

SULFIDED SUPPORTED TUNGSTEN AND MOLYBDENUM CATALYSTS  
PROMOTED BY NICKEL OR COBALT. AN ESR STUDY

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The ESR signals related with the sulfide phase present in  $W(Mo)/SiO_2(\gamma-Al_2O_3)$  are found to disappear as result of nickel or cobalt<sup>2+</sup> introduction. Consequently  $Ni(Co)-W(Mo)/SiO_2(\gamma-Al_2O_3)$  catalysts showed less complex ESR spectra in which only two different ESR signals could be analyzed. This 'promotor' effect is discussed in terms of surface reorganization due to the incorporation of  $Ni^{2+}$  ( $Co^{2+}$ ) ions in the  $WS_2(MoS_2)$  phase.

Adsorption of carbonmonoxide is found to affect the ESR spectra of  $W/SiO_2$  and  $Ni-W/SiO_2$  in different ways, indicating that nickel influences the adsorptive and electronic properties of the catalyst. The effects of CO adsorption can be explained by means of electron transfer from CO to the catalyst.

## INTRODUCTION

Hydrodesulfurization (HDS) of petroleum feedstocks is one of the most important industrial catalytic processes. The HDS reactions can be written as:

Organic sulfur compounds +  $H_2 \rightarrow H_2S$  + desulfurized compounds.  
The catalysts used for this process consist of  $Co(Ni)$  promoted molybdenum or tungsten disulfide supported on alumina. Several models (1, 2, 3) describing the structure of these catalyst systems have been proposed. It is generally accepted by now that the active phase consists of tungsten or molybdenum disulfide crystallites. The catalytic activity of these disulfides can be enhanced ('promoted') by nickel or cobalt ions often referred to as promotor ions. It is in particular this promotor action that is still not well-understood.

Surface  $W^{3+}(Mo^{3+})$  ions connected with sulfur vacancies play the role of the catalytic active center in all models. Since  $W^{3+}$  and  $Mo^{3+}$  are paramagnetic, ESR can be used to study the active centers. The results obtained at our laboratory for the unpromoted  $WS_2$  and  $MoS_2$  catalysts have been reported elsewhere (4). Five different signals could be analyzed in the ESR spectra of these catalysts. Signal I originating from oxo- $M^{5+}$  ions ( $g = 1.93$  for  $Mo^{5+}$  and  $g = 1.78$  for  $W^{5+}$ ) and four signals originating from the disulfide phase. Signal II ( $g = 1.985$  for Mo and  $g = 1.91$  for W) and signal IV ( $g = 2.01$  for W) show a complementary behaviour upon evacuation and  $H_2S$  adsorption and are therefore ascribed to surface paramagnetic species. Signal III, also originating from a surface species, is obtained after a thiophene treatment. It has been attempted (4) to assign signals II, III and IV to surface  $M^{3+}$  or  $M^{5+}$  ions with different sulfur ligand symmetries. The origin of signal V remains unknown but it might be related with the presence of defect structures in the bulk.

In the present study the influence of the promotor ions upon these paramagnetic sulfidic species mentioned above will be demonstrated for the systems Ni-Mo/ $\gamma$ - $Al_2O_3$  and Ni(Co)-W/ $SiO_2$ . The influence on signal I will not be discussed here. The system Ni-W has been studied before by Voorhoeve (5). He reported a correlation between benzene hydrogenation activity and an ESR signal, most probably signal IV in (4). Most likely due to catalyst pretreatment (sulfidation procedure, low  $H_2S$  pressure) the intensities of signal II and V are low in his samples. The drastic change in  $g$ -value and the loss in variety of paramagnetic species upon introduction of promotor ions found in the present work will be discussed in terms of a surface reorganization caused by these promotor ions. The necessity to measure the ESR signal intensities as a function of temperature will be demonstrated.

By means of CO adsorption experiments it is shown that it is difficult to separate the contributions of the distinct signals to the total signal intensity. It is this signal overlap together with a lack of detailed knowledge of the ESR parameters of the signals, that hampers the correlation of ESR results with catalytic activities. Nevertheless ESR is one of the few techniques available that can provide useful information on the interaction of promotor ions with the  $W^{3+}(Mo^{3+})$  ions, which are proposed (1, 2) to be the active species in sulfided HDS catalysts.

## EXPERIMENTAL

All starting materials were free from interfering paramagnetic impurities.

Silica supported catalysts.  $\text{SiO}_2$  (Ketjen F-2) was successively washed with excess ammonia (4.5 N) and distilled water. After drying at 383 K for 16 hr it was calcined in air at 873 K for 2.5 hr. The pore volume was  $1.05 \text{ cm}^3 \text{ g}^{-1}$  and the surface area  $400 \text{ m}^2 \text{ g}^{-1}$ . Aqueous solutions of analytical grade ammonium-metatungstate (Koch-Light Laboratories Ltd.), nickel nitrate (BDH), or cobalt nitrate (Merck) were used for pore volume impregnation. The silica was first impregnated with ammonium-metatungstate, dried 16 hr at 383 K, calcined in air 16 hr at 773 K, and finally sulfided following a standard procedure. Then nickel or cobalt was introduced, followed by drying for 16 hr at 383 K and the standard sulfiding procedure.  $\text{W}(19.3)/\text{SiO}_2$ ,  $\text{Ni}(4)-\text{W}(19.3)/\text{SiO}_2$ , and  $\text{Co}(4)-\text{W}(19.3)/\text{SiO}_2$  were prepared in this way. (Number in brackets represent weight percentages based on  $\text{WO}_3$ ,  $\text{NiO}$  and  $\text{CoO}$  respectively)

Alumina supported catalysts.  $\gamma\text{-Al}_2\text{O}_3$  was prepared by calcining boehmite (Martinswerk GmbH RH6) in air for 2 hr at 873 K. The pore volume was  $0.35 \text{ cm}^3 \text{ g}^{-1}$  and the surface area  $215 \text{ m}^2 \text{ g}^{-1}$ . Aqueous solutions of analytical grade ammoniumheptamolybdate (Merck) and nickel nitrate (Merck) were used for pore volume impregnation. First the alumina was impregnated with ammoniumheptamolybdate, dried 16 hr at 383 K, calcined 16 hr at 773 K. Then nickel nitrate solution was added followed by drying 16 hr, 383 K and calcining 16 hr, 773 K. Finally the catalyst was sulfided under standard conditions.  $\text{Mo}(12)/\gamma\text{-Al}_2\text{O}_3$  and  $\text{Ni}(4)-\text{Mo}(12)/\gamma\text{-Al}_2\text{O}_3$  (Mo wt% as  $\text{MoO}_3$ ) were prepared this way.

Sulfiding procedure. Catalyst samples (200 mg) were treated in  $\text{H}_2$  containing 16% (v/v)  $\text{H}_2\text{S}$  at a flowrate of  $50 \text{ cm}^3 \text{ min}^{-1}$  and using the following temperature programme: 10 min 295 K, linear increase from 295 K to 673 K in 260 Min, 20 hr 673 K, quenching to 295 K. The ESR reactor used to prevent contamination of the sample by oxygen has been described earlier (4). It has been demonstrated (4, 6, 7) that the properties of the sulfided catalysts change upon exposure to oxygen. Hydrogen was deoxygenated over BTS catalyst (BASF R 3-11) and dried over molecular sieves (Union Carbide 4A). Hydrogen sulfide (Matheson CP grade) was used as supplied.

CO adsorption. Freshly sulfided  $\text{W}(19.3)/\text{SiO}_2$  and  $\text{Ni}(4)-\text{W}(19.3)/\text{SiO}_2$  samples were evacuated ( $<10^{-3}$  Torr, 295 K) and contacted with 40 Torr CO (10 min, 295 K and 15 min, 473 K). ESR spectra were recorded after each treatment (sulfiding, evacuation, CO at 295 K, CO at 473 K). Carbon monoxide (Matheson CP grade) was used as supplied.

ESR measurements. The ESR measurements were performed using a Varian E-15 ESR spectrometer equipped with a TE 104 dual sample cavity. A Varian Strong Pitch sample ( $g = 2.0028$ ,  $3 \times 10^{15}$  spins  $\text{cm}^{-1}$ ) was used to calibrate the magnetic field and as a standard for the quality factor of the ESR cavity. Accuracy of the calculated relative and absolute signal intensities was 10% and 25% respectively. In order to determine of the signal intensities

as accurate as possible, ESR spectra were recorded in the temperature range 20-100 K, by means of a liquid helium continuous flow cryostat (Oxford instruments). In this temperature region all samples were found to follow the Curie-Weiss law, but their Curie temperatures are different.

## RESULTS

The ESR signals in the spectra of figures 1-3 are indicated by the approximate position of their low-field peaks, since the low-field peaks of these signals could be detected separately. The quoted g-values have, however, been determined at the turning points. The total number of spins (TNS) has been determined since it is difficult to estimate the contribution of each separated signal. The overall values (resulting from the sum of the signals) of the TNS, g-value, line-width, and Curie temperature of the samples are given in table 1.

Table 1 ESR parameters of standard sulfided catalysts

sample	total number (a) of spins (g cat) <sup>-1</sup>	overall (b) g-value	overall line-width G (c)	Curie temperature $\theta$ K (d)
Mo(12)/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	4.4 x 10 <sup>18</sup>	1.986	130	0
Ni(4)-Mo(12)/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	4.5 x 10 <sup>18</sup>	2.055	180	1
W(19.3)/SiO <sub>2</sub>	8 x 10 <sup>17</sup>	1.906	420	-1
Ni(4)-W(19.3)/SiO <sub>2</sub>	5 x 10 <sup>17</sup>	2.086	200	7
Co(4)-W(19.3)/SiO <sub>2</sub>	7 x 10 <sup>17</sup>	2.090	320	7

(a)  $\pm$  25% (b)  $\pm$  0.005 (c)  $\pm$  10 G (d)  $\pm$  2 K

The ESR spectra measured at 20 K of standard sulfided Mo(12)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ni(4)-Mo(12)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and W(19.3)/SiO<sub>2</sub>, Ni(4)-W(19.3)/SiO<sub>2</sub>, Co(4)-W(19.3)/SiO<sub>2</sub> are shown in figures 1 and 2.

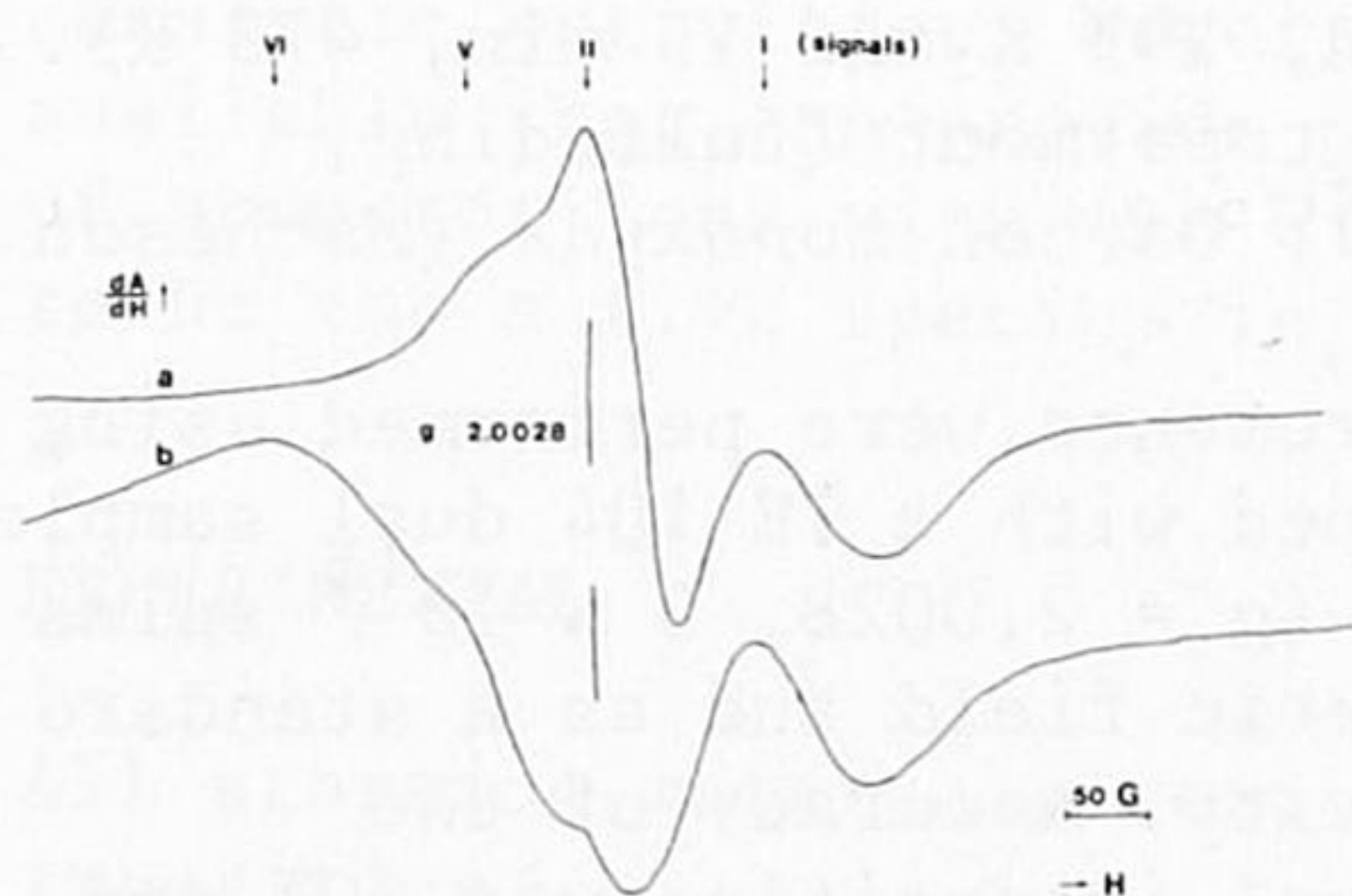


Fig. 1 ESR spectra (20 K) of standard sulfided catalysts:  
 (a) Mo(12)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> spectrometer receiver gain (R.G.)  $10 \times 10^1$ ;  
 (b) Ni(4)-Mo(12)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> R.G.  $5 \times 10^2$

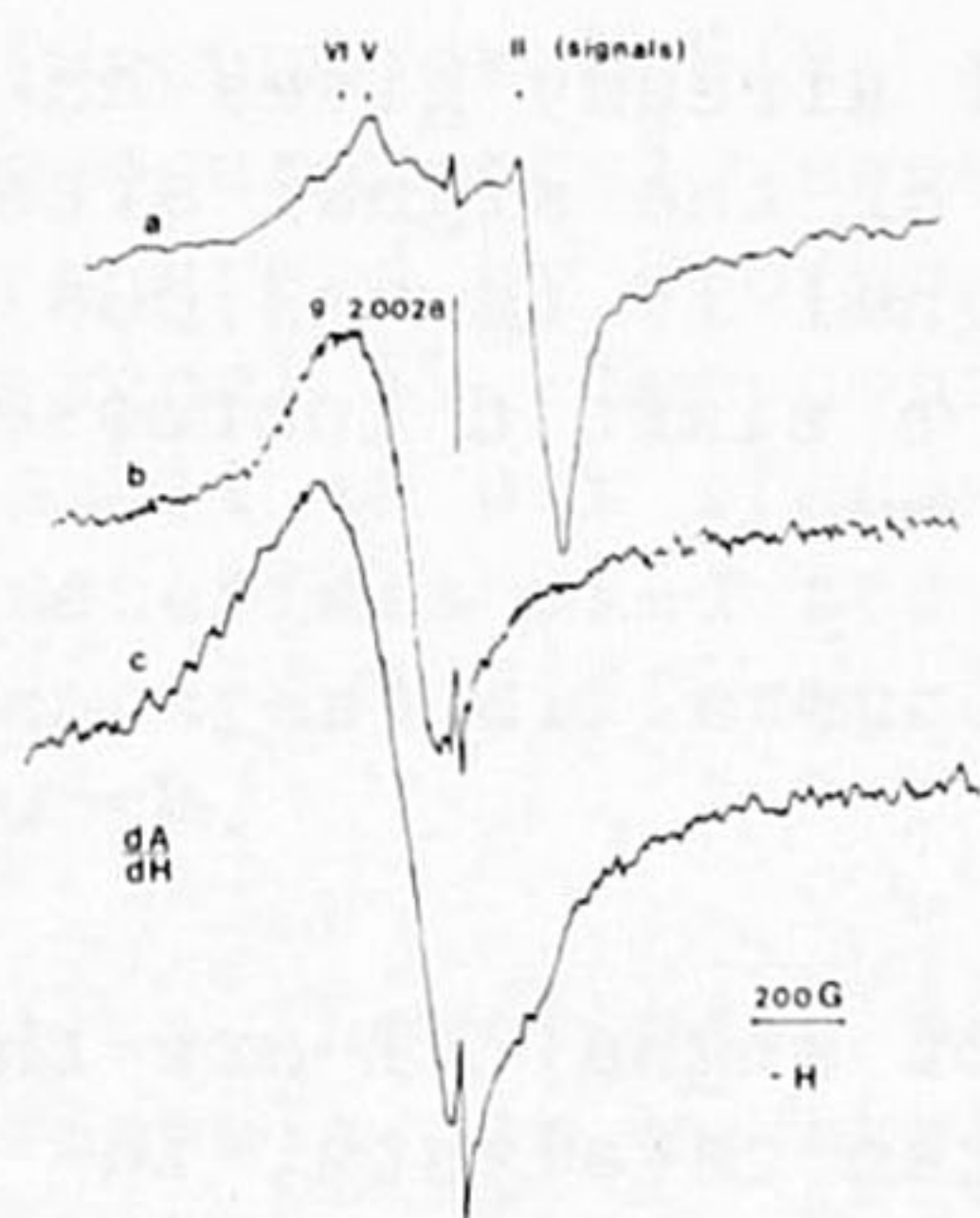


Fig. 2 ESR spectra (20 K) of standard sulfided catalysts:

- (a) W(19.3)/SiO<sub>2</sub> R.G.  $5 \times 10^3$ ;  
 (b) Ni(4)-W(19.3)/SiO<sub>2</sub> R.G.  $4 \times 10^3$ ;  
 (c) Co(4)-W(19.3)/SiO<sub>2</sub> R.G.  $8 \times 10^3$

Incorporation of promotor ions leads to the disappearance of the paramagnetic centers giving rise to signals II and IV. It is difficult to draw conclusions about the intensity of signal V since the new signal VI ( $g = 2.055$  for Ni-Mo and  $g = 2.086$  for Ni(Co)-W) strongly overlaps with signal V and is much stronger but it seems that the intensity diminishes. Note that the linewidth of signal VI is the same for Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni-W/SiO<sub>2</sub> ( $\sim 200$  G). From the spectra of Ni-W/SiO<sub>2</sub> and Co-W/SiO<sub>2</sub> it appears that nickel and cobalt have the same influence on the W/SiO<sub>2</sub> catalyst. The  $g$ -value of signal VI is the same for nickel and cobalt promoted tungsten catalysts although the linewidths differ (200 G for Ni-W, 320 G for Co-W).

The vacuum treatment at 295 K appeared not to influence the ESR spectra of W(19.3)/SiO<sub>2</sub> and Ni(4)-W(19.3)/SiO<sub>2</sub>. The effect of subsequent CO adsorption at 295 K and 473 K is shown in figure 3. For W(19.3)/SiO<sub>2</sub> CO adsorption of 295 K only results in a slight intensity decrease of signal II. At 473 K when CO was adsorbed at 473 K signal II disappeared and a twofold intensity increase of signal IV was observed (subtraction of spectrum b from c clearly shows that it is signal IV that increases).

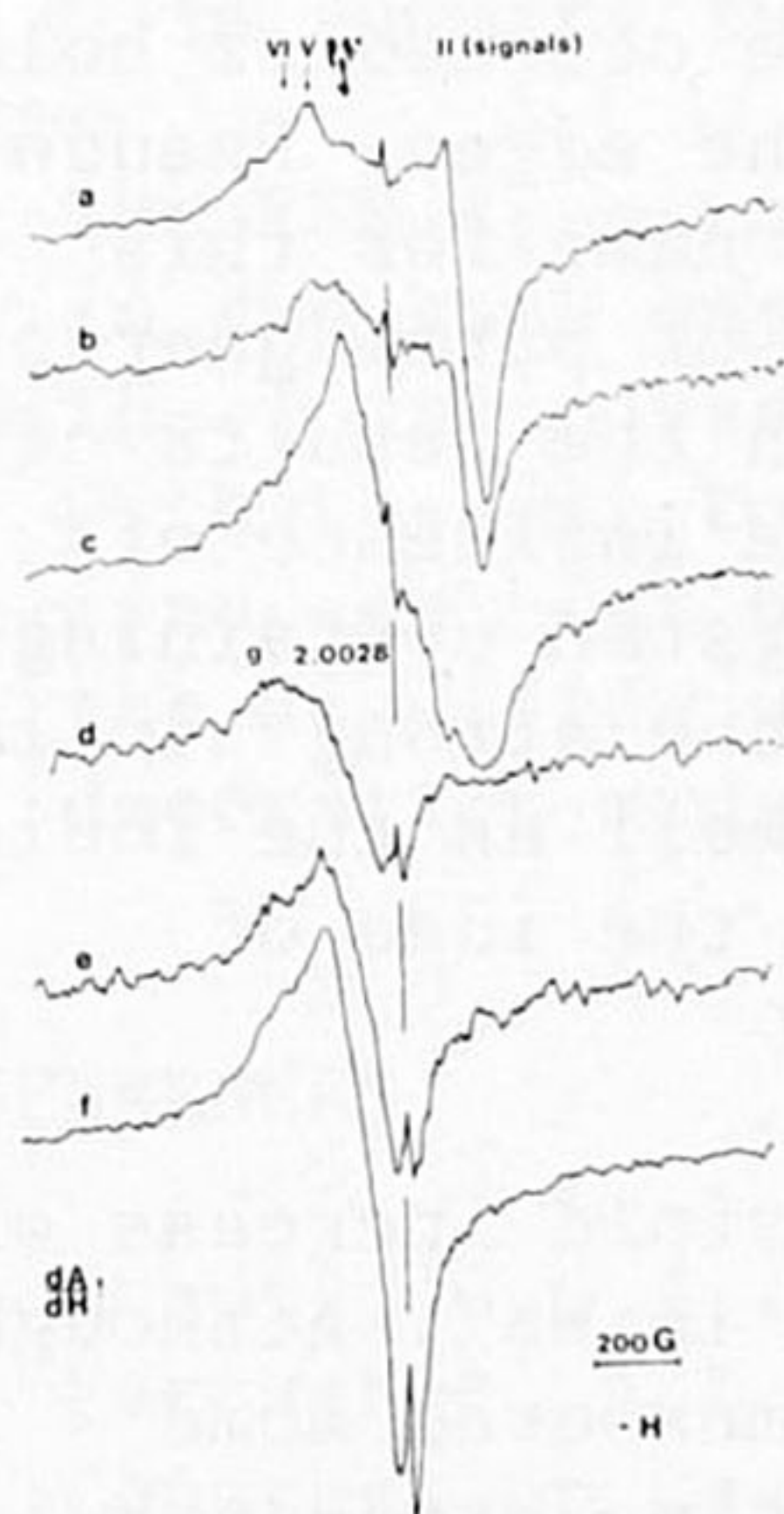


Fig. 3 ESR spectra (20 K):

- (a) W(19.3)/SiO<sub>2</sub> standard sulfided R.G.  $5 \times 10^3$ ;  
 (b) ib (a) + 40 Torr CO at 295 K, R.G.  $5 \times 10^3$ ;  
 (c) ib (b) + 15 min 473 K, R.G.  $5 \times 10^3$ ;  
 (d) Ni(4)-W(19.3)/SiO<sub>2</sub> standard sulfided R.G.  $2 \times 10^3$ ;  
 (e) ib (d) + 40 Torr CO at 295 K, R.G.  $2 \times 10^3$ ;  
 (f) ib (e) + 15 min 473 K, R.G.  $10 \times 10^2$

For Ni(4)-W(19.3)/SiO<sub>2</sub> CO adsorption at 295 K already gives an increase in signal intensity. The parameters of the signal after CO adsorption are slightly different from signal IV ( $g = 2.006$ ,  $\Delta H \sim 180$  G). CO adsorption at 473 K leads to a sixfold increase in TNS.

## DISCUSSION

Within experimental accuracy the linewidths of signal VI are the same for nickel promoted molybdenum or tungsten catalysts, in contrast with the linewidths measured for the unpromoted catalysts. The linewidth of the ESR signals in these samples is most probably determined by dipole-dipole interactions. For the nickel promoted catalysts the magnetic moments and the distances between the paramagnetic centers giving rise to signal VI must be about the same. Different spin-orbit coupling constants for Mo and W and small differences in local symmetry can account for the different  $g$ -value of signal VI in Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Ni-W/SiO<sub>2</sub>. The different linewidth and equal  $g$ -value of signal VI in Ni(4)-W(19.3)/SiO<sub>2</sub> and Co(4)-W(19.3)/SiO<sub>2</sub> can be understood assuming that the distances between the paramagnetic centers differ while the local symmetry is the same.

The ESR spectra of catalysts containing Ni or Co are less complex than the spectra of unpromoted catalysts. Signal VI and possibly a remainder of signal V are the only signals present. This reflects a reduction in the variety of paramagnetic centers that could be caused by a reorganization of the surface and very probably also by a loss of bulk defects (3, 8) of the disulfide crystallites due to the promotor. Farragher and Cossee (2) have shown with electron microscopy the influence of nickel on the edges of WS<sub>2</sub> crystals. The basic idea of their intercalation model is incorporation of promotor ions in the octahedral holes between the disulfide layers, restricted to the edges. Pseudo-intercalation or decoration would be a better name for this phenomena. Decoration should lead to one kind of paramagnetic centers at the edges, which is consistent with the results of our ESR measurements. The observation that the influence of nickel and cobalt upon both molybdenum or tungsten containing catalysts is the same, is in accordance with the strong similarity of the crystal parameters of WS<sub>2</sub> and MoS<sub>2</sub> as well as the ionic radii of Ni<sup>2+</sup> and Co<sup>2+</sup> and therefore supports the idea of decoration.

Voorhoeve (4) reported a twenty- to fiftyfold increase of signal intensity after introduction of nickel in WS<sub>2</sub>. Although in the present study such an increase is not measured some remarks have to be made. The catalyst preparation procedure is not the same and the conditioning of the samples may be different

(vacuum or  $H_2S/H_2$  atmosphere above the samples during the ESR measurements), especially the ESR spectra of unpromoted catalysts reported by Voorhoeve are less complex and consist largely of signal IV. The contribution of signal IV to the TNS is quite small in our standard sulfided catalysts. Furthermore the support materials used are not the same. These facts may account for the apparent differences between Voorhoeves study and the present work.

The effects of CO adsorption upon the intensity of the signals can be explained by the transfer of electrons from CO to tungsten ions. Signal II diminishes after CO adsorption. This is consistent with observations (4) that the intensity of signal II is also reduced after reduction with  $H_2$  or evacuation at 673 K and confirms the assignment to a surface  $M^{5+}$  ion. The increase of signal IV after CO adsorption at 473 K on  $W(19.3)/SiO_2$  can be explained by adsorption of CO on a sulfur vacancy near a  $W^{4+}$  ion followed by electron transfer. This is consistent with the increase of signal IV after evacuation of the sample at high temperature (673 K) and the assignment to a surface  $M^{3+}$  ion (4). The increase in signal intensity upon CO adsorption on  $Ni-W/SiO_2$  at a temperature as low as 293 K could be regarded as an indication for electron transfer via reduction of the promotor ion. The slightly different g-value and linewidth of the signal after CO adsorption can be caused by a small change in the local symmetry due to the presence of CO. The TNS of  $Ni-W/SiO_2$  after CO adsorption at 473 K is two times the TNS calculated for  $W/SiO_2$  (mainly signal IV) after the same treatment. It is not clear by now whether this is merely a kinetic effect or an increase in the number of adsorption sites. Also effects of coupling or decoupling of paramagnetic centers have been omitted in this discussion.

In summary the most important results from the present study are:

- i The ESR spectra of unpromoted Mo or W catalysts are affected in the same way by the incorporation of Ni or Co ions.
- ii The loss in variety of paramagnetic centers and the behaviour with respect to CO adsorption after incorporation of promotor ions can best be accounted for by a strong interaction between the disulfide phase and the promotor ions as proposed in the decoration model.

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