JOURNAL OF CATALYSIS **143**, 601–615 (1993)

Sulfidation of Co/Al_2O_3 and $CoMo/Al_2O_3$ Catalysts Studied by Mössbauer Emission Spectroscopy

M. W. J. CRAJÉ,* V. H. J. DE BEER,† J. A. R. VAN VEEN,‡ AND
A. M. VAN DER KRAAN*

**Interfacultair Reactor Instituut, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands; †Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands; and ‡Koninklijke/Shell-Laboratorium (Shell Research B.V.), Badhuisweg 3, 1031 CM Amsterdam, The Netherlands*

Received December 18, 1992; revised April 29, 1993

The sulfidation of uncalcined and calcined alumina-supported cobalt and cobalt–molybdenum catalysts was systematically studied by means of *in situ* Mössbauer emission spectroscopy (MES) at room temperature. The spectra obtained during the stepwise sulfidation of the uncalcined catalysts clearly resemble those observed for carbon-supported ones. Hence, the interpretation of the spectra of the alumina-supported catalysts is based on the conclusions drawn from the MES studies of the carbon-supported catalysts, which are less complex because Co ions do not diffuse into the support. It is demonstrated that not only in sulfided $CoMo/Al_2O_3$, but also in sulfided Co/Al_2O_3, catalysts Co-sulfide species with a "Co–Mo–S"-type quadrupole splitting can be formed. It is concluded that the Co-sulfide species formed in sulfided Co/Al_2O_3 and $CoMo/Al_2O_3$ catalysts are essentially the same, only the particle size and ordering of the Co-sulfide species may differ, as in the case of Co/C and CoMo/C catalysts. The function of the Mo, which is present as MoS_2, is merely to stabilize very small Co-sulfide particles, which in the limit contain only one single Co atom. Furthermore, it turns out that the value of the electric quadrupole splitting (Q.S. value) of the Co-sulfide phase in the sulfided catalysts depends on the sulfiding temperature and Co content. This observation leads to the conclusion that large Q.S. values point to the presence of very small Co-sulfide entities or particles (the lower limit being "particles" containing only one Co atom, such as proposed in the "Co–Mo–S" model), whereas small Q.S. values point to the presence of large Co-sulfide particles (the upper limit being crystalline Co_9S_8). © 1993 Academic Press, Inc.

INTRODUCTION

For several decades attempts have been made to find a relation between the structure of sulfided CoMo hydrosulfurisation (HDS) catalysts and the synergetic behaviour of Co and Mo in these catalysts. In the beginning the structural investigations leading to the first structural models for these catalysts (*1–4*) were of limited use due to the application of *ex situ* characterization techniques. With the introduction of Mössbauer emission spectroscopy (MES) by Topsøe and coworkers (*5*, *6*), an important step forward was made. MES makes use of 14.4-keV γ-rays and can be applied as an *in situ* technique. In the MES spectra of sulfidic CoMo catalysts a signal was observed that was not present in the spectra of sulfided Co catalysts (without Mo) or in the spectrum of any known crystalline Co(–Mo)-sulfide (*7*). Topsøe *et al.* (*7*) assigned this spectral contribution to a species containing Co + Mo + S and they called this species the "Co–Mo–S" phase. Wivel *et al.* (*8*) reported a linear relation between the amount of Co present as "Co–Mo–S" and the thiophene HDS activity. The latter two findings form the basis of the "Co–Mo–S" model.

The MES studies of Topsøe and co-workers (*7*, *8*) have more recently been extended with results of other techniques, e.g, IR (*9*), AEM (*10*), and *in situ* extended X-ray absorption fine structure (EXAFS) measure-

0021-9517/93 $5.00

ments (*11*), leading to the view that Co is located at edge-sites of MoS_2. However, some problems with the "Co–Mo–S" model still remained, such as: (i) ascribing the synergetic behaviour of Co and Mo to a phase containing Co + Mo + S with a typical MES ("Co–Mo–S") spectrum, (ii) the consequence that the local structure of "Co–Mo–S" has to be identical over a rather large range of Co/Mo ratios, and (iii) the finding of two types of "Co–Mo–S" with rather different catalytic activities as reported. In an attempt to solve some of these problems we performed at first extensive MES and EXAFS studies of Co/C and CoMo/C catalysts the results of which have been reported in the literature (*12–16*). The main conclusion of these studies is that the presence of Mo is not necessary to form a Co-sulfide species with the "Co–Mo–S" structure (according to MES and EXAFS). In fact, it could be concluded that the Co-sulfide species formed in Co/C and CoMo/C catalysts are essentially the same, only the particle size and ordering of the Co-sulfide species may differ. The function of the Mo, which is present as MoS_2, is merely to stabilize very small Co-sulfide particles, which in the limit contain only one single Co atom. From combining the MES and EXAFS results (*16*, *17*), it followed that the variation in particle size and ordering of the Co-sulfide species is reflected in the value of the electric quadrupole splitting (Q.S. value). An increase in particle size and ordering gives rise to a lower Q.S. value.

For the carbon-supported catalysts a consistent picture emerges from the MES and EXAFS results. As industrially applied, CoMo HDS catalysts are generally supported on Al_2O_3, and a consistent picture cannot be formed from the MES results of these catalysts reported in the literature so far, we have extended our study to alumina-supported catalysts. However, it is known from Mössbauer results published previously (*7*, *18*, *19*) that for the latter catalysts the interpretation of MES spectra becomes more complicated because part of the Co diffuses into the alumina support material. As for the carbon-supported catalysts conclusions could be drawn from *trends* in the MES and EXAFS results, so the same systematic approach is applied here to sets of Co/Al_2O_3 and $CoMo/Al_2O_3$ catalysts. First the behaviour of uncalcined catalysts is discussed and subsequently that of some calcined samples. From the experimental results we will try to answer the question whether the Co-sulfide species formed in Co/Al_2O_3 and $CoMo/Al_2O_3$ is essentially the same and whether only their particle size differs like in the case of the carbon-supported catalysts.

EXPERIMENTAL

All catalysts are prepared by pore volume impregnation. A γ-Al_2O_3 (Ketjen 001-1.5E) with a BET area of 271 m^2/g and a pore volume of 0.7 ml/g is used as carrier material. The carrier extrudates were ground and sieved, and only the particle size fraction of 0.5–0.85 mm was used. The pore volume impregnation was carried out using aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ (Merck p.a. or Fluka p.a.) or $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Merck min. 99.9%). For the MES measurements about 1.5 mCi ^{57}Co as aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (ex Amersham) was added to the Co-nitrate solutions. The CoMo catalysts were prepared by a two step procedure with the Mo being introduced first. The Mo/Al_2O_3 is dried in static air at 383 K for 16 h and subsequently calcined in static air at 673 K for 24 h (the temperature was linearly increased to 673 K in 5 h). After Co introduction the catalysts were left in static air at 293 K for 16 h.

Hereafter the majority of the Co/Al_2O_3 and $CoMo/Al_2O_3$ catalysts are subjected to a mild drying treatment in a flow of 50 cm^3 min^{-1} H_2 at 313, 353, and 393 K (24 h at each temperature) resulting in what are referred to as fresh catalysts. The purpose of this treatment, which was already successfully applied in Mössbauer absorption spectroscopy (MAS) studies on Fe and FeMo catalysts supported on carbon (*20*, *21*) and alumina (*18*), is to remove residual nitrate ions. Only one set of Co/Al_2O_3 and one $CoMo/Al_2O_3$ catalyst are calcined in static air (linearly heated up to 773 K in 1 h and holding at 773 K for 2 h). The sulfidation of the samples was carried out in a 10% H_2S/H_2 gas mixture (flow rate of 60 ml/min) at atmospheric pressure in an *in situ* MES reactor.

Catalyst loadings calculated from the impregnation solutions are given in wt% relative to the carrier material. In the figures the following notation is used to indicate the various treatments applied to the catalysts: (S, *a* K, *x*h + *y*h), S stands for 10% H_2S/H_2. During each treatment the catalyst is linearly heated up to *a* K in *x* h and kept at this temperature for *y* h. The catalysts are cooled to room temperature in the reaction gas mixture. In the case that *x* and *y* are not provided, the catalyst is during the whole measurement kept at the temperature indicated. In the text the notation is further condensed to, e.g., $Co(3.0)Mo(8.0)/Al_2O_3(473)$, indicating that the $Co(3.0)Mo(8.0)/Al_2O_3$ catalyst has been treated in 10% H_2S/H_2 according to: (S, 473 K, 1 h + 1 h). Note that the applied sulfidation *temperature* is the only changing parameter and that for each catalyst one and the same sample was successively subjected to the stepwise sulfiding procedure.

The MES measurements were carried out 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 relative to a source of $^{57}Co:Rh$, positive velocities corresponding to the absorber moving away from the source. The velocity scale was calibrated by the Mössbauer spectrum of sodium nitroprusside $Na_2(Fe(CN)_5NO) \cdot 2H_2O$ obtained with the $^{57}Co:Rh$ source.

The spectra were fitted with calculated subspectra consisting of Lorentzian-shaped lines. In the case of quadrupole doublets the linewidths and the absorption areas of the constituent peaks were constrained to be equal.

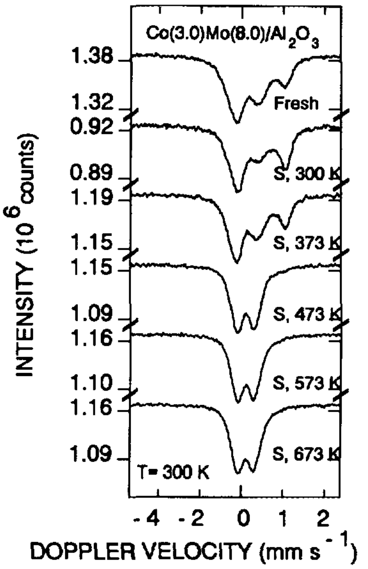

FIG. 1. MES spectra obtained at 300 K with uncalcined $Co(3.0)Mo(8.0)/Al_2O_3$ after various successive sulfidation treatments: fresh catalyst, (S, 300 K), (S, 373 K, 1h + 1h), (S, 473 K, 1h + 1h), (S, 573 K, 1h + 1h), and (S, 673 K, 1h + 1h).

The MES measurements were carried out in a Mössbauer *in situ* reactor, which has been described elsewhere (*22*). However, the heating section as well as the outer container used in this study are made of stainless steel 316. Furthermore,the reactor was placed horizontally so that a small cup of vespel (composite material, DuPont) containing the catalyst particles could be mounted easily.

RESULTS

Sulfidation of the Uncalcined Catalysts

$CoMo/Al_2O_3$. The MES spectra of the $Co(3.0)Mo(8.0)/Al_2O_3$ catalyst recorded after the successive sulfidation steps are presented in Fig. 1 and the results of the analyses of the spectra are given in Table 1. The spectrum changes as a result of exposure of the catalyst to the sulfiding gas mixture at room temperature. The relative contribution of the high-spin 2+ doublet (indicated by the arrows) grows and this doublet shows rather sharp lines compared

TABLE 1

Mössbauer Parameters of Uncalcined Co(3.0)Mo(8.0)/Al_2O_3 after Various Successive Sulfidation Treatments

$T_{Sulf.}$ (K)	Co-sulfide				High-spin 2+			
	I.S. (mm/s)	Q.S. (mm/s)	Γ (mm/s)	A (%)	I.S. (mm/s)	Q.S. (mm/s)	Γ (mm/s)	A (%)
Fresh	0.21[a]	1.26[a]	1.06[a]	72[a]	0.98	2.23	0.65	28
300	0.23	1.28	1.03	52	0.99	2.24	0.66	48
373	0.21	1.18	0.91	65	0.98	2.26	0.60	35
473	0.23	0.85	0.73	100				
573	0.24	0.81	0.71	100				
673	0.25	0.80	0.76	100				

Note. I.S. values are relative to $K_4Fe(CN)_6 \cdot 3H_2O$ measured with a ^{57}Co : Rh source. Experimental uncertainties: I.S. and Q.S. ± 0.03 mm/s; linewidth Γ ± 0.05 mm/s; spectral contribution *A* ± 5%.

[a] This doublet is assigned to a Co-oxide species.

to high-spin 2+ doublets observed in previous MES studies. After sulfidation up to 373 K the spectral contribution of the high-spin 2+ doublet has decreased in favour of a doublet with Q.S. = 1.18 mm/s. The high-spin 2+ doublet has disappeared almost completely after sulfidation at 473 K and the catalyst is characterized by a doublet with Q.S. = 0.85 mm/s. Upon sulfidation at higher temperatures the Q.S. value of this doublet slightly decreases and reaches a value of 0.79 mm/s after sulfidation at 673 K for 4 h (spectrum and parameters not presented in a figure and table).

The sulfidation of the CoMo/Al_2O_3 catalysts with lower Co loading also takes place via a high-spin 2+ intermediate phase. (See for Co(0.013)Mo(8.0)/Al_2O_3 Fig. 2 and Table 2). It is illustrated in Fig. 3 and Table 3 that the lower the Co-loading, the higher the sulfidation temperature needed to remove the high-spin 2+ doublet completely from the spectrum. Furthermore, it can be seen from Table 3 that there is a tendency for the Q.S. value of the dominant spectral contribution to increase with decreasing Co-loading after the sulfidation treatment up to 473 K. For catalysts sulfided at 673 K the Q.S. value systematically decreases with increasing Co-loading, as can be seen in Fig. 4 and Table 4.

Co/Al_2O_3. The results obtained on a Co(3.0)/Al_2O_3 catalyst are presented in Fig. 5 and Table 5. At first sight, the catalyst seems hardly influenced by the sulfidation treatments up to 373 K. However, by drawing some auxiliary lines which connect the

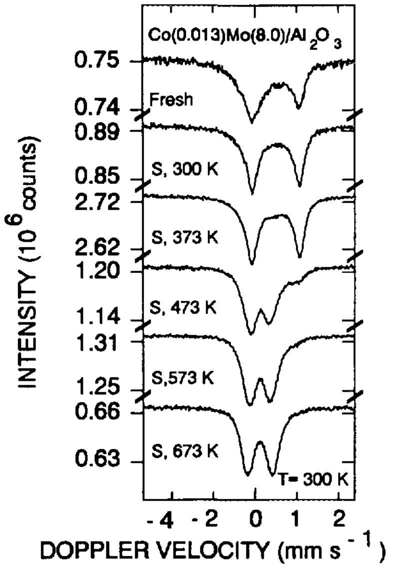

FIG. 2. MES spectra obtained at 300 K with uncalcined Co(0.013)Mo(8.0)/Al_2O_3 after various successive sulfidation treatments: fresh catalyst, (S, 300 K), (S, 373 K, 1h + 1h), (S, 473 K, 1h + 1h), (S, 573 K, 1h + 1h), and (S, 673 K, 1h + 1h).

TABLE 2

Mössbauer Parameters of Uncalcined $Co(0.013)Mo(8.0)/Al_2O_3$ after Various Successive Sulfidation Treatments

$T_{Sulf.}$ (K)	Co-sulfide				High-spin 2+			
	I.S. (mm/s)	Q.S. (mm/s)	Γ (mm/s)	*A* (%)	I.S. (mm/s)	Q.S. (mm/s)	Γ (mm/s)	*A* (%)
Fresh	0.11[a]	1.29[a]	1.51[a]	46[a]	1.00	2.18	0.73	54
300	0.21	1.56	1.10	26	1.00	2.22	0.62	74
373	0.23	1.50	1.10	30	1.00	2.25	0.60	71
473	0.25	0.98	0.80	84	0.92	2.12	0.68	16
573	0.24	1.02	0.76	100				
673	0.24	1.18	0.69	100				

Note. I.S. values are relative to $K_4Fe(CN)_6 \cdot 3H_2O$ measured with a ^{57}Co : Rh source. Experimental uncertainties I.S. and Q.S. ± 0.03 mm/s, linewidth Γ ± 0.05 mm/s, spectral contribution *A* ± 5%.

[a] This doublet is assigned to a Co-oxide species.

minima of the first and third peaks and from the results of the analyses it can be seen that the catalyst is already affected by exposure to the sulfiding gas mixture at room temperature. Due to this treatment the spectral contribution of the high-spin 2+ doublet increases significantly. Upon sulfidation at 373 K the high-spin 2+ contribution has decreased and the spectrum is transformed into one single doublet with a Q.S. value of 0.52 mm/s after sulfidation up to 473 K. During the subsequent sulfidation treatments up to 673 K the Q.S. value of this doublet continuously decreases leading to a MES spectrum which seems to consist of a broadened single line after sulfidation at 673 K for 4 h. This spectrum (spectrum and parameters not presented in a figure and table) was fitted with a quadrupole doublet with Q.S. = 0.27 mm/s, resembling the value of 0.26 mm/s which can be used to fit the spectrum of crystalline Co_9S_8 (*7*). The $Co(0.7)/Al_2O_3$ catalyst shows a quite similar behaviour. However, as can be seen in Table 5, a high-spin 2+ contribution is still present after sulfidation at 473 K.

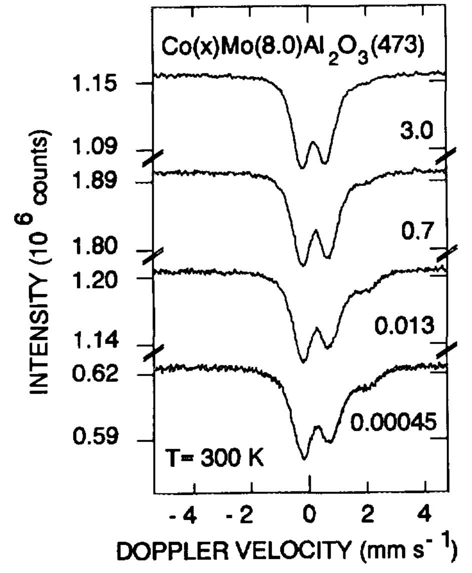

FIG. 3. MES spectra obtained at 300 K with four uncalcined $CoMo/Al_2O_3$ catalysts with different Co/Mo ratios after (S, 473 K, 1h + 1h).

Results of the stepwise sulfidation of $Co(0.013)/Al_2O_3$ are presented in Fig. 6. After exposure of this catalyst to the H_2S/H_2 gas mixture at room temperature the spectrum has changed only slightly, but after sulfidation at 373 K the spectrum consists of two doublets. One high-spin 2+ doublet and a doublet with I.S. = 0.36 mm/s and Q.S. = 1.57 mm/s. This latter doublet dominates the spectrum of the catalyst after sulfidation at 473 K. After the sulfidation at 573 K the spectrum has changed com-

TABLE 3

Mössbauer Parameters of Uncalcined Co(x)Mo(8.0)/Al_2O_3(473) Catalysts with Different Co-Loading x

x (wt%)	Co/Mo ratio (at/at)	Co-sulfide				High-spin 2+			
		I.S. (mm/s)	Q.S. (mm/s)	Γ (mm/s)	A (%)	I.S. (mm/s)	Q.S. (mm/s)	Γ (mm/s)	A (%)
3.0	0.61	0.23	0.85	0.73	100				
0.7	0.14	0.21	0.94	0.70	<100	[a]	[a]	[a]	>0
0.013	0.0026	0.25	0.98	0.80	84	0.92	2.12	0.68	16
0.00045	0.00009	0.24	0.99	0.81	84	0.92	2.12	0.64	16

Note. I.S. values are relative to $K_4Fe(CN)_6 \cdot 3H_2O$ measured with a ^{57}Co : Rh source. Experimental uncertainties: I.S. and Q.S. ± 0.03 mm/s; linewidth Γ ± 0.05 mm/s; spectral contribution A ± 5%.

[a] The small high-spin 2+ contribution visable in the spectrum could not be fitted satisfactorily.

pletely. It is now dominated by a doublet with Q.S. = 0.73 mm/s. Furthermore, a spectral contribution is present with Q.S. = 4.1 mm/s (indicated by the arrows). Doublets with such a huge Q.S. value have also been observed during the sulfidation of Co/C catalysts with very low Co-loadings (below Co(0.0019)/C). This phenomenon will be discussed elsewhere (*23*). After sulfidation at 673 K the catalyst is characterized by a spectrum which can be fitted with a high-spin 2+ doublet and a doublet with I.S. = 0.19 mm/s and Q.S. = 0.91 mm/s.

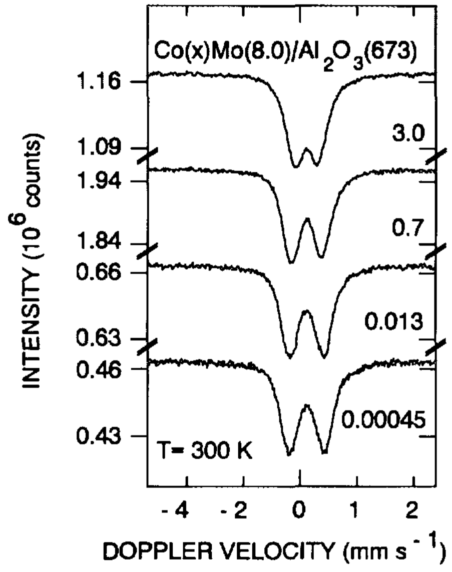

FIG. 4. MES spectra obtained at 300 K with four uncalcined CoMo/Al_2O_3 catalysts with different Co/Mo ratios after (S, 673 K, 1h + 1h).

It is also shown in Fig. 6 that the behaviour of the Co(0.00045)/Al_2O_3 catalyst is quite different from that of the other Al_2O_3 supported catalysts. After each sulfidation step its spectrum is dominated by a high-spin 2+ doublet which shows very broad absorption lines and although minor changes can be observed after a more severe sulfidation treatment, it does not make sense to analyse the spectra of this catalyst in detail.

Sulfidation of the Calcined Catalysts

The MES results obtained on a Co(1.3)Mo(8.0)/Al_2O_3 and a Co(1.3)/Al_2O_3 catalyst,

TABLE 4

Mössbauer Parameters of Uncalcined Co(x)Mo(8.0)/Al_2O_3(673) Catalysts with Different Co-Loading x

x (wt%)	Co/Mo ratio (at/at)	I.S. (mm/s)	Q.S. (mm/s)	Γ (mm/s)
3.0	0.61	0.25	0.80	0.76
0.7	0.14	0.22	1.07	0.72
0.013	0.0026	0.24	1.18	0.69
0.00045	0.00009	0.22	1.22	0.71

Note. I.S. values are relative to $K_4Fe(CN)_6 \cdot 3H_2O$ measured with a ^{57}Co : Rh source. Experimental uncertainties: I.S. and Q.S. ± 0.03 mm/s; linewidth Γ ± 0.05 mm/s; spectral contribution A ± 5%.

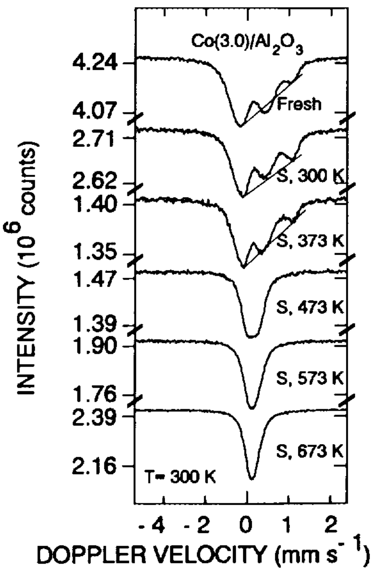

FIG. 5. MES spectra obtained at 300 K with uncalcined $Co(3.0)/Al_2O_3$ after various successive sulfidation treatments: fresh catalyst, (S, 300 K), (S, 373 K, 1h + 1h), (S, 473 K, 1h + 1h), (S, 573 K, 1h + 1h), and (S, 673 K, 1h + 1h).

calcined in air at 773 K for 2 h, are presented in Fig. 7 and Table 6. From the high-spin 2+ contribution in the spectra it follows that even after sulfidation up to 673 K both catalysts were not fully sulfided. The sulfidation of the $Co(1.3)Mo(8.0)/Al_2O_3$ catalyst starts at low temperatures. After exposure of the catalyst to the 10% H_2S/H_2 gas mixture at room temperature the spectrum consists of a high-spin 2+ doublet with rather broad absorption lines and an additional doublet with I.S. $\approx$ 0.25 mm/s and Q.S. $\approx$ 1.2 mm/s. The spectral contribution of this latter doublet clearly increases with increasing sulfidation temperature.

It is difficult to determine at which temperature the sulfidation of the $Co(1.3)/Al_2O_3$ catalyst starts. All spectra of the catalyst are very poorly resolved. The large high-spin 2+ contribution hampers a precise determination of the parameters of the second spectral contribution. Its parameters can be estimated only roughly. The results in Table 6 show that the Q.S. value of both the high-spin 2+ and the additional doublet continuously decrease during sulfidation treatments at elevated temperatures.

DISCUSSION

Sulfidation of the Uncalcined Catalysts

$CoMo/Al_2O_3$. Upon comparing the sulfidation behaviour of the $CoMo/Al_2O_3$ catalysts with that of their carbon-supported counterparts, striking similarities are found. (i) The spectra of the $CoMo/Al_2O_3(673)$ catalysts (see Fig. 4 and Table 4) show a decreasing Q.S. value of the sulfidic doublet with increasing Co/Mo ratio as also found for CoMo/C (*16*, *17*). (ii) The temperature at which the high-spin 2+ doublet has disappeared completely from the spectrum decreases with increasing Co/Mo ratio. Apart from these similarities, there is also an apparent difference. In the case of CoMo/C catalysts with a high Co/Mo ratio (>0.5 at/at) sulfiding at room temperature already results in an almost complete disappearance of the high-spin 2+ doublet from the spectrum and the doublet replacing it has to be assigned to a sulfidic phase on the basis of MES and EXAFS (*16*, *17*). So, the CoMo/C catalysts become completely sulfidic at relatively low sulfidation temperatures. For all alumina-supported catalysts a significant high-spin 2+ contribution is still seen in the spectra after sulfidation at 373 K, even for the $Co(3.0)Mo(8.0)/Al_2O_3$ catalyst with Co/Mo = 0.62 at/at (see Fig. 1, Table 1). This high-spin 2+ contribution disappears completely during sulfidation at elevated temperatures, so it is not plausible to assign it to a fully sulfidic phase. The more so since the combined EXAFS and MES studies on Co(–Mo)/C catalysts (*16*, *17*) reveal that for these systems the high-spin 2+ doublets observed as intermediates during the sulfidation process should be assigned to oxygen containing Co-species.

Due to the presence of the high-spin 2+ spectral contribution the assignment of the second doublet in the spectra observed after sulfidation at 373 K is somewhat uncertain. However, we assign it to a sulfidic species

TABLE 5

Mössbauer Parameters of Uncalcined Co(3.0)/Al_2O_3 and Co(0.7)/Al_2O_3 after Various Successive Sulfidation Treatments

$T_{Sulf.}$ (K)	Co-sulfide				High-spin 2+			
	I.S. (mm/s)	Q.S. (mm/s)	Γ (mm/s)	A (%)	I.S. (mm/s)	Q.S. (mm/s)	Γ (mm/s)	A (%)
				Co(3.0)/Al_2O_3				
Fresh	0.18[a]	1.38[a]	1.07[a]	83[a]	0.96	2.29	0.61	17
300	0.21	1.29	0.95	71	0.98	2.24	0.64	29
373	0.22	1.11	1.11	81	0.99	2.30	0.62	19
473	0.25	0.52	0.68	100				
573	0.25	0.38	0.66	100				
673	0.25	0.30	0.60	100				
				Co(0.7)/Al_2O_3				
Fresh	0.16[a]	1.28[a]	1.29[a]	76[a]	0.96	2.36	0.68	24
300	0.21	1.33	1.14	67	0.98	2.31	0.70	33
373	0.21	1.25	1.08	72	0.98	2.26	0.72	28
473	0.25	0.57	0.87	90	0.89	2.22	0.64	10
573	0.25	0.41	0.74	95	1.0[b]	1.80	0.6[b]	5
673[c]	0.26	0.34	0.63	98	1.0[b]	1.75	0.6[b]	2

Note. I.S. values are relative to $K_4Fe(CN)_6 \cdot 3H_2O$ measured with a ^{57}Co : Rh source. Experimental uncertainties: I.S. and Q.S. ± 0.03 mm/s; linewidth Γ ± 0.05 mm/s; spectral contribution A ± 5%.

[a] These doublets are assigned to a Co-oxide species.

[b] These parameters were fixed during the fitting procedure.

[c] The catalyst was sulfided for four hours at this temperature.

since the spectral contribution of the high-spin 2+ doublet for Co(0.00045)Mo(8.0)/Al_2O_3(373) (not presented) and Co(0.013) Mo(8.0)/Al_2O_3(373) (see Fig. 2) has strongly decreased in favour of a doublet with I.S. = 0.25 (or 0.24) and Q.S. = 0.98 mm/s (or 0.99) after sulfidation at 473 K, and since this spectral contribution further increases during sulfidation at higher temperatures (see Table 3).

In case of Co(3.0)Mo(8.0)/Al_2O_3 the assignment is even more difficult. In Fig. 1 and Table 1 it is shown that besides the high-spin 2+ doublet always a large second spectral contribution (doublet) is present. Clearly this doublet should be assigned to an oxidic phase in the fresh catalyst, whereas it should be assigned to a sulfidic phase in the catalyst sulfided up to 673 K. The problem is therefore to determine at which temperature the oxidic phase is transformed into a sulfidic one. It follows from Fig. 1 and Table 1, that in Co(3.0)Mo(8.0)/Al_2O_3(300) the high-spin 2+ component is increased compared to the fresh sample and that further sulfidation at 373 K results in an partial transformation into the spectral component with I.S. = 0.21 mm/s and Q.S. = 1.18 mm/s. It is plausible on the basis of the similarity in the sulfidation behaviour found between the CoMo/Al_2O_3 and the CoMo/C catalysts that the doublet with I.S. = 0.21 mm/s and Q.S. = 1.18 mm/s should be assigned to a sulfidic phase. This assignment is further supported by the spectra presented in Fig. 3 and the MES parameters given in Table 3 which show that after sulfidation at 473 K the percentage of the Co remaining in a high-spin 2+ phase decreases with increasing Co/Mo ratio. Furthermore, in Co(0.013) Mo(8.0)/Al_2O_3(373) already a contribution of a sulfidic doublet is present (see Fig. 2). (In Table 2 it is shown that already after sulfidation at 300 K, the spectrum can be

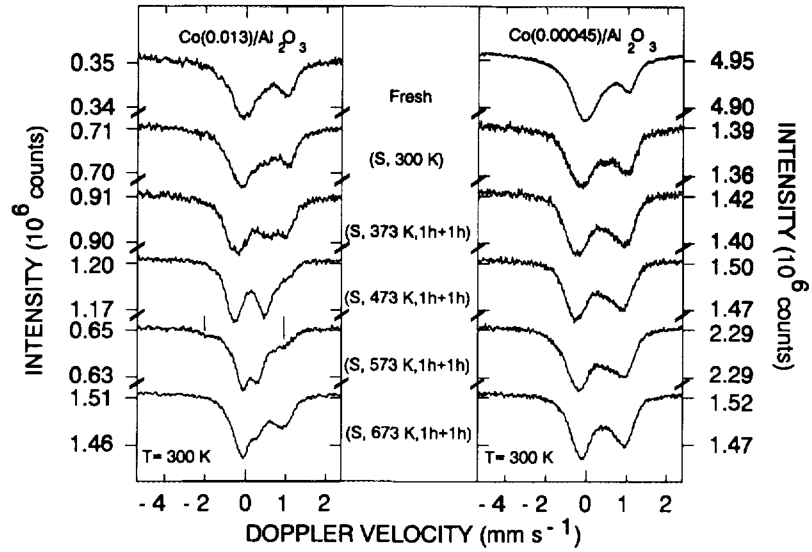

FIG. 6. MES spectra obtained at 300 K with uncalcined $Co(0.013)/Al_2O_3$ and $Co(0.00045)/Al_2O_3$ after the various successive sulfidation treatments indicated in the figure.

analysed in a similar way.) As a consequence, also in $Co(0.7)Mo(8.0)/Al_2O_3(373)$ and $Co(3.0)Mo(8.0)/Al_2O_3(373)$ a Co-sulfide phase must be present since for these catalysts the Co/Mo ratio is much higher. The Co species exhibiting the doublet with I.S. = 0.23 mm/s and Q.S. = 1.28 mm/s in the spectrum of $Co(3.0)Mo(8.0)/Al_2O_3(300)$ can not be distinguished from the oxidic component in the fresh sample (see Table

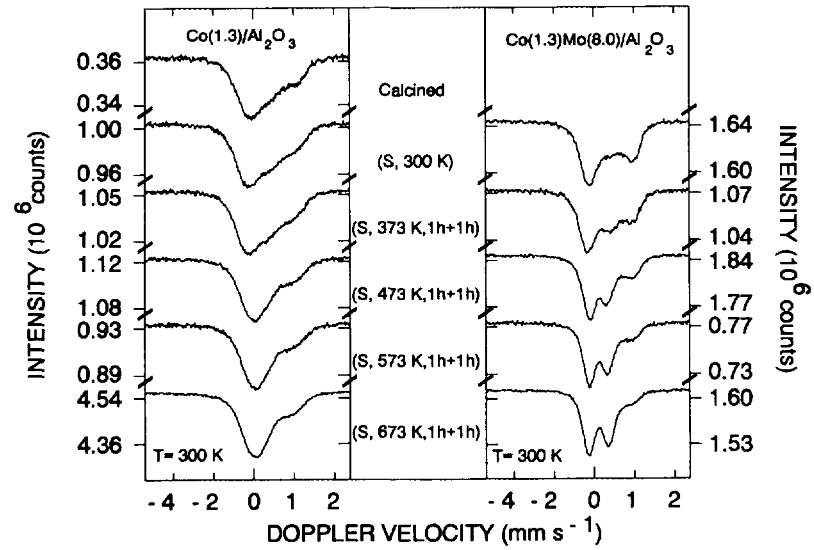

FIG. 7. MES spectra obtained at 300 K with calcined $Co(1.3)/Al_2O_3$ and $Co(1.3)Mo(8.0)/Al_2O_3$ catalysts after the various successive sulfidation treatments indicated in the figure.

TABLE 6

Mössbauer Parameters of Calcined Co(1.3)/Al_2O_3 and Co(1.3)Mo(8.0)/Al_2O_3 Catalysts after Various Successive Sulfidation Treatments

$T_{Sulf.}$ (K)	Co-sulfide				High-spin 2+			
	I.S. (mm/s)	Q.S. (mm/s)	Γ (mm/s)	*A* (%)	I.S. (mm/s)	Q.S. (mm/s)	Γ (mm/s)	*A* (%)
Co(1.3)/Al_2O_3								
Calcined	0.19[a]	1.21[a]	1.17[a]	65[a]	1.03	2.07	0.94	35
300	0.18	1.23	1.19	62	0.97	2.04	1.02	38
373	0.16	1.20	1.13	62	0.92	1.98	1.03	38
473	0.19	0.92	1.11	65	1.00	1.89	0.99	35
573	0.19	0.83	1.13	65	1.01	1.87	1.05	35
673	0.15	0.73	1.19	66	0.98	1.85	1.20	34
Co(1.3)Mo(8.0)/Al_2O_3								
300	0.25	1.18	1.02	44	0.87	2.09	0.87	56
373	0.21	1.25	0.91	55	0.86	2.03	0.88	45
473	0.22	0.93	0.77	65	0.88	2.01	0.82	35
573	0.22	0.95	0.70	73	0.87	2.00	0.79	27
673	0.22	1.01	0.70	82	0.86	1.98	0.72	18

Note. I.S. values are relative to $K_4Fe(CN)_6 \cdot 3H_2O$ measured with a ^{57}Co : Rh source. Experimental uncertainties: I.S. and Q.S. ± 0.03 mm/s; linewidth Γ ± 0.05 mm/s; spectral contribution *A* ± 5%.

[a] This doublet is assigned to a Co-oxide species.

1), and no other indications (trends) are available in the set of measurements to draw conclusions about the nature of this Co species.

Summarizing, it can be stated that the behaviour of the uncalcined CoMo/Al_2O_3 catalysts resembles that of their carbon-supported counterparts in many aspects. Hence, the decreasing Q.S. value with increasing Co loading for the CoMo/Al_2O_3 (673) catalysts indicates an increase in particle size and ordering of a Co-sulfide species associated with MoS_2. The spectrum of Co(3.0)Mo(8.0)/Al_2O_3(673), which can not be explained by a superposition of a "Co–Mo–S" doublet and the spectrum of crystalline "Co_9S_8", supports this indication. A difference observed by us is that the CoMo/Al_2O_3 catalyst with a rather high Co/Mo ratio (0.61 at/at) becomes completely sulfidic at slightly higher temperatures than the CoMo/C catalysts with a comparably high Co/Mo ratio (>0.53 at/at). Apparently, the sulfidation of the alumina-supported catalysts is hampered due to a stronger interaction between the transition metal species and the support.

Co/Al_2O_3. The MES spectra of the low Co-content Co(0.00045)/Al_2O_3 and Co(0.013)/Al_2O_3 catalysts deviate much more from those of their carbon-supported counterparts than in the CoMo case. The spectra of Co/C catalysts showed only high-spin 2+ contributions up to sulfidation at 473 K, which contribution completely disappeared during sulfidation at 573 and 673 K. By combining MES and EXAFS it was found (*16, 17*) that the high-spin 2+ contribution should be assigned to an oxygen containing Co-species. However, the spectrum of Co(0.00045)/Al_2O_3 is dominated by a high-spin 2+ doublet at all sulfidation temperatures and in the spectra of Co(0.013)/Al_2O_3 a substantial high-spin 2+ contribution is always present as well (see Fig. 6). In the spectra of Co(0.7)/Al_2O_3(673) (not shown) and Co(3.0)/Al_2O_3(673) only a very small and no high-spin 2+ contribution can be observed, respectively (see Table 5). Observation of a high-spin 2+ doublet after sulfidation up to 673 K makes it very unlikely that it represents an oxygen containing species similar to the one exhibiting the high-spin 2+ doublet in the Co(–Mo)/C catalysts after low temperature sulfiding. Most probably it represents a Co : Al_2O_3 species. This assumption is supported by the finding that this high-spin 2+ doublet has a much smaller Q.S. value (1.75 mm/s) than the one in the spectra after sulfidation up to 473 K (Q.S. = 2.22 mm/s; see Table 5). Furthermore, it is in accordance with the observation that the relative amount of this species increases with decreasing Co-loading, and by calcination of the catalysts (see Fig. 7 and Table 6). Of course, the presence of Co : Al_2O_3 species in Co(Mo)/Al_2O_3 has often been reported before, but always for calcined material. Apparently, such a species can form even in noncalcined samples. However, we cannot determine whether or not this Co : Al_2O_3 becomes partly sulfided. Finally, the attribution to Co : Al_2O_3 is in line with the interpretation of the MES spectra of Al_2O_3 supported Co(–Mo) catalysts by Topsøe *et al.* (*7*). It is also in agreement with the interpretation of the Mössbauer absorption results on Al_2O_3 supported Fe(–Mo) of Ramselaar *et al.* (*18*).

During sulfidation of Co(0.013)/Al_2O_3 at 300 K only minor changes occur (see Fig. 6), whereas during sulfidation at 373 K a spectral contribution emerges with I.S. = 0.36 mm/s and Q.S. = 1.57 mm/s. As this spectral contribution grows during sulfidation at 473 K and dominates the spectrum, it most probably represents a sulfidic species. The MES parameters of this doublet do not agree with those of any known crystalline Co-sulfide, and are only comparable with those of the so-called "Co–Mo–S" phase (*7*). However, no Mo is present in the catalyst. Thus, as for the Co/C catalysts (*12–14*, *16*), also in Co/Al_2O_3 catalysts a Co-sulfide species is observed with the "Co–Mo–S" MES parameters. And, as in the Co/C catalysts this Co-sulfide species is changing with changing sulfidation temperatures. In Fig. 6 it is shown that the "Co–Mo–S" doublet disappears during sulfidation at 573 K and is transformed into two new doublets. One doublet with Q.S. = 4.05 mm/s, the meaning of which will be discussed elsewhere (*23*) (such a large value of Q.S. is also observed in Co/C catalysts with extremely low Co-loadings, 0.019, 0.0019, 0.0005, after sulfidation up to 573 K and is most likely due to a monatomically dispersed Co-sulfide species with Co atoms in a square planar or in a five-fold coordination), and a doublet with Q.S. = 0.73 mm/s. The latter doublet remains present after sulfidation at 673 K and should be assigned to a sulfidic phase. Due to the presence of a high-spin 2+ subspectrum, the MES parameters of this sulfidic doublet cannot be determined very accurately. But, its Q.S. value is significantly larger than the value for bulk Co_9S_8, (0.26 mm/s). The MES spectra of Co(0.7)/Al_2O_3(673) and Co(3.0)/Al_2O_3(673) show much smaller Q.S. values (0.34 and 0.30 mm/s, respectively; see Table 5). So, the Q.S. value of the sulfidic doublet decreases with increasing Co-loading, like for the Co/C catalysts (*12–14*, *16*).

From Table 5 it is not readily apparent that a Co-sulfide phase with the "Co–Mo–S" MES parameters is formed in the higher Co loading catalysts, viz., Co(0.7)/Al_2O_3 and Co(3.0)/Al_2O_3. Nevertheless, this can be deduced to be the case through applying a similar reasoning as above for Co(3.0)Mo(8.0)/Al_2O_3. It is found that: (i) the spectral contribution of the high-spin 2+ doublet has increased in both Co/Al_2O_3 catalysts after exposure to the H_2S/H_2 gas mixture at 300 K, while it has decreased after sulfidation at 373 K; (ii) Co(0.013)/Al_2O_3 shows a large spectral contribution of a "Co–Mo–S" doublet after sulfidation at 373 K; (iii) the Co atoms in the Co/C, the CoMo/C and the CoMo/Al_2O_3 catalysts become sulfided at lower temperature when the Co-loading is increased. Hence, it is very likely that the doublet, which in addition to the high-spin 2+ doublet is present in the spectra of Co(0.7)/Al_2O_3(373) and Co(3.0)/Al_2O_3(373) has to be assigned to a sulfidic phase. This Co-sulfide phase shows Q.S. values of 1.11 and 1.25 mm/s which fall within the range for "Co–Mo–S" (*24*). The assignment of this doublet to a Co-sulfide phase reveals that the Q.S. value of the Co-sulfide phase that is formed immediately after disappearance of the high-spin 2+ phase from the spectrum is related to the Co-loading (we observe Co(3.0)/Al_2O_3(373): 1.11, Co(0.7)/Al_2O_3(373): 1.25, Co(0.013)/Al_2O_3(473): 1.55 mm/s). Such a relation was also found for Co/C catalysts (*12*, *13*, *16*), and it means that the Co-sulfide particle size/ordering decreases with decreasing Co loading.

The Q.S. values of the Co-sulfide species in the spectra of Co(0.7)/Al_2O_3(473) and Co(3.0)/Al_2O_3(473) are rather small, 0.57 and 0.52 mm/s, respectively. In addition, these Q.S. values decreases during subsequent sulfidation treatments at 573 and 673 K. Despite this decrease the MES parameters of the Co-sulfide formed do not match with those of any known crystalline cobalt sulfide. A similar behaviour was observed in case of the Co/C catalysts (*12*, *13*, *16*).

In summary, during the sulfidation of uncalcined Co/Al_2O_3 catalysts with different Co-loadings, we observed the same trends in the MES parameters as in the case of Co/C catalysts, i.e., during sulfidation treatment up to 473 K, Co-sulfide species are formed which exhibit the "Co–Mo–S" doublet. The sulfidation temperature required to form this doublet decreases with increasing Co-loading and so does the Q.S. value of the "Co–Mo–S" doublet. An elevated sulfidation temperatures the "Co–Mo–S" doublet collapses and a sulfidic phase exhibiting a doublet with a Q.S. value that decreases with increasing sulfidation temperatures is formed. Finally, also the Q.S. value of the sulfidic doublet observed after sulfidation at 673 K decreases with increasing Co-loading. However, as expected, the behaviour of uncalcined Co/Al_2O_3 catalysts differs from that of the carbon-supported counterparts in one respect. In the case of the Co/Al_2O_3 catalysts a stronger Co-support interaction is observed from the behaviour at low sulfidation temperatures and from the contribution of Co : Al_2O_3 in the spectra of fully sulfided Co(0.00045)/Al_2O_3, Co(0.013)/Al_2O_3 and Co(0.7)/Al_2O_3.

Sulfidation of the Calcined Co/Al_2O_3 and CoMo/Al_2O_3 Catalysts

The MES spectra of stepwise sulfided calcined Co(1.3)Mo(8.0)/Al_2O_3 show that the sulfidation starts at low temperature. (The spectral contribution of the doublet with the lowest I.S. and Q.S. values, see Table 5, grows during sulfidation at 373 K). This is in accordance with the observation of Scheffer *et al.* (*25*) that in similarly calcined CoMo/Al_2O_3 catalysts the sulfidation of the Co already starts at room temperature.

After sulfidation at 473 K the main spectral contribution is a doublet with I.S. = 0.22 mm/s and Q.S. = 0.93 mm/s. During sulfidation at 573 and 673 K the Q.S. value of this doublet slightly increases. This behaviour was previously observed for all CoMo/C (*12*, *13*, *16*) and here for uncalcined CoMo/Al_2O_3 catalysts with relatively low Co/Mo ratio (<0.5 at/at), vide supra. It is explained as a redispersion of the Co-sulfide phase over the edges of the MoS_2 crystallites which are only formed at temperatures of about 573 K (*16*, *17*). Clearly part of the Co remains present in a high-spin 2+ phase. The presence of this phase after sulfidation up to 673 K and its rather small Q.S. value (within the range of high-spin 2+ doublets) justify assignment to Co : Al_2O_3, in accordance with the interpretation of their spectra by Topsøe *et al.* (*7*).

The spectra of calcined Co(1.3)/Al_2O_3 are rather poorly resolved. Still, the results previously obtained of uncalcined Co/Al_2O_3 and Co/C catalysts are helpful in order to understand what may happen. Clearly, part of the Co is diffused into the Al_2O_3 support during the calcination treatment. This Co : Al_2O_3 is characterized by a high-spin 2+ doublet. We cannot determine whether or not this Co becomes sulfided. The only indication that this Co might not be sulfided is the finding that the Q.S. value of the high-spin 2+ doublet is relatively small after the sulfidation treatments at 573 and 673 K compared to the Q.S. values of the high-spin 2+ components in the spectra of Co/Al_2O_3 and $CoMo/Al_2O_3$ catalysts sulfided at lower temperatures, which resulted at least in partial sulfidation. The rest of the Co is characterized by a spectral contribution under the peak at the left-hand side of the high-spin 2+ doublet. The MES parameters of this contribution are difficult to derive. A fit with a doublet with adjusted linewidth was applied. From Table 6 it follows that the Q.S. value of this doublet is hardly affected by exposing the catalyst to the sulfiding gas mixture at room temperature, but continuously decreases during the successive sulfidation treatments up to 673 K. After this last sulfidation step a Q.S. value of 0.73 mm/s is analysed, which is in the range of the value for uncalcined $Co(0.013)/Al_2O_3$ (673). This doublet most probably represents a sulfidic phase. The decrease of the Q.S. value points to an increasing Co-sulfide particle size. That also for the calcined Co/Al_2O_3 catalysts the sulfidation starts at room temperature, is in agreement with Arnoldy *et al.* (*26*).

Remarks Concerning the Influence of the Support

As outlined above, the trends observed in the sulfidation of $CoMo/Al_2O_3$ and Co/Al_2O_3 catalysts are essentially the same as those observed in the CoMo/C and Co/C catalysts. Therefore, it is reasonable to assume that the MES spectra of the Al_2O_3-supported catalysts may be interpreted in the same way as those of their C-supported counterparts. That means that also for the Al_2O_3-supported catalysts the Q.S. value depends on the particle size and ordering of the Co-sulfide species formed during the sulfiding process. An increase in particle size and ordering gives rise to a lower Q.S. value. Accordingly, the Co-sulfide species present in Co/Al_2O_3 and $CoMo/Al_2O_3$ catalysts are essentially similar, only the particle size and ordering of the Co-sulfide species differs.

A stronger Co-support interaction is observed in the case of Al_2O_3-supported catalysts, which interaction surely will not be weakened during calcination at 773 K. So, the observation that the sulfidation of calcined $Co(1.3)Mo(8.0)/Al_2O_3$ starts (at least) at 373 K implies that also the sulfidation of uncalcined $Co(0.7)Mo(8.0)/Al_2O_3$ and $Co(3.0)Mo(8.0)/Al_2O_3$ should start at least at this temperature.

Comparing the spectra of Co(4.3)/C(673) (*16*) and $Co(0.7)/Al_2O_3(673)$, it is seen that despite the lower Co-loading (0.25 at/nm^2 versus 0.4 at/nm^2), the Q.S. value of the Co-sulfide species formed on the alumina support is much smaller than that on carbon. Apparently, the Co-sulfide species sinters less easily on the carbon support, and this is probably due to the narrow pore structure of the activated-carbon.

It is interesting to compare the behaviour of uncalcined $Co(0.00045)/Al_2O_3$ and calcined $Co(1.3)/Al_2O_3$. All spectra of $Co(0.00045)/Al_2O_3$ are dominated by a high-spin 2+ doublet due to $Co:Al_2O_3$. The behaviour of calcined $Co(1.3)/Al_2O_3$ is clearly different. This supports our conclusion that only part of the Co diffuses into the Al_2O_3 whereas the rest can normally be sulfided and behaves as in the uncalcined catalysts.

Finally, the present results provide evidence that the Co preferentially adsorbs on the Mo phase during the preparation of the CoMo catalyst. In the $CoMo/Al_2O_3$ catalysts a high-spin 2+ doublet is observed with relatively narrow absorption lines. As these narrow lines are not observed in catalysts without Mo, it indicates that the Co sticks to the Mo phase. Furthermore, the absence of a high-spin 2+ doublet in any of the $CoMo/Al_2O_3(673)$ catalysts makes it clear that after this sulfidation treatment all Co remains located at the MoS_2. Otherwise, (part of) it would have diffused into the Al_2O_3, as was observed for $Co(0.00045)/Al_2O_3$.

However, after the calcination treatment up to 773 K, part of the Co in a $CoMo/Al_2O_3$ catalyst is diffused into the alumina. This can easily be understood in the following way. In the calcination treatment the catalysts are heated up to 773 K in 1 h. It is known from previous MAS and MES (*27*, *28*) studies on the reduction and sulfidation of carbon-supported Fe/Co(–Mo) catalysts that the Fe/Co easily segregates if the catalysts are heated too fast. The segregated Co diffuses into the alumina support.

CONCLUSIONS

The stepwise sulfidation of Co/Al_2O_3 and CoMo/Al_2O_3 catalysts with different Co-loadings has been studied by MES. The trends observed in the spectra of the uncalcined catalysts resemble those observed for carbon-supported catalysts. Therefore, the interpretation of the spectra is based on the conclusions drawn from the MES studies of the Co/C and CoMo/C catalysts (*12*, *13*, *16*).

It is found that a Co-sulfide species exhibiting the "Co–Mo–S" MES spectrum can be formed during sulfidation of Co/Al_2O_3 catalysts. Increasing sulfidation temperature leads to a decrease in Q.S. value which reflects a growth of this Co-sulfide species. In Co/Al_2O_3 catalysts with rather high Co-loading this leads to the formation of Co-sulfide particles nearly exhibiting the MES spectrum (Q.S. = 0.30 mm/s) of crystalline Co_9S_8 (Q.S. = 0.26 mm/s). Apparently, the growth of these relatively large Co-sulfide particles turns out to be easier on alumina than on activated carbon, which is most probably due to the narrow pore structure of the carbon support. In all MES spectra of Co/Al_2O_3 catalysts with low Co-loadings a subspectrum of Co : Al_2O_3 is present.

The MES spectra of fresh CoMo/Al_2O_3 catalysts with rather low Co/Mo ratios show a high-spin 2+ contribution with relatively narrow absorption lines. Although this doublet cannot yet be assigned, such a contribution is not found in the spectra of the Co/Al_2O_3 catalysts and thus it indicates that the Co sticks to the Mo during the preparation of the catalyst. During sulfidation of the CoMo/Al_2O_3 catalysts at low temperatures a Co-sulfide species is formed that exhibits the "Co–Mo–S" MES spectrum. During sulfidation at higher temperatures the Co-sulfide species slightly grows and after sulfidation up to 673 K, very small Co-sulfide particles have been formed which are most likely located at the edge of the small MoS_2 crystallites that are also formed during the sulfidation.

It is concluded that the Co-sulfide species formed in sulfided Co/Al_2O_3 and CoMo/Al_2O_3 catalysts are essentially the same, only the particle size and ordering of the Co-sulfide species may differ, as in the case of Co/C and CoMo/C catalysts. The function of the Mo, which is present as MoS_2, is merely to stabilize very small Co-sulfide particles, which in the limit contain only one single Co atom.

It turned out that the Q.S. value of the Co-sulfide phase in the sulfided catalysts depends on the sulfiding temperature and Co content. This observation leads to the conclusion that large Q.S. values point to the presence of very small Co-sulfide entities or particles (the lower limit being "particles" containing only one Co atom, such as proposed in the "Co–Mo–S" model), whereas small Q.S. values point to the presence of large Co-sulfide particles (the upper limit being crystalline Co_9S_8).

REFERENCES

1. Voorhoeve, R. H. J., and Stuiver, J. C. M., *J. Catal.* **23**, 243 (1971).

2. Farragher, A. L., and Cossee, P., *in* "Proceedings, 5th International Conference on Catalysis," Palm Beach, 1972" (J. W. Hightower, Ed.), p. 301. North-Holland, Amsterdam, 1973.

3. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., *in* "Chemistry in Catalytic Processes," p. 411. McGraw–Hill, New York, 1979.

4. Delmon, B., *in* "Proceedings, 3rd Conference on the Chemistry and Uses of Molybdenum," Ann Arbor, 1979" (H. F. Berry and P. C. H. Mitchell, Eds.), p. 73. Climax Molybdenum Company, Ann Arbor, 1979.

5. Topsøe, H., and Mørup, S., *in* Proc. Int. Conf. Mössbauer Spectr.," Cracow, Poland, 1975" (A. Z. Hrynkiewicz and J. A. Sawicki, Eds.), Vol. 1, p. 305. 1975.

6. Clausen, B. S., Mørup, S., Topsøe, H., and Candia, R., *J. Phys.* **37**, C6–249 (1976).

7. Topsøe, H., Clausen, B. S., Candia, R., Wivel, C., and Mørup, S., *J. Catal.* **68,** 433 (1981).
8. Wivel, C., Candia, R., Clausen, B. S., and Topsøe, H., *J. Catal.* **68,** 453 (1981).
9. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **84,** 386 (1983).
10. Topsøe, N.-Y., Topsøe, H., Sørensen, O., Clausen, B. S., and Candia, R., *Bull. Soc. Chim. Belg.* **93,** 727 (1984).
11. Clausen, B. S., Topsøe, H., Candia, R., and Lengeler, B., *Am. Chem. Soc. Symp. Ser.* **248,** 71 (1974).
12. Van der Kraan, A. M., Crajé, M. W. J., Gerkema, E., Ramselaar, W. L. T. M., and de Beer, V. H. J., Hyperfine Interact. **46,** 567 (1989).
13. Crajé, M. W. J., Gerkema, E., de Beer, V. H. J., and van der Kraan, A. M., *in* "Studies in Surface Science and Catalysis" (M. L. Occelli and R. G. Anthony, Eds.), Vol. 50, p. 165. Elsevier, Amsterdam, 1989.
14. Crajé, M. W. J., de Beer, V. H. J., and van der Kraan, A. M., *Appl. Catal.* **70,** L7 (1991).
15. Crajé, M. W. J., Louwers, S. P. A., de Beer, V. H. J., Prins, R., and van der Kraan, A. M., *J. Phys. Chem.* **96,** 5445 (1992).
16. Crajé, M. W. J., Ph.D. thesis, Delft University of Technology, Delft, 1992.
17. Crajé, M. W. J., Louwers, S. P. A., Prins, R., de Beer, V. H. J., and van der Kraan, A. M., submitted for publication.
18. Ramselaar, W. L. T. M., Crajé, M. W. J., Hadders, R. H., Gerkema, E., de Beer, V. H. J., and van der Kraan, A. M., *Appl. Catal.* **65,** 69 (1990).
19. Van Veen, J. A. R., Gerkema, E., van der Kraan, A. M., Hendriks, P. A. J. M., and Beens, H., *J. Catal.* **133,** 112 (1992).
20. Ramselaar, W. L. T. M., Hadders, R. H., Gerkema, E., de Beer, V. H. J., van Oers, E. M., and van der Kraan, A. M., *Appl. Catal.* **51,** 263 (1989).
21. Ramselaar, W. L. T. M., Crajé, M. W. J., Gerkema, E., de Beer, V. H. J., van Oers, E. M., and van der Kraan, A. M., *Appl. Catal.* **54,** 217 (1989).
22. Van der Kraan, A. M., and Niemantsverdriet, J. W., *in* "Industrial Appl. of the Mössbauer Effect" (G. J. Long and J. G. Stevens, Eds.), p. 609. Plenum Press, New York, 1986.
23. Crajé, M. W. J., de Beer, V. H. J., van Veen, J. A. R., and van der Kraan, A. M., *Appl. Catal. A: General* **100,** 97 (1993).
24. Topsøe, H., Candia, R., Topsøe, N.-Y., and Clausen, B. S., *Bull. Soc. Chim. Belg.* **93,** 783 (1984).
25. Scheffer, B., de Jonge, J. C. M., Arnoldy, P., and Moulijn, J. A., *Bull. Soc. Chim. Belg.* **93,** 751 (1984).
26. Arnoldy, P., de Booys, J. L., Scheffer, B., and Moulijn, J. A., *J. Catal.* **96,** 122 (1985).
27. Crajé, M. W. J., Hadders, R. H., Ramselaar, W. L. T. M., Gerkema, E., de Beer, V. H. J., and van der Kraan, A.M., *Hyperfine Interact.* **57,** 801 (1990).
28. Ramselaar, W. L. T. M., Crajé, M. W. J., Gerkema, E., de Beer, V. H. J., and van der Kraan, A. M., *Bull. Soc. Chim. Belg.* **96,** 931 (1987).