

Sulfidation and activity of Co/C catalysts having extremely low cobalt-loading: A Moessbauer emission spectroscopy and thiophene hydrodesulfurization study

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Sulfidation and activity of Co/C catalysts having extremely low cobalt-loading: A Mössbauer emission spectroscopy and thiophene hydrodesulphurization study

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Abstract

Up to a sulfidation temperature of 473 K, the behaviour of Co/C catalysts with extremely low cobalt-loadings (ppm range) agrees with the trend observed before in the Mössbauer emission spectroscopy (MES) spectra of Co/C catalysts with much higher cobalt-loadings (0.04–4.3 wt.-%). Interestingly, sulfidation at 573 K results in a rather well-defined very highly dispersed (most likely monatomically) 'Co-sulfide' species which shows a doublet with the extremely large value $Q.S. = 4.11$ mm/s. In this species the cobalt atoms may be four-fold (square-planar) or five-fold (square-pyramid) coordinated by sulfur. Sulfidation at 673 K results in the disappearance of this highly dispersed "Co-sulfide" species and the newly formed species are again similar to the one previously found for Co/C catalysts with higher cobalt-loadings. It is worth noting that this finally formed 'Co-sulfide' species does not exhibit the "Co-Mo-S" MES spectrum ($Q.S.$ between 1.0 and 1.3 mm/s) whereas its intrinsic thiophene hydrodesulfurization (HDS) activity equals that of cobalt in the "Co-Mo-S" phase. These observations clearly lead to the conclusion that there is no general relation between the thiophene HDS activity (measured at atmospheric pressure) and the amount of cobalt exhibiting a "Co-Mo-S" MES spectrum.

Keywords: activity; catalyst characterization; cobalt/carbon; hydrodesulphurization; Mössbauer spectroscopy; sulphidation; thiophene

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INTRODUCTION

The main aim of a characterization study of catalysts is to clarify the structure of the catalyst surface on an atomic scale and to relate this structure to the catalytic activity. We systematically applied Mössbauer emission spectroscopy (MES) [1-4] and extended X-ray absorption fine structure (EXAFS) [4-6] in the in-situ characterization of Co/C and CoMo/C hydrodesulfurization (HDS) catalysts. By extensively studying trends we could establish a consistent picture for the local structure of the Co/C and CoMo/C catalysts. It was concluded that the 'Co-sulfide' species present in sulfided Co/C and CoMo/C catalysts are essentially the same, and it is primarily the particle size and concomitant ordering of the 'Co-sulfide' formed after sulfidation that is different at elevated temperatures. In the case of Co/C catalysts the particle size is small only after sulfidation at low temperatures. The Co/C catalysts then exhibit a MES spectrum which cannot be distinguished from that of the so-called "Co-Mo-S" phase which has been defined and reported to be the active phase in CoMo HDS catalysts by Topsøe and co-workers [7-11]. It would be very interesting to ascertain whether the cobalt-species exhibiting this "Co-Mo-S" MES spectrum in Co/C catalysts also shows a high thiophene HDS activity. However, it is not stable at the temperatures at which thiophene HDS tests are usually performed. We have tried to tackle this problem in two ways.

First, we tried to carry out activity tests at temperatures such that the "Co-Mo-S" type species in Co/C is stable, which according to the results in refs. 1, 2 and 4 is at 473 K and below. Unfortunately, the reactor facilities available did not allow reproducible thiophene HDS activity measurements at such low temperatures and attempts to apply more reactive model compounds such as butyl-mercaptan (very malodorous) were not successful so far. The second approach was to determine the thiophene conversions at 673 K for Co/C catalysts with low cobalt-loadings. The MES results obtained during the stepwise sulfidation of a set of Co/C catalysts with different cobalt-loadings showed [1,2,4] that the sulfidation temperature at which the "Co-Mo-S" doublet collapsed was higher for decreasing cobalt-loadings. So, a "Co-Mo-S" MES spectrum could be expected in Co/C catalysts with an extremely low cobalt-loading (much lower than 0.04 wt.-%, see refs. 1, 2 and 4 after sulfidation up to 673 K. Moreover, the Q.S. value in the MES spectra of the Co/C catalysts sulfided up to 673 K [Co/C(673)] systematically increases with decreasing cobalt-loading. It is noteworthy that Vissers et al. [12] reported a relation between the intrinsic activity of cobalt in sulfided Co/C catalysts and the cobalt-loading. They observed an increasing intrinsic activity with decreasing cobalt-loading and predicted that the intrinsic activity of optimally dispersed 'Co-sulfide' will resemble that of "Co-Mo-S".

Therefore, in this paper a number of Co/C catalysts with extremely low cobalt-loadings is investigated by MES. It was expected that these catalysts

would show a "Co-Mo-S" doublet after sulfidation up to 573 or 673 K. For comparison, also molybdenum containing catalysts with comparable low cobalt-loadings were investigated by MES. Finally, thiophene HDS activity tests on Co/C catalysts with very low Co-loading and a set of two CoMo/C catalysts were carried out.

EXPERIMENTAL

All catalysts are prepared by pore volume impregnation. An activated carbon (Norit RX3-extra, particle size 0.5–0.85 mm) with a BET surface area of 1197 m²/g and a pore volume of 1.0 ml/g is used as carrier material. The pore volume impregnation was carried out using aqueous solutions of Co(NO₃)₂·6H₂O (Merck p.a. or Fluka p.a.) or (NH₄)₆Mo₇O₂₄·4H₂O (Merck min. 99.9%). For the MES measurements about 1.5 mCi ⁵⁷Co as aqueous solution of Co(NO₃)₂·6H₂O (ex Amersham) was added to the cobalt-nitrate solutions. The CoMo catalysts were prepared by a two step procedure with the molybdenum being introduced first. Mo/C was dried in static air at 383 K for 16 h. After cobalt introduction the catalysts were left in static air at 293 K for 16 h. Catalyst loadings are given in wt.-% relative to the carrier material and are calculated from the used impregnation solutions.

All catalysts were subjected to a mild drying treatment in a hydrogen flow (flow-rate 50 ml/min) to remove residual nitrate ions [13–15]. During this treatment the catalysts were kept at 313, 353 and 393 K for 24 h at each temperature. They will be referred to as fresh catalysts. The sulfidation of the samples was carried out in a 10% H₂S/H₂ gas mixture (flow-rate of 60 ml/min) at atmospheric pressure in an in-situ MES reactor, which has been described elsewhere [16]. However, the heating section as well as the outer container used in this study are made of stainless steel 316. The following temperature programme was applied: linear increase to the desired maximum sulfidation temperature *a* K in 1 h, holding at this temperature for 1 h and cooling in the H₂S/H₂ gas flow to 293 K. The treatment applied to the catalyst is indicated by: (S, *a* K, 1 h + 1 h). In the text the successive sulfidation procedures will be indicated by their maximum temperature only, i.e. Co(4.3)Mo(7.0)/C(473).

The MES measurements were carried out using a constant acceleration spectrometer in a triangular mode with a moving single-line absorber of K₄Fe(CN)₆·3H₂O enriched in ⁵⁷Fe. The in-situ reactor was placed horizontally so that a small vespel cup (composite material, Dupont) containing the catalyst particles could be easily mounted. Isomer shifts are reported relative to a source of ⁵⁷Co:Rh, positive velocities corresponding to the absorber moving away from the source. The velocity scale was calibrated by the Mössbauer spectrum of sodium nitroprusside Na₂(Fe(CN)₅NO)·2H₂O obtained with the ⁵⁷Co:Rh source.

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

The thiophene HDS activity tests were performed on catalyst samples with other cobalt-loadings than those applied for the ^{57}Co MES measurements. For a *standard* activity test, catalyst samples (200 mg) were sulfided in-situ in a 10% $\text{H}_2\text{S}/\text{H}_2$ gas mixture at a flow-rate of 60 ml/min (atmospheric pressure). The temperature was linearly increased from room temperature to 673 K and kept at that temperature for 2 h. After sulfidation, the reaction gas mixture consisting of 6.2 mol-% thiophene/ H_2 was introduced at a flow-rate of 50 ml/min (atmospheric pressure) while the catalyst was kept at 673 K. In order to increase the conversion, in some experiments one or more parameters (sample weight, thiophene/ H_2 flow) were changed. The reaction products were analyzed by on-line gas chromatography. The thiophene conversion after 2 h run time was taken to calculate the first-order reaction rate constant [k_{HDS} ($\text{m}^3 \text{kg}^{-1} \text{s}^{-1}$)].

RESULTS

MES measurements

The catalysts were subjected to a stepwise sulfidation treatment. In Fig. 1 the MES spectra of a $\text{Co}(0.0005)/\text{C}$ catalyst are presented. After the mild drying treatment in hydrogen, the spectrum is characterized by two doublets, one with $\text{Q.S.} = 0.60$ mm/s and a high spin 2+ doublet, as presented in Table 1. During sulfidation at 300 K the spectral contribution of the high spin 2+ doublet becomes dominant and remains so after sulfidation at 373 K. Upon sulfidation at 473 K, part of the cobalt still exhibits a high spin 2+ doublet, whereas the rest is characterized by a doublet with $\text{I.S.} = 0.21$ mm/s and $\text{Q.S.} = 1.60$ mm/s. After sulfidation at 573 K, part of the cobalt exhibits a quadrupole doublet similar to the latter one. In addition, a new subspectrum of cobalt arises with two sharp lines, one at about +2 and one at -2 mm/s. For various reasons it is unlikely that these lines are the outer lines of a sextuplet. First of all, the hyperfine field would then be only 120 kOe. Furthermore, under the present sulfidation conditions the stable 'Co-sulfide' would be Co_9S_8 , and this 'Co-sulfide' is not magnetic. Finally, magnetic splitting would indicate fairly large 'Co-sulfide' particles, which by itself is very unlikely since we have found very small 'Co-sulfide' particles throughout our investigation of Co/C and CoMo/C catalysts [1-6], and moreover we are dealing with an extremely low cobalt-loading. So, most probably the two lines belong to a quadrupole doublet with $\text{I.S.} = 0.10$ mm/s and $\text{Q.S.} = 4.11$ mm/s. It is remarkable that the lines of this doublet are relatively narrow (0.53 mm/s), indicating a fairly well-defined phase. Besides, the RAA is small (note the large number of counts in

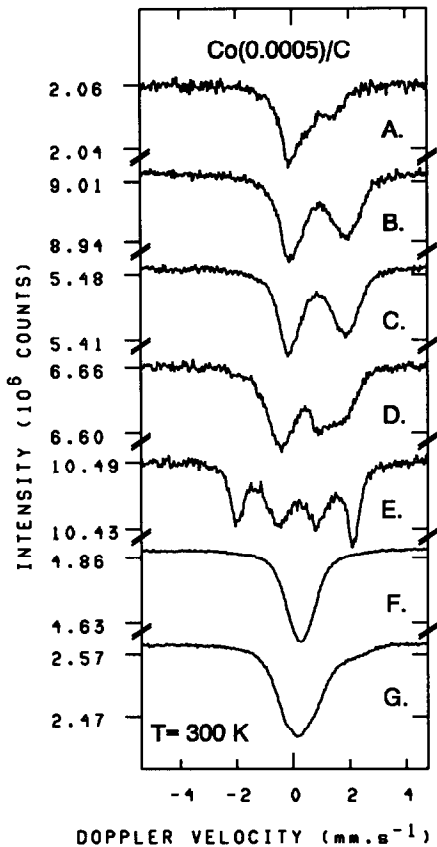


Fig. 1. MES spectra obtained at 300 K with Co(0.0005)/C after various successive sulfidation treatments. A: fresh catalyst; B: (S, 300 K); C: (S, 373 K, 1 h+1 h); D: (S, 473 K, 1 h+1 h); E: (S, 573 K, 1 h+1 h); F: (S, 673 K, 1 h+1 h); G: Reox, ambient air, 2 days.

Fig. 1E). From the spectral analysis (Table 1) it follows that the spectral contribution of this doublet is about 1/3. After sulfidation up to 673 K the subspectrum is still visible but it could no longer be fitted satisfactorily. In addition, the doublet with $Q.S. = 1.40$ mm/s has disappeared after this sulfidation treatment, while a doublet with a much smaller $Q.S. = 0.45$ mm/s has appeared. After a prolonged sulfidation at 673 K for 4 h, the spectral contribution of the doublet with $Q.S. = 4.11$ mm/s has completely disappeared, whereas the $Q.S.$ value of the main spectral contribution has become smaller yet (0.40 mm/s). The spectrum of the catalyst changes drastically upon exposure to air at room temperature. A small but significant high-spin $2+$ contribution arises and the $Q.S.$ value of the other doublet in the spectrum increases considerably.

Two more Co/C catalysts with very low cobalt-loading have been investigated, viz. Co(0.0019)/C and Co(0.019)/C. These catalysts behave quite similarly to the Co(0.0005)/C catalyst. In Fig. 2 the spectra of the three Co/C

TABLE 1

Mössbauer parameters of Co(0.0005)/C determined after various successive sulfidation treatments

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 $\Gamma \pm 0.05$ mm/s, spectral contribution $A \pm 5\%$

T_{sulf} (K)	'Co-sulfide'				High-spin 2+ / 'Co-sulfide'			
	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	0.61 ^a	0.81 ^a	60 ^a	0.70	1.58	0.67	40
300	0.10	0.58	0.46	11	0.94	1.94	0.98	89
373	0.02	0.50	0.42	8	0.90	2.00	0.93	92
473	0.21	1.60	0.86	50	0.83	1.96	0.92	50
573	0.21	1.40	1.13	64	0.10	4.11	0.53	36
673	0.29	0.45	0.91	<100	^b	^b	^b	>0 ^b
Reox	0.24	0.77	1.04	94	1.10	1.83	0.44	6

^aThis doublet is assigned to a cobalt oxide species.

^bThe small spectral contribution visible in the spectrum could not be fitted satisfactory.

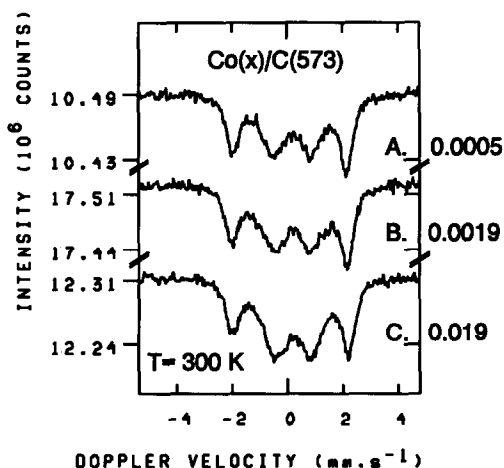


Fig. 2. MES spectra obtained at 300 K with three Co/C catalysts with very low cobalt-loadings after stepwise sulfidation up to 573 K. A: Co(0.0005)/C; B: Co(0.0019)/C; C: Co(0.019)/C.

catalysts recorded after sulfidation up to 573 K are given and they all clearly show the doublet with Q.S. = 4.11 mm/s.

In addition to these Co/C catalysts with very low cobalt-loading, the sulfidation of Co(0.019)Mo(6.84)/C and Co(0.0019)Mo(6.84)/C catalysts has also been studied. For these CoMo/C catalysts a quite similar sulfidation behaviour is found as reported earlier for CoMo/C catalysts with higher cobalt-loadings

TABLE 2

Mössbauer parameters of Co(0.019)Mo(6.84)/C determined after various successive sulfidation treatments

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 $\Gamma \pm 0.05$ mm/s, spectral contribution $A \pm 5\%$

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	0.30 ^a	1.04 ^a	0.85 ^a	49 ^a	0.88	2.10	0.79	51
300	0.25	1.07	0.86	49	0.83	2.53	0.88	51
373	0.25	1.07	0.73	57	0.55	2.25	1.02	43
473	0.24	1.07	0.82	100				
573	0.24	1.13	0.76	100				
673	0.23	1.38	0.77	100				
Reox	0.21	1.43	0.76	100				

^aThis doublet is assigned to a cobalt oxide species.

[1-4], and no indication of a doublet with Q.S. = 4.1 mm/s, as in the Co(0.019)/C catalyst, is observed. The numerical results of the spectral analyses of Co(0.019)Mo(6.84)/C catalyst are given in Table 2.

Thiophene HDS activity tests

As the carbon support material Norit RX3-extra does not show any significant thiophene conversion [17,18] it is justified to ascribe all observed conversion to the 'Co-sulfide' species present in the catalysts.

At first a set of two CoMo/C catalysts was studied. These catalysts were not subjected to the mild drying treatment in hydrogen. For calculating a quasi turn over frequency (QTOF) of the CoMo/C catalysts, the promoter effect was fully attributed to the 'Co-sulfide' species, i.e. the k_{HDS} of Mo(6.84)/C was subtracted from the value of the CoMo(6.84)/C catalyst and from the difference a QTOF value for the 'Co-sulfide' species could be calculated: $QTOF = k_{HDS} \cdot 1.123 \cdot 59 \cdot (wt.\% \cdot 10)^{-1} (s^{-1})$ [1.123 mol thiophene/m³ feed; mass number Co = 59; dimension: (m³ kg⁻¹ s⁻¹ · mol) (m⁻³ · kg mol⁻¹) = s⁻¹]. A QTOF⁻¹ value of 19.2 s was obtained for both Co(1.10)Mo(6.84)/C and Co(0.38)Mo(6.84)/C.

Furthermore, a set of Co/C catalysts with a very low cobalt-loading was tested and these catalysts were subjected to the mild drying treatment in hydrogen as described in Experimental. Several experiments were carried out in which the conversion was increased by applying more catalyst and by using a

lower flow-rate of the 6.2% thiophene/H₂ reaction gas mixture. Changing these parameters increased the conversion but did not significantly influence the calculated QTOF values. The QTOF⁻¹ values calculated from 12 measurements performed (4 with a Co(0.06)/C catalyst, 2 with a Co(0.012)/C catalyst, 5 with a Co(0.006)/C catalyst and 1 with a Co(0.0012)/C catalyst) were averaged and a statistical error has been calculated. A mean QTOF⁻¹ value of 19.4 ± 5.8 s (95% confidence level) has been derived.

DISCUSSION

MES measurements

The main reason for performing these MES studies on the stepwise sulfidation behaviour of Co/C catalysts with very low cobalt-loading was to check whether in these catalysts after sulfidation up to 673 K a 'Co-sulfide' species with the "Co-Mo-S" structure (defined by its Q.S. value between 1.0 and 1.3 mm/s) could be formed. The answer to this question is simply no! From Fig. 1 and Table 1 it follows that the spectrum of Co(0.0005)/C(673) is dominated by a quadrupole doublet with Q.S.=0.45 mm/s. By combining the results of MES and EXAFS [1-6] we demonstrated that such a subspectrum can be assigned to a highly dispersed Co₉S₈-like phase in which the majority of the cobalt atoms has only four sulfur nearest neighbours and some cobalt next-nearest neighbours at 2.51 Å. The 'Co-sulfide' ("Co-Mo-S") species we were looking for is a species in which the cobalt has six sulfur nearest neighbours and some cobalt next nearest neighbours at 2.9 Å, and which exhibits a Q.S. value of about 1.3 mm/s [1-6].

Although we did not observe the expected "Co-Mo-S" doublet upon sulfidation at 673 K, the MES spectra of these Co/C catalysts with very low cobalt-loading show some features which differ from those of the previously studied carbon-supported catalysts with a Co-loading above 0.04 and which need therefore to be discussed.

The observation that the MES spectrum of the Co(0.0005)/C(473) still contains a large contribution of the high-spin 2+ doublet is consistent with the results showing that with decreasing cobalt-loading a more severe sulfidation treatment is necessary to make such a phase disappear [1,2,4]. The additional doublet (I.S.=0.21 mm/s, Q.S.=1.60 mm/s) present in this spectrum should be assigned to a sulfidic cobalt-species. However, this doublet cannot be assigned to any known crystalline 'Co-sulfide' phase [9]. We found previously for Co/C catalysts with higher cobalt-loading, a "Co-Mo-S" spectrum [1,2,4]. Although the observed Q.S. value of 1.60 mm/s in the Co/C catalyst with a very low cobalt-loading is larger than the presented range of 1.0-1.3 mm/s for "Co-Mo-S" by Topsøe et al. [11], we believe that this Q.S.-value is due to a similar sulfidic cobalt-species.

Thus, the response of the Co(0.0005)/C catalyst to sulfidation up to 473 K is consistent with the *trend* we observed before [1,2,4]. Whenever this consistency in response is continued, a "Co-Mo-S" spectrum can be expected after sulfidation of the catalyst up to 573 K. In Fig. 1 and Table 1 it can be seen that indeed the majority of the cobalt exhibits a spectrum with I.S.=0.21 and Q.S.=1.40 mm/s. However, in addition a subspectrum is present characterized by a quadrupole doublet with an extremely large Q.S. value of 4.11 mm/s. Such a large Q.S. value is indicative of the presence of very asymmetrically coordinated cobalt-atoms. The relatively sharp line width of only 0.53 mm/s demonstrates that the cobalt-species should be rather well defined. This phase emerges after the intermediate high-spin 2+ phase disappeared from the spectrum and it is therefore most probably a sulfidic phase. Such a large Q.S. value has been observed in certain Fe high-spin 2+ complexes by Hills et al. [19]. In these complexes the iron is coordinated by four sulfur atoms. A Q.S. value of 4 mm/s has also been observed for several compounds in which iron is five-fold coordinated [20-22]. From the present result we cannot decide whether the cobalt-atoms are four- or five-fold coordinated by sulfur. Moreover, this will be very difficult to determine since no technique is known that can provide structural information under in-situ conditions of a sample containing only 0.0005 wt.-% Co, part of which is in this particular phase.

The sulfidation behaviour of the Co(0.0019)/C and the Co(0.019)/C catalysts resembles that of the Co(0.0005)/C catalyst. It follows from Fig. 2 that the spectral contribution of the particular doublet with Q.S.=4.11 mm/s depends on the cobalt-loading, the lower the cobalt-loading the larger this contribution in the room temperature spectra. The Q.S. value is equal for all three catalysts, indicating that the same species is present in these catalysts. As we have found a relationship between the Q.S. value and the particle size of 'Co-sulfide' species [3,4], the independency of this particular Q.S. value of the cobalt-loading suggests that we are dealing with a monatomically dispersed 'Co-sulfide' species. Such a monatomically dispersed 'Co-sulfide' species is expected to have a relatively low Debye temperature, which indeed appears to be the case according to the strong increase of RAA upon sulfidation at 673 K when this phase has disappeared. It is consistent too with the absence of this phase in the room temperature MES spectra of Co(0.04)/C(473) whereas it is present at 77 and 4.2 K [23]. Interestingly, we also observed in the uncalcined Co(0.013)/Al₂O₃ catalyst a contribution of this doublet with Q.S.=4 mm/s [4,24]. Therefore, it is unlikely that the corresponding subspectrum originates from a cobalt-support interaction.

After sulfidation at 673 K of the Co/C catalyst with very low cobalt-loading the spectrum is dominated by a broad single line that was fitted with a doublet with Q.S.=0.45 mm/s and hence it is difficult to decide whether the subspectrum with Q.S.=4 mm/s is still present (Fig. 1). Low temperature MES measurements of these catalysts should be done in order to be more conclusive at

this point. The doublet with $Q.S.=0.45$ mm/s has to be attributed to a highly dispersed Co_9S_8 -like phase [3-6], growing during the sulfidation treatment at 673 K and so explaining the strong increase of the RAA.

The sulfidation of the $Co(0.019)Mo(6.84)/C$ and $Co(0.0019)Mo(6.84)/C$ catalysts is consistent with the trend already observed for other $CoMo/C$ catalysts [1-4]. The absence of the doublet with $Q.S.=4.11$ mm/s indicates that all the cobalt is present on the molybdenum. Apparently the presence of molybdenum forces the cobalt into a structure in which the strongly asymmetrical coordination giving rise to a very large $Q.S.$ value is not formed. In addition the $Co(0.019)Mo(6.84)/C$ catalyst is not affected by exposure to air at room temperature after the final sulfidation treatment (Table 2). This is in accordance with the trend observed that 'Co-sulfide' phase exhibiting a large (> 1.3 mm/s) $Q.S.$ value is not sensitive to air exposure.

From the above results and those reported elsewhere [1-4] it can be concluded that the MES spectra of $CoMo/C$ catalysts show a similar trend over a very wide range of Co/Mo ratios, from $Co/Mo=1$ at/at down to $Co/Mo=4 \cdot 10^{-4}$ at/at, as discussed elsewhere [1-4]. On the other hand, the MES spectra of Co/C catalysts with very low cobalt-loadings (≤ 0.04 wt.-%) show a spectral contribution at room temperature that has not been observed in Co/C catalysts with higher cobalt-loadings. This doublet with $Q.S.=4.11$ mm/s has been attributed to a well-defined 'Co-sulfide' species in which cobalt is strongly asymmetrically coordinated. However, we cannot decide on a coordination with cobalt in the plane of four sulfur atoms or a five-fold coordination. This species is only observed in catalysts with very low cobalt-loadings and the contribution decreases with increasing cobalt-loading. It has a very low Debye temperature. Therefore, it is most likely related to a very highly dispersed 'Co-sulfide' species, possibly even monatomically dispersed. It is remarkable that also in these Co/C catalysts with very low cobalt-loading a highly dispersed Co_9S_8 type phase with $Q.S. \approx 0.5$ mm/s is formed at higher sulfidation temperatures as we previously observed for Co/C catalysts with much higher cobalt-loadings [1-4].

Thiophene HDS activity tests and MES measurements

Rather similar $QTOF^{-1}$ values of about 19 s were calculated for sulfided $Co(1.10)Mo(6.84)/C$ and $Co(0.38)Mo(6.84)/C$ catalysts. This value agrees with the value reported by Vissers et al. [12] for cobalt in the "Co-Mo-S" phase. Furthermore, the mean $QTOF^{-1}$ value obtained for the Co/C catalysts with very low cobalt-loading [19.4 ± 5.8 s (95%)] equals that of cobalt in the "Co-Mo-S" phase and is in very good agreement with the conclusions of Vissers et al. [12] that the intrinsic activity of optimally dispersed 'Co-sulfide' resembles that of "Co-Mo-S".

Before we carried out these MES and thiophene HDS activity studies on

Co/C catalysts with very low cobalt-loadings, it was assumed that the trends observed in the MES results as a function of the cobalt-loading would continue in the region of low-loading, i.e. we expected to find an increasing Q.S. value of the 'Co-sulfide' species of similar structure with decreasing cobalt-loading. As we could relate the Q.S. value to the particle size of the 'Co-sulfide' species [3,4], it is reasonable to find a relation between the intrinsic activity and the Q.S. value of the 'Co-sulfide'. An intrinsic activity as high as that of "Co-Mo-S" was expected [12] to be found for monatomically dispersed 'Co-sulfide' species and for this species the Q.S. value was expected to be in the range of "Co-Mo-S" (Q.S. \approx 1.3 mm/s). In that case it would be very likely that the activity of both the cobalt and the CoMo catalysts has to be assigned to a very highly dispersed 'Co-sulfide' species. The MoS₂ in the CoMo/C catalysts should function as a secondary support material only.

The thiophene HDS activity test results seem to support the picture presented above: the intrinsic activity of the 'Co-sulfide' species in the CoMo/C catalysts is the same as that of the 'Co-sulfide' species formed in Co/C catalysts with very low cobalt-loading. However, if we try to relate the activity results to the MES data, it is seen that the CoMo/C catalysts are characterized by doublets with Q.S. $>$ 0.9 mm/s whereas the Co/C catalysts are characterized by doublets with Q.S. \approx 0.5 mm/s. So, the particle size of the 'Co-sulfide' species (where the particle size indicates the number of cobalt atoms that is associated with a 'Co-sulfide' particle) in the Co/C catalysts with extremely low cobalt-loadings is larger than in the CoMo/C catalysts, but nevertheless they exhibit the same intrinsic activity. This result is very interesting. It indicates that no clear relation exists between the intrinsic HDS activity and the particle size of the 'Co-sulfide' species. However, it might also indicate that the activity of the Co/C catalysts is not necessarily caused by the highly dispersed Co₉S₈-like cobalt species (Q.S. \approx 0.5 mm/s) but by the monatomically dispersed 'Co-sulfide' species exhibiting the doublet with Q.S. \approx 4 mm/s. It would be interesting to investigate this by an extensive thiophene HDS activity study. The aim of such a study should be to draw conclusions from *trends*, just as we did in the case of the MES and EXAFS investigations. To this end, a series of Co/C and CoMo/C catalysts with cobalt-loadings varying from 0.0001 wt.-% up to 10 wt.-% should be investigated. Whatever the outcome of this future study will be, it is already clear from the above findings that there is no general relation between the thiophene HDS activity and the amount of cobalt exhibiting a "Co-Mo-S" MES spectrum.

CONCLUSIONS

The behaviour of CoMo/C catalysts with very low cobalt loadings during step-wise sulfidation in H₂S/H₂ up to 673 K is, as far as can be verified by MES, in accordance with what was to be expected based on the trend observed

[1-3] and discussed [4] earlier for CoMo/C catalysts having a considerable higher cobalt-loading.

The behaviour of the Co/C catalysts with very low cobalt-loadings agrees only up to a sulfidation temperature of 473 K with the trend observed in the MES spectra of considerably higher loaded Co/C catalysts. After sulfidation up to 573 K, a rather well-defined very highly dispersed (most likely monatomically) 'Co-sulfide' species is observed which shows a doublet with the extremely large value $Q.S. = 4.11$ mm/s. In this species the cobalt atoms may be present in a square-planar or in a five-fold coordination. After sulfidation up to 673 K sintering occurred and a highly-dispersed 'Co-sulfide' species is formed as was previously found for Co/C catalysts with higher cobalt-loading. Thiophene HDS activity tests at 673 K, reveal that the intrinsic activity ($QTOF^{-1}$) of the cobalt in the Co/C catalysts with very low cobalt-loading equals that of cobalt in the "Co-Mo-S" phase. In addition, the catalysts in question do *not* exhibit the "Co-Mo-S" MES spectrum. This clearly shows that there is no general relation between the thiophene HDS activity and the amount of cobalt exhibiting a "Co-Mo-S" MES spectrum.

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