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# A $^{57}$Co Mössbauer Emission Spectrometric Study of Some Supported CoMo Hydrodesulfurization Catalysts

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A suite of 11 CoMo/$Al_2O_3$ (and one CoMo/$SiO_2$) catalysts has been prepared employing four preparation routes, viz. one sequential-impregnation route and three different coimpregnation routes. Speciation of the Co present in the oxidic precursors (octahedral vs tetrahedral Co) and in the activated, sulfided catalysts (CoMoS, $Co_9S_8$, and unsulfided Co) was effected with the aid of $^{57}$Co Mössbauer emission spectroscopy (MES). A linear relation between the thiophene-hydrodesulfurization (HDS) activity and wt% Co-in-CoMoS was observed for each preparation route, but no unique correlation was found to exist. This was traced to the fact that the preparation routes differ in the amount of CoMoS I and CoMoS II they produce in the activated catalyst. Although these two phases differ in specific activity, CoMoS II being twice as active in thiophene HDS as CoMoS I, they cannot be distinguished on the basis of their Mössbauer parameters. It appears that octahedral Co is easier to sulfide than tetrahedral Co, but a substantial fraction of the latter is also found to be capable of entering CoMoS upon sulfidation. The reduced effectiveness of high-loading catalysts is traced to their being prone to $CoMoO_4$ formation in the calcination step. A rationalization of this behavior is offered.

## INTRODUCTION

An understanding, and therefore a rational exploitation, of the influence of the preparation method on the hydrodesulfurization (HDS) activity of Co(Ni)Mo/$Al_2O_3$ catalysts has long been hampered by the difficulty of establishing in a quantitative manner which Co(Ni)Mo phases are present on the alumina surface after calcination and sulfidation. As far as Co speciation is concerned, it would appear that $^{57}$Co Mössbauer emission spectroscopy (MES), whose application to HDS catalysts was pioneered by Topsøe *et al.* (*1, 2*), is by far the most powerful technique. On the basis of results obtained by this and other methods, Topsøe *et al.* (*1–3*) have concluded that there is only one really active phase, designated CoMoS, which consists of $Co^{2+}$ ions sitting on the edges of (small) $MoS_2$ crystallites, the thiophene-HDS activity being proportional to the amount of Co in CoMoS. Furthermore, it is found that the CoMoS phase is formed from well-dispersed octahedral Co and well-dispersed Mo present on the support surface after calcination (*4*). Other phases often encountered in sulphided catalysts, such as $Co_9S_8$, unsulfided Co, and unpromoted $MoS_2$, have negligible activity. However, Candia *et al.* (*5*) have recently shown that there are (at least) two CoMoS phases: these are designated type I, in which the Mo is not fully sulfided, so that some bridging oxygen ions between Mo and Al remain, and type II, in which Mo is fully sulfided, so that the interaction between active phase and the subjacent alumina is only of the van der Waals type. This distinction into two modifications is important in that the latter type is more active, per Co in CoMoS, than the former in the HDS of thiophene (*5*). However, apparently the CoMoS I and II phases cannot be distinguished by $^{57}$Co MES measurements: not only has a comparison between the Mössbauer parameters of the two

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phases never been given by Topsøe *et al.*, but they use the activity criterion to distinguish the phases (*6*)! In this connection it is also relevant to note that Göbölös *et al.* (*7*) have found that CoMoS activity can be greatly altered via severe pretreatments without the Mössbauer parameters changing appreciably. Since one can expect the Mo–$Al_2O_3$ interaction to vary with the preparation method employed, and the extent of sulfidation under standard conditions in its turn to vary with that interaction, it may well be that there is no universal $k$(HDS) vs Co-in-CoMoS curve, but that while a straight line is obtained for each preparation route, the slope of that line will depend on the relative amounts of CoMoS I and II generated (the $k$(HDS) vs Co-in-CoMoS curve does not even have to be straight, since the ratio I/II may depend on catalyst loading).

In order to verify the reported linear relationship between thiophene-HDS activity and the amount of Co in the CoMoS phase (*1*) we have applied MES to study the relationship "preparation–structure–HDS activity." The results are reported here. In passing, we also studied the question as to whether in fact only Co(oct.) is capable of entering the CoMoS phase. Recently van der Kraan *et al.* (*8*) reported the observation of the so-called CoMoS phase in carbon-supported cobalt sulphide catalysts by MES. Their results show that the formation of a cobalt species like the one present in the CoMoS phase does not necessarily require the presence of molybdenum disulphide. This implies that from a fundamental point of view this special type of cobalt species, defined by an MES spectrum consisting of a quadrupole doublet (QS = 1.0–1.3 mm/s), should not be referred to as CoMoS; however, we will still use CoMoS here as a notation to avoid misunderstandings while comparing our results with those reported in the literature (*1–7*), in particular because there appears to be little doubt that in CoMo systems the Co giving rise to the quadrupole doublet is in fact (mainly) associated with the $MoS_2$.

Although we have exploited our results through the CoMoS model, we do not wish to imply that there is in any way a consensus on the structure and function of catalyst and promoter in CoMo HDS catalysts. For a recent review of the various views on this matter, see Ref. (*9*).

## EXPERIMENTAL

The CoMo/$Al_2O_3$ samples were prepared via the sequential route described by Wivel *et al.* (*4*) and via three different coimpregnation routes, viz. routes using (a) phosphoric acid-containing solution, (b) ammoniacal solution, and (c) near-neutral solution containing nitrilotriacetic acid (NTA). In the case of the Mössbauer samples $^{57}$Co was added to the impregnation solution as its nitrate in 0.07 $M$ $HNO_3$ (ex Amersham). In the case of the samples destined for activity measurements only the nitric acid was added. In some cases an adverse effect of the acid on the catalyst activity was noted, which, however, could be counteracted by neutralizing it with $Co(OH)_2$ or $NH_4OH$. The $Co(OH)_2/NH_4OH$-modified routes were used for both the Mössbauer and activity samples. The reproducibility of the catalyst preparation cum activity test is satisfactory: the spread in catalyst activity for separate preparations is always within 5% relative, except at the highest loadings (e.g., ±10% for samples such as No. 241). Catalyst loadings are given in Table 1. The amount of $^{57}$Co in the Mössbauer samples was of the order of 4 mCi $g^{-1}$.

As support we employed a Shell $\gamma$-$Al_2O_3$ with a surface area of 250 $m^2\ g^{-1}$ and a pore volume of 0.75 ml $g^{-1}$, in one case modified by $NH_4F$ treatment to remove the basic OH groups (*10*). The HDS of thiophene at atmospheric pressure was used as the activity test. The setup was similar to one described in the literature (*11*), the standard conditions being as follows: sulphidation, 2 h at 350°C in $\frac{1}{6}$ v/v $H_2S/H_2$; testing, 5 h at 350°C in $H_2$, loaded with 6 vol% thiophene, the performance at $t$ = 5 h being taken as the catalyst activity (by this time a plateau had long been

TABLE 1

Metal Loading and Preparation Route of the $CoMo/Al_2O_3$ Catalysts Studied

| Catalyst no. | Metal loading | | Preparation route[a] |
|---|---|---|---|
| | Co, %w | Mo, %w | |
| 124 | 2.9 | 8.3 | s.i. (Mo) |
| 125 | 2.9 | 8.3 | s.i. (Co) |
| 126 | 2.0 | 9.3 | a |
| 127 | 2.4 | 11.1 | a |
| 129 | 1.5 | 7.8 | c |
| 234 | 0.91 | 4.2 | a |
| 235 | 0.53 | — | |
| 237 | 2.1 | 6.0 | b |
| 238[b] | 1.3 | 7.5 | c |
| 239 | 2.5 | 7.5 | b |
| 241 | 2.7 | 13.2 | a |
| 268 | 2.6 | 7.9 | b |

[a] s.i., sequential impregnation [( ) indicates component impregnated first]
a,b,c: coimpregnation routes, c involving the presence of an organic ligand.

[b] Support, $SiO_2$.

reached in the conversion vs time plot in practically all cases).

The MES experiments were carried out *in situ* at room temperature using a constant acceleration spectrometer in a triangular mode with a moving single-line absorber of $K_4Fe(CN)_6 \cdot 3H_2O$ enriched in $^{57}Fe$. Isomer shifts are reported with respect to a source of $^{57}Co$ in metallic Rh, positive velocities corresponding to the absorber moving away from the source. The velocity scale was calibrated by the Mössbauer spectrum of sodium nitroprusside (SNP) obtained with the $^{57}Co$ in Rh source. Mössbauer spectra were fitted by computer with calculated subspectra consisting of Lorentzian-shaped lines, by varying the Mössbauer parameters in a nonlinear, iterative minimization routine. In the case of quadrupole doublets the linewidths and the absorption areas of the constituent peaks were constrained to be equal.

Sulfidation of the catalysts for the MES experiments was performed in a Mössbauer *in situ* reactor, which has been described elsewhere (*12*). However, the heating section as well as the outer container used in this study was made of stainless steel, while the Mylar windows were replaced by beryllium windows, vacuum-brazed on the outer container. Sulfidation was carried out in a 50 $cm^3 min^{-1}$ flow of 10 mol% $H_2S$ in $H_2$ gas mixture. After flushing the reactor with the $H_2S/H_2$ mixture at room temperature for 30 min, the temperature was linearly increased by 10 K $min^{-1}$ (in some cases 2 K $min^{-1}$) up to $T = 673$ K, and kept at this temperature for 1 h. Subsequent cooling was effected in argon.

The spectrometer was placed in a vertical position so that the catalysts, which had been prepared as $\frac{1}{16}$-in. extrudates, could be measured as such.

## RESULTS

Mössbauer Emission Spectroscopy of $^{57}Co$-doped Co-containing catalysts can yield information about the Co-containing phases via the $^{57}Fe$ atoms produced by the decay of the $^{57}Co$. However, the observed valence and spin states of the $^{57}Fe$ daughter atoms may be different from those of the parent $^{57}Co$ atoms due to so-called chemical after-effects (*13*). Although these after-effects can be neglected in conducting materials, they are quite important in insulators. It seems worthwhile to emphasize that due to the after effects, MES can only be used as a finger-print technique. However, within a framework of the same kind of catalysts (same constituent atoms, same kind of support) valuable information about the Co-containing phases can be obtained from mutual comparison of the spectra of the catalysts and by comparing the spectra of the catalysts with those of appropriate model compounds. In this study we have used the results of model compounds as published by Wivel *et al.* (*4*) for the oxidic precursors and by Topsøe *et al.* (*1*) for Co and CoMo sulfides.

Although we are dealing with $^{57}Fe$ atoms produced by the decay of the $^{57}Co$, we ascribe the various resonant absorption spectra to Co species.

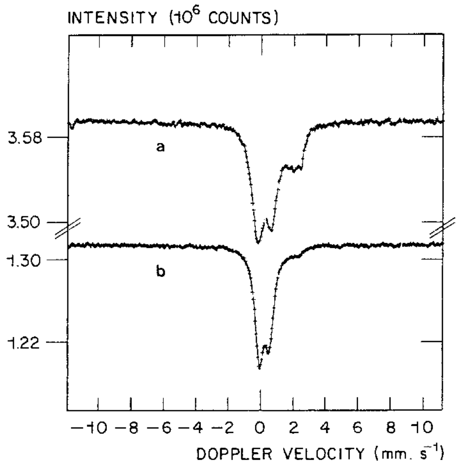

FIG. 1. Room-temperature Mössbauer spectra of calcined $CoMo/Al_2O_3$, prepared via sequential impregnation. (a) Mo first, No. 124, (b) Co first, No. 125.

### *Oxidic Catalyst Precursors*

Figure 1 presents the room-temperature Mössbauer spectra of the calcined versions of the catalysts prepared by the sequential impregnation routes of Wivel *et al.* (*4*). In the case that the Co has been deposited first on the $\gamma$-$Al_2O_3$ support, the spectrum contains a contribution of about 90% from $Co_3O_4$, as expected, and a contribution of about 10% from a high-spin $Co^{2+}$ compound (Fig. 1b). When Mo is deposited first on the support, $Co_3O_4$ is not in evidence (Fig. 1a). However, from Fig. 1 it is obvious that the Mössbauer spectrum of $Co_3O_4$ falls completely within the resonant region of the spectrum of Fig. 1a. The possible presence of a small amount of $Co_3O_4$ in sample 124 cannot, therefore, be entirely ruled out, and it will hardly be possible to analyze spectra such as that shown in Fig. 1a in a proper unique way, for lack of more detailed spectral information.

Nevertheless, we have checked the proposed relationship between octahedral Co in the oxidic precursor and Co in CoMoS after sulphidation (*4*). Since we have worked with low Co/Mo atomic ratios the formation of $Co_3O_4$ during the calcination step will be highly improbable (as long as both elements are present together). Therefore, we have applied in the analysis of the spectra the same basic ideas about tetrahedrally and octahedrally coordinated Co species as Wivel *et al.* (*4*). The results of such a computer analysis of the spectrum of Fig. 1a are presented in Table 2.

Close inspection of the spectrum of Fig. 1a reveals that the outer wing of the resonant absorption lines at positive velocities is rather sharp (cf. Fig. 3, below), indicating the presence of a well-crystallized species. In view of the deduced Mössbauer parameters (Table 2) this species could be $\alpha$-$CoMoO_4$ (cf. Ref. (*4*)). Compounds that are nominally $CoMoO_4$, do not, however, appear to give invariably the same Mössbauer spectrum (*1, 4*). Hence, we were unable to constrain the $CoMoO_4$ parameters in such a way as to be able to determine the spectral contribution of $CoMoO_4$. On the other hand, the presence of this phase is evident from X-ray diffraction data, as is shown in Fig. 2c.

The influence of the applied preparation method on the composition of the oxidic catalyst precursor can be gauged from Fig. 3, in which a Mössbauer spectrum of one sample of each applied preparation route is presented, the sequential impregnation, with Co first, being excluded. Manifestly, there are only rather subtle differences between the samples, made via the three completely inorganic routes, while coimpregnation method c, which involves the presence of an organic ligand (NTA), leads to an essentially different Mössbauer spectrum. The latter has been analyzed with only one $Co^{3+}$ and one $Co^{2+}$ component; spectra 3a–3c have been analyzed in the same way as the one in Fig. 1a. The numerical results are presented in Table 2.

The sample prepared following route c has only been dried at 383 K, and was not calcined afterward, in order to prevent the decomposition of the Co–Mo–NTA complex before the sulphidation step. The Mössbauer spectrum of this sample (Fig. 3d)

TABLE 2

Mössbauer Parameters[a] of the Oxidic Catalyst Precursors

| Catalyst no. | $Fe^{3+}$ component | | | | | | $Fe^{2+}$ component | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | tet | | | oct | | | tet | | | oct | | |
| | IS | QS | A | IS | QS | A | IS | QS | A | IS | QS | A |
| 124 | 0.27 | 0.74 | 37 | 0.27 | 1.31 | 19 | 1.06 | 1.47 | 19 | 1.00 | 2.71 | 25 |
| 125 | 0.22 | 0.65 | 60 | 0.10 | — | 30 | 1.27 | 0.87 | 4 | 1.00 | 2.66 | 6 |
| 126 | 0.31 | 0.71 | 28 | 0.30 | 1.19 | 39 | 1.09 | 1.67 | 11 | 1.02 | 2.69 | 22 |
| 127 | 0.32 | 0.63 | 33 | 0.32 | 1.15 | 26 | 1.08 | 1.35 | 11 | 1.02 | 2.65 | 30 |
| 129 | 0.29 | 0.15 | 30 | | | | | | | 1.03 | 2.53 | 70 |
| 234 | 0.21 | 0.85 | 45 | 0.44 | 1.17 | 12 | 0.83 | 1.33 | 4 | 0.74 | 2.54 | 39 |
| 235 | 0.16 | 0.67 | 63 | | | | 0.66 | 1.96 | 37 | | | |
| 237 | 0.24 | 0.69 | 32 | 0.31 | 1.18 | 4 | 0.90 | 1.29 | 35 | 0.87 | 2.66 | 29 |
| 239 | 0.25 | 0.72 | 46 | 0.34 | 1.24 | 6 | 0.87 | 1.27 | 17 | 0.79 | 2.59 | 31 |
| 241 | 0.26 | 0.64 | 46 | 0.36 | 1.21 | 3 | 0.91 | 1.25 | 23 | 0.87 | 2.56 | 28 |
| 268 | 0.24 | 0.78 | 44 | 0.37 | 0.98 | 19 | 0.98 | 1.54 | 15 | 0.85 | 2.52 | 22 |

[a] IS and QS in mm $s^{-1}$; A is the spectral contribution in %.

shows a relatively small resonant absorption area, indicating an effective Debye temperature much lower for the Co-phase than for those in the calcined samples. As apparent below, the effective Debye temperature is strongly increased upon sulphidation.

Figure 4 shows the room-temperature Mössbauer spectra of a series of oxidic catalyst precursors prepared following the coimpregnation route a. In this series the total metal loading has been increased while keeping the Co/Mo atomic ratio constant at 0.35. The spectra have been analyzed as described above, and the Mössbauer parameters obtained are again given in Table 2. Visual inspection of the spectra suggests that at higher loadings (samples 127 and 241) $CoMoO_4$ should be present, and in fact the parameters of the $Co^{2+}$ spectral components are similar to those of a model $\alpha$-$CoMoO_4$ compound (*4*). That $CoMoO_4$ is present only at higher loadings is also corroborated by X-ray diffraction; see Fig. 2, diffractograms a and b.

The Mössbauer spectra of samples prepared via coimpregnation route b are quite similar to those of their route a counterparts, and the results of their analyses are collected in Table 2. $CoMoO_4$ is again in evidence (sample 239), especially when an $NH_4F$-treated $Al_2O_3$ is taken as a support (sample 237, cf. X-ray diffractogram in Fig. 2d).

The Mössbauer spectrum of CoMo (NTA)/$SiO_2$ (sample 238) is identical with that of its $Al_2O_3$ analogue, as reported before (*14*).

### *Activated Catalysts*

In Fig. 5 we present the Mössbauer spectra at room temperature of the samples prepared by sequential impregnation in sulfided form (see Fig. 1 for the oxidic precursors). It is seen that, as reported before (*4*), $Co_3O_4$ is transformed upon sulfiding into $Co_9S_8$ (spectrum 5b). The spectrum of the model compound $Co_9S_8$ consists of one doublet and one singlet with an intensity ratio of 8 : 1, the ratio of the number of tetrahedral and octahedral positions in the crystal structure (*4*). In the computer analysis, however, the broad absorption line obtained (cf. 5b) can be fitted with one small-quadrupole doublet (QS = 0.26 mm $s^{-1}$) to as good an ap-

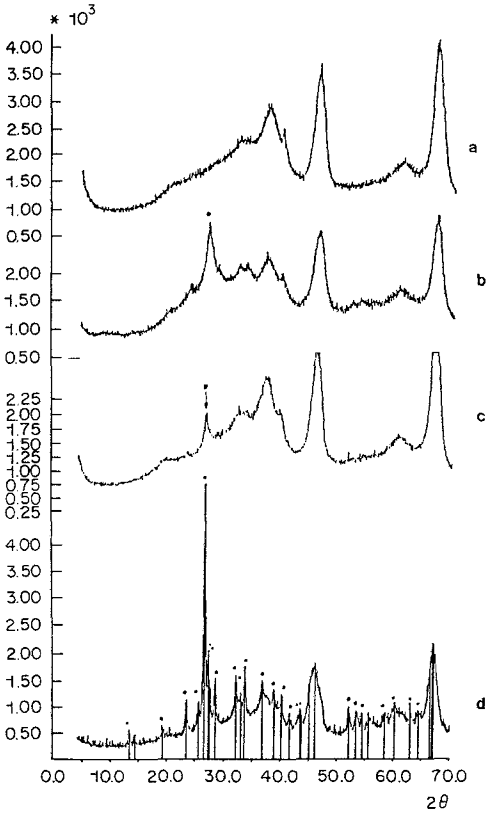

FIG. 2. X-ray powder diffractograms of some calcined CoMo/$Al_2O_3$ samples. (a) 6.5% Mo, route a; (b) 12% Mo, route a; (c) 8.8% Mo, s.i. (Mo); (d) 8.6% Mo, route b, fluorided $Al_2O_3$ support. The lines indicated with dots are due to α-$CoMoO_4$ (JCPDS Powder Diffraction File 21-868).

proximation as the doublet cum singlet described above. In the following, the one-doublet approximation with a constraint QS of 0.26 mm $s^{-1}$ is applied.

Figures 6 and 7 show the spectra of the activated catalysts of Figs. 3 and 4, respectively. The spectra consist mainly of an electric quadrupole doublet, which has been ascribed to the so-called CoMoS phase by Topsøe *et al.* (*1*). The spectra have been analyzed taking into account the CoMoS and $Co_9S_8$ phases, as well as a high-spin $Co^{2+}$ component. The results are collected in Table 3.

From an extensive study of FeMo/carbon HDS catalysts, Ramselaar *et al.* (*15*) have found that the Mössbauer spectrum of the FeMoS phase (defined by analogy with the CoMoS phase) can best be analyzed by a set of two, instead of one, electric quadrupole doublets. Although such an approach leads here to a better fit of the spectrum in all cases, there appears to be no system in the partitioning into a high- and a low-QS contribution, nor are improved *k*(HDS) vs Co(CoMoS) correlations obtained (cf. below). We report, therefore, only the results obtained with a single doublet for the so-called CoMoS phase (Table 3).

As to the identification of CoMoS II, as opposed to CoMoS I, Candia *et al.* (*5*) have reported the formation of the former phase upon sulfidation at high temperatures (well above 675 K). As the Mössbauer parameters of CoMoS II were not reported, we have studied the effect of 873 K sulfidation on the spectrum of sample 126. Results are collected in Fig. 8 and Table 4.

## *Reoxidized Catalysts*

After the *in situ* Mössbauer measurements the activated catalysts were exposed to air at room temperature. If MES is performed immediately after exposure to air, no direct effect on the spectrum is apparent (cf. Fig. 9d). After standing in air for a few days, however, samples become oxidized:

TABLE 3

Mössbauer Parameters[a] of the Activated Catalysts

| Catalyst no. | CoMoS | | | $Co_9S_8$[b] | | $Co^{2+}$ | | |
|---|---|---|---|---|---|---|---|---|
| | IS | QS | A | IS | A | IS | QS | A |
| 124 | 0.23 | 0.92 | 75 | 0.23 | 23 | 0.64 | 1.20 | 2 |
| 125 | | | ~10 | 0.28 | ~90 | | | |
| 126 | 0.22 | 0.99 | 83 | 0.19 | 8 | 0.52 | 1.45 | 9 |
| 127 | 0.24 | 1.03 | 72 | 0.23 | 21 | 0.83 | 1.82 | 7 |
| 129 | 0.20 | 0.99 | 100 | | | | | |
| 234 | 0.24 | 1.07 | 74 | 0.14 | 10 | 0.64 | 2.27 | 16 |
| 235 | | | | 0.27 | 73 | 0.73 | 2.24 | 27 |
| 237 | 0.21 | 1.11 | 36 | 0.23 | 58 | 0.74 | 1.87 | 6 |
| 238 | 0.20 | 1.00 | 100 | | | | | |
| 239 | 0.19 | 1.08 | 63 | 0.20 | 33 | 0.69 | 1.89 | 4 |
| 241 | 0.25 | 1.05 | 45 | 0.22 | 45 | 0.75 | 2.40 | 10 |
| 268 | 0.23 | 0.92 | 87 | 0.18 | 6 | 0.84 | 1.77 | 7 |

[a] IS and QS in mm $s^{-1}$; A is the spectral contribution in %.
[b] QS ($Co_9S_8$) constrained to 0.26 mm $s^{-1}$.

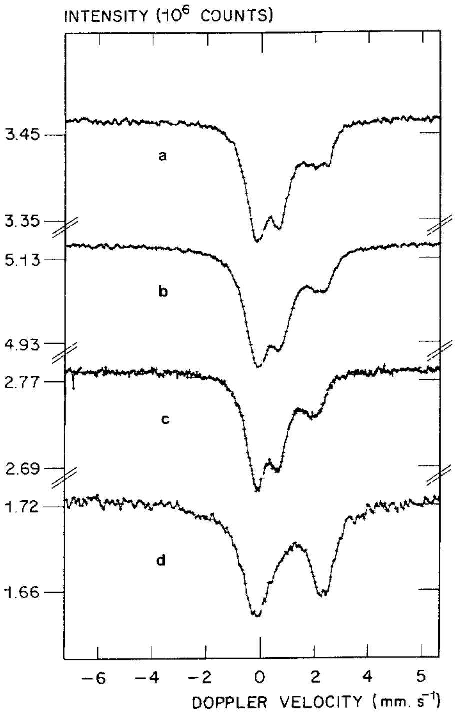

FIG. 3. Room-temperature spectra of calcined $CoMo/Al_2O_3$ catalysts prepared via various routes. (a) s.i. (Mo), sample No. 124; (b) route a, No. 126; (c) route b, No. 268; (d) route c, No. 129.

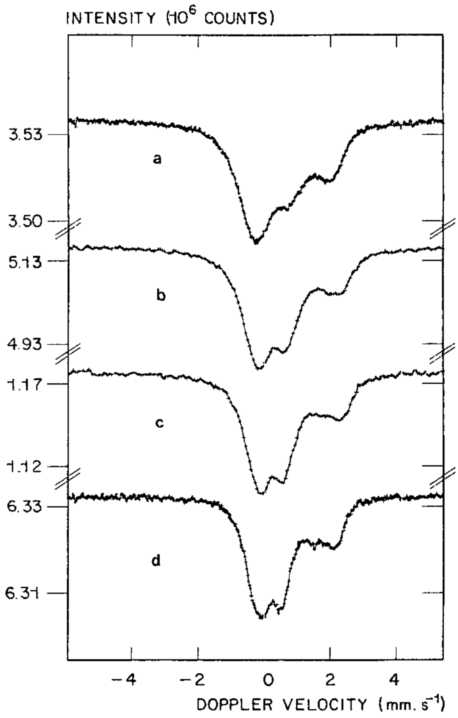

FIG. 4. Room-temperature spectra of calcined $CoMo/Al_2O_3$ prepared via coimpregnation route (a). Co, Mo loadings in wt%: (a) 0.9, 4.2; (b) 2.0, 9.3; (c) 2.4, 11.1; (d) 2.7, 13.2.

for sample No. 125 one observes that only 20% of the original $Co_9S_8$ remains, the spectrum being dominated by new Co phases ($Co^{3+}$ and $Co^{2+}$); for samples 124 and 129 a high-spin $Co^{2+}$ phase is seen to have formed (26 and 16%, respectively). Whether in the latter cases the central doublet is to be ascribed to CoMoS alone, or whether also an $Fe^{3+}$ (ox.) component is present, we have not attempted to ascertain, the Mössbauer parameters of these phases being quite similar (Tables 2 and 3, cf. Ref. (*16*)); in view of the observed isomer shift of 0.20 mm $s^{-1}$, however, it seems probable that CoMoS is at least the major component.

## DISCUSSION

In order to construct a plot of HDS activity vs wt% Co-in-CoMoS, we take the latter quantity to be equal to the wt% Co in the catalyst times the spectral contribution of the CoMoS signal to the room-temperature Mössbauer spectrum.

Figure 10 is a plot of thiophene-HDS ac-

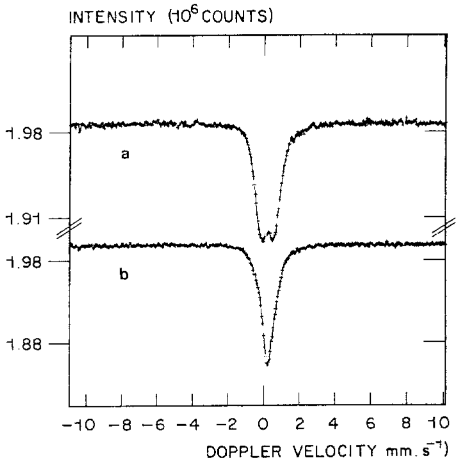

FIG. 5. As Fig. 1, after sulfiding.

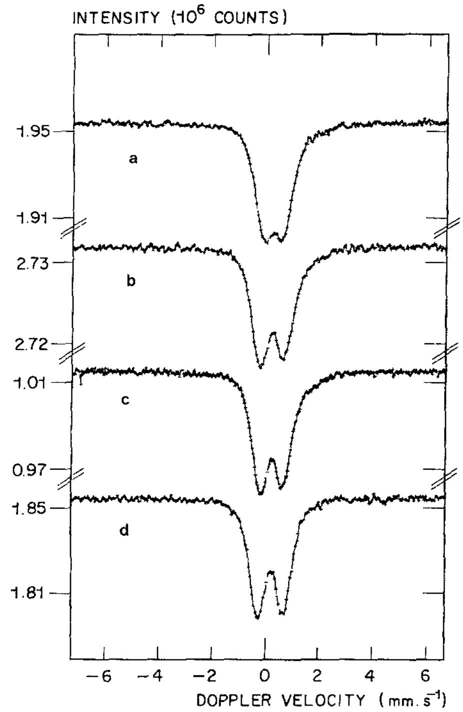

FIG. 6. As Fig. 3, after sulfiding.

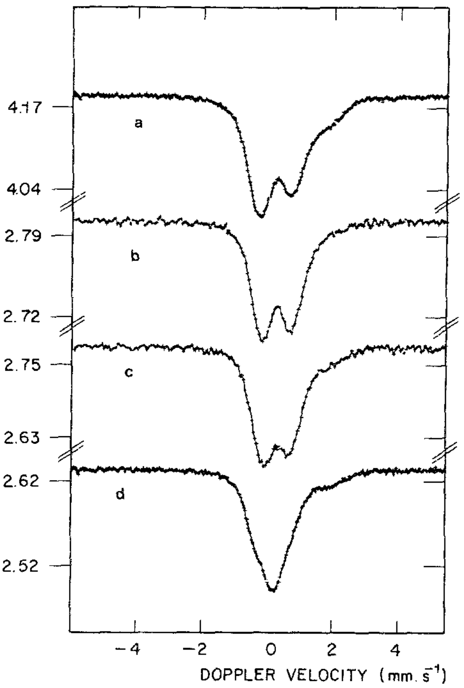

FIG. 7. As Fig. 4, after sulfiding.

tivity, expressed as a pseudo-first-order rate constant against wt% Co-in-CoMoS, obtained as described above. It appears that there is no single correlation line, but that the data points segregate into three groups: (i) those obtained for catalysts prepared via coimpregnation route b or sequential impregnation, with Mo first, (ii) those obtained for catalysts prepared via coimpregnation route a, and (iii) those obtained for catalysts prepared via coimpregnation route c. Curve (i) is labeled CoMoS I, because the sequential impregnation route leads to that phase, according to Topsøe *et al.* (*1, 5*), while curve (iii) is labeled CoMoS II, because, as we have argued elsewhere (*14*), route c, involving the application of an organic ligand (e.g., NTA), results in that phase exclusively (as long as the calcination step is omitted). We note in passing that the specific activity of

TABLE 4

The Influence of Sulfiding Temperature on the Mössbauer Parameters of CoMoS (CoMo/$Al_2O_3$, Cat. No. 126)

| $T^a$(K) | $Co_9S_8$ | | | Co–Mo–S | | |
|---|---|---|---|---|---|---|
| | IS (mm s$^{-1}$) | QS (mm s$^{-1}$) | A (%) | IS (mm s$^{-1}$) | QS (mm s$^{-1}$) | A (%) |
| 673 | | | 3 | 0.24 | 0.95 | 97 |
| 873 | 0.23 | 0.26 | 33 | 0.28 | 1.02 | 67 |
| 873$^b$ | 0.21 | 0.26 | 22 | 0.25 | 0.96 | 78 |

[a] Temperature of *in situ* sulfiding.

[b] After sulfidation at 673 K and subsequent exposure to air.

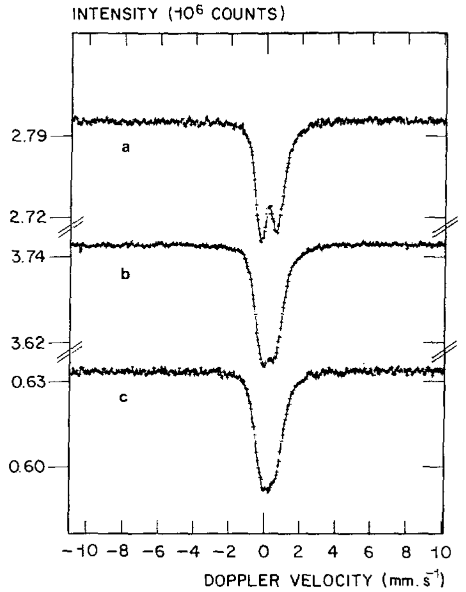

FIG. 8. Room-temperature Mössbauer spectra of sulfided CoMo/$Al_2O_3$ sample No. 126 (a) sulfided at 673 K, (b) sulfided at 673 K, exposed to air, resulfided at 873 K, (c) sulfided at 873 K.

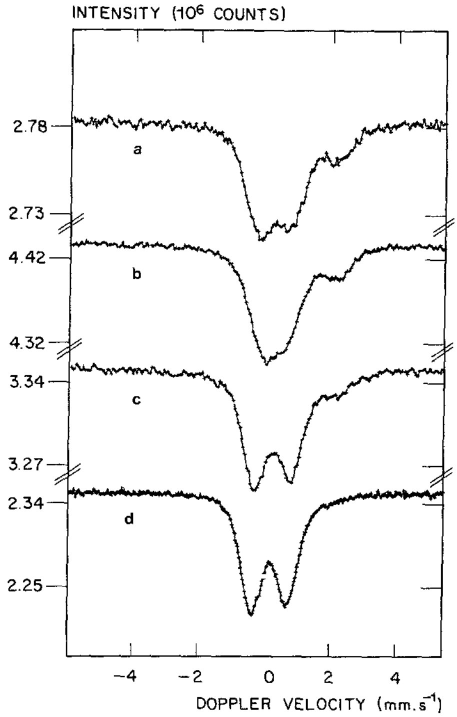

FIG. 9. Room-temperature Mössbauer spectra of sulfided CoMo/$Al_2O_3$ catalysts, after exposure to ambient air. (a) No. 124, (b) No. 125, (c) No. 129, (d) No. 238.

CoMoS II for the HDS of thiophene is about twice that of CoMoS I, in agreement with the report of Candia *et al.* (5).

The line obtained for catalysts prepared via route a is intermediate between the CoMoS I and II curves, showing that in fact a certain amount of phase II can be prepared using a quite conventional, fully inorganic impregnation solution; since the line is straight the relative formation of I and II seems to be independent of catalyst loading. The implication is that, as suggested in the Introduction, no general *k*(HDS) vs Co-in-CoMoS correlation exists, but that its precise form will, in general, depend on the preparation route used. The situation would have been different if MES were capable of distinguishing between CoMoS I and II, but as far as the Mössbauer parameters derived from room-temperature spectra are concerned, Tables 3 and 4 make it obvious that this is not the case. The wt% Co-in-CoMoS

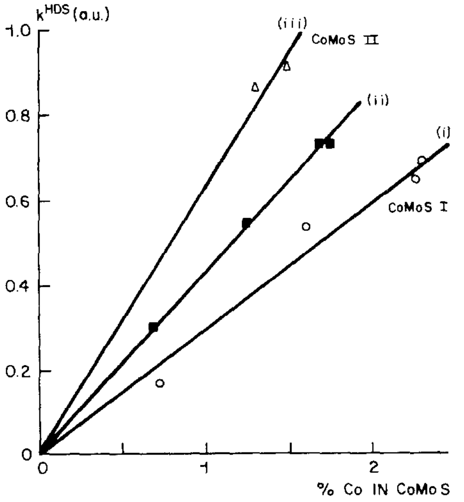

FIG. 10. Plot of the pseudo-first-order rate constant (arbitrary units) for thiophene hydrodesulfurization, $k^{HDS}$, vs wt% Co in CoMoS. (○) s.i. (Mo) and route b; (■) route a; (△) route c.

has been determined by the spectral contribution of the CoMoS signal to the room temperature Mössbauer spectrum. However, due to different Debye temperatures of the different spectral components, the spectral composition should have been corrected. This correction has not been applied here for two reasons. First, it turned out that upon correcting the spectral contributions using the Debye temperatures for CoMoS ($\theta_D$ = 200 K) and for bulk $Co_9S_8$ ($\theta_D$ = 305 K) given by Topsøe *et al.* (*1*), the correlations given in Fig. 10 are not seriously affected. Second, it can be assumed that in our catalysts the $Co_9S_8$ will not be bulk-like, but will be present as rather small particles. Hence, in practice, the difference in effective Debye temperature will be less than that given above.

We add two further comments:

(i) Considering that sample No. 125 contains only very little Co-in-CoMoS, its HDS activity is surprisingly high: $k$ = 0.27 a.u. (cf. Fig. 10). This activity must be due to the $Co_9S_8$ and $MoS_2$ present in the catalyst. However, there is no apparent need to correct for any $Co_9S_8/MoS_2$ contribution to the activity of the other samples. To decide whether we have a problem here, we would obviously need to do some further work. One thing we can say about sample No. 125 is that its $Co_9S_8$ appears to be rather highly dispersed, since it becomes almost totally oxidized in a matter of a few days upon exposure to air (cf. Results above).

(ii) Since the sequential impregnation route of Topsøe *et al.* and our coimpregnation route b lead to catalysts, which fit the same $k$(HDS)–Co(CoMoS) correlation, it is illustrative to compare the effectiveness of both methods in producing CoMoS. Route b is a difficult one, in the sense that slight variations in solution composition can greatly affect its stability and, hence, its effectiveness in generating an active catalyst. Sample No. 268 has been prepared using a perfectly stable solution, and it is seen (Table 3) that the coimpregnation route can be slightly more effective in generating the CoMoS phase than the sequential impregnation one (87 vs 75%).

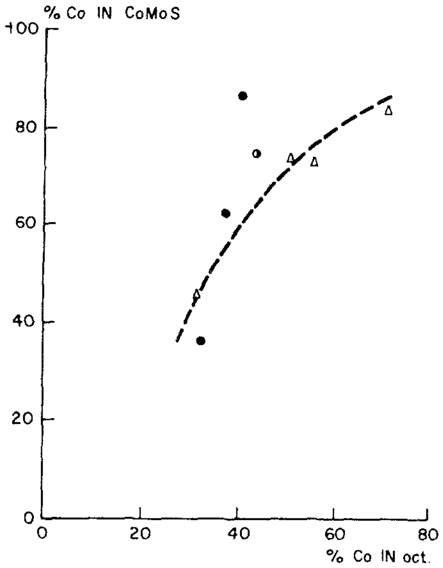

FIG. 11. Plot of wt% Co in CoMoS in the sulfided catalyst vs wt% octahedral Co in the calcined precursor, both quantities being determined through $^{57}$Co MES.

Let us now address the question of whether it is only octahedral Co in the calcined precursor that can end up in the so-called CoMoS phase upon sulfidation. Our results pertaining to this question are graphically displayed in Fig. 11. The answer is clearly not affirmative, although it does seem that the efficiency of CoMoS formation increases with increasing Co(oct) content in the catalyst precursor. Our data strongly indicate that, in contrast to the report by Wivel *et al.* (*4*), a substantial part of Co(tet) can easily be sulfided.[1]

To gain more insight into the latter point, we have prepared a 0.5% $Co/Al_2O_3$ catalyst via impregnation with $Co(NO_3)_2$, drying,

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[1] Our samples appear to contain more Co in a tetrahedral environment than those of Wivel *et al.* (*4*). This is not an artifact of the computer analysis, as is already obvious from a mere visual inspection of the respective Mössbauer spectra.

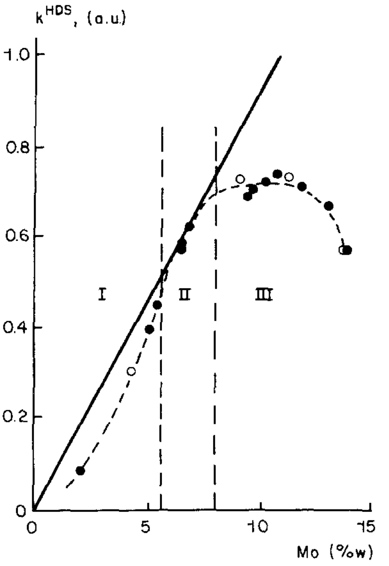

FIG. 12. Thiophene-HDS activity (arbitrary units) as a function of Mo loading. CoMo/$Al_2O_3$ prepared via impregnation route a. Co/Mo constant at 0.35 at/at. Open symbols: catalysts of composition corresponding to those used in the $^{57}$Co MES experiments. For discussion of the regions I–III, see text.

and calcining at 600°C for 4 h. The blue color of the resulting sample indicates the absence of $Co_3O_4$ formation, and the Mössbauer analysis (Table 2, sample No. 235) substantiates the expected predominant tetrahedral coordination of the Co ions. Sulfidation of this material under standard conditions shows that this Co(tet) is to a large extent readily transformed into $Co_9S_8$ (73% conversion, Table 3). We conclude, therefore, that the Co(tet) formed in the preparation of the oxidic precursor is not at all lost for subsequent sulphidation and is, to a certain extent at least, able to enter the CoMoS phase (provided, of course, Mo is present in the catalyst).

The last point to be discussed is why the effectiveness of CoMo declines at higher metal loadings. To illustrate this decline we have plotted in Fig. 12 the thiophene-HDS activity against Mo loading for catalysts prepared via coimpregnation route a. On the basis of our Mössbauer results we can distinguish three regions in this plot. In region I, at low Mo loadings, CoMoS formation is less than total, because some of the Co ions present are not in close contact with the Mo-ox. phase and either remain unsulfided or form $Co_9S_8$ upon sulfidation (sample No. 234, Table 3). We have no Mössbauer data for catalysts in region II, but we think that in that region CoMoS formation is more or less complete. At still higher Mo loadings, in region III, the Mössbauer and X-ray diffraction results indicate the formation of $CoMoO_4$, which is not a good precursor for the active phase, sulfidation leading mainly to $Co_9S_8$ (*17*). The formation of (bulk) $CoMoO_4$ can be expected in cases where the Mo-support interaction is weak or nonexistent (*17*). It is further reasonable to assume that only the Mo that is adsorbed by the alumina is in strong interaction with it. Seeing that the adsorption capacity of $\gamma$-$Al_2O_3$ with respect to Mo is limited (*19–21*), we then conclude that, while in regions I and II, the Mo loading is sufficiently low for the Mo to be able to enter into a strong interaction with the $Al_2O_3$ support in the impregnation/drying step; beyond those regions Mo is no longer adsorbed, leading to the $CoMoO_4$ formation noted above. In fact, the Mo-adsorption capacity in the presence of phosphoric acid (*22*) practically coincides with the Mo loading at the II/III boundary observed here.

It has been found that $NH_4F$ treatment reduces the Mo-adsorption capacity of an alumina (*10, 20*), and so the above conclusion can be easily tested by applying an $NH_4F$-treated $\gamma$-$Al_2O_3$. The result (sample No. 237, Table 3 and Fig. 2d) unequivocally supports our hypothesis, showing a strong presence of $CoMoO_4$ in the calcined and much $Co_9S_8$ in the activated catalyst (although route b instead of a was used in the preparation of this particular sample, this does not detract from the argument).

That $CoMoO_4$ is detected in sample No. 239 and was prepared via route b and of relatively low Mo loading is due to the fact that in this case a slightly unstable impregnation solution has been applied, leading to a

Co–Mo precipitate, which is here the precursor of the $CoMoO_4$ phase in the calcined material. In the $CoMo/Al_2O_3$ : F case, referred to above, as for sample No. 268, a perfectly stable solution was used (vide supra).

## CONCLUSIONS

The present $^{57}Co$ MES study of a suite of $CoMo/Al_2O_3$ samples, prepared by four different preparation routes, has led to the following findings:

(i) The so-called CoMoS I and II phases are not distinguishable in MES, at least as far as the Mössbauer parameters deduced from room-temperature spectra are concerned.

(ii) The thiophene-HDS activity is in general proportional to wt% Co-in-CoMoS, but since different preparation routes lead to different ratios of phase I to phase II, varying from 100% of the one to 100% of the other, no unique relation exists. In the present case three correlation lines are observed, two preparation routes leading to the same CoMoS phase distribution.

(iii) It is not only the octahedral Co in the oxidic precursor that can end up as Co-in-CoMoS in the activated catalyst, although the view that octahedral Co is easier to sulfide than its tetrahedral counterpart is not inconsistent with our data.

(iv) The fact that at high metal loadings the effectiveness of CoMo decreases can be rationalized by assuming that at Mo loadings beyond the adsorption capacity of the $Al_2O_3$ carrier, the Mo–support interaction will be slight, thereby favoring $CoMoO_4$ formation in the calcination step and leading to relatively inactive $Co_9S_8$ in the activated catalyst.

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