JOURNAL OF CATALYSIS 91, 318–326 (1985)

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

II. Catalytic and Physicochemical Properties of Nickel-Promoted Catalysts

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Received March 28, 1984; revised October 23, 1984

The promotional effects of nickel on the catalytic activities of MoS_2 and WS_2 have been investigated. A series of unsupported Ni–W sulfides with a composition ratio, r = Ni/{Ni + W} (atom), varying from 0.0 to 1.0, and two unsupported and fully sulfided nickel–molybdenum catalysts (one prepared by comaceration method and the other by homogeneous sulfide precipitation method) with $r = 0.25$ have been tested for cyclohexane isomerization, cyclohexene hydrogenation, and thiophene hydrogenolysis at 305°C and 30 bars of hydrogen pressure. Surface area, X-ray diffraction, and ESR measurements on Ni–W samples show that in the low composition range, $r < 0.05$, the surface area decrease is associated with the formation of large crystallites. The ESR study shows the presence of W(V), W(III), and sulfur-containing paramagnetic species in the sample with $r = 0.00$. At the synergetic composition range, r = 0.15 to 0.40, the surface area versus composition plot shows a wide maximum, while the ESR results indicate the presence of certain ferromagnetic nickel-containing phase. It is shown that a strong electronic interaction takes place between two sulfide phases.

1. INTRODUCTION

MoS_2 and WS_2, which have the same crystallographic structure, are the basic active substances in hydrodesulfurization catalysts. The activity of MoS_2 and WS_2 can be enhanced considerably by group VIII metals, of which Co and Ni are the most widely employed. Molybdenum or tungsten, and cobalt, nickel, or iron act synergetically in determining the catalytic activity. Although, the optimum atomic ratio of the group VIII metal to the group VI metal (corresponding to the maximum activity in hydrodesulfurization and hydrogenation) differs with different authors, it is usually found to vary between 0.2 and 1.0 (*1, 2*). However, it can be remarked that, whatever the preparation method employed, the activity versus composition curves have the same volcano shape (*3, 4*), including mechanical mixture of the pure sulfides (*5*). Four hypotheses (*6–10*) have been proposed to explain the role of the promoter in MoS_2 or WS_2 hydrodesulfurization catalysts (see Ref. (*10*) for recent review). Previous work in our group (*12–16*) indicates that the synergetic effect occurs in quite a variety of Co–Mo catalysts (supported or unsupported) and also in the case of the sulfided unsupported Ni–Mo system (*14*). The association Fe–Mo behaves similarly (*15, 16*). Although the results obtained by these systems are consistent with the "synergy by contact" or "remote control" models (*8, 9*), it has not been possible to rule out the occurrence of some intercalation (*7*), or mixed Co–Mo–S phase (*10*).

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0021-9517/85 $3.00

Intercalation model was supported essentially by experimental results on the Ni–W system, and hence we undertook the present investigation on that system, but used the comaceration method. We expected to discern what is independent from the preparation method in the Ni–W system, and to relate the previously published results on Ni–W to our own result on the other systems. The Co–Mo–S model derives its support mainly from the results on Fe–Mo and Co–Mo catalysts (*10*). It is claimed that it can be extended to explain the results obtained with other hydrotreating catalyst systems (*10, 11*). In order to determine if such a mixed amorphous phase plays any role in the nickel promoted catalysts, we prepared two unsupported, sulfided Ni–Mo catalysts. The first was prepared by the comaceration method while the second sample was prepared by the method recommended by Topsøe *et al.* (*11*) for maximizing the formation of the mixed amorphous phase, e.g., Ni–Mo–S phase. On account of the fact that the Ni-based system lends itself to extensive investigation in ESR, and that many previous ESR results (*17–35*) have been published on this system, we placed some emphasis on the ESR method (*36*). Catalytic activity measurements involved the study of hydrogenolysis of thiophene, hydrogenation of cyclohexene, and isomerization of cyclohexane at 305°C and 30-bars pressure. In addition, the catalysts were characterized by determinations of BET surface area and X-ray diffraction. The ESR results obtained on Ni–W system will be presented here.

2. EXPERIMENTAL PROCEDURE

2.1. *Catalysts Preparation*

The catalysts were prepared by comaceration method described earlier (see Ref. (*8*)). The samples are denoted by r-0.00, r-0.01, r-1.00 etc., where 0.00, 0.01, etc., give the composition ratio Ni/(Ni + W). A mechanical mixture (of tungsten disulfide, r-0.00, and nickel sulfide, r-1.00) having a composition ratio of 0.35, was prepared for ESR measurements and was identified as r-mm-0.35.

A Ni–Mo sample having a composition ratio of 0.25 was prepared by comaceration method while another sample with $r = 0.28$ was prepared by the homogeneous sulfide precipitation (HSP) method (*11*). This method involves the coprecipitation of nickel and molybdenum sulfides from very dilute solutions by the addition of 20% (aq.) ammonium sulfide solution (*11*).

2.2. *Surface Areas*

The surface areas of these catalysts were determined gravimetrically, using nitrogen adsorption, by the BET method.

2.3. *Catalytic Activity*

The activity measurements were made by treating a feed containing 70% (by wt) cyclohexane and 30% (by wt) cyclohexene to which 5000 ppm thiophene was added. The reaction was carried out at 305°C and 30 bars of hydrogen pressure. The H_2 (gas NTP)/hydrocarbons (liquid) ratio was 600; LHSV was 18. The products were collected every half-hour for 6 hr and analyzed by gas chromatography. It will be shown that the activity stabilizes after 3 hr or less. Steady-state conversions cited in this work were taken after 6 hr; the activities in various reactions were defined as follows:

$$A_{\mathrm{HDS}} = \text{HDS activity} = (\text{initial thiophene} - \text{final thiophene}) \times 100/\text{initial thiophene/g catalyst}.$$

$$A_{\mathrm{HYD}} = \text{hydrogenation activity} = (\text{initial cyclohexene} - \text{final cyclohexene}) \times 100/\text{initial cyclohexene/g catalyst}.$$

$$A_{\mathrm{ISO}} = \text{isomerization activity} = (\text{initial cyclohexane} - \text{final cyclohexane}) \times 100/\text{initial cyclohexane/g catalyst}.$$

A stands for the specific activity, i.e., percentage raw conversion at steady state per

TABLE 1

Catalytic and Physical Properties of Unsupported, Sulfided Ni–Mo, Co–Mo, and Ni–W Catalysts[a]

Catalyst	Surface area (m^2/g)	% Conversion/ g catalyst		First order rate const[b]		A_{HDS}/A_{HYD}
		HDS	HYD	HDS $\times 10^3$	HYD $\times 10^1$	
Ni–Mo-0.25[c]	14.3	86.0	58.0	5.62	1.50	0.038
Ni–Mo-0.28[d]	17.1	85.0	59.0	5.42	1.52	0.035
Co–Mo-0.25[c,e]	25.0	80.0	15.0	4.60	0.28	0.164
Ni–W-0.25[c]	13.7	83.2	75.6	5.09	2.40	0.021

[a] Weight of catalyst, 1 g; temperature, 305°C.

[b] Specific rate constant in mol hr^{-1} g^{-1}.

[c] Comacerated sample.

[d] HSP method described in Refs. (*10, 11*).

[e] Data taken from Ref. (*39*).

gram catalyst, while *A* gives the first-order rate constant per unit surface area of the catalyst.

2.4. *X-Ray Diffraction Studies*

X-Ray diffraction measurements were made using a Philips X-ray diffractometer type PW 1010 with CoK_α radiation.

2.5. *ESR Measurements*

A Varian E-line Century Series ESR spectrometer with an E-102 microwave bridge (dual cavity) was used to record the spectra. Experimental details are given in Part I (*36*). Before introduction into the sample tube, the Ni–W samples, in addition to the treatment described above, were subjected to the following treatments:

(1) Equilibration of the samples with a mixture of 20% H_2S in H_2 (v/v) at 400°C for 4 hr. Samples are denoted by W-0.00, NW-0.35, and NW-MM-0.35.

(2) Reduction of the samples from treatment 1 (W-0.00 etc.) by treatment with pure hydrogen at 400°C for 4 hr. The samples are denoted by R-0.00-(4) etc., where "R" stands for the reduced sample, and the number in the parenthesis gives the duration of treatment.

(3) Sulfidation of pure WS_2-based sample from previous treatment (R-0.00-(4)) with pure hydrogen sulfide at 400°C for 4 hr. The sample will be referred to as S-0.00-(4).

3. RESULTS

3.1. *Surface Areas*

Surface areas of two Ni–Mo samples and a NW-0.25 are compared in Table 1, while those of the Ni–W series are presented in Fig. 1. The surface area of Ni–W samples is found to go through a sharp minimum for low nickel contents, then to a maximum in the composition range, where a synergetic effect is observed, and then to decrease.

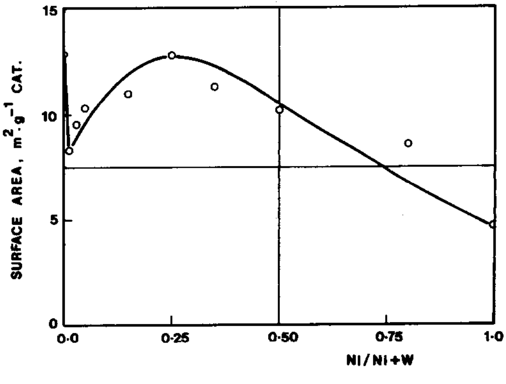

FIG. 1. Variation of surface area as a function of composition ratio for Ni–W catalysts.

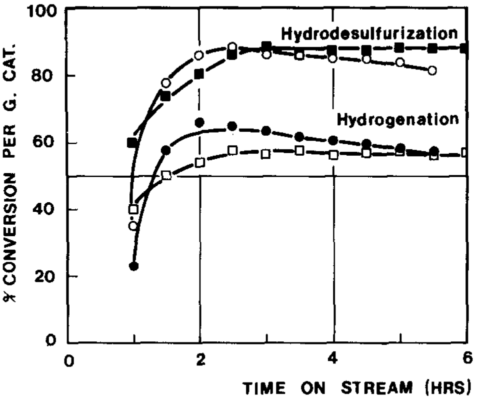

FIG. 2. HDS and hydrogenation activities of Ni–Mo catalysts prepared by comaceration method (represented by squares) and HSP method (represented by circles).

3.2. *Catalytic Activity*

Figure 2 compares the table activities (A_{HDS} and A_{HYD}) of two Ni–Mo catalysts prepared by different methods, while Table 1 presents a comparison of the activities of Ni–Mo samples with those of Co–Mo catalysts (*39*). Figure 3 gives activity variations for Ni–W catalysts with different typical compositions, as a function of time (in hours), in the hydrogenolysis of thiophene, hydrogenation of cyclohexene, and isomerization of cyclohexane. Activities stabilize before 3 hr in all cases (Fig. 3).

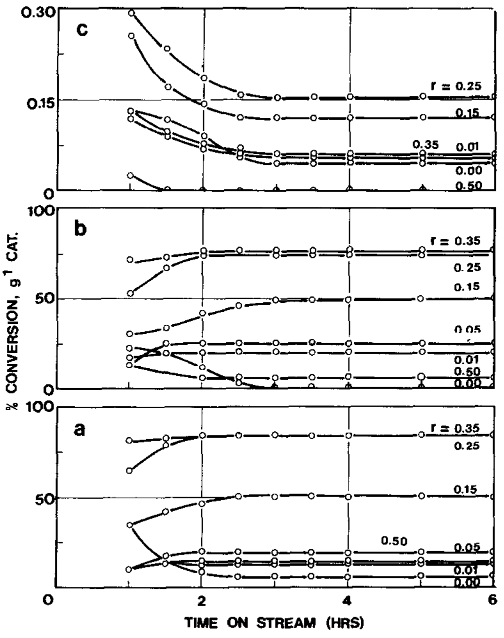

FIG. 3. Activity–time curves for various Ni–W catalysts. (a) HDS, (b) HYD, (c) ISO.

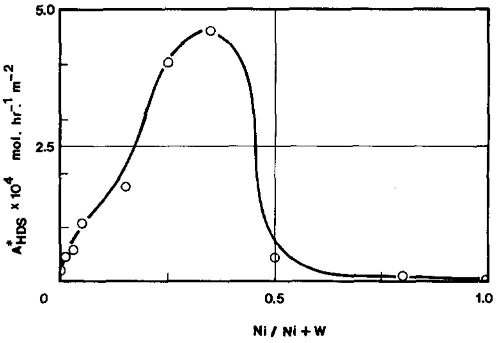

FIG. 4. Variation of activity in thiophene hydrogenolysis as a function of composition ratio of Ni–W catalysts.

Stable activities (A^*), i.e., rate constants per unit surface area of the catalyst (Figs. 4, 5, and 6) increase with increasing promoter concentration, reaching a maximum value between $r = 0.05$ and 0.30 (isomerization), or $r = 0.20$ to 0.40 (other reactions), and then decline sharply.

3.3. *X-Ray Analysis*

The X-ray diffraction patterns of MoS_2 samples showed only those lines corre-

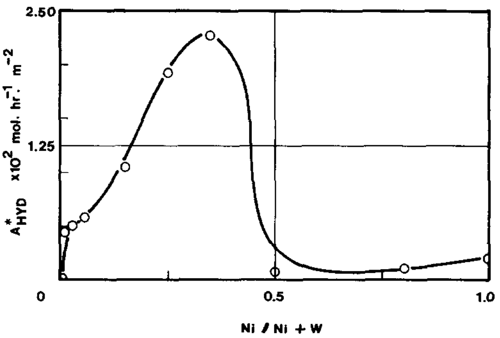

FIG. 5. Variation of activity in cyclohexene hydrogenation as a function of composition ratio of Ni–W catalysts.

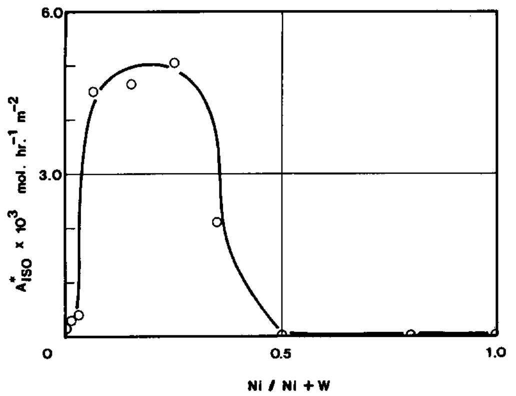

FIG. 6. Variation of activity in cyclohexane isomerization as a function of composition ratio of Ni–W catalysts.

sponding to very strong reflections of MoS_2. The X-ray analyses of the Ni–W samples treated by a mixture of H_2S/H_2 for 12 hr showed no lines attributable to the oxides, and especially to tungsten dioxide (WO_2), which could be observed in those treated for a shorter duration. All the samples we used were treated for 12 hr. The samples exhibited only a few broad lines, corresponding to the most intense reflections of WS_2. The X-ray lines corresponding to nickel sulfide appeared only at $r = 0.50$. The sample with $r = 1.0$ (pure NiS) was found to be very well crystalline.

3.4. ESR Measurements

Figure 7 presents the ESR spectra of pure WS_2 samples after they received various pretreatments. The ESR signals have been identified by I, II, III, and IV in this figure, and their ESR characteristics are listed in Table 2. Figure 8 corresponds to the influence exerted by the addition of 35% (atom) nickel on the ESR absorptions of WS_2. The broad signals observed for the equilibrated and reduced samples are designated by V and V_R, respectively.

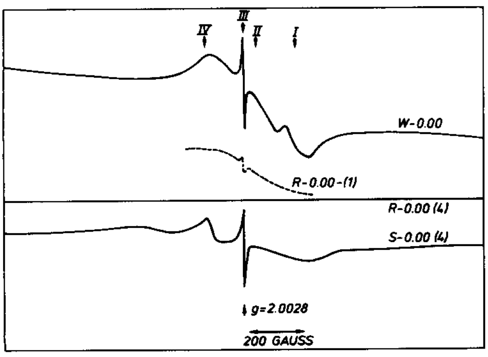

FIG. 7. ESR spectra of various WS_2 samples: (A) W0.00, (B) R0.00, and (C) S0.00.

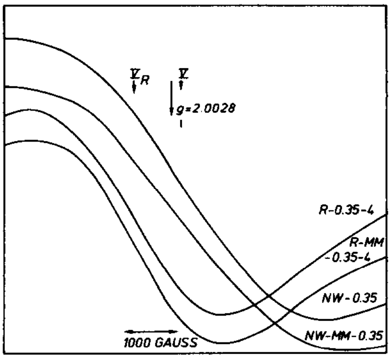

FIG. 8. ESR spectra of NW-0.35 and NW-MM-0.35 samples.

4. DISCUSSION

4.1. Extent of Sulfidation of the Samples

X-Ray data indicate that a 4-hr sulfidation time was not sufficient for the complete conversion to WS_2. The rate of sulfidation of WO_3, thus, seems to be much slower than that of MoO_3 (*37*). The slow reduction-sulfidation of WO_3 is in agreement with the views expressed by Ng and Hercules (*38*).

TABLE 2

ESR Parameters of Various Signals Present on Ni–W Catalysts

Signal	Recording temp. (K)	g	ΔH (G)
I	93 and 293	1.90	80
II	93 and 293	1.987	260
III	93 and 293	2.003	10
IV	93 and 293	2.046	60–70
V	93 and 293	1.97	1800
V_R	93	2.55	>1800

4.2. *Surface Area*

Surface areas of these nickel based samples are very similar, and compare favorably with the data given by Topsoe (*10*) for a Co–Mo sample with the same composition ratio.

For Ni–W catalysts there is a noticeable, though modest, decrease in the surface area (about 35% decrease) at $r \leq 0.05$ followed by a maxima at $0.2 < r < 0.4$ (Fig. 1). This result is similar to those obtained on Co–Mo (*8, 15*) and Ni–Mo (*14*). Furimsky and Amberg (*4*) have also reported such a decrease in surface area of Ni–W catalysts prepared in a totally different way.

4.3. *Activity Results*

4.3.1. Ni–Mo catalysts. A comparison of the activities of two Ni–Mo samples prepared by different methods (Fig. 1 and Table 1) shows that both samples exhibit a comparable performance in HDS and hydrogenation. Breysse *et al.* (*40*) have recently shown that the Co–Mo catalysts prepared by the method suggested by Topsoe group (*11*) is significantly more active than that prepared by the comaceration method. At present, we do not have any plausible explanation for this discrepancy. The high activity exhibited by the two Ni–Mo samples is consistent with the "remote control theory" (*9*), and the Co–Mo–S or Ni–Mo–S theory (*10, 11*). However, if we adopt the latter model, the present results suggest that the comaceration is also equally effective in producing the Ni–Mo–S phase.

A comparison of the activities of Ni–Mo and Co–Mo catalysts presented in Table 1 shows that while their HDS activities are almost comparable the former is 5 times more active in hydrogenating cyclohexene than the latter. These results are in agreement with the findings of Kasztelan *et al.* (*41*), and suggest the usefulness of Ni-promoted catalysts in the processes, where extensive hydrogenation is desired. While Ni–W catalyst with same composition shows highest activity for both reactions, Co–Mo catalyst gives better selectivity toward HDS reaction.

4.3.2. Ni–W catalysts. The general trends for various activities of Ni–W versus composition curves are similar (Figs. 4 through 6). However, there are small differences especially when comparing the isomerization activity with those of hydrogenolysis and hydrogenation. The maximum for the former is reached for $r = 0.05$ to 0.30, while for the other reactions, it is attained for $r = 0.20$ to 0.40.

A distinctive feature of the Ni–W system, in comparison with the molybdenum-containing systems, Co–Mo (*8*), Ni–Mo (*14*), and Fe–Mo (*16*), is that there is no minimum in the intrinsic activity for small promoter concentrations ($r = 0.01$ to 0.03). However, there is an increase, which is quite modest with respect to that observed at higher proportions of nickel ($r = 0.15$ to 0.40); the rate per unit surface area is further increased by a factor of 7–8 for hydrodesulfurization, 4.5 for hydrogenation, and 1.5 for isomerization, when going from $r = 0.03$ to the synergetic range ($r = 0.15$ to 0.40). The increase in the hydrogenation activity by association of nickel with WS_2 is in agreement with the earlier reported results in the literature (*42, 43*).

Thus, a high amount of nickel ($r = 0.15$ to 0.40) is actually necessary for bringing about most of the beneficial effect than what is sufficient for intercalation (*7*) or decoration model (*44*). Similar conclusion emerged from the results presented by Farragher and Cossee in the discussion of their article (see Fig. 3 of Ref. (*7*)). For the sample with Ni/W ratio of 0.1 (or Ni/(Ni + W) of 0.09) the activities in hydrogenation of benzene and cyclohexene were 9 and 3 times larger, respectively, than those observed in the composition necessary to achieve full intercalation (Ni/W < 0.05). The increase in activity with an increase in promoter content (in the composition range of 0.1 to 0.3) is in accordance with the predictions of "remote control theory" (*9*) and the Co–Mo–S theory (*10, 11*). The present results indicate that this additional amount plays an essential role, either by way of activating sites more effectively through the hydrogen spill-over from the promoter phase to the host sulfide as proposed by Delmon (*9*), or by increasing the amount of mixed amorphous Ni–W–S phase after Topsoe *et al.* (*10, 11*).

4.4. ESR Results

In this section, we shall discuss the effects of various chemical treatments on the signals identified by I, II, III, IV, V, and V_R, some of which have been described earlier (*36*).

(a) Signal I has been assigned to W(V) ions for the reasons given earlier (*36*). It should be noted that this signal disappears upon reduction and reappears on sulfidation (Fig, 7).

(b) In order to confirm the assignment of signal II to W(III) species, reduction of the sample W-0.00 was carried out with an expectation that this treatment would result in an increase in the intensity of II. On the contrary, the results presented in Fig. 7B show that the reduction of the W-0.00 sample with pure hydrogen at 400°C for 4 hr removes this signal. Recently, a more elaborate study carried out by Konings *et al.* (*22*) has shown that the CO adsorption (very mild reduction or electron transfer process) causes an increase in the intensity of this signal, while the hydrogen reduction (severe reduction) brings about a decrease in its intensity possibly because of the over-reduction of W(III) to W(II) species. The latter findings of Konings *et al.* (*22*) explain the absence of signal II in the R-0.00-(4).

The sample R-0.00-(4) was subsequently sulfided in hydrogen sulfide atmosphere a 400°C for 4 hr with an expectation that it would give rise to this signal. However, the results proved to be otherwise. At this time, it is worthwhile recalling the results of Voorhoeve (*18*) who showed that the adsorption of benzene, cyclohexene, and hydrogen sulfide reduces the intensity of this signal. Considering these results, we feel that the adsorption of H_2S on these sites must be responsible the absence of this signal in the S-0.00-(4) sample.

The above-mentioned results together with those of Voorhoeve (*18*) and Konings *et al.* (*20, 22*) lead us to assign this signal to trivalent tungsten species located on the surface on WS_2.

(c) Signal III, which has the ESR characteristics close to those of radicals, has been attributed to sulfur radicals (*17, 18, 20, 22*) on molybdenum and tungsten-containing catalysts. Figure 7 shows that the reduction with pure hydrogen results in the disappearance of this signal while the sulfidation of the reduced sample makes it reappear. These results give additional support to the assignment of this signal to sulfur species as mentioned earlier (*36*).

(d) Signal IV was detected as a separate absorption in the sample S-0.00-(4). It is likely that this signal is also present in the sample W-0.00 but cannot be detected because of a considerable overlap from Signal II. Konings *et al.* (*22*) have assigned a signal with similar *g*-value and ΔH to trivalent tungsten ions. In the present study, we note that the H_2S treatment gives rise to this signal along-with the signal III. If we accept with Konings *et al.* (*22*) that the signal arises from the W(III) species, it is tempting to speculate about the presence of these two signals, viz. III and IV, in the sample S-0.00-(4) as follows:

$$\mathrm{W(IV)} + \mathrm{H_2S} \rightarrow \mathrm{W(III)} + 2\mathrm{H}^+ + \mathrm{S}^- \quad (1)$$

(e) The broad signal V observed in the sample containing 35% nickel (Fig. 8) has a ferromagnetic character, the origin of which has been ascribed to ferromagnetic nickel sulfide, analogous to CoS_2 (*36, 48*). We have no explanation for the fact that the signal shifts to the low field side upon reduction of the samples in hydrogen. Metallic nickel can, in principle, be formed during reduction with hydrogen (*45–49*).

Another important fact in Fig. 8 that warrants special attention is that the ESR spectra of the comacerated NW-0.35 sample is identical to that of the mechanical mixture, NW-MM-0.35, and that it is modified in a similar way upon reduction. We could not obtain any ESR signal for pure nickel sulfide (NW-1.00), which is consistent with the findings of Voorhoeve (*18*). In this context, it is striking to note that the signals present in pure WS_2 are no longer detected in the mechanical mixture, although the latter contains 65% atomic proportion of tungsten. In other words, a simple contact of WS_2 with nickel sulfide suppresses the ESR signals present in pure WS_2 (W-0.00). The present results suggest that the electronic interactions occurring in a comacerated sample upon various treatments are identical to those experienced by a mechanical mixture, and hence the former can be considered largely biphasic. However, it is not possible to rule out the possibility of a small amount of mixed Ni–W–S phase being present in our samples for the reasons given earlier (*11, 16, 36*). The Mössbauer studies of Candia *et al.* (*11*), made on the Co–Mo catalysts prepared by the comaceration method, showed less than 10% of the total Co being present as Co–Mo–S phase, while the rest (about 90% of total Co) was present in Co_9S_8 form. Recently, the ESCA and ISS studies of Carver *et al.* (*50*) have also shown that about 90% of the total Ni (in Ni–Mo catalysts) exists as nickel sulfide.

Several authors (*51–54*) have proposed schemes for the electron transfer reactions between nickel and tungsten ions responsible for generating the HDS sites. All of them suggest the participation of W(III) ions in thiophene hydrogenolysis. Topsoe *et al.* (*10, 11*) also proposed a mechanism involving the electron transfer between Mo(III) or W(III) ions and cobalt ions in the Co–Mo–S phase for the HDS reactions. Our results corroborate well with the reported literature (*8–11, 48, 50, 53, 54*), and lead us to believe that the ineraction between ferromagnetic nickel sulfide and W(III) species in WS_2 is responsible for the synergetic effect exhibited by the comacerated samples. More experiments are underway to determine whether these electronic interactions have their origin in the remote control mechanism (*9*) or the Co(Ni)–Mo(W)–S phase.

5. CONCLUSIONS

Activities of Ni–Mo samples prepared by comaceration and HSP methods are identical suggesting that both methods are equally efficient in producing the Ni–Mo–S phase.

The activities of Ni–W sulfides have been found to increase with an increase in nickel content in accordance with current theories such as remote control theory (*8, 9*) or Co–Mo–S theory (*10, 11*). The maximum for isomerization activity occurs at $r = 0.05$ to 0.30, while that for HDS and hydrogenation lies between $r = 0.20$ to 0.40. Hydrogenation and HDS activities show the following order: Ni–W > Ni–Mo > Co–Mo.

The ESR studies show the presence of W(III) ions and ferromagnetic nickel sulfide phase. Based on the results presented here, we believe that the interaction between the ferromagnetic nickel sulfide and W(III) ions present in WS_2 brings about the beneficial effect in comacerated samples.

ACKNOWLEDGMENTS

We gratefully acknowledge many fruitful discussions with Dr. V. H. J. de Beer, Dr. D. C. Koningsberger, and Dr. A. J. A. Konings, whose expertise was decisive in interpreting our results. We also acknowledge the support of the Services de Programmation de la Politique Scientifique (Belgium) in the frame of the "Actions Concertees Interuniversitaires Catalyse" and the fellowship received by one of us (D.S.T.) from the Ministere de l'Education Nationale et de la Culture Francaise.

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