 Å. At 100°C, there is a further increase in the Co–O coordination, to 1.7 at a distance of 2.01 Å, and a small additional decrease in $N_{Co–S}$.

In previous studies, the Co–S coordination number of (Co)MoS_2/alumina was found to be about five, and the bridging and terminal Co–S distances could not be resolved. In this study, we find that exposure to O_2 at 20°C leads to a loss of about one Co–S at a distance of 2.29 Å. This distance is consistent with that for the terminal Ni–S bond in (Ni)WS_2 on carbon and alumina supports.[6] While the terminal Co–S is reactive to O_2, the remaining four Co–S are not, and are likely bridging bonds. Figure 2 shows a structural model of the (Co)MoS_2/alumina catalyst based on this analysis.

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