

Relation between Hydrodesulfurization Activity and the State of Promoters in Precursor Calcined Ni-Co-Mo/Al₂O₃ Catalysts

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Two series of NiCo-Mo/Al₂O₃ hydrodesulfurization (HDS) catalysts prepared by different procedures were investigated. In each series the Mo loading and the total content of promoters (Co + Ni) were kept constant but the Co/(Co + Ni) atomic ratio was varied from 0 to 1. The two series of catalysts were prepared by a sequential wet impregnation technique. In series I, the impregnations of both Mo and promoters were carried out at the pH of the impregnating aqueous solutions, employing an intermediate calcination; in series II, Mo was impregnated at pH 10, while the promoters were added in aqueous ethanol solutions without intermediate calcination. Catalysts in their calcined state were characterized by reduction in H₂ at 500°C, O₂ chemisorption, and infrared spectroscopy of adsorbed NO. The HDS activity and the optimum Co/(Co + Ni) atomic ratio were different for the two series, in agreement with our previous studies, HDS activity being generally higher for series II than for series I. Dispersion of Mo (as estimated from O₂ chemisorption) and NO adsorption on Mo in reduced catalysts (as judged from the intensity of the band at about 1705 cm⁻¹) were not substantially different for the two series of catalysts and did not correlate with HDS activity. However, adsorbed NO on promoters in oxidized catalysts (bands at about 1880 and 1800 cm⁻¹) followed roughly the same trend as HDS activity, suggesting that the active sites may be related to the Co and Ni atoms adsorbing NO. Possible reasons for the differences between HDS activity of the two series are considered. © 1986 Academic Press, Inc.

INTRODUCTION

Molybdena/alumina catalysts promoted with minor amounts of metal (Co or Ni) are commonly used in hydrodesulfurization (HDS) processes. The scientific literature on Co-Mo binary systems is abundant. By contrast, only a few studies concerning catalysts containing more than two metals have been reported (1-5), although an enhanced HDS activity of multicomponent systems is frequently claimed in patent literature (6, 7).

In a first paper, Beuther *et al.* (1) found that the addition of a certain amount of Ni to Co-Mo/Al₂O₃ catalysts resulted in an improvement of their HDS activity. In a further study Trifirò *et al.* (2) tried to modify the surface properties of the carrier by add-

ing dopant ions, viz., Ca²⁺, Fe²⁺, and Zn²⁺; they concluded that Fe²⁺ and Zn²⁺ ions may partially substitute Co, with either no effect or a slight increase of the HDS rate. Later, Martínez and Mitchell (3) studied the effect on the structure and HDS activity of adding Zn²⁺ or Mg²⁺ ions to a commercial Co-Mo/Al₂O₃ catalyst. Recently, Gil Llambías *et al.* (4) confirmed the enhancement effect of Ni on the gas-oil HDS activity of Co-Mo/Al₂O₃ catalysts produced by partial substitution of Co²⁺ by Ni²⁺ ions, with an optimum for a Co/(Co + Ni) atomic ratio of about 0.7. More recently, Brito *et al.* (5) reported also a secondary promotional effect on a NiCo-Mo/Al₂O₃ catalyst series, but the optimum Co/(Co + Ni) atomic ratio was found to be around 0.3. Such difference in the optimum atomic ratio between the two reported catalytic studies on NiCo-Mo/Al₂O₃ catalysts could be related to differences in surface structure,

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since different preparation procedures and/or pretreatment conditions were used.

Although Co and Ni have generally a similar behavior, the simultaneous presence of both Co and Ni as promoters may result in a more complex catalyst since, for example, the oxides of these transition metals show differences in reducibility, in the degree of their interaction with MoO₃ and/or Al₂O₃, and in their preferential coordination. On the other hand, recent studies (8–14) have demonstrated the usefulness of NO as a probe molecule for infrared study of HDS catalysts, providing selective information on the sites associated with Co (or Ni) and Mo atoms.

In view of the lack of characterization of the catalysts of the previous work (5), a comparative study of the two series of NiCo–Mo/Al₂O₃ catalysts should give more insight into the secondary promotional effect of such a catalytic system. The present work reports thiophene HDS activity results for such catalysts, together with characterization of their calcined state using H₂ reduction, O₂ chemisorption, and infrared spectroscopy of adsorbed NO.

EXPERIMENTAL

Preparation of Catalysts

The same two series of catalysts as described in Refs. (4, 5), designated here as series I and II, respectively, were used.

Catalysts of series I (4) were prepared by wet impregnation of the γ -Al₂O₃ (Girdler T-126, $S_{\text{BET}} = 188 \text{ m}^2 \text{ g}^{-1}$, pore volume $0.39 \text{ cm}^3 \text{ g}^{-1}$, particle size 0.84–1.19 mm) with aqueous solutions of ammonium heptamolybdate at pH 6 (first impregnation) to obtain an MoO₃ loading of 8.5 wt%, followed by a second wet impregnation with cobalt and/or nickel nitrate to obtain a total promoter content of $3.0 \pm 0.3 \text{ wt}\%$ and Co/(Co + Ni) atomic ratios in the range 0–1. Both impregnations were carried out in a rotary evaporator at 80°C and 27 kN m^{-2} . After each impregnation the samples were dried at 110°C, heated at 380°C in a flow of air for 2.5 h, and then calcined at 550°C for 4.5 h.

TABLE I
Composition of Catalysts

Catalysts	MoO ₃ ^a (wt%)	CoO (wt%)	Ni (wt%)	CoO + NiO (wt%)	Co/(Co + Ni) atomic ratio
Series I	8.5	—	—	—	—
		2.80	0.00	2.80	0.00
		2.61	0.31	2.92	0.11
		2.40	0.70	3.10	0.23
		1.70	1.60	3.30	0.49
		0.65	2.45	3.10	0.79
		0.00	2.90	2.90	1.00
Series II	10.4	—	—	—	—
		3.55	0	3.55	0.00
		2.61	0.57	3.18	0.10
		2.40	1.07	3.47	0.20
		1.86	1.24	3.10	0.31
		1.71	1.64	3.35	0.51
		1.03	2.32	3.35	0.60
		0.62	2.50	3.12	0.69
		0.30	2.68	2.98	0.82
		0.00	3.55	3.55	1.00

^a Average Mo content.

Catalysts of series II (5) were also prepared by a two-step impregnation method. The γ -Al₂O₃ (0001.5 EHP Akzo Ketjen, $S_{\text{BET}} = 213 \text{ m}^2 \text{ g}^{-1}$, pore volume = $0.51 \text{ cm}^3 \text{ g}^{-1}$, $\frac{1}{16}$ -in. extrudates) was first wetted in an NH₄OH–NH₄NO₃ buffer aqueous solution (pH 10) and then stirred in an ammonium heptamolybdate solution in the same buffer at room temperature for 48 h. The remaining solution was drained and the impregnated sample was dried under vacuum at 90°C for 1 h and subsequently at 120°C for 12 h. Portions (30 g) of the dried molybdenum-impregnated sample (10.4 wt% MoO₃) were impregnated with 100 ml aqueous ethanol solutions of cobalt and/or nickel nitrate in appropriate concentrations to achieve a constant promoter content of $3.2 \pm 0.3 \text{ wt}\%$ of MeO in all the catalysts. The excess of solvent was removed in a rotary evaporator at 60°C. The catalysts were dried at 120°C overnight and calcined at 500°C in a flow of air for 24 h. The chemical compositions of the catalysts, determined by atomic absorption spectrometry, are given in Table 1.

Reduction Measurements

Reduction measurements were carried

out in a Cahn microbalance connected to a high-vacuum line and gas-handling system. The samples (120 mg) were first evacuated at room temperature and then at 110°C to remove the molecular water, and then slowly heated to the desired reduction temperature (510°C) which was maintained until constant weight. Then the samples were contacted with 40 kN m⁻² of H₂ (99.995% purity) and the integral kinetic curves of reduction were recorded. A trap at liquid-nitrogen temperature (-196°C) placed near the sample condensed the water produced in the reduction. All experiments were carried out under essentially isobaric conditions because the dead volume of the microbalance was large compared to the negligible volume of H₂ required for the reduction. A more detailed description is given elsewhere (15).

Oxygen Chemisorption

Reduced samples (see above) were subsequently evacuated under dynamic high vacuum at 510°C for 3 h and then cooled to -196°C. When the weight of the samples was constant, oxygen (13.3 kN m⁻²) was adsorbed on the reduced catalysts. After equilibrium with oxygen was attained, the samples were evacuated until constant weight so as to remove only the physically adsorbed oxygen. The extent of O₂ chemisorption was obtained from the weight change of the sample after contacting with O₂.

Infrared Measurements

Self-supporting wafers of the calcined samples (12–15 mg cm⁻²) were prepared by pressing the powdered catalysts at 710 kN m⁻². These samples were placed inside a special IR cell with greaseless stopcocks, and evacuated under dynamic high vacuum at 500°C for 15 h. After this, 2.7 kN m⁻² of NO were contacted with the sample at room temperature for 0.5 h, and then the gas phase was condensed in a trap at liquid-nitrogen temperature (-196°C). An analogous procedure was followed with samples

previously reduced with 13.3 kN m⁻² at 500°C for 1 h. All spectra were recorded at room temperature with a Perkin-Elmer 680 double-beam grating spectrophotometer. Constant extinction coefficients and peak areas in transmittance mode were considered in calculations.

Activity Measurements

Activity measurements for hydrodesulfurization of thiophene were carried out at 400°C at atmospheric pressure in a continuous-flow system connected to an on-line gas chromatograph. The activity is referred to as thiophene conversion. Activity measurements on both presulfided (250 mg) and nonpresulfided (500 mg) powdered catalyst samples were performed. For presulfiding, the sample was first treated at 300°C in H₂ for 1 h before H₂S admission and then sulfided with H₂S at 400°C for 2 h. For activity tests on nonpresulfided sample, prior to reaction the catalyst was pretreated at 400°C in a helium flow for 1 h.

RESULTS

Hydrodesulfurization Activity

The steady-state thiophene conversions of both presulfided and nonpresulfided catalysts of series I and II are compared in Fig. 1. A secondary promotional effect by partial replacement of Co by Ni in both series of catalysts was observed, in good agreement with previous results (4, 5). For series I, the maximum in activity occurred at an atomic ratio, r , of about 0.8 or 0.7, depending on pretreatment, whereas for series II it was at about 0.2–0.3. It is seen that all catalysts of series II have a higher activity for hydrodesulfurization than those of series I. In addition, in both series of catalysts the presulfided samples showed higher activity than nonpresulfided ones.

Catalyst Reduction

The reduction results expressed in terms of the extent of reduction, α , for the two series are shown in Fig. 2. The extent of

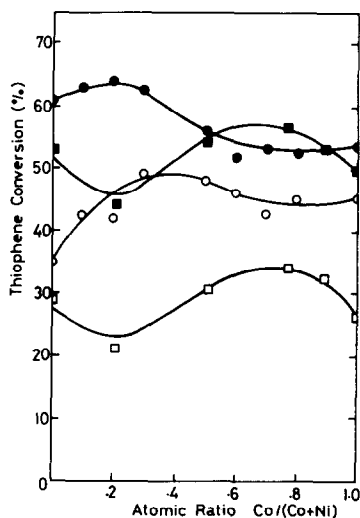


FIG. 1. Dependence of thiophene conversion on the atomic ratio $\text{Co}/(\text{Co} + \text{Ni})$ for series I (\square , \blacksquare) and II (\circ , \bullet) catalysts. Samples nonpresulfided (\square , \circ) and presulfided (\blacksquare , \bullet).

reduction is based on the catalyst weight loss obtained after hydrogen treatment compared to that calculated for reduction of MoO_3 to MoO_2 , NiO to Ni , and CoO to Co .

It is evident that the reducibility of the two catalyst series was substantially different, the extent of reduction being clearly higher for series II than for series I. In both series the extent of reduction of the catalyst

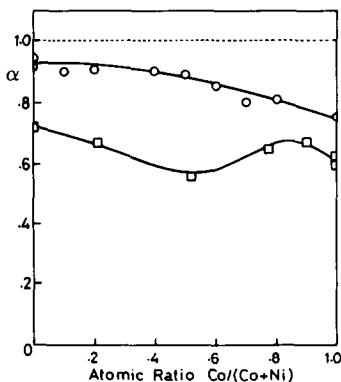


FIG. 2. Extent of reduction at 510°C as a function of the atomic ratio $\text{Co}/(\text{Co} + \text{Ni})$ for series I (\square) and II (\circ) catalysts.

containing only Ni–Mo ($r = 0$) was higher than that of the catalyst containing only Co–Mo ($r = 1$), in agreement with previous results (4). However, the extent of reduction decreased monotonically with r in series II whereas in series I a relative minimum (at about $r = 0.5$) and a relative maximum (at about $r = 0.8$) were found. It is also noted that the extent of reduction for the Ni–Co-containing molybdena catalysts of series II was slightly higher than that expected from the behavior of the single Co (or Ni)-promoted catalysts.

In addition, the general tendency of the extent of reduction for series I in the composition range $0.5 < r < 1.0$ was apparently different from that reported previously for the same catalyst series (4). This apparent difference is probably due to differences in the reduction temperatures and in the reduction procedure used. In the present study a trap at liquid-nitrogen temperature placed near the catalyst sample was used to remove the water formed during the reduction process, avoiding, in this case, the reoxidation of the catalysts (12).

Oxygen Chemisorption

The oxygen chemisorption results for the calcined catalysts as a function of their $\text{Co}/(\text{Co} + \text{Ni})$ atomic ratio are shown in Fig. 3. For the catalysts of series I, no appreciable variation in the oxygen uptake was observed. For the catalysts of series II, a slight decrease in the oxygen uptake at high atomic ratio seems to occur, although the

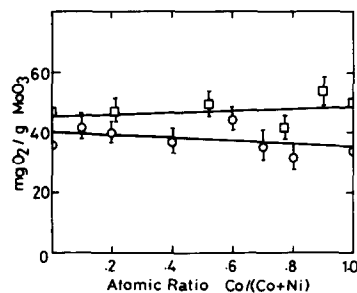


FIG. 3. Oxygen uptake as a function of the atomic ratio $\text{Co}/(\text{Co} + \text{Ni})$ for series I (\square) and II (\circ) catalysts.

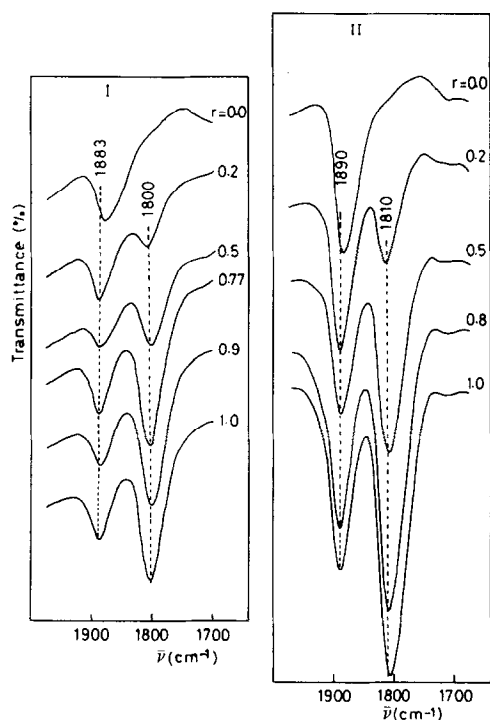


FIG. 4. IR spectra of NO adsorbed on series I and II catalysts after treatment under vacuum at 500°C.

variation is close to the experimental error. It can also be seen that the oxygen uptakes of the catalysts of series I were slightly higher than those of series II at high Co/(Co + Ni) atomic ratio, but they were not significantly different at low atomic ratio, suggesting that the fraction of reduced Mo able to chemisorb oxygen is not significantly higher for series I than for series II.

For the parent Mo/Al₂O₃ samples used for preparing the Co-Ni-promoted catalysts, the oxygen uptake was found to be 72.5 and 67.5 mg O₂ per g MoO₃ for series I and II, respectively.

IR Spectra

Typical spectra of adsorbed NO at room temperature on calcined catalysts evacuated at 500°C for 15 h, after the gas phase was condensed, are shown in Fig. 4. The Ni-Mo-containing catalysts ($r = 0$) gave rise to a single band at about 1870 cm⁻¹ (series I) or 1880 cm⁻¹ (series II), whereas

the Co-Mo-containing catalysts ($r = 1$) exhibited two bands at 1800 and 1883 cm⁻¹ (series I) or 1805 and 1890 cm⁻¹ (series II). The band at about 1870–1880 cm⁻¹ may be due to dinitrosyl species on Ni atoms octahedrally coordinated (14) and the doublet around 1800 and 1880 cm⁻¹ has been attributed to dinitrosyl or dimeric species on Co atoms octahedrally coordinated (11). The Ni-Co-Mo-containing catalysts also showed two bands at 1800 and 1880 cm⁻¹ for series I and at 1810 and 1887–1890 cm⁻¹ for series II. It is clear that the high-frequency band contains contributions from NO chemisorbed on both Co and Ni atoms, and its intensity was observed to remain virtually constant, since the Co + Ni composition is constant, whereas the low-frequency band is practically associated only with Co and, therefore, its intensity decreased with decreasing Co content.

A weak broad band centered at about 1705 cm⁻¹, which appeared in series II, indicates that some reduced Mo species may be present on this series after evacuation at 500°C. This is particularly noteworthy in the catalyst with $r = 0$, where also a shoulder at about 1810 cm⁻¹ appears. In the spectra of series I, the weak band at about 1705 cm⁻¹, and the shoulder at about 1810 cm⁻¹ for $r = 0$, were not detected.

It is also evident in Fig. 4 that, in general, catalysts of series II exhibit more intense bands than catalysts of series I. This is more clearly seen in Fig. 5, where the intensities of the band at about 1800 cm⁻¹ (adsorption on Co) and the band at about 1880 cm⁻¹ (adsorption on both Co and Ni) as a function of the Co/(Co + Ni) atomic ratio are compared for the two series. In series I the intensities of the two bands at about 1800 and 1880 cm⁻¹ were found to be at a maximum for $r = 0.8$. Although no similar maximum was observed in series II, it is, however, significant that the Ni-Co-containing catalysts showed higher intensities than those expected if an additive behavior exists between the extreme ($r = 0$ and $r = 1$) catalysts.

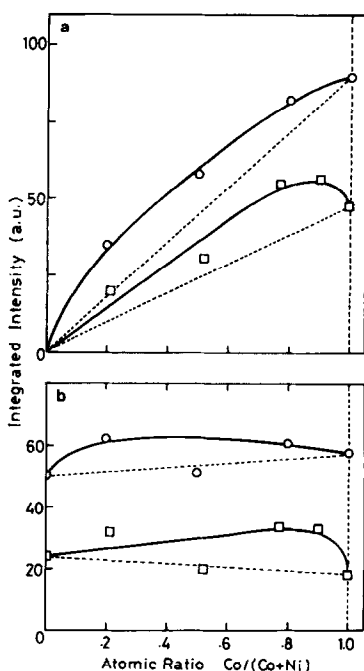


FIG. 5. Effect of the atomic ratio $\text{Co}/(\text{Co} + \text{Ni})$ for series I (\square) and II (\circ) catalysts on the integrated intensity of the IR bands of adsorbed NO: (a) on Co (at about 1800 cm^{-1}) and (b) on Co + Ni (at about 1880 cm^{-1}). From spectra of Fig. 4.

Spectra of adsorbed NO at room temperature on catalysts reduced at 500°C for 1 h, after the gas phase was condensed, are shown in Fig. 6. The salient features of the spectra after reduction as compared with those of only-evacuated catalysts were: (i) shifts of about $3\text{--}5\text{ cm}^{-1}$ toward low frequencies in the bands associated with Ni and Co, predominantly for catalysts of series II (i.e., from 1880 to 1877 cm^{-1} for $r = 0$, and from 1805 and 1890 to 1802 and 1885 cm^{-1} , respectively, for $r = 1$); (ii) the appearance of a broad band at about 1705 cm^{-1} , due to a dinitrosyl complex (8, 12) or to a NO dimer (10–12) adsorbed on reduced Mo species, whose intensity for the binary catalysts (Co– or Ni–Mo) was apparently similar for the two series, whereas for the ternary catalysts (Co–Ni–Mo) it was slightly higher for series II; and (iii) a relative increase in the intensity of the band at about 1800 cm^{-1} (series I) or at about 1805

cm^{-1} (series II) of the Co-containing catalyst, also due to the contribution of NO adsorbed on reduced Mo species. Since the content of Co of the catalysts varies, the intensity of the 1800-- or 1805 cm^{-1} band was observed to vary as a function of the $\text{Co}/(\text{Co} + \text{Ni})$ atomic ratio.

DISCUSSION

The above results show clearly that marked differences in surface properties occur between the series I and II of Co–Ni–Mo/ Al_2O_3 catalysts, as a result of the variations in several parameters of the preparation, including the use of the alumina supports from different sources.

The differences in HDS activity between the two series are significant; they could be due, generally speaking, to variations in the surface distribution of the various possible Mo and/or promoter species. We will ex-

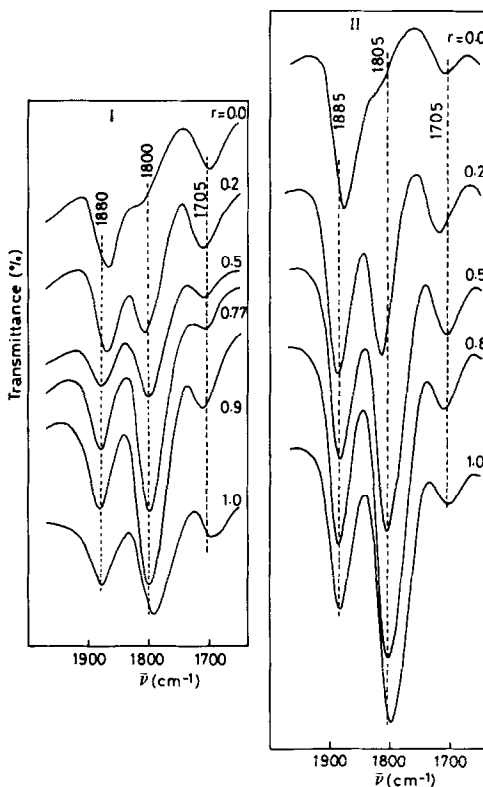


FIG. 6. IR spectra of NO adsorbed on series I and II reduced catalysts.

amine first whether the differences in HDS activity could be related to changes in Mo dispersion or not, since the two series differ, apart from other preparation parameters, in the alumina support, and slightly in Mo coverage (wt%/m²). The importance of such effects on the structure and HDS activity of Ni-Mo/Al₂O₃ catalysts has recently been shown (16). However, in the present catalysts the differences in the characteristics of the alumina and Mo coverage do not seem to be significant, since the oxygen uptakes of the two parent Mo/Al₂O₃ samples corresponding to the catalysts of series I and II were very similar. Consequently, as oxygen chemisorption provides a relative measure of the dispersion of Mo in reduced supported-molybdena catalysts (17, 18), it can be concluded that the parent Mo/Al₂O₃ samples have similar dispersions and, therefore, the first step of the preparation (Mo impregnation) cannot be responsible for the differences in HDS activity between the two series of catalysts.

Upon addition of Co and/or Ni to the Mo/Al₂O₃ samples, the oxygen uptake did not vary significantly with the Co/(Co + Ni) atomic ratio for each of the series I and II (Fig. 3). Consequently, the dispersion of Mo remains practically constant in each of the series and is slightly larger for series I than for series II, which is contrary to the order for HDS activity. However, as the intensity of the band at about 1705 cm⁻¹ (adsorption on Mo) changed slightly with the Co/(Co + Ni) atomic ratio (Fig. 6), it can be interpreted that the distribution of the various Mo species present on the catalysts is not uniform along the series. Nevertheless, for each of the series, the intensity of this Mo band does not correlate with HDS activity. In general, all these changes in dispersion of Mo and in the amount of Mo phase adsorbing NO are small as compared with that found for the HDS activity. Thus, comparing series I with series II, it is seen (Figs. 1 and 3) that while the HDS activity for the nonpresulfided samples in-

creased by 25% (catalyst $r = 0$) or about 72% (catalyst $r = 1$), the corresponding oxygen uptake only increased by 12 or 35%, respectively. For some of the catalysts containing both Co and Ni, this difference in the increases can be even larger. Similar inconsistency arises when comparing the HDS activity of the presulfided samples with the oxygen uptake. Thus, it appears that the differences in HDS activity between series I and II and, also, between catalysts within each series, are, in principle, not directly related to the dispersion of Mo, nor to the NO adsorption on Mo.

The marked difference between the reducibility of the catalysts of series I and II (Fig. 2) may then reflect differences in the distribution of the various Co (or Ni) species present in the catalysts, i.e., promoter ions entering into the alumina matrix (non-reducible species) and those which are on or near or in the surface molybdate layer (reducible species). The possibility that the difference in reducibility (Fig. 2) could be only or mainly due to a difference in the dispersion or the distribution of Mo species is highly unlikely in view of the above discussion, particularly on the basis of the small or no difference found between the NO adsorption on Mo of series I and II. It is reasonable, therefore, that the higher reducibility of series II as compared with that of series I can be taken as due to the presence of a larger fraction of octahedrally coordinated Co and/or Ni surface species in series II than in series I (Fig. 5); it is known (19, 20) that Co and Ni atoms located in octahedral coordination are relatively more reducible than those in tetrahedral coordination. Another interesting point is that the reducibility of catalysts and the corresponding HDS activity tend to vary almost similarly with the Co/(Co + Ni) atomic ratio; this rough analogy is better observed for the series I, where the maxima for reducibility and HDS activity appear at approximately similar range (0.7–0.8) of Co/(Co + Ni) atomic ratio. This can be taken

as indicating that the changes in HDS activity are related to the variations of the fraction of octahedral Co and/or Ni species.

The infrared results of NO chemisorption on Co and Ni atoms (Fig. 5) provide further evidence that variations in HDS activity seem to be related to the octahedral Co and Ni surface species. Thus, the NO adsorption on Co (band at about 1800 cm^{-1} , Fig. 5a) and on Co + Ni (band at about 1880 cm^{-1} , Fig. 5b) was clearly larger for series II than for series I, and it has been shown that NO adsorption occurs preferentially on the Co (or Ni) ions that at least before NO adsorption were octahedrally coordinated (11). It is also interesting that the variation of NO adsorption on the promoters (Fig. 5b), and the corresponding variation of HDS activity on nonpresulfided samples (Fig. 1) with Co/(Co + Ni) atomic ratio have almost similar trends. This is particularly notable for series I, where both the HDS activity and the NO adsorption on the promoter showed a maximum at about the same Co/(Co + Ni) atomic ratio. For series II, such parallelism is, however, less satisfactory probably due to less marked differences between the catalysts, but the Ni-Co-containing catalysts showed more NO adsorption on the promoter than expected from the behavior of the singly promoted catalysts. All these facts suggest that the higher activity of the nonpresulfided samples of series II as compared with that of series I is likely to be associated with the large amount of NO-adsorbing exposed octahedral promoter atoms present in the former series, and presumably interacting strongly with the Mo phase. Recently, Topsøe and Topsøe (14) have also reported a good correlation between HDS activity and the amount of NO adsorbed on the Co or Ni atoms for calcined and sulfided Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts. However, from the present study it cannot be decided whether the maximum in activity for each of series I and II corresponds to an optimization of the exposed octahedral Co (or Ni) or of both Co and Ni atoms,

because in the case of Ni-Co-containing catalysts the infrared results do not provide separate information on Ni atoms adsorbing NO.

Although the present results do not permit a more precise description of the structures of the two series of catalysts studied, and a correlation with the preparation procedure, it can nevertheless be concluded that the differences observed seem to be related to the second step of the preparation of the catalyst (the impregnation of the promoters) or to the pretreatment conditions (the calcination temperature). This may lead to changes in the Co/(Co + Ni) atomic ratio at which the promoter phase (probably octahedral species adsorbing NO) associated with the Mo produces an optimum situation. In this respect, we are presently studying the effect of the calcination temperature on the surface structure and HDS activity of one of the Ni-Co-Mo/Al₂O₃ catalyst series, since this preparational parameter may affect the distribution of the Co and/or Ni species on the surface.

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