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The Role of Group VIII Metal Promoter in MoS_2 and WS_2 Hydrotreating Catalysts

I. ESR Studies of Co–Mo, Ni–Mo, and Ni–W Catalysts

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ESR spectroscopic measurements have been carried out on unsupported Co–Mo, Ni–Mo, Ni–W sulfide catalysts with two objectives: the first is to determine the role of Group VIII metal promoter atom in hydrotreating catalysts, while the second is to identify differences, if any, between Mo and W based catalysts. This study shows two ranges of promoter concentrations which deserve more attention, viz., low promoter concentration range (r = Group VIII metal atom/{Group VIII + Group VI-B} metal atoms < 0.05), and high promoter concentration ($0.1 < r < 0.5$). The presence of trivalent Group VI-B metal species has been detected in both cases. In the low concentration range, addition of Group VIII metal atom has been found to suppress ESR signals due to defects present in the host dichalcogenide (MoS_2 or WS_2). In the region corresponding to high promoter content, strong ferromagnetic behavior is observed. These results are explained invoking current theories proposed for HDS catalysis. A comparison of ESR spectra of Mo and W catalysts shows that although paramagnetic properties of Mo-based catalysts are not very different from those exhibited by W-based catalysts and their responses to addition of Group VIII metal are quite similar, a stronger electronic interaction is observed in WS_2-based catalysts. © 1985 Academic Press, Inc.

1. INTRODUCTION

Hydrotreating catalysts containing Co or Ni on one hand, and Mo or W on the other hand, have been subjected to extensive physicochemical characterization in order to elucidate the chemistry of these most widely used catalysts (*1–8*). Difficulties arising from metal–support interaction have been overcome (*2–4*) by adopting a simpler way of using the unsupported catalysts in their studies (*5–22*). Both oxidic and sulfidic forms of Mo or W catalysts promoted by Co or Ni (unsupported) have been examined by techniques, such as ESCA, ESR, adsorption of probe gases, and magnetic measurements (*1–8, 15, 22–39*) to determine the role of promoter in the HDS catalysis. It is generally believed that a strong interaction between the active phase (Mo or W) and promoter (Co or Ni) takes place. Four models have been proposed to explain this electronic interaction. They are "intercalation model" (*1, 22*), "synergy by contact or remote control model" (*4, 5*), "incorporation of Co in molybdenum sulfide" (*7*), and "formation of a mixed "promoter-active element-S" phase (*8*).

In order to understand the role of promoter in these catalysts, we focused our attention on the preparation and structural characterization (X-ray diffraction, SEM, TEM, and microprobe analysis) of various unsupported hydrotreating catalysts based on Fe–Mo, Co–Mo, Ni–Mo, Co–W, and Ni–W sulfides (*9–19*). Recently, Grange (*5*)

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has summarized these results and pointed out several similarities in the variations of physicochemical properties and catalytic activity as a function of promoter content (see Ref. *5*, Fig. 7).

Catalytic and magnetic measurements of Delvaux *et al.* (*14, 15*) have shown a correlation between the catalytic hydrogenation activity and magnetic moments of Co–Mo catalysts, while their ESCA results (*14*) have indicated an abnormal variation of Mo valencies with increase in Co content. These results led us to initiate the present investigation, to determine the oxidation states of Mo and W in these catalysts. Electron spin resonance (ESR) spectroscopy, an extremely sensitive technique for this purpose, has been employed by several investigators to study cobalt and nickel containing hydrotreating catalysts (*20–38, 41*). The species expected to yield ESR signals in Mo or W containing samples (tri- and pentavalent Mo or W ions), are considered to be active centers (*5, 14, 16, 22–26*). Di-, tetra-, and hexavalent species do not give ESR signals. The ESR intensity of W(III) or Mo(III) species has been correlated with benzene hydrogenation activity by Voorhoeve (*22*), and with thiophene HDS activity by Konings *et al.* (*23, 24*), while a correlation between intensity of the sulfur coordinated Mo(V) ESR signal and dibenzothiophene HDS activity has been established by Silbernagel *et al.* (*26*).

Although, overall structural and catalytic properties of both molybdenum and tungsten sulfides are influenced in almost identical ways by addition of Group VIII metals, there are some differences between these two systems (*6, 19*), which need more careful attention. First, addition of a small amount of promoter ($<5\%$) results in a decrease in the *c*-parameter of molybdenum sulfide catalysts but not that of tungsten based catalysts. Second, in low promoter concentration range, Mo catalysts (prepared by comaceration method) show a decrease in HDS activity (*9, 19*), while W catalysts exhibit a modest increase. Furimsky (*6*) has recently pointed out that prediction of properties of W catalysts, based on results obtained with Mo catalysts is not always valid. The aim of this communication is to compare ESR spectra of Co–Mo, Ni–Mo, and Ni–W catalysts, and to point out the major differences, if any, in their paramagnetic properties.

2. EXPERIMENTAL PROCEDURE

2.1. Catalyst Preparation

Several catalysts with the composition ratio, r = Co(Ni)/Co(Ni) + Mo(W), varying from 0.0 to 1.0 were prepared by comaceration method described elsewhere (*4, 5, 9–14*). The X-ray analyses of W samples treated in H_2S/H_2 for 4 to 6 hr showed a few lines due to WO_2 and consequently the Ni–W samples received longer sulfidation treatment. For some measurements, a mechanical mixture of pure MoS_2 (WS_2) and pure cobalt sulfide (nickel sulfide) was prepared. The mechanical mixture was ground in an agate mortar for 5 min and identified by "MM."

All catalysts received the H_2S/H_2 equilibration treatment at 400°C for 4 hr. Unpromoted samples were denoted by M0.00 and W0.00, while the promoted samples were termed as CM0.01, NM0.01, and NW0.01 etc., for Co–Mo, Ni–Mo, and Ni–W samples, respectively, with 0.00 etc. giving the composition ratio, Group VIII/(Group VIII + Group VI-B). Treatments were carried out *in situ* in a specially designed all glass/quartz reactor with grease-free joints and stopcocks, attached to a standard vacuum system.

2.2. ESR Measurements

A Varian Model E-line Series ESR spectrometer (with E 102 microwave bridge) was used to record spectra at 293 and 93 K. Sample tube had an internal diameter of 3 or 1 mm, depending upon the sample under investigation, e.g., 1-mm-i.d. tube was used for samples containing high concentrations

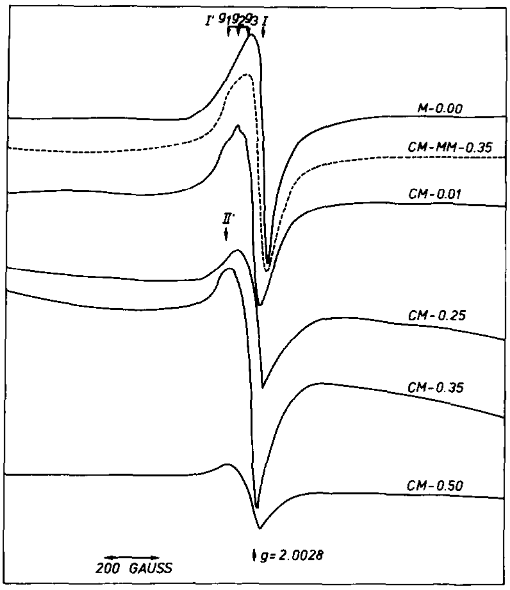

FIG. 1. ESR spectra of various Co–Mo samples recorded at 293 K.

of nickel or cobalt. The sample bed height was always 40 mm. A Varian strong pitch sample ($g = 2.0028$) was used to calibrate the magnetic field, and as a standard for the quality factor of the ESR cavity. The working frequency was 9.26 MHz. Its modulation corresponded to 100 kHz. The scan range was 2000 G for samples M-0.00, NM-0.01, and CM-series, while it was 10,000 G for those containing more than 10% (atomic) nickel.

3. RESULTS

Figures 1 and 2 present ESR spectra of various Co–Mo and Ni–Mo sulfided samples, respectively, after treatment in H_2S/H_2, evacuation at 400°C for 2 hr, and subsequent cooling to room temperature in vacuum. Signals have been recorded at 293 K. Figures 3A and B display ESR spectra of Ni–W sulfided catalysts, W-0.00, 0.01, and 0.03, recorded at 293 and 93 K, respectively. Figure 4 illustrates the influence exerted by the presence of Ni (in higher proportions) on the ESR spectra; the recording temperatures for Figs. 4A and B were 293 and 93 K, respectively. The various ESR signals have been indicated by arrows in Figs. 1 to 4. The ESR characteristics of Co–Mo, Ni–Mo, and Ni–W are summarized in Table 1, while Table 2 compares literature data on the ESR parameters of sulfur radicals on various substrates.

3.1. Molybdenum-Based Catalysts

Signal I is present in M-0.00 sample; its intensity decreases on addition of Co or Ni. It is difficult to estimate the signal intensity because of overlap with other signals. A shift to the low-field side on addition of a small amount of promoter is obvious. This signal is also exhibited by the mechanical mixture, CM-MM-0.35.

Signal I' (3-g value signal) appears in the sample containing 1 atom% Co or Ni in

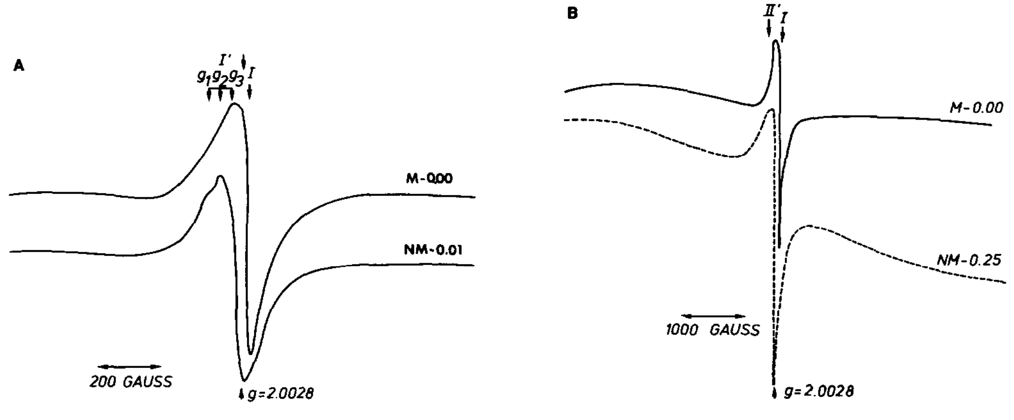

FIG. 2. ESR spectra of various Ni–Mo samples recorded at 293 K.

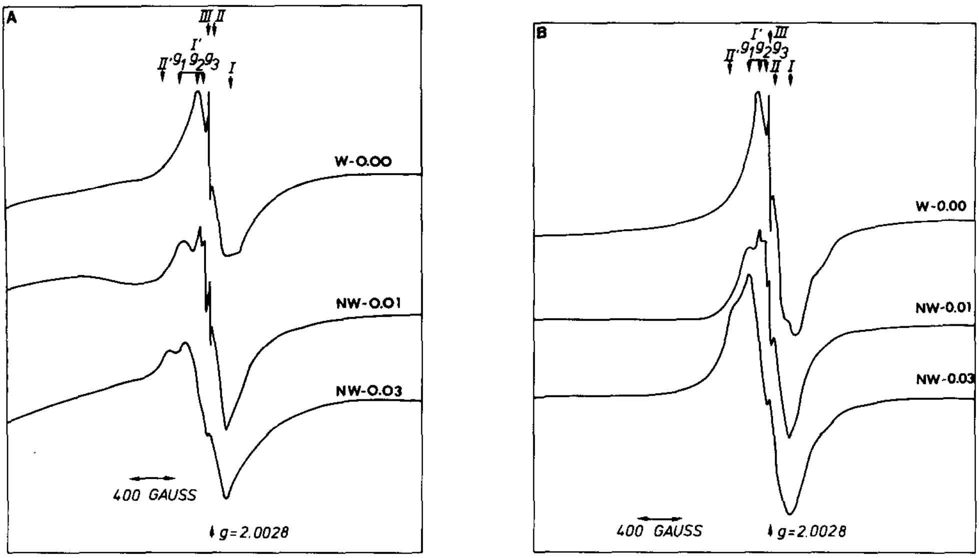

FIG. 3. ESR spectra of Ni–W samples containing small amounts of nickel: (A) recorded at 293 K, and (B) recorded at 93 K.

MoS_2 (sample NW-0.01). Such a signal has also been observed in NW-0.01. Its *g*-values are listed in Tables 1 and 2. It disappears on further increase in Co or Ni content.

Signal II′ appears as a shoulder on the left-wing of the Co–Mo and Ni–Mo spectra. It is difficult to detect its presence in CM- and NM-0.01 samples, probably because of a considerable overlap from Signal I′. Its intensity increases with an increase in Co or Ni content. Its *g*-values are 2.067 and 2.063 for Co–Mo and Ni–Mo samples, respectively. Although, it was difficult to estimate its intensity, it seems to be maximum in the composition range, $0.1 < r < 0.4$, concident with a maximum in HDS activity (*6, 9–14*).

3.2. *Tungsten-Based Catalysts*

Various signals present in Ni–W samples have been identified by I, I′, II, II, II′, V,

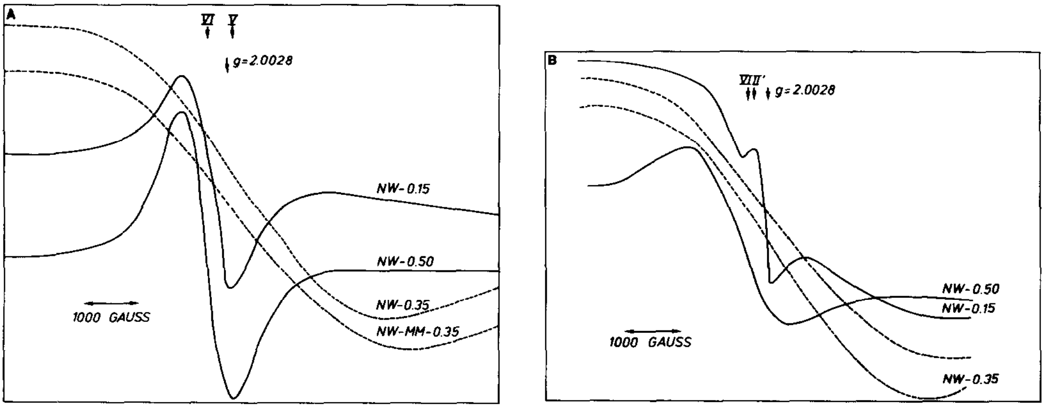

FIG. 4. ESR spectra of Ni–W samples containing high amounts of nickel: (A) recorded at 293 K, and (B) recorded at 93 K.

TABLE 1

ESR Parameters of Various Signals

Signal	Catalyst	g	ΔH (G)
I	M-0.00	2.00	90
I′	Co–Mo, Ni–Mo (CM- and NM-0.01)	$g_1 = 2.067$ $g_2 = 2.04$ $g_3 = 2.02$	
II′	Co–Mo, Ni–Mo (CM- and NM-0.25 etc.)	2.07	
I	Ni–W (W-0.00)	1.9	80
II	Ni–W (W-0.00, NW-0.01, and 0.03)	1.987	260
III	Ni–W (W-0.00, NW-0.01, and 0.03)	2.003	10
I′	Ni–W (NW-0.01 and 0.03)	$g_1 = 2.115$ $g_2 = 2.0499$ $g_3 = 2.024$	
II′	Ni–W (NW-0.01, 0.03, and 0.15)	2.19	
V	Ni–W (NW-0.35)	1.987	1800
VI	Ni–W (NW-0.15 and 0.50)	2.32[a] 2.20[b]	1800[a] 900[b]

[a] Recording temperature, 93 K.
[b] Recording temperature, 293 K.

and VI in Figs. 3 and 4. These signals are described below:

Signal I which is present in sample W-0.00 is better resolved when recorded at 93 K than at 293 K (Fig. 3). This signal, with $g = 1.9$ and $\Delta H = 80$ G disappears by addition of nickel; the intensity of this signal can also be altered by reduction in hydrogen or by sulfidation in hydrogen sulfide (*19*).

Sample W-0.00 gives signal II which has a g-value close to 2.0 and ΔH of 260 G. This signal disappears slowly on addition of nickel; it is also absent in the mechanical mixture of pure tungsten disulfide and nickel sulfide.

TABLE 2

ESR Parameters of Sulfur Radicals Adsorbed on Different Substrates

Catalyst	g_1	g_2	g_3	Ref.
W-based	2.115	2.0499	2.024	This work
Mo-based	2.067	2.04	2.02	This work
Mo-based	2.029	2.007	2.003	(*25*)
W-based	2.048	2.027	1.994	(*25*)
MoS_3–MoS_2	2.048	2.034	2.004	(*21*)
Ni-zeolite	2.12	2.067	2.032	(*40*)
Co–Mo/Al_2O_3	2.053	2.03	2.000	(*41*)

Signal III is normally observed in samples containing pure WS_2 and very small amounts of nickel. Its ESR characteristics ($g = 2.003$ and $\Delta H = 10$ G) are very similar to that of a free electron. Signal III is observed at both recording temperatures, viz. 93 and 293 K.

Signal I′, a sharp 3 g-value signal, is easily discernible in the sample NW-0.01; it loses intensity progressively with increase in nickel content. However, an increase in nickel content from 1 to 3 atom% gives rise to another signal on the left wing of the spectra (signal II′). The ESR parameters of these signals are listed in Table 1.

Signal V observed in samples NW-0.35 and NW-MM-0.35 is extremely broad indicative of a ferromagnetic character. Signal VI is detected on the samples NW-0.15 and NW-0.50. It shows temperature-dependent g-values: $g = 2.20$ at 293 K and $g = 2.32$ at 93 K.

4. DISCUSSION

The comaceration method used in this study for preparation of MoS_2 and WS_2 (reaction of their trioxides with aq. ammonium sulfide solution) can lead to formation of trisulfides (e.g.):

$$MoO_3 + 3\,(NH_4)_2S + 3\,H_2O \rightarrow MoS_3 + 6\,NH_4OH \quad (1)$$

The trisulfide thus formed transforms into disulfide under reducing or sulfiding conditions or in a vacuum at moderate temperatures of 300°–600°C (*5, 13*). However, the synthetic dichalcogenides are known to have a very disordered structure with a stoichiometric composition $Mo_{1-X}S_2$ ($W_{1-X}S_2$) (*5, 12, 13*). Disorder in the structure is determined by the value of X (the higher the value of X, the higher the disorder) and is normally accompanied by the presence of excess sulfur, metal vacancies and stacking faults. Progressive reorganization occurs upon prolonged heating (*13*). With sulfur release from trisulfide (for example WS_3), W(V), (IV), and (III) species with electronic configurations $5d^1$, $5d^2$, and $5d^3$, respectively, are formed. Thus, in Co or Ni promoted Mo and W based samples Mo or W(V) and (III) containing species, Co or Ni ions, and polysulfur ions formed by the interaction of hydrogen sulfide are expected to yield ESR spectra (*10, 16, 20–43*).

4.1. Molybdenum-Based Catalysts

Unpromoted MoS_2 catalyst gives an ESR signal (Signal I) with *g*-value around 2 which can be assigned to Mo(V) ions. On the other hand, unpromoted WS_2 exhibits four signals, three of which (I, II, III) are discussed in this article while the fourth signal will be described in the following article. Signals due to sulfur radicals are readily discernable in WS_2. It will be shown that these signals have their origin in structural defects and that they are modified on addition of promoter.

Signal I. Co–Mo and Ni–Mo catalysts studied in this investigation yield signal I; its ESR parameters compare favorably with those of Mo(V) signal reported by Hagenbach *et al.* (*10*) and Canesson *et al.* (*16*). Silbernagel *et al.* (*26*) and Busetto *et al.* (*21*) have also reported Mo(V) signals in their unsupported, sulfided Mo-based samples, the ESR parameters of which correspond fairly well to those obtained in the present study. These results lead us to believe with Silbernagel *et al.* (*26*) that the ESR signal present in the Co–Mo and Ni–Mo should be related to the pentavalent Mo ions, located on defect sites. The fact that the presence of Co or Ni brings about a decrease in its intensity is supported by the findings of Konings *et al.* (*23, 24*) and indicates the removal of these defect sites and attainment of better crystallinity on addition of cobalt or nickel to MoS_2. Konings *et al.* have, however, attributed this signal to trivalent Mo ions.

Signal I′. Addition of 1 atom% Co or Ni gives rise to this 3-*g* value signal. It is also observed in the NW-0.01 sample. Konings *et al.* (*25*) have also detected a triplet signal on MoS_2, which has been ascribed to sulfur radicals. A comparison of *g*-values of sulfur radicals (Table 2) suggests that this signal originates from sulfur-containing paramagnetic species fixed on Co or Ni ions (*40*).

Signal II′. Signal II′ is also generated when Co or Ni is added to MoS_2. Konings *et al.* (*23, 24*) have described a signal with a *g*-value of 2.06 on samples containing 4 wt% of nickel oxide, attributing its presence to trivalent Mo or W ions. It is interesting to note that intensity increases with increasing Co content up to 35% (atom/atom), beyond which a decline is observed (Fig. 1). The NM-0.25 sample also shows the presence of signal II′ with better resolution and higher intensity as compared to NM-0.01 sample (in the latter case, because of considerable overlap from signal I′, it is not possible to identify it separately). This signal with slightly higher g-value is also observed on NW-0.01 and NW-0.03 samples. Considering the results of Delvaux *et al.* (*14*), we feel that it should have its origin in trivalent Mo or W containing species (*22–24*). The possible electronic reactions for the formation of Mo(III) are suggested by de Beer and Schuit (*49*), Laine *et al.* (*50*), and Topsøe *et al.* (*8*).

4.2. Tungsten-Based Catalysts

We shall discuss each signal separately and compare our results with those reported in the literature (*22–26, 33–38*).

Signal I. Voorhoeve (*20, 22*) was first to detect an ESR signal in tungsten sulfides and Ni–W sulfides with parameters very similar to that of Signal I reported here. Konings *et al.* (*23, 24*) reported a signal on the bulk WS_2 samples, the ESR characteristics of which correspond fairly well with those of signal I. The adsorption of CO on WS_2 catalysts resulted in the disappearance of this signal (*24*). Our own results (*19*) show that reduction of W-0.00 sample in hydrogen causes the signal I to disappear. We feel, in agreement with Konings *et al.* (*23, 24*) that it originates from pentavalent species.

Signal II. A comparison of ESR parameters of the W(III) signal ($g = 2.0$ and $\Delta H = 260$ G) (*20, 22–24*) with those of Signal II leads us to attribute the latter signal to W(III) ions. This assignment was further confirmed by ESR measurements on W-0.00 sample subjected to reduction and sulfidation; a detailed discussion is given in Part II of this series (*19*).

A decrease in the intensity of this signal by addition of Ni is in agreement with results obtained by Konings *et al.* (*23, 24*). It should be pointed out that several researchers have observed better crystallinity in bulk MoS_2 and WS_2 by addition of minute amounts of Group VIII metals (*5, 6, 12, 22*). Based on these findings, we proposed that the interaction of Group VIII metal with the Group VI-B metal sulfide starts a nucleation process by controlling stoichiometric composition (close to MoS_2) and reducing defects/disorder (*12, 13*). We concur with Konings *et al.* that these paramagnetic ions (Signal II in the present study and signal IV in Ref. *23, 24*) located on the defect sites, are removed by interaction with nickel.

Signal III. Voorhoeve (*20, 22*) and, later Konings *et al.* (*23, 24*) attributed this sharp signal in their unsupported WS_2 samples signal to a carbonaceous deposit or grease contamination, while Conesa *et al.* (*33*) assigned this signal with $g = 2.002$ in their tungsten-containing samples to free electrons. The latter experiments (*33*) were carried out in a grease-free vacuum system, very similar to that used in the present study. The Figs. 3A and B clearly show that the intensity of Signal III decreases on addition of small amounts of nickel to WS_2 indicating some interaction between nickel and the paramagnetic species giving rise to Signal III. These results corroborate well with those of Conesa *et al.* (*33*), and suggest that Signal III is not due to carbonaceous deposition, but, rather, it is inherent in the WS_2 samples and should be attributed either to the free electrons after Conesa *et al.* (*33*), or to vacancies/defects (*21, 26*), or to some sulfur containing paramagnetic species (*21*) (see the discussion of signal II′). The results of Delvaux *et al.* (*14*) on analogous Co–Mo catalysts prepared by the same method support the assignment to sulfur species.

Signal I′. The sharp triplet, referred to as signal I′, has been detected in samples containing very small amounts of nickel (<3%) at 93 and 293 K. Recently, Ezzmarty *et al.* (*40*) have reported a 3-g value signal (due to sulfur species) generated by adsorption of hydrogen sulfide on Ni-exchanged zeolites. Konings *et al.* (*25*) have also described a triplet signal due to S_n^- on MoS_2 and WS_2. A comparison of the ESR parameters of sulfur-containing species listed in Table 2 shows that the present results are in excellent agreement with those of Ezzmarty *et al.* (*40*). Hence, we feel that the signal I′ must be originating from sulfur radicals, as suggested by Ezzmarty *et al.* (*40*).

Signal II′. Before proceeding to the discussion of signal II′, it is necessary to point out that the intensity of signal III present in pure WS_2 gradually decreases with an increase in nickel content (Fig. 3, samples NW-0.01 and 0.03). The reaction of paramagnetic species giving rise to signal III with nickel can be represented as

$$\mathrm{Ni(II)} + e \rightarrow \mathrm{Ni(I)} \qquad (2)$$

or

$$\mathrm{Ni(II)} + \mathrm{S}_n^- \rightarrow \mathrm{Ni(I)} + \mathrm{S}_n \qquad (3)$$

while electron transfer from Ni(I) to W(IV) can be written as follows (*49, 50*):

$$\mathrm{Ni(I)} \rightarrow \mathrm{Ni(II)} + e \qquad (4)$$

$$\mathrm{W(IV)} + e \rightarrow \mathrm{W(III)} \qquad (5)$$

A trace amount of nickel (less than 3 atom%) seems to be sufficient for complete removal of signal III. The signal II′ appears as a shoulder on I′ and gains intensity with increase in nickel content to 3% (atomic). Note that complete disappearance of signal III is accompanied by better resolution of signal II′ in sample NW-0.03 compared to NW-0.01. ESR spectra of NW-0.15 show the presence of this signal (see Fig. 4B). However, at higher nickel loadings, due to considerable overlap from the ferromagnetic signal, it is not possible to distinguish this signal. In view of its ESR parameters and the fact that its intensity increases with an increase in nickel content (compare the spectra of NW-0.01 with NW-0.03 in Fig. 3 and NW-0.15 in Fig. 4A), we feel that the signal II′ should be attributed to W(III) ions, in agreement with Konings *et al.* (*24*).

Signals V and VI. Signal V observed in the sample containing 35% nickel (atomic) is extremely broad and suggests a strong ferromagnetic character. At present, we have no explanation for the fact that the sample NW-0.35 yields an ESR signal, which is different from those observed in NW-0.15 and NW-0.50. Signal VI is observed in samples NW-0.15 and NW-0.50. Its characteristics, presented in Table 1, are similar to those reported on Ni–W (*33, 35*) and Ni–Mo (*34, 36, 37*), and are found to be dependent on the temperature at which the spectra were recorded. Upon cooling the sample from 293 to 93 K, its *g*-value changes from 2.2 to 2.32, while ΔH increases from 900 to 1800 G in agreement with the results of Sivasanker *et al.* (*35*) and Galiasso and Menguy (*34*). These authors have attributed it to the ferromagnetic resonance of metallic nickel.

The broad signals observed in nickel-containing systems (*33–37*) are normally ascribed to metallic nickel formed during reduction and reduction–sulfidation. However, the sulfiding conditions employed in our work, and thermodynamic data on nickel sulfide (*44, 45*) suggest that formation of metallic nickel is unlikely. Moreover, ESCA studies of Ng and Hercules (*46*) have shown the presence of nickel sulfides (NiS or Ni_3S_2) in the Ni–W samples treated with 9% H_2S in H_2. We, therefore, feel that the presence of some ferromagnetic nickel sulfide (analogous to ferromagnetic CoS_2 (*15*)) in very small amounts could be responsible for the observed ferromagnetic behavior. In fact, Klier (*47*) has reported a ferromagnetic nickel sulfide. Unfortunately, the ferromagnetic properties of this sulfide are not qualitatively understood on account of the difficulties encountered in preparation of a single crystal (*47, 48*). It seems likely that minute amounts of such ferromagnetic nickel sulfide present in our samples might give rise to the broad signal.

4.3. Comparison of MoS_2 and WS_2 Catalysts

The results presented above indicate two ranges of composition, $0.00 < r < 0.05$ and $0.1 < r < 0.5$, which warrant more attention. We shall discuss these two composition ranges separately.

Low promoter concentration ($0.00 < r < 0.05$). Most striking similarity is that paramagnetic centers on the defect sites are progressively removed on addition of Co or Ni to MoS_2 or WS_2 supporting our earlier results (*12*). In both cases (MoS_2 or WS_2), addition of 1 atom% Co or Ni results in the formation of sulfur-containing paramagnetic species, and further addition of Group VIII metal results in the formation of trivalent Mo or W species.

The main difference in these two systems that pure MoS_2 yields only one signal due to Mo(V) species whereas pure WS_2 gives one due to W(III) and the other due to W(V). At this time we do not have any plausible explanation for this difference. Another interesting observation is that the species, such as trapped S_n^- or electrons are easily discernible in the ESR spectra of pure WS_2. We feel that these species are likely to be present in MoS_2 sample, but they remained unresolved or undetected for the reasons not known at this time.

High promoter concentration ($0.1 < r < 0.5$). In this composition range the presence of trivalent Mo(W) species and ferromagnetic Group VIII metal sulfide is detected.

The spectra of Co–Mo and Ni–Mo samples are almost identical while that of Ni–W system are somewhat different as compared to Ni–Mo catalysts. Nevertheless, the overall electronic effects seem to be comparable.

The mechanical mixture of Co–Mo sulfides exhibited a spectrum identical to the parent MoS_2, whereas that of Ni–W sulfides showed no signals due to pure WS_2 but on the contrary yielded a spectra identical to that given by a comacerated sample of same composition. These results suggest a stronger interaction between Ni and W species as compared to Co and Mo species. More experiments are needed to explain the exact nature and mechanism of this interaction.

5. CONCLUSIONS

The present study shows a clear distinction between the two promoter concentration ranges. At lower promoter composition, the ESR spectra can be used as a probe to measure qualitatively the extent of disorder in Group VI-B sulfides. An improvement in crystallinity can be followed by monitoring the decrease in defect signals as a function of Group VIII metal content.

At a higher range of promoter concentration ($0.1 < r < 0.5$), ferromagnetic phases of Group VIII metal sulfides are formed (*15, 18*). The main feature deduced from ESR results is the presence of trivalent Mo or W species in agreement with literature data (*14, 22, 24*). This study together with many other results (*15*) suggest that the interaction of these ferromagnetic sulfides with the host dichalcogenides is most probably responsible for increased activity in this range.

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