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# On the Promoting Effect in Sulfided Ni–Mo/$Al_2O_3$ Catalysts as Studied by Chemisorption

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Two series of thiophene-sulfided Ni–Mo/$Al_2O_3$ catalysts, with constant molybdenum content (7 and 16 wt% $MoO_3$, respectively) and variable nickel concentration have been characterized by their thiophene hydrodesulfurization activities and their chemisorption capacities measured *in situ*. Carbon monoxide adsorption was performed at 0°C and oxygen uptake at 60°C. Both adsorbate molecules exhibit similar behavior in the series and are thought to be good probes for anion vacancies. For the first series of catalysts, the characterizations distinguish three concentration ranges according to the Ni/Mo ratio. The main enhancement of activity is observed in the range $0.2 < \text{Ni/Mo} < 0.6$ with a simultaneous slight increase in gas consumption. Comparison of the data with similar characterizations of Ni/$Al_2O_3$ catalysts indicates that the promoting effect is not associated with an excess of anion vacancies. The whole set of samples leads to three different kinds of correlation between activity and chemisorption, thus revealing different actions of nickel ions on the molybdenum-based catalyst. For the second series, chemisorption results are not clearly influenced by the Ni content.

## INTRODUCTION

Hydrodesulfurization (HDS) is usually performed on catalysts which associate, in a sulfide form, Mo or W with Co or Ni, dispersed on a γ-alumina support. In these mixed catalysts, Mo or W are thought to act as active components and their activity is enhanced by the presence of Co or Ni. The influence of the so-called promoter Group VIII elements depends on their loading and it is well established that a maximum promoting effect is encountered for a Co(Ni)/Mo(W) atomic ratio in the range 0.2–0.6 (*1–4*).

The role of the promoter ions in the catalytic couple has not yet received any satisfactory explanation, in spite of the numerous investigations published on the subject (for reviews, see Refs. (*1–4*)). The controversy hinges on the nature of the promoted active phase, mainly discussed in respect of Co-Mo studies. This phase is variously regarded as slightly or widely different from that proposed for supported Mo catalysts. Thus, the molybdenum layer is thought by some to remain in the presence of cobalt, but is supposed to be stabilized (*1*) or better dispersed on the support (*5*). Other models are based on the assumption that the molybdenum is present in the sulfide phase as $MoS_2$ crystallites and consequently the models may apply to both supported and unsupported catalysts. According to these models, the promoter effect arises from intercalation of Co ions between the slabs (*6*), or more probably at the slab edges (*7, 8*), of the layered $MoS_2$ structure. Another view is that the Co–Mo catalyst acts by synergy (*9*) as a result of a close contact between the two separate $MoS_2$ and $Co_9S_8$ stable sulfide phases. In a more recent description of the promoted catalyst (*10*), Co is considered to be associated with $MoS_2$ in a Co–Mo–S phase, with Co atoms probably located in substitutional positions at the edges of S–Mo–S slabs. On the other hand, the concept of Co being a promoter is questioned, since cobalt has been regarded as a catalyst by itself, even in the absence of molybdenum (*11, 12*).

Whatever the true situation, any ap-

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proach to understanding the promoting effect must involve a study of the catalytic sites, since the observed increase in activity reflects modifications in the surface state. In this respect, a better knowledge of the active sites, and especially their titration on promoted catalysts will be of fundamental significance to promoter action. This aspect will be examined in the present report, and the implications for the structural arrangement of the active phase will be discussed in the following paper (*13*).

Application of probe molecules, as developed for metal catalysts, seems very appropriate to the study of the HDS sulfide catalyst surface, in spite of the experimental necessity of performing measurements *in situ* due to the extreme sensitivity of sulfided catalysts toward air. First assays carried out by a pulse dynamic method on unsupported $MoS_2$ by Tauster *et al.* (*14*), and on sulfided $Ni/Al_2O_3$ catalysts in our group (*15*) demonstrated that oxygen uptake varies linearly with HDS activity. Examination of sulfided $Mo/Al_2O_3$ catalysts led us to conclude that both carbon monoxide and oxygen are valuable adsorbates for titrating active sites (*16*).

The results reported here deal with sulfided $Ni–Mo/Al_2O_3$ catalysts. This system has received much less attention than the Co–Mo couple, but is also of interest in view of the needs for more selective catalysts, especially for the hydrogenation of unsaturated compounds or hydrodenitrogenation. In addition, comparison with the "one-component" $Ni/Al_2O_3$ and $Mo/Al_2O_3$ catalysts previously studied is directly available (*15–18*). Carbon monoxide and oxygen uptakes measured by a dynamic method will be compared with catalytic activity data for thiophene HDS and propene hydrogenation reactions. In these studies, the promoting effect will be examined on catalysts with constant Mo concentration and variable Ni content. The influence of the overall Ni/Mo atomic ratio will be checked on two Mo-based catalysts with different loadings, 7 and 16% $MoO_3$, since previous characterization of $Mo/Al_2O_3$ catalysts indicated very different behavior according to the Mo concentration (*17*). Examination of an industrial catalyst will complete the series.

## EXPERIMENTAL

### Catalysts

The $Ni–Mo/Al_2O_3$ catalyst preparation involves two successive impregnations by pore volume filling. The $\gamma$-alumina (Rhone Poulenc, surface area 238 $m^2\ g^{-1}$, pore volume 0.6 $cm^3\ g^{-1}$, sieved 90–190 mesh) is first impregnated with ammonium heptamolybdate solution, dried for 12 h at 110°C in air, and calcined for 2 h at 500°C under air circulation. Nickel is then introduced by a second impregnation with nickel nitrate, followed by drying and a final calcination for 1 h at 500°C. The samples are recalcined for 2 h at 500°C just prior to their introduction in the reactor.

Two series of $Ni–Mo/Al_2O_3$ samples have been prepared in this way, with constant molybdenum content (6.9 or 15.7% $MoO_3$) and variable nickel concentrations ($x$ or $y$ NiO%). These series are denoted Mo-7–Ni-$x$ ($0.4 < x < 4$) and Mo-16–Ni-$y$ ($0.5 < y < 8.3$). The industrial Procatalyse HR 346 catalyst (14% $MoO_3$, 3.5% NiO) has been compared with the second set of Ni–Mo samples.

For both series, the nickel concentration parameter will be expressed either as NiO% when comparison between $Ni–Mo/Al_2O_3$ and $Ni/Al_2O_3$ catalysts is looked for, or as Ni/Mo atomic ratio. The use of the latter parameter minimizes the slight differences in Mo concentrations and thus allows us to a first approximation to include the industrial Procatalyse HR 346 catalyst in the Mo-16–Ni-$y$ series.

### Procedure

Sulfidation of the sample, catalytic activity tests for thiophene HDS or propene hydrogenation reactions, and dynamic oxygen or carbon monoxide uptakes are performed in the same flow apparatus working at atmospheric pressure. Thus, the three measurements are successively carried out on the same sample without transfer of the sulfided catalyst. The equipment has been previously set up for examination of Ni and Mo/$Al_2O_3$ catalysts; details are reported elsewhere (*15–18*).

*Sulfidation and catalytic activity.* The calcined Ni–Mo/$Al_2O_3$ sample is sulfided in the reactor directly with a $H_2$ (700 Torr)–thiophene (60 Torr) reaction mixture at 420°C without presulfidation. Stabilization is achieved in 24 h and followed by the measurement of the catalytic HDS activity, which is expressed as the rate of thiophene hydrogenolysis at initial conversions, $r_{HDS}$ (mol $h^{-1}$ $g^{-1}$). For conversions higher than 0.05, $r$ values are derived from a pseudo-first-order behavior, as generally assumed in test experiments. Following this test, a feed of propene is added for 30 min in the thiophene–$H_2$ flow and the hydrogenation rate of the olefinic compound, $r_{Hyd}$ (mol $h^{-1}$ $g^{-1}$), is determined in the same way as $r_{HDS}$. The ratio $r_{Hyd}/r_{HDS}$ is used to characterize the catalyst selectivity.

*Chemisorption measurements.* At the end of the 24-h period needed for stabilization and activity tests, the sulfided catalyst is subsequently flushed with argon for 2 h at 420°C, then measured for its oxygen or carbon monoxide capacity in the reactor itself by a dynamic method. Successive pulses are run onto the sulfided catalyst held at 60°C (oxygen) or 0°C (carbon monoxide) until cumulative adsorption ($N_O$, mol O $g^{-1}$ and $N_{CO}$, mol $g^{-1}$) remains constant. At these temperatures, the support has no effect, and side reactions ($SO_2$ or COS formation) are avoided. According to previous studies (*15–18*) oxygen is fixed irreversibly on sulfide catalysts. The temperature dependence of the oxygen uptake shows that 60°C marks a frontier between surface and bulk oxidation. By contrast, carbon monoxide uptake is really chemisorbed. However, $N_{CO}$ measured at 0°C by the pulse method represents only a fraction of the total capacity of the catalyst: chemisorption would be complete at much lower temperature, but it cannot be achieved by pulses since CO adsorbs at a slow rate. Measurements at low temperature were carried out on typical samples (Ni-8, Mo-7, and Mo-7–Ni-1.6) as follows. The purged sulfided catalyst is first swept at −133°C for 3 h with pure CO flow to allow both physisorption and chemisorption to take place; in a second step, physisorbed CO is selectively eliminated by flushing the sample with helium for 20 h at the same temperature and finally the amount of gas remaining on the catalyst (chemisorbed CO) is desorbed by warming the sample up to 250°C in flowing helium.

## RESULTS

### Catalytic Activities

Since sulfidation and stabilization of initially oxidic Mo/$Al_2O_3$ catalysts under thiophene–$H_2$ was found to stretch over a period of 24 h, the HDS reaction rates on Ni–Mo/$Al_2O_3$ catalysts reported here have been measured after this standard running time. However, it is worth mentioning that the apparent stabilization period varies with the nickel content. In this respect, low Ni/Mo samples behave like the Mo-7 or Mo-16 reference catalysts and reach steady state activities after about 10 or 20 h, respectively; this period shortens with increasing Ni concentration and finally high Ni/Mo catalysts stabilize after 5 h on stream, as the Ni/$Al_2O_3$ catalysts.

Rate data are given in Table 1 and plotted in Fig. 1 as a function of the Ni/Mo ratio. They are in line with those previously obtained by many investigators, since they clearly show the positive effect of nickel addition upon both the HDS and hydrogenation activities of the Mo catalysts. However, the promoting action is rather weak at low Ni concentration (Ni/Mo-7) $< 0.2$; (Ni/Mo-16) $< 0.1$. The main effect occurs in the range 0.2 (0.1) $<$ Ni/Mo $<$ 0.6 (0.5), for which the HDS reaction rates gradually increase; for the most active catalyst, a four

TABLE 1

Characterization of Ni–Mo/$Al_2O_3$ Catalysts

| Catalyst | | | Activities | | | Chemisorption | |
|---|---|---|---|---|---|---|---|
| Symbol | NiO (wt%) | Atomic Ni/Mo | $10^3$ $r_{HDS}$ (mol $h^{-1}$ $g^{-1}$) | $10^3$ $r_{Hyd}$ (mol $h^{-1}$ $g^{-1}$) | Selectivity | Oxygen (60°C) $10^4$ $N_O$(mol O $g^{-1}$) | CO (0°C) $10^4$ $N_{CO}$(mol $g^{-1}$) |
| Mo-7(6.9% $MoO_3$) | — | — | 2.56 | 3.40 | 1.33 | 1.75 | 0.27 |
| Mo-7–Ni-0.4 | 0.37 | 0.10 | 2.96 | 3.90 | 1.32 | 2.13 | 0.30 |
| Mo-7–Ni-0.6 | 0.61 | 0.17 | 3.23 | 3.77 | 1.17 | 2.14 | 0.31 |
| Mo-7–Ni-1.2 | 1.20 | 0.33 | 6.06 | 5.27 | 0.87 | 2.50 | 0.38 |
| Mo-7–Ni-1.6 | 1.62 | 0.45 | 8.70 | 7.29 | 0.84 | 2.92 | 0.43 |
| Mo-7–Ni-2 | 1.99 | 0.55 | 10.31 | 8.46 | 0.82 | 2.99 | 0.47 |
| Mo-7–Ni-2.2 | 2.24 | 0.62 | 10.74 | 9.26 | 0.86 | 3.04 | 0.48 |
| Mo-7–Ni-2.7 | 2.71 | 0.78 | 10.98 | 9.12 | 0.83 | 3.31 | 0.48 |
| Mo-7–Ni-3.2 | 3.21 | 0.92 | 10.96 | 9.25 | 0.84 | 3.68 | 0.49 |
| Mo-7–Ni-4 | 3.96 | 1.11 | 10.97 | 9.23 | 0.84 | 4.00 | 0.51 |
| Mo-16(15.7% $MoO_3$) | — | — | 5.78 | 10.00 | 1.73 | 3.56 | 0.67 |
| Mo-16–Ni-0.7 | 0.7 | 0.09 | 7.11 | 9.88 | 1.39 | 3.67 | 0.57 |
| Mo-16–Ni-1.2 | 1.16 | 0.14 | 9.52 | 10.71 | 1.13 | 3.78 | 0.55 |
| Mo-16–Ni-4.3 | 4.29 | 0.53 | 31.03 | 16.40 | 0.53 | 3.80 | 0.63 |
| Mo-16–Ni-8.3 | 8.32 | 1.04 | 28.02 | 15.56 | 0.56 | 4.25 | 0.63 |
| HR 346[a] | 3.5 | 0.48 | 31.70 | 17.37 | 0.55 | 3.75 | 0.50 |
| Ni-1[b] | 1.09 | — | 0.22 | 0.12 | 0.55 | 0.6 | — |
| Ni-4 | 4.02 | — | 0.75 | 0.36 | 0.49 | 2.0 | 0.07 |
| Ni-8 | 7.84 | — | 1.38 | 0.58 | 0.42 | 4.2 | 0.13 |

[a] Industrial catalyst: 14% $MoO_3$.

[b] Ni/$Al_2O_3$ catalysts.

(five)-fold increase in $r_{HDS}$ is observed. Further nickel addition has no more influence in the Mo-7–Ni-$x$ series, and tends to lower the reaction rate in the Mo-16–Ni-$y$ series.

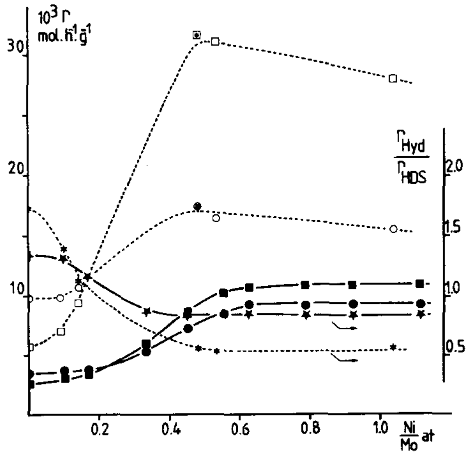

FIG. 1. Ni–Mo/$Al_2O_3$ catalysts. Activities for HDS (square symbols) and hydrogenation (circled symbols) as a function of the Ni/Mo molar composition ratio. Selectivities ($r_{Hyd}/r_{HDS}$) denoted by starred symbols. (■, ●, ✱) Mo-7–Ni-$x$ catalysts. (□, ○, ＊) Mo-16–Ni-$y$ catalysts. (▣, ◉, ✱) HR 346 catalyst.

Activity for propene hydrogenation follows the same general trends, but from the selectivity curves it is seen that nickel addition affects hydrogenolysis more strongly than hydrogenation.

However, the selectivity values are different in each of the Ni–Mo series. For the Mo-7–Ni-$x$ catalysts, $r_{Hyd}/r_{HDS}$ seems at first constant at 1.3, up to Ni/Mo $< 0.2$; this level corresponds to that observed for the reference Mo-7 sample. It then decreases with increasing Ni/Mo ratio and finally stabilizes at 0.8 for Ni/Mo $> 0.6$. In the Mo-16–Ni-$y$ series, the selectivity starts at a higher level, 1.6, and sharply decreases; for Ni/Mo higher than 0.5, it remains constant at 0.5, close to the value obtained in the case of Ni/$Al_2O_3$ catalysts. The HR 346 industrial catalyst is well included in the latter series; its catalytic properties locate this sample at the maximum of the curves.

### *Oxygen and Carbon Monoxide Uptakes*

The amounts of oxygen $N_O$ (60°C) and carbon monoxide $N_{CO}$ (0°C) that can be taken up by the sulfided Ni–Mo/$Al_2O_3$ catalysts by the pulse chemisorption method are collected in Table 1. Figure 2 presents the variation of $N_O$ and $N_{CO}$ with Ni/Mo or NiO% in the Mo-7-$x$ series. Results for the two probe molecules lead to different curve shapes: from the $N_O$ data points, an almost straight line can be drawn in the whole Ni/Mo range, while Ni/Mo $\simeq$ 0.6 distinguishes two regions in the case of $N_{CO}$.

Figure 2 and Table 1 also include chemisorption data for Ni/$Al_2O_3$ catalysts treated in the same conditions; for those samples, increasing Ni content on alumina leads to a proportional increase in chemisorption of both gases, as long as the active phase remains dispersed, i.e., up to 13% NiO (*18*). Comparison with Ni–Mo/$Al_2O_3$ catalysts can be given by the slopes $\Delta N_O(N_{CO})/\Delta$Ni. It is seen that the $N_O$ lines run parallel in both Ni–Mo and Ni/$Al_2O_3$ catalysts, so that nickel ions added either to the Mo-7/$Al_2O_3$ catalyst or to the alumina leads to the same proportional increase in oxygen uptake, almost one O atom per two Ni atoms. Results are different when considering carbon monoxide chemisorption.

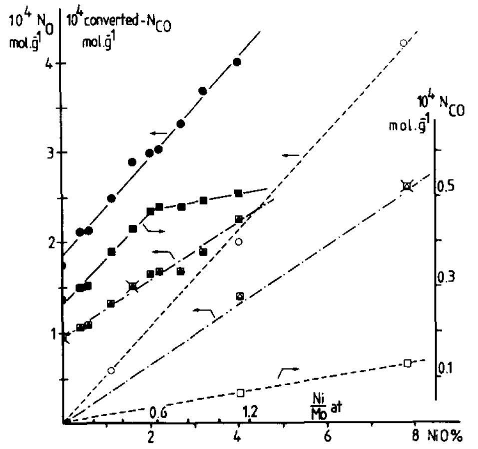

FIG. 2. Oxygen and carbon monoxide chemisorptions by Ni–Mo/$Al_2O_3$ (Mo-7–Ni-$x$) and Ni/$Al_2O_3$ catalysts as a function of the nickel content. Oxygen uptake 60°C ($N_O$) ●, Ni–Mo/$Al_2O_3$; ○, Ni/$Al_2O_3$. Carbon monoxide chemisorption: 0°C ($N_{CO}$) ■, Ni–Mo/$Al_2O_3$; □, Ni/$Al_2O_3$, −133°C ⊠, Mo-7 and Mo-7–Ni-1.6; ⊠, Ni-8. Converted-$N_{CO}$ (see text) ▣, Ni–Mo/$Al_2O_3$; ▨, Ni/$Al_2O_3$.

In the range Ni/Mo < 0.6, the Ni–Mo catalysts show a much larger increase in $N_{CO}$ than the Ni/$Al_2O_3$ samples, while for higher Ni concentration the slopes are rather similar in both systems.

Such different behaviors of the two adsorbates towards the Ni–Mo catalysts is intriguing, since striking similarities have been observed in the case of "one-component" Mo/$Al_2O_3$ and Ni/$Al_2O_3$ catalysts (*16, 18*).

As described in the experimental section, performing CO adsorption by the pulse method at 0°C does not measure the total capacity of the catalyst. Based on the few experiments carried out at −133°C, one can see from Fig. 2 that the Mo-7–Ni-1.6 sample is able to chemisorb 3.5 times more CO at −133°C than in the pulse test at 0°C. The same ratio holds for the Mo-7 sample but a factor as high as 20 is found in the case of the Ni-8/$Al_2O_3$ catalyst. Thus, the two linearities of the $N_{CO}$ (0°C) pulse curve observed for the Ni–Mo catalysts may arise from different fractions of sites detected by the probe at 0°C according to the Ni/Mo composition ranges.

Since oxygen uptake $N_O$ at 60°C expresses the complete detection of surface sites for the whole set of catalysts, it follows that for correct comparison in the site titration by the two adsorbates one should convert $N_{CO}$ measured at 0°C into the total CO capacity of the catalysts. It is found (Fig. 2) that for all the Mo-7–Ni-$x$ catalysts, complete carbon monoxide uptakes reasonably lie on a straight line, as does $N_O$, when treating the conversion of $N_{CO}$ (0°C) data as follows. For the Ni–Mo catalysts belonging to the composition range Ni/Mo < 0.6, a 3.5 factor is applied to $N_{CO}$, according to the $N_{CO(-133°)}/N_{CO(0°C)}$ ratio observed for the typical Mo-7–Ni-1.6 catalyst; in the range Ni/Mo > 0.6, since the slopes $\Delta N_{CO(0°C)}/\Delta$Ni are rather similar for Ni–Mo and Ni/$Al_2O_3$ catalysts, it is assumed that beyond Ni/Mo $\simeq$ 0.6, CO behaves toward the Ni–Mo catalyst similarly as toward the Ni/$Al_2O_3$ catalyst, and thus obeys the conversion factor

20. As an example, the measured $N_{CO}$(0°C) value of $0.5 \times 10^{-4}$ for the Mo-7–Ni-4 catalyst (Ni/Mo = 1.11) (Table 1) is composed of $0.48 \times 10^{-4}$ up to Ni/Mo = 0.6 and $(0.51-0.48) \times 10^{-4}$ beyond. Its total CO capacity is then the following sum $\{[0.48 \times 3.5] + [(0.51 - 0.48) \times 20]\}10^4 = 2.28 \times 10^{-4}$ mol $g^{-1}$.

Finally, nickel addition to the molybdenum Mo-7 sample leads to a proportional increase in both total gas capacities of the catalysts.

The proportionality constants compare well in the Mo-7–Ni-*x* and Ni-*x* series, namely, almost 0.5 oxygen atom and about 0.25 CO molecule as one nickel atom is added.

In case of the Mo-16–Ni-*y* series, chemisorption is not clearly influenced by the Ni content: the amounts of $O_2$ or CO consumed at 60 or 0°C seem approximately constant for all the samples studied, except the Mo-16–Ni-8.2 catalyst, which leads to a higher $N_O$ value than the reference Mo-16 catalyst. The industrial HR 346 catalyst is in line with these results.

### *Relationship between HDS Activity and Gas Adsorbate Capacity*

The rate of thiophene hydrogenolysis on the various Mo-7–Ni-*x* catalysts is plotted in Fig. 3 against the chemisorption capacities. For oxygen as the probe molecule, $N_O$ measured at 60°C is plotted directly on the *x* axis; in the case of carbon monoxide, the $N_{CO}$ value measured in the test experiment at 0°C has been converted into the total capacity of the samples as described in the preceding section. On the same plot are shown the corresponding values, $N_O$ and converted-$N_{CO}$, for the "one-component" $Ni/Al_2O_3$ and $Mo/Al_2O_3$ samples (*16*).

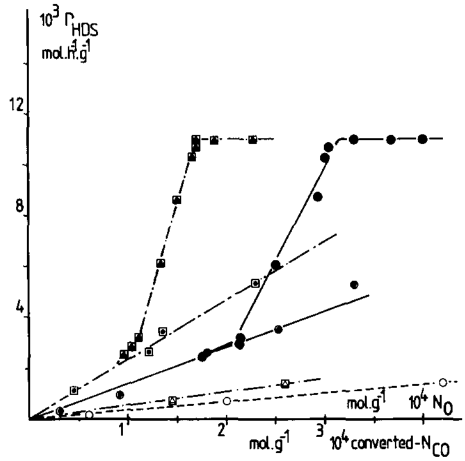

FIG. 3. Correlation between HDS activity and oxygen uptake, $N_O$ (circles) or carbon monoxide capacity, converted-$N_{CO}$ (squares). Ni–$Mo/Al_2O_3$ catalysts (Mo-7–Ni-*x*) ●, ■; $Mo/Al_2O_3$ catalysts: ◉, ▣; $Ni/Al_2O_3$ catalysts: ○, ⊠.

For each adsorbate, the Ni–$Mo/Al_2O_3$ catalysts of the Mo-7–Ni-*x* series are displayed along a broken line with three linear sections. Three correlation ranges are thus distinguished; they correspond to the different promoting effects observed on HDS activity upon nickel addition to the Mo-7-based catalyst in Fig. 1. The first domain (Ni/Mo < 0.2) is very narrow, so that the slope of the correlation line is not well defined, due to a lack of data. However, the numerical values, which express the activity per oxygen or CO detected site (apparent turnover numbers, TON) appear slightly higher than those observed on well-dispersed $Mo/Al_2O_3$ catalysts, much higher than on $Ni/Al_2O_3$.

More interestingly, the second set of samples (0.2 < Ni/Mo < 0.6) shows compared to the first one a five- to sixfold increase in TON for both probe molecules. In this domain, which corresponds to the main promoting action of nickel, the TON values are at least 20 times larger than those found on $Ni/Al_2O_3$ catalysts.

Finally, in the last section, HDS reaction rates remain approximately constant in spite of a further increase in gas consumption.

With respect to the Mo-16–Ni-*y* series, with high molybdenum content, our results do not allow us to derive such a correlation since chemisorption data do not vary so much with the nickel concentration.

## DISCUSSION

Application of the $O_2$ and CO molecules as probes on sulfided Ni–Mo/$Al_2O_3$ catalysts may be used to gain insight on the promoting effect. The discussion is mainly devoted to the Mo-7–Ni-$x$ series for which the wide experimental data allows good reliability. Two fundamental points are put forward: (i) titration by means of probe molecules does not reveal any considerable increase in catalytic site number upon adding nickel in the promotion range, and (ii) three different activity-chemisorption correlations are observed according to the amount of nickel added.

### *Active Sites Detected by $O_2$ or CO*

In the Mo-7–Ni-$x$ series, the chemisorption values for the two probe molecules change similarly with Ni concentration, as shown in Fig. 2 from the nearly straight lines observed for $N_O$ and converted-$N_{CO}$ data points. From the numerical values, the sulfided surface is able to accommodate about twice as many oxygen atoms as CO molecules. These results are fully in line with those previously reported for sulfided Ni/$Al_2O_3$ and Mo/$Al_2O_3$ catalysts (*18, 16*). They confirm our previous statement that the two adsorbates selectively detect the same kind of sites, in spite of a completely different adsorption process. Moreover, they suggest that the same kind of sites are present on the three types of catalysts.

Millman and Hall (*19*) have correlated oxygen uptake with anion vacancies on partially reduced molybdena catalysts. In the case of sulfided samples, the vacancy site specificity of the oxygen molecule is also likely to occur (*20, 21*), and is best demonstrated by the equivalent stoichiometries O/Mo and □/Mo found by Massoth (*22*) on sulfided Mo and Co–Mo/$Al_2O_3$ catalysts. From our work, in view of the irreversibility of the uptake, we are led to think that oxygen adsorbs dissociatively at coordinatively unsaturated transition metal ions and reacts simultaneously with adjacent sulfur, so that one vacancy would be counted per two consumed O atoms.

With respect to carbon monoxide chemisorption over sulfided catalysts, comparison of our results with the literature data is missing. However, since the total capacity of the catalyst (converted-$N_{CO}$) runs similarly to oxygen uptake, it is strongly suggested that the adsorption also takes place at vacancies. This statement may find further support from the electronic properties of the CO molecule, which make it naturally adsorb at vacancy sites. Moreover, the perfect reversibility of the chemisorption process allows us to suppose that carbon monoxide is a selective probe for vacancies, without further reaction with sulfur. Thus, one CO molecule would be able to detect one vacancy.

### *Low Molybdenum Content Ni–Mo/$Al_2O_3$ Catalysts*

*Titration of vacancies.* For the set of catalysts with low Mo concentration (Mo-7–Ni-$x$ series), oxygen uptake and CO capacity increase with increasing Ni content (Fig. 2, $N_O$ and converted-$N_{CO}$ lines). This indicates that more vacancies are present on the catalytic surface.

More precisely, both titrations agree in detecting 0.25 created vacancy as one Ni atom is added. Moreover, the similar slopes $\Delta N_O$ ($\Delta$ converted-$N_{CO}$)/$\Delta$Ni for Ni–Mo and Ni/$Al_2O_3$ catalysts show that the increase amounts to what a simple addition of nickel is expected to bring on its own. However, one must object to this comparison in that on alumina-supported catalysts, a fraction of the Ni ions (essentially dependent on the calcination and sulfidation temperatures) react into the surface spinel $NiAl_2O_4$ which is inactive for chemisorption (*15*). As shown in the following paper (*13*) by selective extractions, the presence of molybdenum partially hampers the migration of the Ni ions into the alumina lattice. Thus a Ni–Mo/$Al_2O_3$ catalyst shows less nickel aluminate species than a Ni/$Al_2O_3$ sample containing the same amount of nickel and pretreated in the same conditions. Hence, based on the amount of active Ni, it is clear that a promoted catalyst is characterized by a lower concentration of unsaturated sites compared to the sum brought by the individual components.

Our chemisorption results thus rule out the foregoing interpretations of the promoting effect which ascribe to the Co(Ni) ions the ability to create more vacancies (*4*, *6*).

*Evidence for different promoting actions of nickel.* In the Mo-7–Ni-*x* series, the increase in vacancy concentration is directly proportional to the amount of promoter added. Since three domains stand out for HDS activity, it results that the plot of activity versus chemisorption (Fig. 3) gives rise to three different correlation sections. This indicates that the vacancies which are regularly created upon nickel addition to the Mo-7 catalyst favor the HDS reaction to different extents. Specially, it is clear from the second linear section in Fig. 3 that the surface sites on the Ni–Mo catalysts ranging in the $0.2 < \mathrm{Ni/Mo} < 0.6$ composition ratio range are much more active than on the "one-component" $Mo/Al_2O_3$ or $Ni/Al_2O_3$ samples.

From the chemisorption studies, one must assume that the main action of nickel on the reference $Mo\text{-}7/Al_2O_3$ catalyst is to change the nature of the active sites, increasing their intrinsic activity. Wivel *et al.* (*23*) have drawn the same conclusion from the kinetic parameters of the thiophene HDS reaction, in connection with the amount of promoter present in a Co–Mo–S phase.

Finally it should be noted that chemisorption cannot discriminate between vacancies belonging to either molybdenum or nickel atoms in the Ni–Mo couple, so that the alternative interpretation of nickel acting as a catalyst instead of as a promoter remains (*12*).

However, the above interpretations of the role of nickel in Ni–Mo catalysts do not cover the whole Ni concentration range. Thus, at low Ni content ($\mathrm{Ni/Mo} < 0.2$), the number of vacancies and the HDS activity increase almost as on a $Mo/Al_2O_3$ catalyst, while at high Ni concentration ($\mathrm{Ni/Mo} > 0.6$), the third correlation section makes the Mo-7–Ni-*x* catalysts essentially resemble $Ni/Al_2O_3$ samples. For those sets of catalysts, the promoting effect is considerably reduced.

### *High Molybdenum Content Ni–Mo/Al₂O₃ Catalysts*

For the second $Ni\text{–}Mo/Al_2O_3$ series studied (16% $MoO_3$, *y*% NiO), gas uptake is not influenced by nickel addition, as far as we may conclude from the incomplete set of samples investigated. It follows that (i) these catalysts are not characterized by more vacancies than the reference Mo-16 sample, and (ii) the promoting effect is not detected by chemisorption. Thus, the high HDS activity of these samples, including the industrial catalyst, may also arise from an activation of the vacancy sites already present on the Mo-based catalyst. However, our chemisorption results appear in conflict with those reported by Burch and Collins (*20*), who observe an increase in $O_2$ uptake for a 15% $MoO_3$ $Ni\text{–}Mo/Al_2O_3$ series. The reason may presumably arise from the activation procedures of the samples, stabilization under thiophene/$H_2$, or presulfiding by $H_2S/H_2$.

### *Limitations of the Chemisorption Method*

When considering the chemisorption results obtained on different sulfide catalysts (Ni, Mo, and different promoted Mo catalysts), it appears that gas uptake is more or less sensitive to changes in HDS activity. These different behaviors have led to much debate about the HDS site specificity of the oxygen molecule and raise questions about the validity of the chemisorption method. Based on the lack of a general correlation between HDS activity and oxygen uptake for a wide range of supported Co–Mo catalysts, Zmierczak *et al.* (*24*) conclude that $O_2$ chemisorption reflects the dispersion of the active phase rather than that it provides the titration of HDS sites, as previously stated by Tauster *et al.* (*14*).

In fact, the evaluation of HDS catalysts on the unique consideration of vacancies, as detected by the $O_2$ and CO probe molecules, is not unambiguous since those sites do not function in isolation in the HDS mechanism. An increase in SH sulfur anion concentration, or their activation by hydrogen transfer in the reaction network could also lead to a higher activity. Such an interpretation has been postulated for Mo/$Al_2O_3$ catalysts containing more than 10% $MoO_3$ (*17*). Accordingly, an $O_2$-activity correlation would be interpreted as meaning a constant ratio SH/vacancy, while large variations from one series of catalysts to another would explain the absence of a general correlation.

## CONCLUSION

Application of carbon monoxide and oxygen chemisorption to thiophene-activated Ni–Mo catalysts strongly indicates that the enhanced activity of a Mo catalyst upon nickel addition is not the effect of an increased concentration in anion vacancies. The promoting effect could result in an activation of the surface sites, which is more pronounced for HDS than for hydrogenation.

Although the absence of presulfidation may have influenced the results, it is found that chemisorption measurements are sensitive to the promoting effect in the case of a Mo-based catalyst with low Mo content. They reveal that the promoter ions act in three different ways according to their concentration. By contrast, gas uptakes do not detect the increase in activity of the high Mo content promoted catalyst. Then, the technique appears to fail in the evaluation of industrial catalysts. Nevertheless, oxygen and carbon monoxide probe molecules may be very useful in an easy way to obtain titration of vacancies on sulfided catalyst, which remain an important characterization of the catalytic system.

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