MÖSSBAUER STUDIES OF THE ACTIVATED STATE
OF Co-Mo HYDRODESULFURIZATION CATALYSTS

B. S. CLAUSEN, S. MØRUP

Laboratory of Applied Physics II
Technical University of Denmark, DK-2800 Lyngby, Denmark

H. TOPSØE and R. CANDIA

Haldor Topsøe Research Laboratories, DK-2800 Lyngby, Denmark

Résumé. — Des Co-Mo catalyseurs à hydrodésulfuration ont été étudiés par application de spectroscopie Mössbauer. En état calciné les Co ions se trouvent localisés dans le support en alumine. Pendant l'activation, une structure de surface se forme contenant Co, Mo, et S. Les résultats de mesures indiquent que le procédé catalytique est associé avec un changement en valence des Co ions.

Abstract. — Co-Mo hydrodesulfurization catalysts have been studied by the use of Mössbauer spectroscopy. In the calcined state the Co ions are found to be located in the alumina carrier. During activation a surface structure containing Co, Mo, and S is formed. The measurements indicate that the catalytic process is associated with a valence change of the Co ions.

1. **Introduction.** — The need for reducing sulfur pollution has made hydrodesulfurization an important catalytic process for removing sulfur from oil fractions. Commonly, this is done by passing at high temperature the oil together with hydrogen over a catalyst consisting of Co and Mo supported on a high surface area alumina. In this way the sulfur is removed as H_2S. Extensive research on this catalyst system has been carried out, but neither its structure nor its mode of operation has been completely clarified.

The catalyst is prepared by impregnation of a γ-Al_2O_3 carrier with a solution containing Co and Mo. The catalyst is then calcined in air at about 780 K and is activated for instance by exposure to a H_2/H_2S gas mixture at 500-600 K. Two different structures of the catalyst in the activated state have been proposed, namely the surface model and the intercalation model.

In the surface model [1] the (110) planes are the predominant surface planes of the alumina. In the calcined state Mo is assumed to be present in a surface layer of MoO_3 having the same symmetry as the surface plane of the alumina carrier. The location of cobalt (Co^{2+}) is assumed to be a tetrahedral position somewhere within the alumina, i. e. below the surface layer. During operation the catalyst is in a sulfided state, and it is assumed that sulfur ions replace the oxygen ions at the surface.

In the intercalation model [2, 3] the sulfided catalyst is assumed to consist of a surface layer of MoS_2 with a structure consisting of slabs, each of which is comprised of a plane of Mo atoms sandwiched between two hexagonal closed-packed planes of sulfur atoms. The Co ions are then assumed to be incorporated (intercalated) in octahedral holes between the slabs. Although intercalation is not possible in an ideal MoS_2 crystal, it has been postulated [3] that it may occur to a certain extent provided the crystals are small.

Recently, it was proposed [4] that in the calcined state the catalyst has a monolayer structure, but that during sulfidation small crystals of MoS_2 are formed, giving rise to an intercalation structure. Both IR and UV reflectance spectra [5], however, suggest that the cobalt ions remain in the alumina after sulfidation.

In order to achieve further information concerning not only the structure of the Co-Mo/Al_2O_3 catalyst, but also the chemical behavior of the Co ions, *in situ* Mössbauer spectroscopy studies of the catalyst have been carried out. This is a new technique for investigation of this particular catalyst ; at present only one Mössbauer study [6] dealing with this system is known.

2. **Experimental.** — The samples were prepared by impregnating powdered alumina with a solution containing Fe, and/or Co, and/or Mo ions. The Mössbauer sources and absorbers were prepared by compressing the material into thin wafers. Six different samples have been studied :

Sample 1 : Is a Co-Mo/Al_2O_3 catalyst in which a small fraction of the Co was replaced by ^{57}Fe. Some of the results have been reported in an earlier publication [6].

Sample 2 : In this sample all the Co was replaced by Fe.

Sample 3 : Contains no iron, but some of the Co was introduced as ^{57}Co. In this way the Co atoms are investigated by using the catalyst as a source.

Sample 4 : Similar to sample 3, but without Mo.

Sample 5 : Pure MoS$_2$ doped with ^{57}Co.

Sample 6 : Pure MoS$_2$ doped with ^{57}Fe.

Samples 1-4 were calcined in air at 780 K before they were placed in a Mössbauer cell which allowed treatments of the samples at high temperatures in different gaseous environments (H$_2$, H$_2$/H$_2$S, H$_2$/thiophene (C$_4$H$_4$S), and air) while the spectra were recorded.

The Mössbauer spectra were obtained by the use of conventional constant acceleration Mössbauer spectrometers. A source of ^{57}Co in Pd was used giving a line width of about 0.23 mm/s with a thin absorber of metallic iron. The experiments with samples doped with ^{57}Co (samples 3, 4, and 5) were carried out with a moving absorber of K$_4$Fe(CN)$_6\cdot$3 H$_2$O, enriched in ^{57}Fe.

In the absorber experiments positive velocity corresponds to the source approaching the absorber. For convenience we have defined positive velocity in the source experiments for the absorber moving away from the source. Thus, the isomer shifts become immediately comparable.

3. Results.

— Figure 1 shows some spectra of sample 3 after various treatments. Spectrum (a) is obtained after calcination of the sample. This spectrum resembles that of ^{57}Co diffused into Al$_2$O$_3$ obtained by Wertheim and Buchanan [7]. The spectrum indicates that both Fe^{2+} and Fe^{3+} are present after the decay of ^{57}Co. The spectra (b), (c), and (d) are obtained at 600 K, 300 K, and 80 K, respectively, after sulfidation of the sample at 600 K in H$_2$/H$_2$S. These spectra were decomposed into two quadrupole doublets, Q_1 and Q_2, with the parameters $\delta_{Fe}(Q_1) = 0.33$ mm/s, $\Delta(Q_1) = 1.13$ mm/s, $\delta_{Fe}(Q_2) = 1.06$ mm/s, $\Delta(Q_2) = 1.78$ mm/s at 300 K. It is noteworthy that the two quadrupole splittings are temperature dependent. Spectrum (e) is obtained at 300 K after reduction in H$_2$ at 600 K. In this spectrum the relative area of the quadrupole doublet, Q_2, has increased. After resulfidation (f), the spectrum is identical with (c). The spectra (g) and (h) were obtained at 300 K after exposure of the catalyst to a H$_2$/thiophene gas mixture at 600 K and after subsequent reduction in H$_2$ at 600 K. The changes in the spectra (c), (e), and (g), (h) were found to be reversible. The spectrum (i) was obtained at room temperature after exposure of the sulfided sample to air at 600 K. Similar changes were found when the sample was oxidized at 300 K. It was found that subsequent exposure of the sample to H$_2$/H$_2$S at 600 K reestablished the spectrum (c).
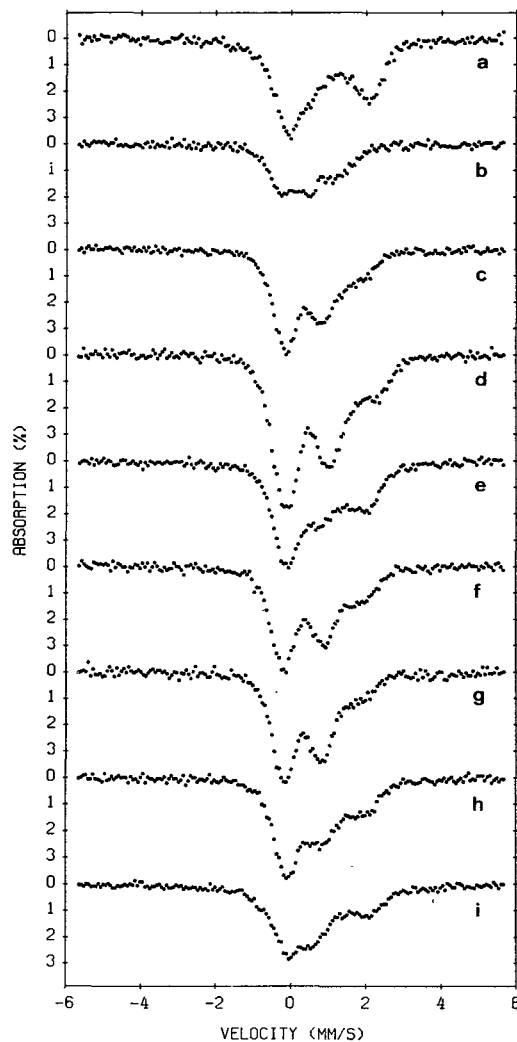

Fig. 1. — Mössbauer spectra of sample 3 : *a*) in the calcined state at 300 K ; *b*), *c*) and *d*) in the sulfided state at 600 K, 300 K, and 80 K, respectively ; *e*) after reduction in H$_2$ at 600 K ; *f*) after resulfidation ; *g*) after exposure to H$_2$/thiophene at 600 K ; *h*) after reduction in H$_2$ at 600 K ; *i*) after exposure to air at 600 K. The spectra *e*)-*i*) were obtained at 300 K.

The spectra of samples 1 and 2 in the sulfided and reduced states were in most respects similar to those of sample 3.

Figure 2 shows spectra of sample 4 (γ-Al$_2$O$_3$ doped with ^{57}Co) and sample 5 (MoS$_2$ doped with ^{57}Co). (a) is the room temperature spectrum of sample 4 after calcination in air at 780 K. This spectrum is quite similar to figure 1*a*. Sulfidation in H$_2$/H$_2$S at 600 K (spectrum (b)) increases the relative area of the doublet with the larger isomer shift. Reexposure to air at 300 K (spectrum (c)) gives rise to a spectrum similar to (a).

The spectra of sample 5 ((d), (e), and (f)) show a quadrupole doublet with a line separation decreasing from 1.4 mm/s at 80 K to 0.8 mm/s at 690 K. The isomer shift at room temperature is $\delta_{Fe} = 0.31$ mm/s.
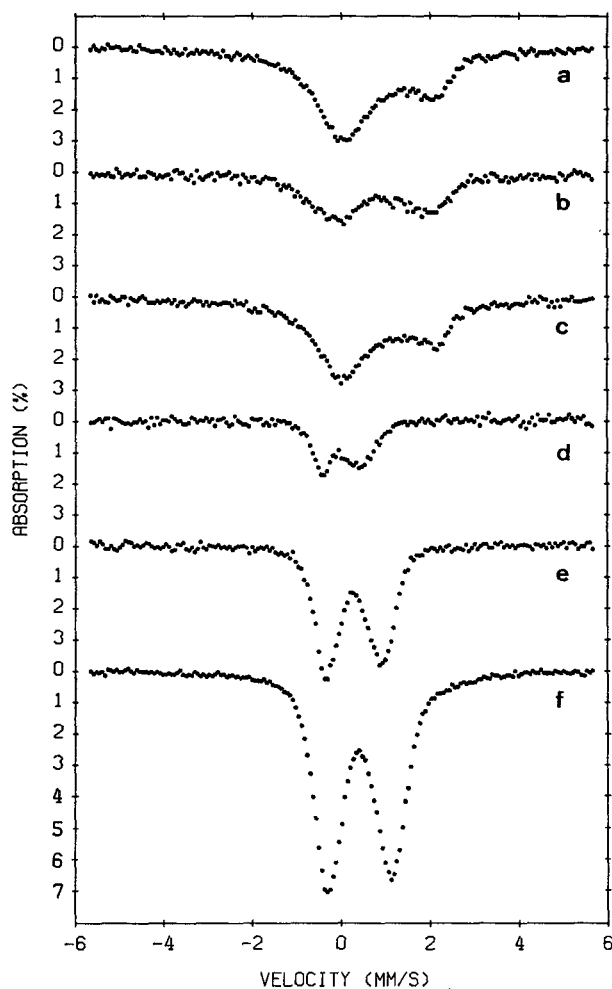
The spectra of sample 6 are essentially similar to

FIG. 2. — Mössbauer spectra of samples 4 and 5 : a) sample 4 after calcination ; b) after sulfidation at 600 K ; c) after reexposure to air at 300 K. The spectra a)-c) were obtained at 300 K ; d), e) and f) are spectra of sample 5 obtained at 690 K, 300 K, and 80 K, respectively.

those of sample 5, but the quadrupole splitting is about 0.3 mm/s smaller at all temperatures.

4. **Discussion.** — It is evident from the Mössbauer spectra of the catalysts that the Fe ions are strongly affected by the exposure of the samples to the various gas mixtures.

However, it is important to note that the industrially used catalysts do not contain iron but cobalt. The Mössbauer spectra only give information about the state of iron ions which are supposed to substitute cobalt (in samples 1 and 2) or iron ions which are produced by the decay of ^{57}Co in the catalyst (sample 3). In the latter sample the lattice positions of the iron ions may be assumed to be identical with the cobalt positions. However, some of the observed chemical states might be produced by the Auger cascade following the electron capture in ^{57}Co, although the similarities of the spectra of samples 1, 2, and 3 in the sulfided

states indicate that this is not the case. This will be discussed in detail elsewhere.

4.1 THE CALCINED STATE. — The similarity of the spectra (1a) and (2a) suggests that Co occupies similar positions in the calcined states of sample 3 and sample 4. It is therefore likely that in the calcined state of the catalyst, Co is located in the γ-Al_2O_3 lattice, and the Mo ions have no influence on the Mössbauer spectra. The Mössbauer parameters indicate that iron is present in the Fe^{3+} and the Fe^{2+} high spin states. In the calcined states of samples 1 and 2 only Fe^{3+} in the high spin state was detected.

4.2 THE ACTIVATED (SULFIDED) STATE. — Exposure of sample 3 to the H_2/H_2S gas mixture at 600 K changes considerably the Mössbauer spectra. It is seen in figure 1 that the quadrupole doublets, Q_1 and Q_2, both have a temperature-dependent quadrupole splitting. The isomer shift and the quadrupole splitting of Q_2 are typical of Fe^{2+} in the high spin state. The small isomer shift of Q_1 ($\delta_{Fe} = 0.33$ mm/s at 300 K) is consistent with Fe^{3+} in the low spin state, Fe^{2+} in the low spin state, or Fe^{3+} in the high spin state. However, the temperature dependence of the quadrupole splitting suggests that the two latter possibilities can be excluded, indicating that iron is present as Fe^{3+} in the low spin state.

Exposure of sample 4 to H_2/H_2S gave rise to an increased amount of high spin Fe^{2+}, presumably due to the reducing effect of H_2. This is opposite to the change of sample 3 during sulfidation. Therefore, the sites of Co in the catalyst in the sulfided state are strongly affected by the presence of Mo.

The quadrupole doublets of samples 5 and 6 (^{57}Co and ^{57}Fe in MoS_2) closely resemble the quadrupole doublet Q_1 of sample 3 in the sulfided state. It therefore seems likely that Co ions in the catalyst occupy positions similar to those of Co in MoS_2. If the Co ions intercalate in the MoS_2 lattice, it should give rise to an increase in the distances between the layers. However, x-ray diffraction experiments on sample 6 did not show clear evidence of intercalation. In an earlier x-ray investigation [8] it was found that the layer spacing decreases upon diffusion of small amounts of Co into MoS_2. This was explained in terms of a formation of a solid solution in which Co ions substitute Mo in the MoS_2 structure.

The occurence of low spin Fe^{3+} is presumably due to the presence of sulfur ions surrounding the iron ions. In several iron sulfides low spin Fe^{2+} ions have been observed [9-11]. In oxides Fe^{2+} and Fe^{3+} ions are normally found in the high spin states.

4.3 CHEMICAL REACTIONS IN THE ACTIVATED CATALYST. — The reduction of the sulfided catalyst in H_2 (Fig. 1e) changes the area ratio of the two quadrupole doublets towards a relatively larger area of the Fe^{2+} doublet. After subsequent sulfidation the spectrum

(1 f), which is similar to (1c), is obtained. Alternative exposure of the catalyst to H_2/thiophene and H_2 (Figs 1g and 1h) gave rise to similar changes in the spectra. These processes were found to be reversible. Thus, the valence change of iron seems to be closely related to the catalytic process.

The exposure of the catalyst (sample 3) to air at 600 K or 300 K also affected the spectrum. The quadrupole doublet with the smaller isomer shift has now broader lines and, furthermore, the splitting of this doublet did not show any significant temperature dependence. Therefore, the iron seems to be converted into Fe^{3+} in the high spin state. After exposure of the oxidized sample to H_2/H_2S a spectrum similar to figure 1c was obtained again.

5. Conclusion. — The present measurements indicate that in the calcined state of the catalyst the Co ions are located in the alumina lattice, but during sulfidation a large fraction of the Co ions diffuse to positions near the surface, where a structure containing Co, Mo, and S is formed. It also seems likely that Co ions in the catalyst occupy the same positions as when diffused into MoS_2.

The present measurements together with the x-ray results [8] may be interpreted in terms of a structure, where Co ions substitute Mo ions in the layer structure. The conversion of Fe^{3+} in the low spin state into Fe^{3+} in the high spin state, when the sulfided catalyst is exposed to air at room temperature, suggests that sulfur ions surrounding the Co are replaced by oxygen. This suggests that some Co ions may be located closer to the surface than previously supposed [1, 3].

The reversible process occurring during alternative treatments with H_2/H_2S and H_2 gases may be expressed by the following reaction scheme :

$$2 Fe^{2+} + H_2S \leftrightarrows 2 Fe^{3+} + S^{2-}(ads) + H_2 .$$
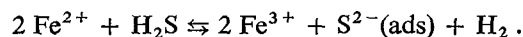
This reaction does occur in the Co-Mo/Al_2O_3 sample (sample 3), but not in the Co/Al_2O_3 sample (sample 4), i. e. the valence change occurs only when Co and Mo are associated in the catalyst. Thus the present measurements suggest that Co ions play an active role during hydrodesulfurization catalysis.

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