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Hydrodesulfurization Catalysts Prepared from $X(MS_4)_2^{2-}$ Thioheteroanions Containing Ni or Co and Mo or W: Correlation of ESR Signal Intensity with Thiophene Conversion

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Hydrodesulfurization catalysts were prepared by impregnating silica and alumina with aqueous solutions of thioheteroanion complexes containing Ni or Co and Mo or W. Their catalytic activities are comparable to those of conventionally prepared catalysts and the ESR spectra are also very similar. Under H_2S/H_2 atmosphere the thioheteroanions transform into metal sulfides. Combining the results obtained with catalysts prepared via the new method with those of conventionally prepared catalysts, a larger spread in catalytic activities for thiophene hydrodesulfurization and ESR signal intensities was obtained than for conventional catalysts only. As a result a correlation could be established between the intensity of the ESR signal from Mo^{3+} and W^{3+}, in interaction with nickel or cobalt promoter ions at the surface of MoS_2 or WS_2 crystallites, and the catalytic activity for thiophene hydrodesulfurization.

INTRODUCTION

Commercial hydrodesulfurization catalysts such as Co–Mo, Ni–Mo, and Ni–W supported on alumina are usually delivered by the manufacturers in the oxidic state. Upon use they become sulfidic to a certain degree. Although in the past models have been proposed that attribute the catalytic activity of these catalysts to molybdenum or tungsten cations surrounded by oxygen as well as sulfur anions (*1*, *2*), it is widely accepted now that the catalytic activity resides in the Mo or W ions at the surface of a MoS_2 or WS_2 phase. The nature of the promoter action by nickel or cobalt is still not well understood, albeit that, in several models (*3*, *4*), close contact between active phase and promoter is regarded as essential. It is further known that during catalyst preparation the formation of bulk $CoMoO_4$ and of corresponding nickel- or tungsten-containing compounds has to be avoided since these compounds exhibit low hydrodesulfurization (HDS) activity and are difficult to sulfide (*1*).

Guided by these ideas we have undertaken a study of unconventional HDS catalysts, prepared by impregnating alumina and silica with aqueous solutions of thiocomplexes containing Ni or Co and Mo or W. The conditions under which such catalysts are prepared promote close contact between Mo (W) and Co (Ni), decrease the interaction between support and transition metal ions, and prevent the formation of mixed oxides like $CoMoO_4$. The preparation of thioanions of the form $[X(MS_4)_2]^{2-}$ (X = Ni, Co; M = Mo, W) has been described by Müller *et al.* (*5*, *6*). The molar ratio $X/M = 0.5$ is within the range used for commercial catalysts.

With these catalysts we have tested the hypothesis that the catalytic active phase is MoS_2 (WS_2) and that intimate contact between active phase and promoter is necessary. Catalytic testing has been done by means of thiophene hydrodesulfurization

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measurements at atmospheric pressure while physical characterization has been performed by ESR measurements. The results are compared with those obtained for catalysts prepared in the conventional oxidic way as reported earlier (*7*).

EXPERIMENTAL

Catalyst Preparation

All starting materials were free from interfering paramagnetic impurities. The support materials were taken from the same batches as used in previous studies (*7*, *8*): Ketjen F-2 silica, with surface area and pore volume being 400 $m^2\ g^{-1}$ and 1.1 $cm^3\ g^{-1}$, respectively, and γ-Al_2O_3 prepared from boehmite (Martinswerk RH6) by calcination at 873 K for 2 h resulting in a surface area of 215 $m^2\ g^{-1}$ and pore volume of 0.35 $cm^3\ g^{-1}$. Aqueous solutions of the thioheteroanion complexes were made by the addition of a nickel nitrate or cobalt nitrate solution to an ammonium tetrathiotungstate or -molybdate solution (*5*, *6*). The support material was added to this solution. Excess water was evaporated at 313 K in a rotating film evaporator. The remaining slurry was dried for 16 h at 383 K in air.

In the following sections the catalyst loadings with Ni (Co) and/or Mo (W) will be indicated by numbers in parentheses. In order to facilitate a comparison with catalysts prepared via a conventional oxidic route, the loadings are calculated on the basis of hypothetical NiO, CoO, MoO_3, and WO_3 weight percentages, respectively.

Sulfiding Procedures and Activity Measurements

Although the catalysts are prepared in a sulfidic form, reoxidation, at least of the surface, due to exposure to air, cannot be excluded. The samples are therefore sulfided before use. For the ESR measurements the sulfidation was carried out in a special reactor (*8*) to preclude subsequent contact with air. Two hundred milligrams of catalyst was sulfided in $H_2S/H_2 = 1/6$, at a flow rate of 50 $cm^3\ min^{-1}$, using the following temperature program: 10 min at 295 K, a linear increase to 673 K in 260 min, 20 h at 673 K, and quenching to 295 K. Prior to thiophene HDS activity measurements the 200-mg catalyst samples were sulfided in the flow microreactor using the same gas mixture and flow rate as mentioned above. The temperature program applied was: 10 min at 295 K, an increase to 673 K in 1 h, and 2 h at 673 K. Then the gas flow was changed to hydrogen containing 7% v/v thiophene, with the flow rate being 50 $cm^3\ min^{-1}$.

Thiophene conversion experiments were performed at atmospheric pressure and 673 K in a continuous-flow reactor (*9*) with 200 mg catalyst. The reaction rates were calculated on the basis of pseudo-first-order reaction in thiophene. The activity data used were obtained from catalysts that had been stabilized for 2 h.

ESR Measurements

ESR measurements were performed with a Varian E-15 spectrometer, equipped with a TE 104 dual-sample cavity and a liquid helium continuous-flow cryostat (Oxford Instruments). Thus a Varian strong-pitch sample ($g = 2.0028$, 3×10^{15} spins cm^{-1}) could be used to calibrate the magnetic field and to standardize the quality factor of the ESR cavity. The sample temperature could be varied in the range 4–300 K.

RESULTS

ESR Measurements

The results of the ESR measurements are presented in Table 1 and Figs. 1 and 2. Note that catalysts prepared via the conventional oxidic route are marked with (C). The total number of spins (TNS) of the signals from the sulfidic phase (signals II–VI) per gram of catalyst, is calculated as described earlier (*7*). The relative intensity of the signals in each spectrum is indicated in Table 1. The spectra given in the figures are measured at 20 K and the signals are indicated by arrows at the approximate position of

TABLE 1

Catalyst Composition, Total Number of Spins (TNS), Relative Signal Intensities, and Thiophene HDS Reaction Rate

Catalyst composition[a]	TNS $\times 10^{-18}$ (g^{-1})	Signal						r_{HDS} $\times 10^3$ (mol h^{-1} g^{-1})
		I	II	III	IV	V	VI	
W(17.6)/γ-Al_2O_3	0.9	—	W	—	—/VW	S	—	1.1
Ni(2.7)–W(16.9)/γ-Al_2O_3	1.3	—	—	—	—	W	VS	28.6
Ni(3.5)–W(16.7)/γ-Al_2O_3	1.5	—	—	—	—	W	VS	31.2
Co(2.7)–W(16.9)/γ-Al_2O_3	1.1	—	—	—	—	W	VS	14.8
Ni(2.7)–Mo(10.5)/γ-Al_2O_3	1.0	W	—	—	—	—	VS	18.0
Co(2.7)–Mo(10.5)/γ-Al_2O_3	—	S	W	—	—	W	VS	12.4
W(17.6)/SiO_2	1.5	—	S	—	VW	S	—	4.7
Ni(2.7)–W(16.9)/SiO_2	0.9	—	VW	—	—	W	VS	40.1
Ni(3.5)–W(16.7)/SiO_2	0.6	—	W	—	—	S	S	18.7
Co(2.8)–W(16.9)/SiO_2	0.7	—	W	—	—	S	S	12.4
Ni(2.7)–Mo(10.5)/SiO_2	0.4	—	—	—	—	—/VW	VS	6.8
Co(2.7)–Mo(10.5)/SiO_2	1.3	—	—	—	—	S	S	11.2
W(19.3)/γ-Al_2O_3 (C)	2.9	—	VS	—/VW	—/VW	S	—	2.8
W(19.3)/SiO_2 (C)	0.8	—	S	—	VW	S	—	3.8
Ni(0.4)–W(19.3)/SiO_2 (C)	0.8	—	W	—/VW	—/VW	S	W/S	18.0
Ni(4)–W(19.3)/SiO_2 (C)	0.5	—	—	—	—	W	VS	25.3
Mo(12)/γ-Al_2O_3 (C)	4.4	S	VS	—/VW	—/VW	S	—	8.4
Mo(12)/SiO_2 (C)	5.4	VW	VS	—/VW	—/VW	VS	—	8.9
Ni(4)–Mo(12)/γ-Al_2O_3 (C)	4.5	S	—	—	—	W	VS	30.3
Ni(4)–Mo(12)/SiO_2 (C)	3.5	S	VW	—	—	S	S	35.9
Co(4)–Mo(12)/SiO_2 (C)	3.5	S	W	—	—	S	S	29.4

Note. — = not observable; W = weak; VW = very weak; S = strong; and VS = very strong.

[a] The numbers in parentheses indicate weight percentage NiO, CoO, MoO_3, or WO_3. Conventionally prepared catalysts are marked with (C).

their low-field peaks which are found to be better resolved than the high-field peaks (*7*, *8*). Only those signals clearly observable are indicated.

Tungsten-containing catalysts. In Fig. 1 the spectra of: (a) W(17.6)/SiO_2; (b) W(19.3)/SiO_2 (C); (c) W(17.6)/γ-Al_2O_3; and (d) W(19.3)/γ-Al_2O_3 (C) are given. The TNS for these catalysts are 1.5, 0.8, 0.9, and 2.9 $\times 10^{18}$ spins g^{-1}, respectively.

Figure 1 shows that there is not much difference between the ESR spectra of the unpromoted catalysts prepared via the conventional or the unconventional method. The only differences seem to be that spectrum c contains less signal II than spectrum d, and that the differences in TNS between alumina- and silica-supported catalysts prepared from tetrathiomolybdate or -tungstate, are opposite to those of the conventionally prepared samples.

For the promoted tungsten-on-alumina samples the spectra are similar to those of the corresponding conventional catalysts (showing mainly signal VI), except for the TNS which is two to three times higher in the case of the conventionally prepared ones. Besides signals VI and V, spectra of the promoted tungsten-on-silica catalysts also contain signal II and they resemble more the spectra obtained from Ni (Co) (0.4)–W(19.3)/SiO_2 (C) (*7*). Their TNS values are comparable with those calculated for catalysts prepared via an oxidic route using the double-sulfiding procedure to prevent formation of $NiWO_4$ or $CoWO_4$ on silica (*7*).

Molybdenum-containing catalysts. In

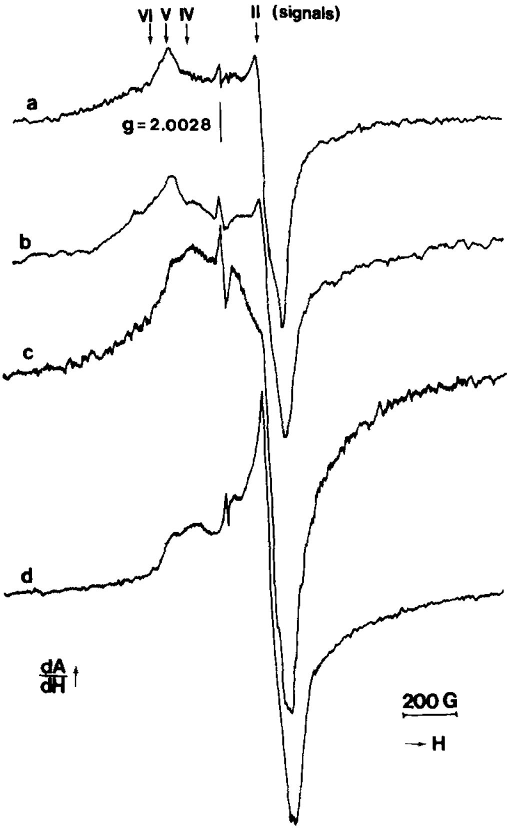

FIG. 1. ESR spectra of unpromoted tungsten catalysts (recorded at 20 K): (a) W(17.6)/SiO_2, sulfidic route, receiver gain (*R.G.*) = 2 × 10^3; (b) W(19.3)/SiO_2 (C), oxidic route, *R.G.* = 5 × 10^3; (c) W(17.6)/γ-Al_2O_3, sulfidic route, *R.G.* = 4 × 10^3; (d) W(19.3)/γ-Al_2O_3 (C), oxidic route, *R.G.* = 1 × 10^3.

Fig. 2 the spectra of: (a) Ni(2.7)–Mo(10.5)/γ-Al_2O_3; (b) Ni(4)–Mo(12)/γ-Al_2O_3 (C); (c) Co(2.7)–Mo(10.5)/γ-Al_2O_3; (d) Ni(2.7)–Mo(10.5)/SiO_2; and (e) Co(2.7)–Mo(10.5)/SiO_2 are shown. The spectra of the nickel-promoted catalysts consist mainly of signal VI with the addition of signal I in the alumina-supported samples. In spectra of the cobalt-promoted catalysts, however, also a strong contribution of signal V is observable, and the γ-Al_2O_3-supported catalyst also shows a signal due to Co^{2+} in the alumina. As a consequence no TNS could be calculated for the latter sample. The TNS values are three to nine times lower than

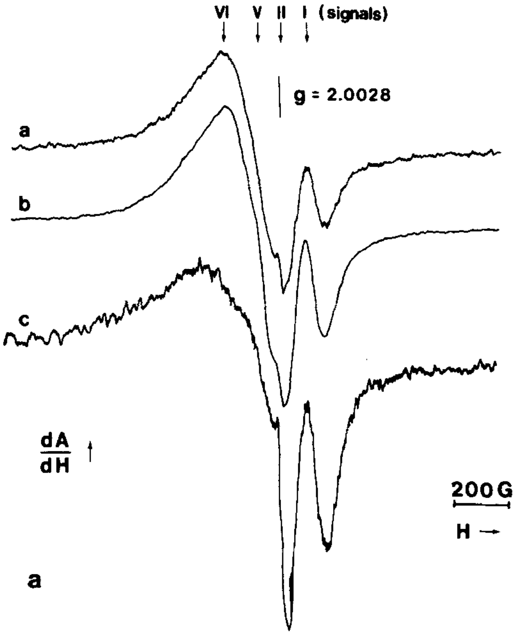

FIG. 2a. ESR spectra of promoted molybdenum-on-alumina catalysts (recorded at 20 K): (a) Ni(2.7)–Mo(10.5)/γ-Al_2O_3, sulfidic route, *R.G.* = 2 × 10^3; (b) Ni(4)–Mo(12)/γ-Al_2O_3 (C), oxidic route, *R.G.* = 5 × 10^2; (c) Co(2.7)–Mo(10.5)/γ-Al_2O_3, sulfidic route, *R.G.* = 4 × 10^3.

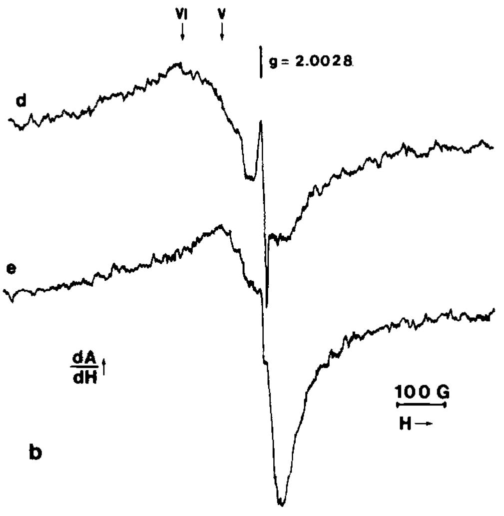

FIG. 2b. ESR spectra of promoted molybdenum-on-silica catalysts (recorded at 20 K): (d) Ni(2.7)–Mo(10.5)/SiO_2, sulfidic route, *R.G.* = 8 × 10^3; (e) Co(2.7)–Mo(10.5)/SiO_2, sulfidic route, *R.G.* = 4 × 10^3.

those of catalysts prepared in the conventional oxidic way.

HDS Activity Measurements

The results of thiophene HDS activity measurements are presented in Table 1. It is clear that the reaction rates of tungsten-containing catalysts are not greatly affected by the preparation method chosen. In the case of molybdenum-based catalysts, however, the conventional preparation method leads to reaction rates that are 1.5–5.0 times higher than those from preparation via heterothioanions.

DISCUSSION

Our results demonstrate that hydrodesulfurization catalysts of the type Ni (Co)–W (Mo)/γ-Al_2O_3 (SiO_2) can be prepared directly from sulfidic precursors. They have catalytic properties comparable to those of catalysts prepared via the conventional oxidic route and also the ESR spectra of both catalyst types are very similar: the same signals are present as in the spectra of conventionally prepared samples, the intensities, however, differ and thus appear to be sensitive to the preparation method. The presence of signal I (oxo-Mo^{5+}) in molybdenum-on-alumina catalysts prepared via the sulfidic route indicates that during preparation the molybdenum complex interacts with the alumina.

Signal I is absent in tungsten-on-alumina catalysts, most probably because those oxo-W^{6+} species that resist sulfidation are also hardly reducible to W^{5+} (*10, 11*).

The differences in TNS between conventionally and unconventionally prepared catalysts indicate that factors other than the interaction with the support are also important. Probably the dispersion of the transition metal compounds is different in both cases as a result of which the number of disulfide growth nuclei is different.

A correlation between the thiophene HDS activity and the intensity of signal VI was suggested earlier (*7*). For tungsten-containing catalysts the strong overlap of signals VI and V circumvented the unequivocal establishment of such a correlation. For molybdenum-containing catalysts, however, these signals are better separated and the intensity of signal VI can be estimated reasonably well. For instance, the intensity of signal VI in the spectrum of Ni(2.7)–Mo(10.5)/γ-Al_2O_3 (Fig. 2a, spectrum a) represents almost 100% of the TNS. For Ni(4)–Mo(12)/SiO_2 (C) (Fig. 1c in Ref. (*7*)) signals V and VI are the main contributors to the TNS. Assuming Gaussian lineshapes for both signals, the TNS consists of about 75% of signal VI. All other spectra are analyzed in the same way. In Fig. 3 the estimated intensity of signal VI is plotted versus the thiophene HDS reaction rate for several molybdenum-containing catalysts. In spite of considerable scatter it appears that there is a definite correlation between the intensity of signal VI and the thiophene hydrodesulfurization reaction rate.

Figure 3 also shows the same plot (intensity of signal VI versus r_{HDS}) for tungsten-containing samples. Although it is now harder to estimate intensities of signal VI, it appears that again a correlation with the HDS activity exists. For catalysts prepared along the conventional oxidic route the spread in catalytic activities for thiophene HDS and intensities of ESR signals VI was not large enough to establish a correlation between these two phenomena. It is only when the results from conventionally prepared catalysts are combined with those from catalysts prepared according to the new method described above that such a correlation could be perceived. This is because of the larger spread in activities and intensities so obtained.

Voorhoeve (*12*) reported a correlation between the intensity of an ESR signal in Ni–W–S systems and the benzene hydrogenation rate constant. Most probably this signal is identical to signal VI described in the present study although we have mentioned earlier (*7*) that several of Voorhoeve's experimental results concern-

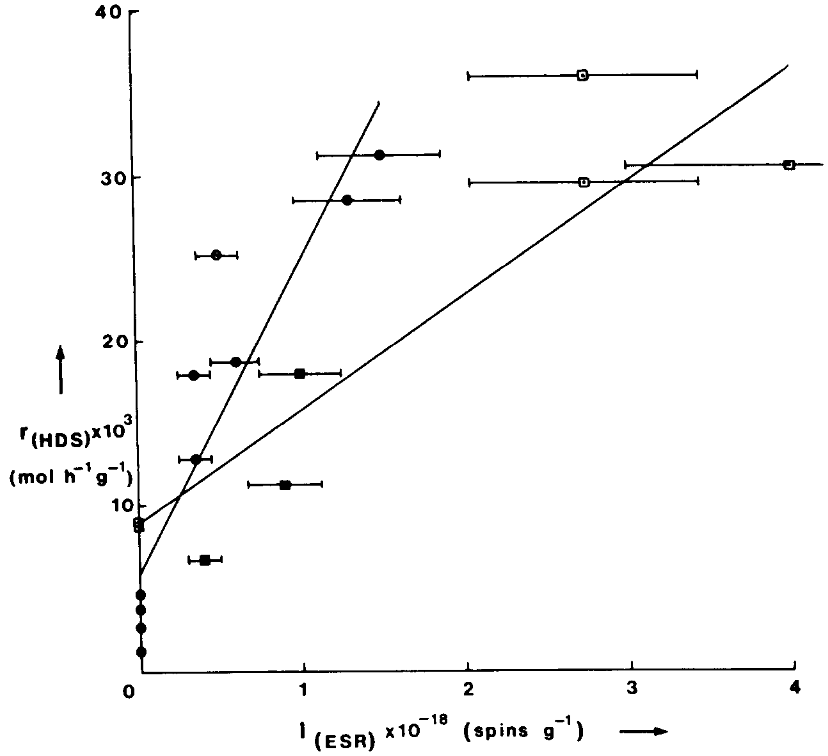

FIG. 3. Thiophene reaction rate versus ESR signal VI intensity for molybdenum-containing catalysts (□, conventionally prepared; ■, sulfidic route), and for tungsten-containing catalysts (○, conventionally prepared; ●, sulfidic route).

ing the intensity of this signal could not be reproduced.

Our results show that catalysts prepared from thioheteroanion complexes are generally less active for thiophene HDS than conventionally prepared catalysts. The influence of the "slurry" method versus the impregnation method on the dispersion of the sulfide phase is unknown, however, and the method has not been perfected yet.

The similarity in catalytic and paramagnetic properties between catalysts prepared via an oxidic route and those prepared using thio compounds, leads to the conclusion that in both cases the MoS_2 or WS_2 phase is the stable form of the molybdenum and tungsten atoms under hydrodesulfurization conditions as is also expected on thermodynamic grounds. It seems worthwhile to try to optimize the new preparation method, because the fact that it does not require a calcination step may minimize the loss of Co (Ni) and Mo (W) ions in the support material. The relatively low intensity of the signal originating from Co^{2+} in alumina for Co(2.7)-W(16.9)/γ-Al_2O_3 and Co(2.7)-Mo(10.5)/γ-Al_2O_3 indicates that cobalt has hardly been able to interact with the alumina. The same holds for molybdenum since the intensity of signal I (oxo-Mo^{5+}) in Ni(2.7)-Mo(10.5)/γ-Al_2O_3 is about five times weaker than in Ni(4)-Mo(12)/γ-Al_2O_3 (C). These observations strongly indicate that indeed less transition metal ions are lost in the carrier when catalysts are prepared according to the new method.

The main conclusion from the present study is that there exists a correlation between the intensity of an ESR signal, viz., signal VI arising from Mo^{3+} or W^{3+} in interaction with promoter ions at the surface of MoS_2 or WS_2 crystallites, and the thiophene hydrodesulfurization reaction rate for promoted molybdenum- or tungsten-containing catalysts.

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