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SO-CALLED "Co-Mo-S" PHASE OBSERVED IN CARBON-SUPPORTED Co AND Co-Mo SULFIDE CATALYSTS BY MÖSSBAUER EMISSION SPECTROSCOPY

A.M. VAN DER KRAAN, M.W.J. CRAJÉ, E. GERKEMA, W.L.T.M. RAMSELAAR and V.H.J. DE BEER*

Interfacultair Reactor Instituut, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands

* *Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

In-situ Mössbauer Emission Spectroscopy (MES) has been used to study the type of phases present in sulfided activated carbon-supported Co and Co-Mo hydrodesulfurization (HDS) catalysts. Most of the reported MES studies are performed on Co-Mo/Al₂O₃ catalysts. Co species in the so-called "Co-Mo-S" phase, so far only observed in sulfided catalysts containing Co and Mo, should govern the HDS activity. The present observations show that the same Co species in sulfided Co/C and Co-Mo/C catalysts, with the same quadrupole splitting as "Co-Mo-S" can be formed. Furthermore, it turns out that the QS-value of the "active phase" in the sulfided Co/C and Co-Mo/C catalysts depends on the sulfiding temperature and Co content. Hence, it seems unlikely that there will be only one well defined active sulfide phase which governs the HDS activity.

1. INTRODUCTION

Hydrotreating catalysts are of great importance. These catalysts are used in the oil-refining industry for upgrading of fossil fuel fractions in the presence of hydrogen (5-15 MPa at 600-700 K). Several reactions take place simultaneously, such as removal of carbon-bonded impurities via so-called hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and hydrodemetallization (HDM) reactions, hydrogenation of olefinic and aromatic hydrocarbons as well as hydrocracking. At present, industrial hydrotreating catalysts consist of Mo or W sulfide promoted by Co or Ni dispersed on a high-surface area alumina-support. It is shown that the use of carbon instead of alumina as carrier material results in an improvement of the catalytic activity [1-6]. Vissers et al. [7] explained the higher activity of Mo/C compared to Mo/Al₂O₃ by differences in the structure of sulfide phases and differences in electron density around the transition metal ions present in these active phases. The latter explanation is in accordance with the results of a combined Mössbauer, HREM and HDS activity study by van Veen et al. [8] which strongly suggest the existence of a beneficial electronic effect in the case of carbon-supported Co-Mo sulfide catalysts. The role and the chemical state of the Co or Ni promoter ions in the promoted sulfide catalysts, is much debated [9-11].

Mössbauer spectroscopy is an excellent technique for in-situ investigation of catalysts, due to the high penetrating power of the γ -radiation applied and the sensitivity of the spectral parameters for chemical state and local environment of the Mössbauer atoms. As neither Co nor Mo contain Mössbauer isotopes it is not possible to apply the common Mössbauer absorption spectroscopy to Co-Mo sulfide catalysts. However, by doping Co-containing catalysts with radioactive ⁵⁷Co, they can be used as sources in Mössbauer Emission Spectroscopy (MES).

Clausen et al. [12] were the first to study the nature of the cobalt phases present in a working Co-Mo HDS catalyst by means of MES. Later, Topsøe et al. [13,14] and Mørup et al. [15] showed that Co may be present in several different types of phases and it was observed that the HDS activity was almost completely governed by the presence of the so-called "Co-Mo-S" phase [16]. This "Co-Mo-S" phase was defined by its Isomer Shift and Quadrupole Splitting which did not match those of any known Co sulfide and Co molybdenum sulfide compound. It was only

observed in the presence of Co, Mo and S and was found to consist of Co ions at the edges of MoS₂ crystallites [10,17,18].

Recently we have briefly reported [19] that the room temperature Mössbauer spectra of Co(0.04)/C sulfided at 473 K and Co(0.04)-Mo(6.84)/C sulfided at 673 K both exclusively consist of an identical quadrupole doublet, which doublet is similar to the doublet ascribed by Topsøe et al. [14] to the so-called "Co-Mo-S" phase. In the present paper we present more detailed information about our MES study on sulfided Co/C and Co-Mo/C catalysts. The thermal stability of the sulfide phases formed has been investigated by applying a stepwise sulfidation procedure to the samples and furthermore we have varied the Co content.

2. EXPERIMENTAL

The carbon carrier used was a Norit (RX3-Extra) activated carbon with a surface area of 1190 m²/g and a pore volume of 1.0 cm³/g. The Co/C catalysts were prepared by pore volume impregnation of the carrier with aqueous solutions of Co(NO₃)₂·6H₂O (Merck "for analysis"), to which a solution of ⁵⁷Co nitrate (ex Amersham) was added. Co-Mo/C catalysts were prepared by a two step pore volume impregnation procedure. The Mo-phase was introduced first by impregnation with an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O (Merck, min 99.9%) followed by an intermediate drying in static air at 383 K for 16 h and the introduction of Co as described above. After Co introduction the catalyst samples were dried in ambient air at 293 K for 16 h.

Precursor catalyst compositions (without ⁵⁷Co) were determined by means of atomic absorption spectroscopy using a Perkin-Elmer 300 AAS spectrometer. The catalysts are denoted as Co(x)/C or Co(x)-Mo(6.84)/C with x and 6.84 representing the wt% Co and Mo respectively. Prior to the sulfidation, the samples were subjected to an additional drying treatment in a H₂-flow (flow rate 50 cm³/min) and kept under an H₂ atmosphere. During this treatment the sample is kept at 313, 353 and 393 K for 24 h at each temperature.

Sulfidation of the catalysts was carried out in a Mössbauer in-situ reactor, which has been described elsewhere [20]. However, the heating section as well as the outer container used in this study are made of stainless steel, while the mylar windows are replaced by beryllium windows, vacuum brazed on the outer container. Sulfiding was carried out in a 10 mol% H₂S in H₂-gas mixture at a flow rate of 60 cm³/min. During the sulfiding procedure the following temperature program was sequentially applied: linear increase to the desired maximum sulfidation temperature in 1 h, holding at this temperature for 1 h and cooling in the H₂S/H₂ flow to 293 K.

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 K₄Fe(CN)₆·3H₂O enriched in ⁵⁷Fe. The spectrometer was placed in a vertical position, so that the catalysts which had been prepared as extrudates, could be measured as such. Isomer shifts are reported relative to a source of ⁵⁷Co in Rh, while positive velocities correspond to the absorber moving away from the source. The velocity scale was calibrated by the Mössbauer spectrum of sodium nitroprusside (SNP) obtained with the ⁵⁷Co in Rh source. Mössbauer spectra were fitted by computer with calculated subspectra consisting of Lorentzian-shaped lines, by varying the Mössbauer parameters in a non-linear, iterative minimization routine. In the case of quadrupole doublets the line widths and the absorption areas of the constituent peaks were constrained to be equal.

3. RESULTS

In the preparation process of HDS catalysts, sulfidation of the oxidic precursors is a crucial step because it results in the formation of the actual active catalyst. From our extensive Mössbauer absorption spectroscopic study of activated carbon-supported Fe-Mo catalysts [21,22] it followed that the sulfidic catalyst structure is influenced by the sulfidation procedure. When during the 1 h sulfiding procedure, the catalyst precursor is heated from room temperature to 673

K instead of 623 K, a large amount of Fe_{1-x}S is observed while a decrease in the activity for thiophene HDS is measured. Therefore, we have studied the sulfidation of the activated carbon-supported Co and Co-Mo catalysts in a stepwise manner. First a MES spectrum was recorded at 293 K while the sample was kept in static $\text{H}_2\text{S}/\text{H}_2$ at atmospheric pressure. Next, the same sample was subjected to various successive sulfidation treatments as described in the section Experimental.

3.1 $\text{Co}(x)\text{-Mo}(6.84)/\text{C}$ catalysts

In Figure 1 the room temperature Mössbauer spectra of the $\text{Co}(0.04)\text{-Mo}(6.84)/\text{C}$ and $\text{Co}(2.25)\text{-Mo}(6.84)/\text{C}$ catalysts are presented after the successive $\text{H}_2\text{S}/\text{H}_2$ -treatments together with those of the catalyst precursors after the drying treatment in a H_2 -flow. These last spectra are analyzed with two quadrupole doublets. One doublet ascribed to high-spin Fe^{2+} and one doublet belonging to Fe^{3+} species (after electron capture). The results of computer analyses of the spectra are given in Table 1.

Fig.1. In-situ Mössbauer emission spectra of sulfided $\text{Co}(0.04)\text{-Mo}(6.84)/\text{C}$ and $\text{Co}(2.25)\text{-Mo}(6.84)/\text{C}$ catalysts at 293 K after various successive sulfidation treatments in a $\text{H}_2\text{S}/\text{H}_2$ gas mixture.

It is clear from Figure 1 that the spectra of the catalyst precursors already changed after they were exposed to the $\text{H}_2\text{S}/\text{H}_2$ gas mixture at room temperature. At increasing sulfidation temperature, the spectral contributions of the high-spin Fe^{2+} -phases decreased and finally disappeared while roughly speaking one new quadrupole doublet appears in the spectra. Although the computer fits were improved by using two doublets instead of one, in Table 1 only the numerical

Table 1.

Mössbauer parameters obtained at 293 K of Co/C and Co-Mo/C catalysts after various successive treatments in $\text{H}_2\text{S}/\text{H}_2$ gas mixture. Experimental uncertainties: IS: 0.03 mm/s, QS: 0.05 mm/s, A: 5%. The QS-value of Co_9S_8 is constrained to 0.26 mm/s.

Treatment	Fe^{3+} *			Fe^{2+} *			"active phases"			Co_9S_8		
	IS	QS	A	IS	QS	A	IS	QS	A	IS	QS	A
	(mm/s)		(%)	(mm/s)		(%)	(mm/s)		(%)	(mm/s)		(%)
Co(0.04)-Mo(6.84)/C												
[393 K, H_2]	0.24	0.85	63	0.86	1.92	37						
[293 K, H_2S]				0.75	2.28	30	0.32	1.19	70			
[373 K, H_2S]												
[473 K, H_2S]							0.32	1.20	100			
[573 K, H_2S]							0.23	1.11	100			
[673 K, H_2S]							0.22	1.30	100			
Co(2.25)-Mo(6.84)/C												
[393 K, H_2]	0.30	0.95	71	0.89	2.09	29						
[293 K, H_2S]				0.89	2.09	11	0.20	1.22	89			
[373 K, H_2S]							0.24	1.20	100			
[473 K, H_2S]							0.25	0.90	100			
[573 K, H_2S]							0.22	0.85	100			
[673 K, H_2S]							0.21	0.87	100			
Co(0.04)/C												
[393 K, H_2]	0.32	0.80	72	0.79	1.85	28						
[293 K, H_2S]	0.30	0.85	26	0.99	2.01	74						
[373 K, H_2S]				0.98	2.08	71	0.20	1.35	29			
[473 K, H_2S]							0.20	1.35	100			
[573 K, H_2S]							0.23	0.65	74	0.22	0.26	26
[673 K, H_2S]							0.22	0.76	83	0.23	0.26	17
Co(2.45)/C												
[393 K, H_2]	0.34	1.02	64	0.75	2.44	36						
[293 K, H_2S]				0.64	2.58	10	0.24	1.18	90			
[373 K, H_2S]							0.20	1.18	100			
[473 K, H_2S]							0.23	0.79	82	0.23	0.26	18
[573 K, H_2S]							0.25	0.73	53	0.23	0.26	47
[673 K, H_2S]							0.26	0.73	50	0.23	0.26	50

* ^{57}Fe atoms produced by the decay of ^{57}Co . However, in MES experiments the observed valence and spin states of ^{57}Fe may be different from those of the parent ^{57}Co atoms.

results of the analyses with one doublet are presented. The sulfiding temperature at which the transition of the catalyst precursor into the active sulfide phase took place was found to decrease with increasing cobalt content. Furthermore, for the Co(0.04)-Mo(6.84)/C sample the value of the quadrupole splitting of the newly formed Co species is increasing with increasing sulfidation temperature, while for Co(2.25)-Mo(6.84)/C the observed quadrupole splitting is decreasing with increasing sulfidation temperature.

After the catalyst samples sulfided at 673 K were measured by MES they were first exposed to Ar and then to air at room temperature. It was observed that the sulfidic phase formed in the Co(0.04)-Mo(6.84)/C is very stable upon exposure to air at room temperature while this is not the case for the catalyst with the relatively high cobalt content Co(2.25)-Mo(6.84)/C.

3.2 Co(x)/C catalysts

Figure 2 shows the room temperature Mössbauer spectra of the Co(0.04)/C and Co(2.45)/C catalysts after the successive H₂S/H₂-treatments together with the spectra of the catalyst precursors which were subjected to the drying treatment in flowing hydrogen. Also for these catalysts we have analyzed the spectra of the precursors with two quadrupole doublets. One doublet due to high-spin Fe²⁺ and one doublet belonging to Fe³⁺ species respectively. The results of computer analyses of the spectra are also given in Table 1.

As soon as the H₂-flow treated catalyst precursors are exposed at room temperature to the sulfiding H₂S/H₂ gas mixture, the spectra are changed (see Figure 2). In the case of Co(0.04)/C mainly a high-spin Fe²⁺ spectral component is formed, which is still present after the sulfidation treatment at 373 K. Sulfiding at higher temperatures causes the spectrum to change drastically. As reported before [19], after the sulfidation treatment at 473 K the spectrum consists exclusively of a quadrupole doublet, with Mössbauer parameters (IS and QS) identical to those of the doublet observed for Co(0.04)-Mo(6.84)/C sulfided at 673 K (see Table 1). This measured quadrupole doublet is similar to the one which is ascribed by Topsøe et al. [14] to the "Co-Mo-S" phase.

However, it turned out that this particular Co species is not stable at sulfiding temperatures of 573 K and higher (see Figure 2). For the Co(2.45)/C catalyst the high-spin Fe²⁺ spectral component is hardly observable after sulfidation at room temperature. The spectrum consists mainly of a newly formed quadrupole doublet, which is still present after sulfidation at 373 K. As shown in Table 1, this doublet is also observed in the spectra of the Co(2.25)-Mo(6.84)/C catalyst sulfided at room temperature and 373 K. The Mössbauer parameters of the observed doublet are also in the range given by Topsøe et al. [17] for the "Co-Mo-S" phase. As is shown in Figure 2, increasing of the sulfiding temperature caused a drastic change of the spectrum. These spectra are analyzed by one free quadrupole doublet and one doublet with a quadrupole splitting constrained to 0.26 mm/s. The latter splitting can be considered as a good simulation of the spectrum of Co₉S₈. The deduced numerical values are summarized in Table 1.

4. DISCUSSION

In spite of numerous studies devoted to hydrodesulfurization catalysts, it has been difficult to obtain detailed structural information on the promoter phase. Efforts aiming at the clarification of the structure and the related HDS activity of these complex catalyst systems resulted in different structural models in which especially the role and chemical state of the Co or Ni promoter ions in the sulfided catalysts remained much debated [9-11]. It is largely due to recent Mössbauer Emission Spectroscopy studies by the Topsøe group that a quantitative picture of the structure of cobalt in HDS catalysts has emerged [14,16-18]. So far, most of the reported MES studies are performed on Co-Mo/Al₂O₃ catalysts and only a few are concerning to Co/C and Co-Mo/C [13,17,23]. Topsøe and coworkers showed that the cobalt atoms are situated at MoS₂ crystallite edges in the "Co-Mo-S" structure and that the amount of this Co-phase in the MES spectrum governed almost completely the HDS activity. The Co species in "Co-Mo-S" phase are defined by a

Fig.2. In-situ Mössbauer emission spectra of sulfided Co(0.04)/C and Co(2.45)/C catalysts at 293 K after various successive sulfidation treatments in a $\text{H}_2\text{S}/\text{H}_2$ gas mixture.

MES spectrum, consisting of a quadrupole doublet ($QS=1.0-1.3$ mm/s) which is so far only observed in sulfided catalysts containing both Co and Mo.

However, we have shown recently that an identical quadrupole doublet can be observed in the MES spectra recorded for sulfided Co(0.04)/C and Co(0.04)-Mo(6.84)/C catalysts, and that this doublet is similar to the one ascribed by Topsøe et al. [14] to the "Co-Mo-S" phase (see also the Figures 1 and 2). This result proves that the definition of the "Co-Mo-S" phase by its Mössbauer parameters is not unequivocally. The formation of a Co species like the one present in the so-called "Co-Mo-S" phase does not necessarily require the presence of MoS_2 .

Although in sulfided Co/C and Co-Mo/C catalysts the same Co species can be formed, it follows from comparison of the spectra in Figures 1 and 2 that in the case of Co/C catalysts this particular Co species is not stable at increasing sulfiding temperature. After the sulfiding at 673 K, the temperature at which thiophene HDS-activity tests are often performed, differences in the spectra of Co/C and Co-Mo/C catalysts are observed. Visser et al. [24] observed an activity

for optimally dispersed pure cobalt sulfide supported on activated carbon which was nearly as high as that of a Co-Mo/C catalyst. Based on this finding they concluded that the activity of sulfided Co-Mo/C catalysts is most likely completely due to the cobalt sites and suggested that the role of MoS₂ in these catalysts is mainly to function as a support for optimally dispersed cobalt ions. Our results will be in agreement with the conclusions of Visser et al. [24] when the quadrupole splitting of the "active phase" decreases upon sintering of this phase.

Our findings that the QS-value of the doublet in the spectra of Co-Mo/C catalysts depends on the applied sulfiding temperature as well as the Co content support such an effect. For Co(2.25)-Mo(6.84)/C the QS-value changes from 1.20 mm/s (sulfidation at 373 K) to 0.87 mm/s (sulfidation at 673 K) which value is significantly smaller than reported by Topsøe et al. [17] for "Co-Mo-S". The observed decrease in the QS-value for Co(2.45)/C is even larger. However the QS-values remain much larger than the values reported for Co₉S₈ (IS=0.22 mm/s, QS=0.26 mm/s), CoS₂ (IS=0.23 mm/s, QS=0.32 mm/s) and Co₃S₄ (IS=0.17 mm/s, QS=0.18 mm/s), while the observed IS-values exclude an assignment to bulk CoS_{1+x} (IS₁=0.35 mm/s, QS₁=0.29 mm/s; IS₂=0.38 mm/s, QS₂=0.67 mm/s) [14].

The sulfided Co species in the spectrum of Co(0.04)-Mo(6.84)/C catalysts after sulfidation at 673 K has the largest QS-value (QS=1.30 mm/s). It is interesting to notice that this particular sulfided Co species is highly stable upon exposure to air at room temperature, which is not the case for the sulfided Co species in the Co(2.25)-Mo(6.84)/C catalysts with a QS=0.87 mm/s.

So, it seems that in both Co/C and Co-Mo/C catalysts the same Co species is formed at relatively low sulfiding temperatures and that the Co species gradually changes at increasing sulfiding temperatures. Such a change is more pronounced for the Co/C, in which also Co₉S₈ is formed, than for the Co-Mo/C catalysts. In this respect it is important to mention also the results recently obtained by Bouwens et al. [25] via characterization of a Co(4.1)/C and Co(1.5)-Mo(7.7)/C catalyst by means of EXAFS and XANES. They found that as a result of sulfidation similar Co-phases are formed in these catalysts i.e. in both cases a high sulfur coordination of the Co atoms was observed.

Recently in our institute Ramselaar [22] and Ramselaar et al. [26] have also found indications that in sulfided Fe and Fe-Mo catalysts supported on alumina as well as activated carbon, Fe species are formed with Mössbauer parameters ascribed to the so-called "Fe-Mo-S" phase. Therefore we have started a detailed comparative Mössbauer study between sulfided Fe (Fe-Mo) and Co (Co-Mo) catalysts supported on activated carbon as well as alumina.

5. CONCLUDING REMARKS

It has clearly been shown that due to the applied stepwise sulfidation procedure it was possible to observe the same Co species in sulfided Co/C and Co-Mo/C catalysts. This Co species has the same quadrupole splitting as the "Co-Mo-S" phase described by Topsøe et al. [14]. From the fundamental point of view this implies that this Co species should not be referred to as "Co-Mo-S".

It turns out that the QS-value of the active Co "phase" formed in the sulfided Co/C and Co-Mo/C catalysts depends on the sulfiding temperature and Co content. Hence, it seems unlikely that there will be only one well defined active sulfide phase (with specific spectral characteristics) which governs the HDS activity or the QS-value of the "active phase" decreases upon sintering.

Finally, Co ions diffuse not into the carbon support as in the case of an alumina support. The high-spin Fe²⁺-phase in the alumina-supported catalysts which can not be sulfided, and the possibly accompanying high-spin Fe³⁺-aliovalent species [27], are absent in the carbon-supported ones. Therefore the MES spectra of the sulfided carbon-supported catalysts are less complex. So, characterization of carbon-supported Co sulfide and Co-Mo sulfide catalysts by means of the ⁵⁷Co-MES technique is a very promising approach in studies on the role of Co in commercial Co-Mo sulfide catalysts.

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