At the same time, the Co terminal Co reacts to O₂. By contrast, at the Mo ions, oxidation with O₂ is more, it is observed that only the long, nonbridging Co atoms of MoS₂/alumina and (Co)MoS₂/alumina catalysts after chemisorption and partial oxidation with O₂. 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 O₂. By contrast, at the Mo ions, oxidation with O₂ 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 350°C for 1 h at atmospheric pressure in a flow of 5% H₂ in He (150 cc/min). The EXAFS data were collected at room temperature in 5% O₂/He. Following reduction and purging with He, the catalyst was treated in 5% H₂/He at room temperature and at 100°C. After each oxidative treatment, EXAFS data were collected at room temperature in 5% O₂/He.

The EXAFS signal is composed of a linear combination of the absorption fine structure of each scattering path in the sample. 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 MoS₂, if oxygen is adsorbed to the edge of the MoS₂ 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 MoS₂ catalyst and the same sample oxidized at 100°C.

Results and Discussion

At 100°C, the Mo–O coordination number, NMo–O, is 1.3 at a distance of 1.66 Å, which is significantly shorter than the 1.77 Å in Na₂MoO₄, i.e., Mo⁶⁺–O. Also, there are decreases of about 0.7 and 0.4 in NMos–S and NMos–Mo, respectively. The replacement of Mo–S by Mo–O disrupts the MoS₂ structure, as evidenced by the smaller Mo–Mo coordination; however, much of the MoS₂ structure remains unchanged.

While the EXAFS spectrum of catalyst oxidized at 100°C could be fit by standard analysis procedures, the spectrum for MoS₂/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 MoS₂/alumina catalyst and two difference spectra.

At the Co edge the results are more striking. Exposure to O₂ at 20°C leads to the formation of 0.9 Co–O bonds per Co atom, at a distance of 1.98 Å, which is considerably shorter than the 2.13 Å in CoO. At the same time, the Co–S coordination number decreases by 0.6 at a distance of 2.29 Å. The Co–S bond,
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. 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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