JOURNAL OF CATALYSIS 76, 300–315 (1982)

Surface Properties of Sulfided Mo/Al_2O_3 Catalysts

J. BACHELIER, M. J. TILLIETTE, J. C. DUCHET, AND D. CORNET

"Structure et Réactivité d'Espèces Adsorbées (E.R.A. 824)," I.S.M.R.A., Université de Caen, 14032 Caen Cédex, France

Received July 27, 1981; revised January 21, 1982

Three types of measurement have been successively performed on a series of sulfided Mo/Al_2O_3 catalysts with initial contents ranging from 3 to 21 wt% MoO_3, namely (i) catalytic activity for thiophene hydrogenolysis and propene hydrogenation reactions (420°C, 1 atm total pressure), (ii) dynamic oxygen chemisorption at 60°C, and (iii) selective dissolution of molybdenum in a basic medium. Correlation between the three sets of data brings a new approach to the active surface species. They reveal that catalysts activated under thiophene bear different Mo species according to the loading. It is suggested that the molybdenum ions are grouped as polythiomolybdate clusters bound to the alumina support. The isolated polyions characterized in the less concentrated catalysts tend to polymerize further at higher Mo contents. Oxygen is a good probe molecule for titration of HDS active sites associated with the smaller Mo units. The stoichiometry of the polythiomolybdate entities cannot be precisely established, but it is clearly a function of the sulfiding conditions.

INTRODUCTION

Petroleum refining processes need more and more active and selective catalysts, due to more precise specifications imposed on the refined oil, and on the heavier oil fractions to be treated. Therefore, a better knowledge of the operating catalysts is desirable, especially in the case of the hydrorefining catalysts.

Most of the industrial processes use Co–Mo or Ni–Mo type catalysts. They are prepared as alumina-supported oxides, and then converted into sulfides before use. Many authors have characterized the catalysts by means of various techniques, and recent reviews (*1–3*) emphasize the great complexity of the system studied. The main questions are: what is precisely the role of molybdenum (with or without promoter ions) in the successive steps of the HDS reaction, and how can structural models account for the proposed surface state? No unequivocal answer has yet been given to these questions, although clarification is in progress, mainly from the investigations of Massoth, and the groups of de Beer and Delmon (*4–6*). We have looked at the behavior of the Mo/Al_2O_3 catalyst itself, before examining the difficult problem of the promoter influence.

Even though preparative conditions of the Mo/Al_2O_3 catalysts have not been standardized (alumina type, impregnation and calcination steps), it is generally accepted that molybdenum ions in the oxidic precursor are deposited as a monolayer, up to about 20% MoO_3, and that they interact strongly with the alumina carrier (*7*). However, several authors observe that alumina adsorbs at most 10% MoO_3 from solutions, leaving a large fraction of its surface uncovered (*8, 9*). The nature and the distribution of the molybdenum species (tetrahedral and octahedral coordination, existence of a separate MoO_3 phase) are not definitely established, probably because different preparation procedures are used (*8, 10–12*).

The sulfide form of the Mo/Al_2O_3 catalysts is far more difficult to characterize, since the solid is extremely sensitive toward air (*13*). Therefore, studies have to be performed in the reactor itself. The picture of the sulfide catalyst is still a matter of

0021-9517/82/080300-16$02.00/0

controversy. Essentially, two descriptions emerge: on the one hand, Massoth (*14*), following the hypothesis of Schuit and Gates (*15*), argues that the sulfidation treatment does not destroy the interaction between alumina and molybdenum which prevails in the oxidic precursor. On the other hand, the model first introduced by Voorhoeve and Stuiver (*16*) and now advocated by de Beer *et al.* (*17*) ascribes the active phase to small bulk MoS_2 crystallites lying on the support. In any case, the surface sites are thought to be associated with anion vacancies and surface sulfur ligands, both involved in the hydrogenolysis of S compounds (*18*).

The present paper reports our studies of the Mo/Al_2O_3 catalysts in the sulfide form, which is really the active form in hydrodesulfurization. New characterization elements have been introduced by means of methods which have not been widely applied to sulfide catalysts, namely, the chemisorption of oxygen as a specific adsorbate molecule, and molybdenum extraction by chemical attack of the catalyst. We have tried to correlate the results of such measurements with activity data for thiophene hydrogenolysis and propene hydrogenation reactions, performed at atmospheric pressure. The same procedure applied to sulfided Ni/Al_2O_3 catalysts proved to be very efficient and allowed us to correlate directly oxygen uptake at 60°C and HDS activity (*19*). A similar relationship has recently been established by Tauster *et al.* (*20*) in the case of bulk MoS_2 catalysts tested for dibenzothiophene hydrodesulfurization. In one instance only, measurements have been extended to the more complex catalysts using alumina as a carrier (*21*). Generally, for these supported systems, chemisorption of various molecules, O_2 (*22–24*), CO (*25*), or H_2 (*25*), has been examined on prereduced samples; in such conditions, the surface state of the catalyst is not representative of the sulfide form, and no correlation has been found with HDS activity, when measured (*24*).

Ultimately, the relationship between chemisorption and activity has to be interpreted in terms of a structural model, which should account for the metal–support interaction. The selective extraction of molybdenum in basic solution, applied to the oxidic catalysts (*7, 27–29*), has been extended here to the sulfides in order to distinguish between different types of molybdenum. This procedure may also reveal changes attending the sulfidation of the Mo oxide layer.

EXPERIMENTAL

Catalysts

A series of MoO_3/Al_2O_3 catalysts containing 3–21% MoO_3 by weight has been prepared by dry impregnation of γ-alumina (GFS C Rhône Poulenc, surface area 238 $m^2\ g^{-1}$, pore volume 0.61 $cm^3\ g^{-1}$) with ammonium heptamolybdate aqueous solutions. After drying for 12 h at 110°C in air, the samples are calcined for 2 h at 500°C under air circulation. The catalysts are then sieved (90–190 mesh) and again fired for 2 h at 500°C in air immediately prior to use.

Procedure

Catalytic activity tests and dynamic oxygen uptake are performed in the all-glass flow apparatus already described (*19*). Slight modifications have been made in order to introduce both thiophene and propene in the H_2 flow; this enables us to run two reactions on the same sample, viz. thiophene hydrogenolysis and propene hydrogenation in the presence of a thio compound. The equipment allows us to make successive measurements of activity and chemisorption without any transfer of the powder.

Reaction conditions. Initially oxidic catalyst (0.240 g) is introduced in the reactor and generally sulfided with a H_2 (700 Torr)–thiophene (60 Torr) mixture at 420°C and a total flow rate of 30 $cm^3\ min^{-1}$. This process is denoted as "T-sulfiding."

After 24 h on stream, the mixture from the reaction $C_4H_4S + H_2 \rightarrow H_2S + C_4$ hydrocarbons is analyzed by on-line chromatography (20% OV_1 column, 5 m, $\frac{1}{8}''$ o.d., 50°C, 20 cm^3 min^{-1} He, thermistor detection). The HDS activity for these T-sulfided samples is expressed as the reaction rate, r_{HDS} (mol h^{-1} g^{-1}), at initial conversion. For noninitial conversions, a first-order behavior is assumed to obtain r_{HDS}. Following HDS activity measurement, a feed of propene (6.12×10^{-3} mol h^{-1}) is added to the H_2-thiophene flow by means of a motor-driven syringe. The conversion into propane is measured by VPC on a dual Porapak Q–silicagel column. The hydrogenation rate at initial conversion r_{hydr} is then derived.

In some experiments, dimethyl disulfide (DMDS, 23 Torr) provided by a separate saturator is used as a presulfiding agent of the oxidic catalyst ("D-sulfiding"). In order to obtain the activity of the presulfided samples, thiophene is substituted for DMDS in the H_2 flow by switching on the second saturator. The rate of thiophene hydrogenolysis is then measured, immediately after the pretreatment (activity for the D sulfided catalysts) and then 20 h later (activity for the D, T sulfided catalysts).

In the computation of reaction rates, the raw data have been corrected for the activity of the support itself: r_{HDS} 0.03×10^{-3} mol h^{-1} g^{-1}, r_{hydr} 0.12×10^{-3} mol h^{-1} g^{-1}.

Oxygen uptake measurement. Oxygen uptake by the sulfided catalyst is measured in the reactor itself by a dynamic method. After the activity tests have been completed at 420°C, the catalyst is swept by a flow of deoxygenated argon for 2 h, then cooled to 60°C. Oxygen pulses are then run onto the catalyst, and the quantity irreversibly adsorbed is estimated by thermistor detectors: cumulative adsorption N_O (mol O per gram catalyst) remains constant after a few pulses. No oxygen uptake can be detected on sulfided alumina at this temperature.

Molybdenum extraction. Molybdenum is extracted from both oxidic and sulfided catalysts by selective dissolution at room temperature in 12 N ammonium hydroxide solution. Sulfided samples experience oxygen chemisorption at 60°C prior to Mo extraction. The standard procedure involves a 24 h basic attack; the maximum amount of Mo that can be extracted from the catalyst is estimated after 7 days standing in ammonia. The Mo content of the basic solution is measured by atomic absorption spectrometry.

Sulfur analysis. The sulfided catalysts are collected after oxygen uptake at 60°C and sulfur analysis is carried out in a microanalytical combustion apparatus. A small addition of V_2O_5 prevents sulfation of the alumina. The sulfur contents given here are corrected for a slight sulfidation of the support at 420°C.

RESULTS

Catalytic Activities

Stabilization. Sulfidation of the initially oxidic Mo/Al_2O_3 catalysts under thiophene–H_2 mixture (T-sulfiding) needs a relatively long time before a steady-state is reached. After a short activation period, the rates of both thiophene hydrogenolysis and propene hydrogenation steadily go down during the first 24 h, then more slowly (Mo-21 sample, Fig. 1). The decrease in activity runs parallel for both reactions, as exemplified by the nearly constant selectivity ratio r_{hydr}/r_{HDS}. Steady-state activities are reached more rapidly when the Mo content of the catalyst is lower.

Presulfidation by dimethyl disulfide reduces the stabilization period to 7 h. HDS activity measured immediately after such a pretreatment (D-sulfiding) is enhanced, but does not hold with time: prolonged contact of the presulfided catalyst with thiophene as the only sulfur compound considerably lowers the activity. After 20 h working in these conditions (D, T-sulfiding), the rate of thiophene hydrogenolysis is close to that observed without pretreatment.

We thus confirm the observation reported by Massoth (*4*) who finds that stabilization

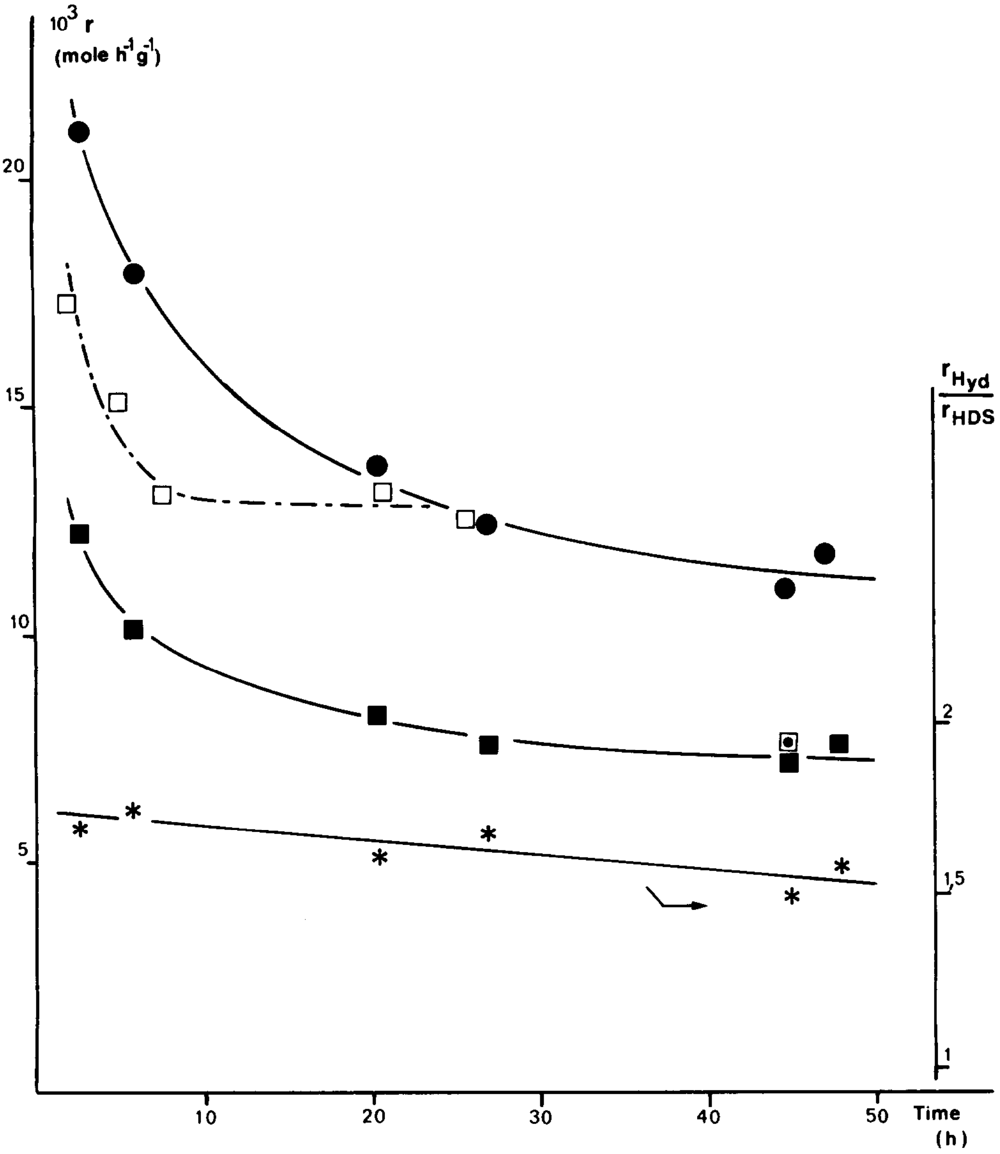

FIG. 1. Sulfided Mo/Al_2O_3 catalyst, 21.6% MoO_3. Dependence of thiophene hydrodesulfurization and propene hydrogenation reaction rates with running time. T-sulfiding: ■, HDS; ●, hydrogenation; *, Hydr/HDS; D-sulfiding: □, HDS; D,T-sulfiding: ▣, HDS. Conditions: see footnotes in Table 1.

of a presulfided 8% Mo/Al_2O_3 (12% MoO_3) catalyst needs an overnight period in a thiophene–H_2 stream.

Steady-state activities. Since the activities of the catalysts apparently do not decrease much after 24 h in a thiophene–H_2 stream, mesurements taken at this standard time have been considered as representative of steady-state activities. They vary with the Mo content as shown in Table 1. In terms of specific activities, *a*, per mole of molybdenum, there is (Fig. 2) a threshold at about 3% MoO_3 for hydrogenolysis, whereas this does not seem to exist for hydrogenation. A significant maximum is observed for both specific activities at about 10% MoO_3 in the oxidic precursor; the selectivity hydrogenation/HDS first sharply

TABLE 1

Characterization Data of Mo/Al_2O_3 Catalysts

Catalyst		Sulfiding conditions[a]	Activities[b]		Oxygen uptake 60°C $10^4 N_O$ (mol g^{-1})	Sulfidation degree at. S/Mo	10^3 extractable Mo(g g^{-1})		
Symbol	MoO_3 wt%		$10^3 r_{HDS}$[c] (mol h^{-1} g^{-1})	$10^3 r_{Hydr}$ (mol h^{-1} g^{-1})			Oxidic	Sulfided	
								24 h	7 days
Mo-3	3.1	T	0.31	0.66	0.31	0.98	15.0	12.8	
Mo-4	4.5	T	0.95	1.32	0.91	1.03	22.1	17.7	
Mo-7	7.0	T	2.63	3.81	1.79	1.21	32.1	30.5	
		D	5.43	—	1.62	1.71	—	26.9	40.3
		D,T	2.60	—	1.47	1.67	—	25.2	35.1
Mo-7-E-500	2.4	T	0.22	—	0.19	—	10.2	10.5	10.5
Mo-7-E-80		—	—	—	—	—	4.8	—	—
Mo-8	8.0	T	3.51	5.68	2.53	1.26	38.6	35.3	
Mo-13	13.3	T	5.32	8.79	3.32	1.47	58.9	41.8	
Mo-16	15.7	T	5.96	10.05	3.56	1.37	67.9	42.6	
Mo-19	19.3	T	7.27	11.97	3.58	1.44	88.2	43.9	—
		D	15.50	—	2.86	—	—	51.3	107
		D,T	7.21	—	2.75	1.56	—	47.1	89.9
Mo-21	21.6	T	7.60	12.58	3.55	1.35	93	43.6	98.4
		D,T	7.76	—	2.98	1.56		43.2	—
Mo-21-700	19.7	—					76.6		
Mo-21-E-500	6.6	T	1.89	—	1.44	0.91	25.5	26.2	
Mo-21-E-80		T	2.34	—	1.40	1.02	14.6	25.3	
Mo-21-E-20		—	—	—	—	—	5.8		

[a] T = 24 h, thiophene 60 Torr–H_2 700 Torr; D = 24 h, DMDS 23 Torr–H_2 737 Torr; D,T = 24 h DMDS, plus 24 h thiophene.

[b] Conditions: 420°C; 0.240 g catalyst; F. thiophene: 6.26×10^{-3} mol h^{-1}; F. propene: 6.12×10^{-3} mol h^{-1}.

[c] Measurement after 24 h on stream for T catalysts; immediately after the pretreatment for D catalysts and 20 h later for D,T catalysts.

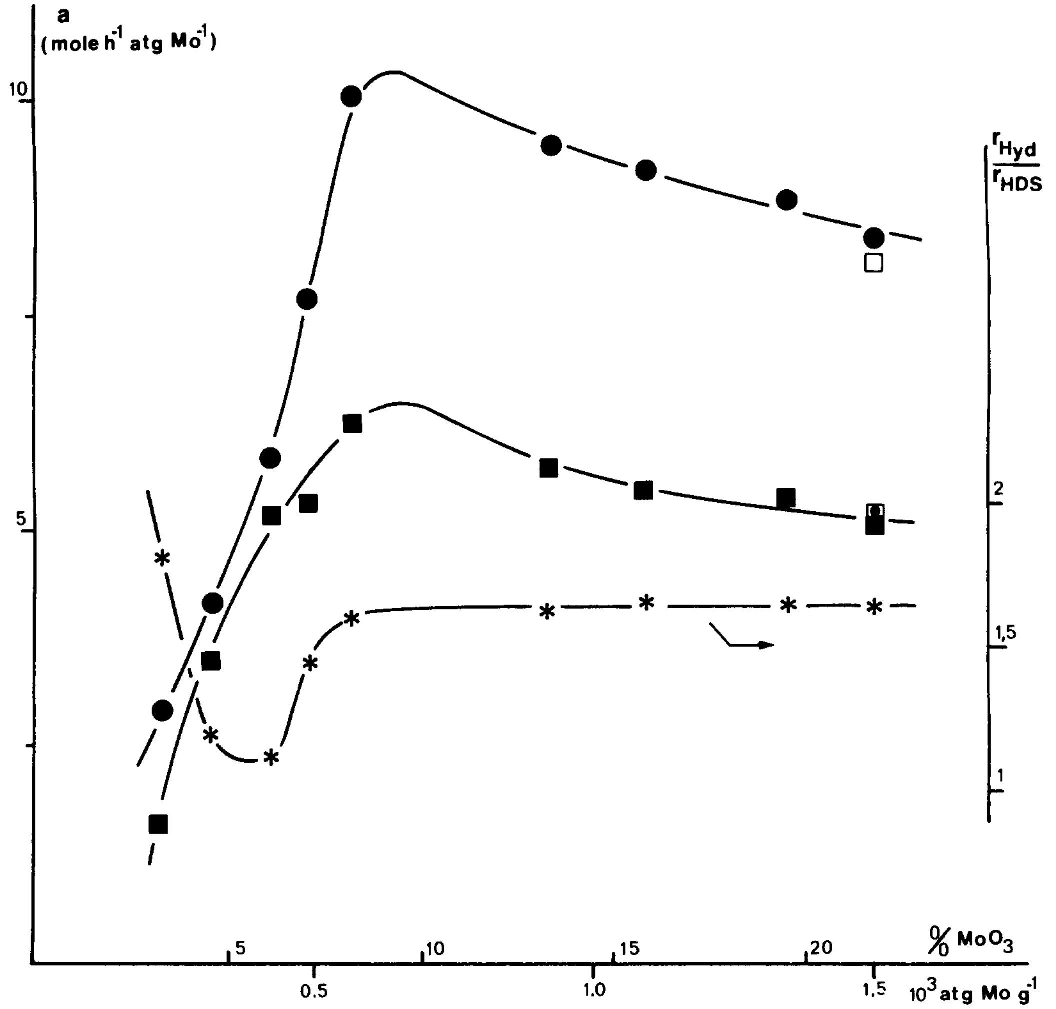

FIG. 2. Sulfided Mo/Al_2O_3 catalysts. Specific activity of molybdenum as a function of the Mo content. T-sulfiding: ■, HDS; ●, hydrogenation; *, Hydr/HDS; D-sulfiding: □, HDS; D,T-sulfiding: ▣, HDS; Conditions: see footnotes in Table 1.

decreases, then stabilizes at 1.6 for the more concentrated samples.

The effect of presulfiding the catalyst is also shown in the same diagram: as mentioned above, the high activity of the (D) presulfided samples, measured immediately after the pretreatment, stabilizes to a considerably lower level under the (D, T) H_2–thiophene feed.

Sulfur Content

Sulfur contents measured on stabilized catalysts are collected in Table 1 and represented in Fig. 3. Values reported are not underestimated due to partial reoxidization of the sample at 60°C prior to sulfur analysis: in this sense, it has been verified, in agreement with Massoth (*1*), that any SO_2 eventually produced during oxygen uptake would remain on the catalyst at this temperature.

The percentage of sulfur on the catalysts increases linearly with the Mo content. However, the plot shows an intercept on the *x* axis at about 1.5% MoO_3, indicating that the very first Mo atoms deposited on

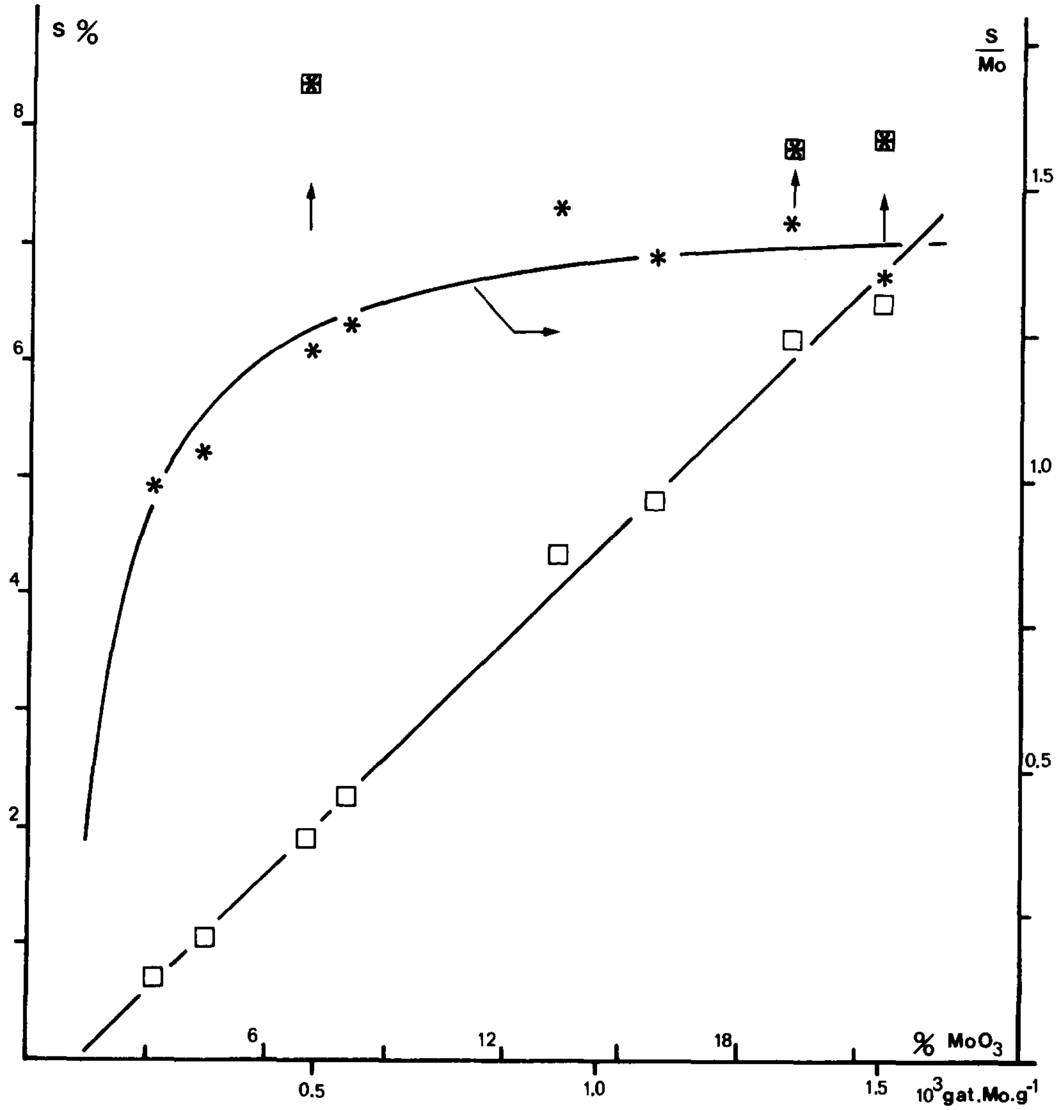

FIG. 3. Sulfided Mo/Al$_2$O$_3$ catalysts. Sulfur content and sulfidation degree of molybdenum as a function of the Mo content. T-sulfiding: □, S percent; *, sulfidation degree S/Mo; D,T-sulfiding: ⊞, sulfidation degree S/Mo.

the support do not sulfide. In terms of stoichiometry, the atomic ratio S/Mo is rather low for the less concentrated catalysts; the ratio increases with the catalyst loading up to about 10% MoO$_3$, then tends to stabilize at 1.5.

However, excluding the first Mo under the threshold, all the catalysts have the same stoichiometry S/Mo $\simeq$ 1.5. Thus, activation under thiophene leads to an incomplete sulfiding of the molybdenum atoms, as compared to MoS$_2$. This trend is in agreement with the results of Okamoto *et al.* (*29*).

Pretreatment of the catalyst with DMDS greatly enhances the sulfur level (sample Mo-7 D in Table 1), which however does not attain S/Mo = 2. The high sulfidation degree of this presulfided catalyst is maintained when the sample is allowed to reach steady-state under the thiophene–H$_2$ stream. The effect of presulfidation is more pronounced for low-molybdenum catalysts than for more concentrated samples, so that the S/Mo ratio on stabilized catalysts does not vary much with Mo content (Fig. 3).

Oxygen Uptake

Measurement of dynamic oxygen uptake by sulfided catalysts in the reactor itself guarantees that the surface state is representative of the working catalyst. Furthermore, as the oxygen consumption has small values (see Table 1), our results confirm that testing a sulfided sample after transfer of the powder may lead to hazardous conclusions about the active components.

In the chromatographic method used, the first oxygen pulses are quantitatively adsorbed, producing a rapid saturation since no further oxygen uptake is observed.

Oxygen consumption by the sulfided Mo catalysts is strongly temperature dependent. It is detected at temperatures as low as −90°C, and increases with temperature. As for Ni/Al_2O_3 catalysts (*19*), the temperature dependence of oxygen consumption shows two different zones of increasing uptake, separated by a short plateau around 60°C which indicates two different behaviors of the sulfided Mo catalysts toward oxygen. Hence, oxidation of the catalyst under carefully controlled conditions is limited to the surface.

Reproducibility is good, provided that the catalysts have reached stabilization in the sulfiding atmosphere, and that a sufficient purge with argon (2 h at 420°C) has been carried out.

Oxygen chemisorption at 60°C by thiophene-sulfided Mo catalysts in shown in Fig. 4 versus Mo loading. Chemisorption starts at about 3% MoO_3, increases linearly with Mo content up to 10% MoO_3; then a further increase in Mo content results in a constant oxygen uptake. Hence, a maximum stoichiometry O/Mo ratio is found at 10% MoO_3 which corresponds to about 0.45 oxygen atom taken up per molybdenum.

Finally the chemisorption values are plotted against the rate of thiophene hydrogenolysis in Fig. 5. A good linear relationship exists as long as the catalytic activity remains low, i.e., less than about 5.10^{-3} mol h^{-1} g^{-1}; the proportionality does not hold beyond this limit since oxygen consumption stays constant in spite of a further increase in activity. This feature was not reported by Tauster *et al.* (*20*) for bulk MoS_2 catalysts. In our case, the linear part of the curve corresponds to catalysts with a low Mo content, containing at most 10% MoO_3, while the second section belongs to more concentrated samples.

Presulfided Mo/Al_2O_3 samples show a significantly lower oxygen uptake, unaffected by subsequent treatment with thiophene. The corresponding N_O and r_{HDS} values do not fall on the graph established from thiophene-sulfided catalysts.

Solubility of Molybdenum

Treatment with aqueous ammonia as described in the experimental section does not extract all of the molybdenum contained in the catalysts, neither in the oxide nor in the sulfide form (Fig. 6). The maximum amount of extractable molybdenum is found to vary with the firing temperature and the sulfidation procedure.

The oxidic precursors of the Mo/Al_2O_3 catalysts have been calcined at 500°C. From these, a constant fraction (66%) of the molybdenum can be removed in basic solution. After sulfidation with thiophene, the Mo ultimately dissolved amounts exactly to the same value, i.e., 66%; by contrast, more molybdenum (85%) may be extracted from the DMDS-presulfided catalysts.

Marked differences between oxidic and sulfided samples are observed when considering the solubility rates of molybdenum: it is found that molybdenum from the sulfided samples goes into solution much more slowly than from the oxidic forms. The rate of dissolution varies with Mo loading, but is independent of the sulfidation procedure. As an example, maximum extraction from the sulfided Mo-21 catalyst needs 1 week

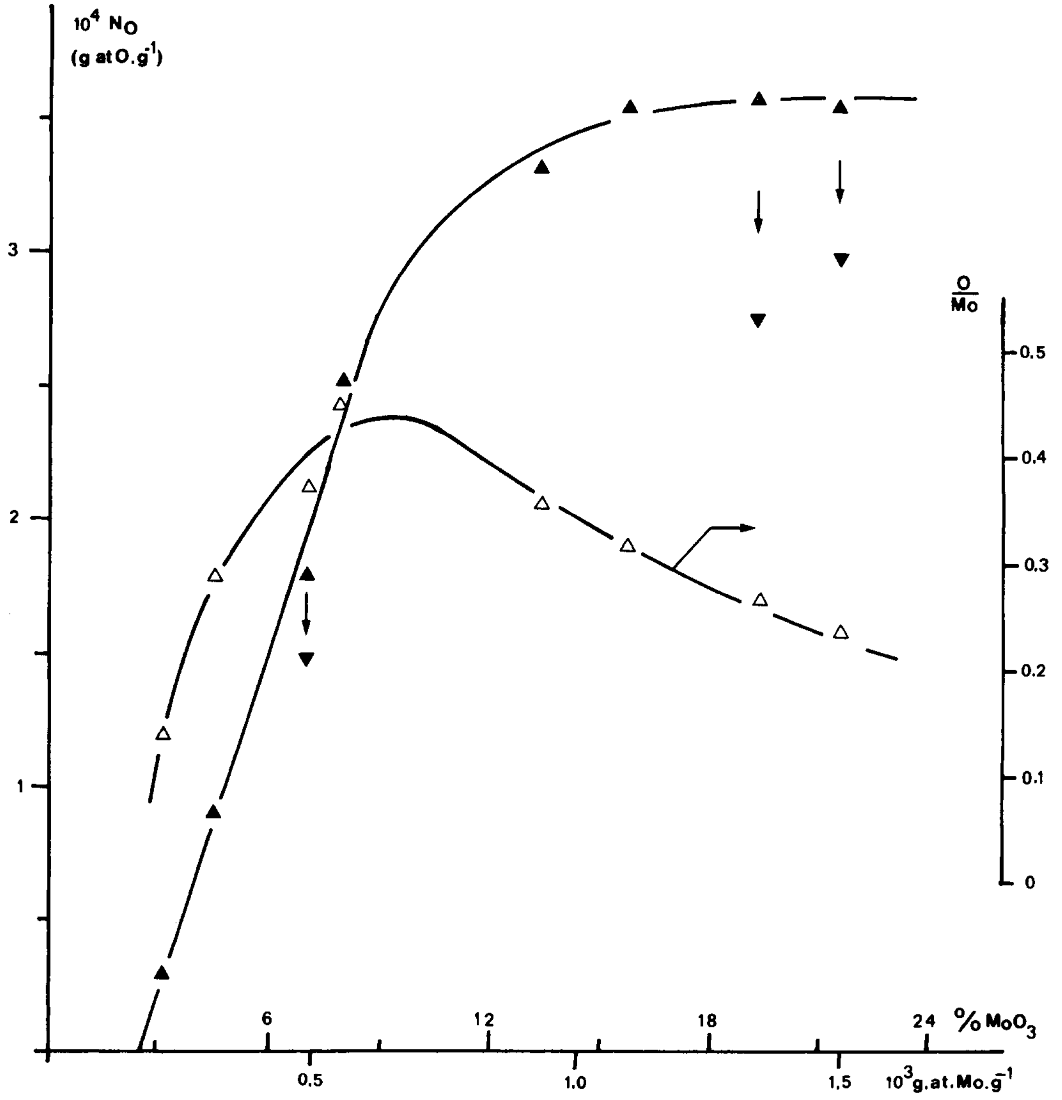

FIG. 4. Sulfided Mo/Al_2O_3 catalysts. Oxygen uptake at 60°C as a function of the Mo content. T-sulfiding: ▲, oxygen uptake; △, stoichiometry O/Mo; D,T-sulfiding: ▼, oxygen uptake.

standing in ammonia, whereas it is achieved in 6 h in the case of the corresponding oxidic form. Comparison of the solubility rates among the sulfided catalysts of the series is made possible by measuring the amount of molybdenum extracted during a standard attack time, namely 24 h. It is seen (Fig. 6) that in the low concentration range, up to 10% MoO_3, the amount of molybdenum extracted in 24 h from the sulfided samples corresponds to the maximum labile fraction, exactly as in the oxidic precursor; on the other hand, beyond this loading a constant amount of molybdenum goes into solution, 0.043 g Mo/g of catalyst.

Finally, results in Table 2 give the relative amounts of extratable and nonextractable molybdenum for several calcination temperatures of the oxidic catalyst or various treatments of an extracted oxidic sample. Thus, firing at 700°C the Mo-21 oxidic catalyst already calcined at 500°C gives less

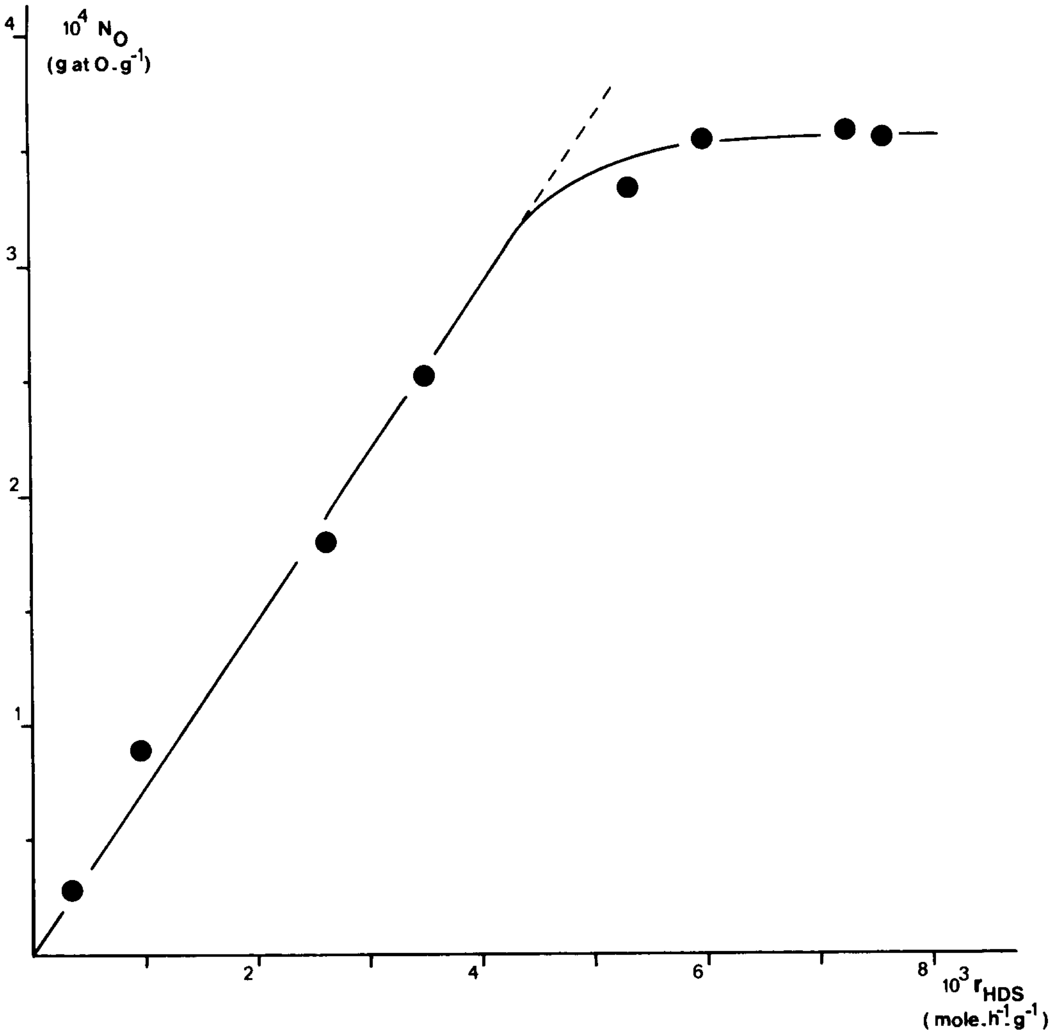

FIG. 5. Thiophene-sulfided Mo/Al_2O_3 catalysts. Correlation between oxygen capacity at 60°C and the rate of thiophene hydrodesulfurization.

extractable Mo (58 versus 66%). Successive ammonia washings have been applied to the oxidic catalysts. After a first basic attack of the Mo-21 catalyst had removed the whole soluble molybdenum, leaving 6.6% MoO_3 on the support, the powder, denoted Mo-21-E in Tables 1 and 2, was then recalcined at 500°C and again soaked into ammonia solution: again a large fraction (58%) of the remaining molybdenum was dissolved, nearly as much as in the case of untreated oxidic catalysts calcined at the same temperature (see Fig. 6). Even upon drying the Mo-21-E sample at 80°C or at room temperature under vacuum, thus omitting the recalcination step, basic attack again extracted some molybdenum, but to a smaller extent (33 and 13%, respectively). Upon sulfiding with thiophene, both dried (80°C) and recalcined Mo-21-E samples exhibit 60% of labile molybdenum, about as much as the normal unwashed sulfide catalysts (see Fig. 6). Similar observations are obtained from the Mo-7 catalyst. Further characterizations of the Mo-21-E and Mo-7-E samples by means of specific surface

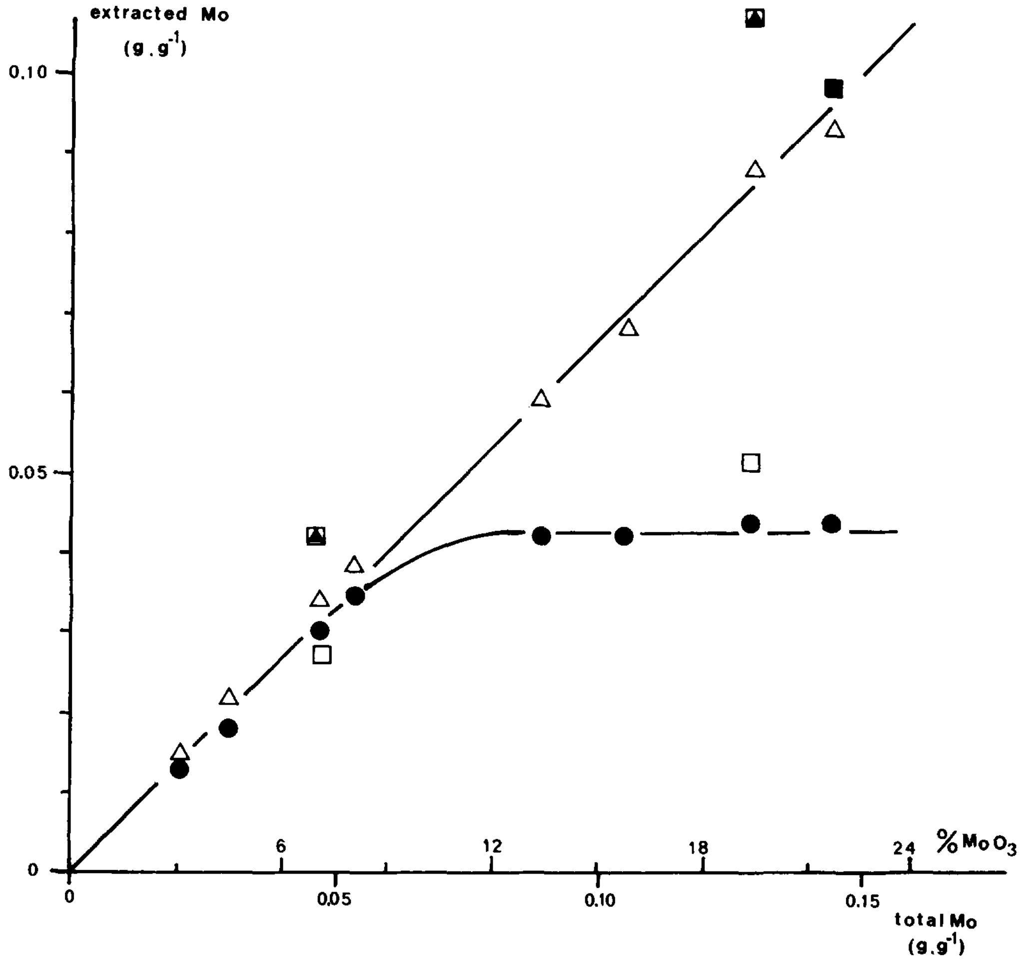

FIG. 6. Sulfided Mo/Al$_2$O$_3$ catalysts. Extraction of molybdenum with ammonium solution as a function of the Mo content. Oxidic catalysts: △, 24 h; T-sulfided catalysts: ●, 24 h; ■, 7 days; D-sulfided catalysts: □, 24 h; ▣, 7 days.

area, catalytic HDS activity, sulfur content, and oxygen uptake (Table 1) clearly demonstrate that a washed catalyst behaves as an unwashed one of the same concentration. This finding agrees well with the observations mentioned by Kotera *et al.* (*28*) for Co–Mo/Al$_2$O$_3$ studies. Thus, redistribution of molybdenum on the surface readily occurs upon heat treatment, calcination, or sulfidation.

In the case of oxidic samples, our results are in line with those reported in the literature. Hence, the extraction measurements really distinguish between soluble (free molybdenum or Mo ions in weak interaction with the support) or insoluble (strongly held) Mo species. We have verified that continuing the attack in ammonia for 5 days or carrying out the attack in a larger volume of basic solution (100 ml) does not bring any change in the amount of molybdenum extracted; furthermore, fresh alumina does not adsorb molydenum when contacted with the extraction solution containing the molybdenum extracted from another sample.

DISCUSSION

Characterization of sulfided Mo/Al$_2$O$_3$ catalysts by means of catalytic activity, ox-

TABLE 2

Mo/Al$_2$O$_3$ Catalysts: Influence on Successive Ammonia Washings on the Fraction of Extractable Molybdenum

Successive treatments	Mo-21					Mo-7		
Calcination (°C)	500		500		700	500		500
Sulfidation (°C)	No		420		No	No		420
First NH$_4$OH washing: % Mo extracted	65		68		58[a]	69		65
	Mo-21-E					Mo-7-E		
Drying (°C)	500		80		20	500		80
Sulfidation (°C)	No	420	No	420	No	No	420	No
Second NH$_4$OH washing: % Mo extracted	58	60	33	58	13	65	66	30

[a] Computed from the effective total Mo content of the recalcined catalyst, after the slight loss due to volatile MoO$_3$.

ygen chemisorption, and selective dissolution of molybdenum reveals that:

(i) The surface state of Mo varies according to the Mo content. This was established for catalysts activated under thiophene–H$_2$.

(ii) This surface state is very sensitive to the sulfiding conditions (thiophene or DMDS).

(iii) Redistribution between soluble and insoluble Mo readily occurs upon heating.

The methods used here provide a new approach to the problem of active Mo surface species in the operating catalysts, and offer an opportunity to check earlier proposals about structural models of HDS catalysts.

Influence of Molybdenum Concentration

The most salient finding concerning the series of catalysts activated under thiophene is the abrupt change in properties according to the Mo content: 10% MoO$_3$ marks a maximum in the specific activities, a saturation in the amount of chemisorbed oxygen at 60°C, and a slackening in the solubility rate of molybdenum from sulfided samples upon standard ammonia extraction. Thus, two different behaviors of molybdenum are observed at low and high concentration in these catalysts. These trends do not clearly appear from catalytic activity tests reported in the literature (*29, 30*), probably due to incomplete stabilization which is especially pronounced in the high loading region. The maximum in specific activity can thus easily be shifted, or missed. It is noteworthy that a transient state of the catalyst cannot be detected by the hydrogenation/HDS reaction rate ratio since both reactions change similarly with time.

Oxygen chemisorption measurements provide the best distinction between two types of catalysts: in the low concentration range, a good proportionality exists between oxygen uptake at 60°C by sulfided samples and the rate of thiophene hydrogenolysis, whereas this does not hold for the more concentrated catalysts.

Individual Catalytic Sites

Since it is generally accepted that two kinds of sites exist on these catalysts, the change in catalytic behavior at a particular value of the Mo content is interpreted as a change in the distribution of these sites. Accordingly, the classical HDS mechanism pictures the active Mo site as a coordinatively unsaturated surface ion which is in the trivalent state (*16*). The anion vacancy associated with this Mo is thought to adsorb sulfur compounds, either through the S atom, or through the double bond (*31*). A second type of site is postulated since hydrogen transfer follows the C–S bond rupture. It is assumed that sulfur anion groups, bonded to surface Mo atoms, activate hydrogen from the gas phase and transfer it, probably as protons, to the organic molecule.

The marked difference between dilute and more concentrated Mo catalysts suggests a change in the distribution of the two kinds of active site on the surface. The linearity between N_O and r_{HDS} found in the first region (low Mo content) indicates that oxygen is a good probe molecule for HDS active sites operating on this set of samples. The proportionality implies a constant ratio between vacancies and active sulfurs since, according to Massoth and Kibby (*18*), the HDS reaction rate follows the product of both site concentrations. Such a correlation has been reported by Tauster *et al.* on unsupported molybdenum disulfide (*20*) and interpreted by the authors as meaning chemisorption of the oxygen molecule on the edge planes of the MoS_2 crystallites, responsible for HDS activity. Thus, the number of sites is determined by the topography of the surface.

In the case of sulfided Mo/Al_2O_3 catalysts, since the correlation does not hold in the whole concentration range studied, we infer that other factors determine the number of sites.

Precise information about the mode of chemisorption of oxygen on sulfided Mo catalysts at 60°C would be necessary to convert oxygen uptake into site concentration. One may reasonably assume that oxygen fills up anion vacancies by analogy with the chemisorption results on partly reduced molybdena on alumina at 78 K, as reported by Millman and Hall (*23*). However, on the sulfided catalysts this process is not reversible, and it is likely that the oxygen molecule splits up, reacting with an anion vacancy and also with a sulfide or SH group attached on the same ion. Finally, for the less concentrated samples, the observed stoichiometry O/Mo, when corrected for the first 0.17×10^{-3} mol Mo which is unreactive toward chemisorption, amounts to a constant value, i.e., 0.5 O atom per Mo atom. This indicates that in the concentration range 3–10% MoO_3 the catalyst surface is made up of a juxtaposition of equivalent Mo-containing entities which present a constant distribution of the two types of active sites.

Beyond 10% MoO_3, the increase in activity without simultaneous increase in oxygen uptake indicates that the active sites which ensure a higher activity are not detected by oxygen. Since oxygen consumption remains constant, we infer that those catalysts do not develop more anion vacancies than the 10% MoO_3 sample. Therefore at high Mo loadings the catalysts would show increasing SH/□ ratios, which could ensure a higher (□) × (SH) value, and thus a higher activity. The fact that oxygen fails to detect these extra SH groups would indicate that they are isolated, not directly connected with a vacancy.

Polymolybdates and Polythiomolybdates as Active Surface Species

The concept of two different operating sites applies to each of the two structural models actually proposed, i.e., the monolayer model and the MoS_2 crystallite model. In the monolayer model (*14, 15*), Mo ions are disposed on the surface in registry with the alumina lattice, and sulfidation keeps them in strong interaction with the support. The second model, advocated by de Beer *et al.*, is based on a complete reorganization of the oxidic structure during the sulfidation step, resulting in small MoS_2 patches diluted by the carrier. Since we observe that the Mo surface species are different at low and high loadings, dilute catalysts could be described by the first model, and more concentrated samples by the second one. However, it is then difficult to explain why two different structures could lead to the same molybdenum extraction data, that is a constant fraction of the molybdenum remaining on the sulfided catalyst after prolonged ammonia washing, whatever the loading.

Thus the best description of the catalyst probably arises from a single model. Obviously, our extraction and sulfur analysis results rule out the MoS_2 crystallite model; they could better fit with the monolayer model for which molybdenum strongly interacts with alumina in both the oxide and sulfide form. However, such a model does not foresee any change in the catalyst properties at approximately half-coverage of the carrier (10% MoO_3 for an alumina with 238 m^2 g^{-1} specific area).

The model we have in mind describes molybdenum as forming polyanion groups on the surface, these groups being held on the support by means of some Mo ions embedded into the upper alumina layer. Basic extraction would selectively dissolve those Mo ions not connected to alumina. The genesis of this bound-cluster structure has to be found in the oxidic state, since the same Mo fraction is extracted from both oxide and sulfide catalysts. Thus, no major change in the arrangement of molybdenum occurs upon sulfiding with thiophene. The surface entities could be written as follows:

Wang and Hall (*12*) have recently invoked the concept of bound polymolybdate species for Mo/Al_2O_3 catalysts. Their size, however, cannot be defined at present, but analogy with compounds of known structure, both in solution or in the solid state, suggests that they are rather small: $x = 7$ is common in polymolybdates, and $x = 6$ and 12 have been reported for sulfur-containing anions (*32*). The size of the clusters may well depend upon the pretreatment temperature; extraction data only show that the number of anchoring points increases as calcination temperature goes from 500 to 700°C.

The picture which emerges for the catalyst is as follows. At the lowest Mo concentrations, up to 3% MoO_3, spectroscopic evidence (*10, 27*) is in favor of isolated Mo in tetrahedral coordination. We suggest that some of the vacant cation sites in exposed layers of the alumina support may accommodate at least a fraction of these Mo, making them unreactive toward sulfidation, chemisorption, and HDS. This conclusion, however, is not unambiguous, since a constant fraction of these Mo remains extractable whereas activity tests (HDS and hydrogenation), sulfidation, and chemisorption revealed thresholds at somewhat different Mo content.

In the intermediate concentration range (3 to 10% MoO_3) the catalyst is constituted of juxtaposed isolated clusters fixed on the support, all of them showing the same specifications, namely, a constant size, and a uniform distribution of catalytic sites created upon sulfiding as revealed by the fact that excluding the first Mo's of the threshold, the stoichiometry O/Mo and the activity per Mo atom are at a constant value in the range 3–10% MoO_3. This description holds for catalyst loadings which do not exceed half coverage of the alumina carrier. For more concentrated catalysts, steric factors lead to an interaction between the Mo islands, and the clusters condense by means of sulfur bridges. It is reasonable to think that condensation occurs through unsaturated Mo atoms, so that increasing Mo content, that is multiplying the number of clusters, does not result in an increase in vacancy concentration. Finally, the distribution between linked and free Mo still exists, but the larger size of the islands makes them more difficult to extract.

With regard to the effect of sulfiding, the comparison between thiophene and DMDS is first evidenced by extraction experiments: they confirm that thiophene sulfidation is rather mild, since the frame of the Mo phase is similar in oxide and sulfide samples. By contrast, more severe sulfiding is achieved by DMDS: the higher H_2S/H_2 ratio on the surface partly destroys the oxidic structure, and the fraction of free molybdenum increases upon sulfiding. Presulfiding with DMDS is thought to tear out some of the bound Mo ions (such an effect has been observed in the case of Ni/Al_2O_3 catalysts); the liberated Mo could contribute to enlarge the size of the remaining clusters. The sulfidation degree of the molybdenum is in line with the mild or severe sulfiding conditions.

CONCLUSION

The salient findings reported here can be summarized as follows:

(1) Active site titration on sulfided Mo/Al_2O_3 catalysts can be achieved by chemisorption. The oxygen probe molecule detects simultaneously the vacancy and anion in the coordination sphere of a molybdenum ion. Oxygen adsorption confirms that HDS activity of sulfided Mo/Al_2O_3 catalysts cannot be predicted only by titration of the anion vacancies present on the catalytic surface.

(2) A new conclusion is suggested from the structural point of view: molybdenum ions are grouped in cluster arrangements, bound to the alumina via molybdenum. Isolated clusters of small size which present the same concentration in active sites can be formed at low loadings. In such a structural arrangement Mo ions exhibit the highest intrinsic efficiency. Higher Mo content does not favor the catalytic properties since the cluster size increases without increasing the number of active sites.

(3) Mo catalysts are very sensitive to the sulfiding process. Changes in structure occur when increasing H_2S partial pressure.

Studies of the influence of promoter ions on the different Mo phases put forward in this paper are presently in progress.

ACKNOWLEDGMENTS

This work has received financial support from D.G.R.S.T., Contract No., 79.7.0957. We wish to thank Dr. G. Martino and Dr. Y. Jacquin for very helpful discussions.

REFERENCES

1. Massoth, F. E., *Adv. Catal.* **27,** 266 (1978).
2. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes," Chap. V. McGraw-Hill, New York, 1979.
3. Le Page, J. F., "Catalyse de Contact," Chap. 4. Technip, Paris, 1978.
4. Massoth, F. E., *J. Catal.* **47,** 316 (1977).
5. De Beer, V. H. J., Van Der Aalst, M. J. M., Machiels, C. J., and Schuit, G. C. A., *J. Catal.* **43,** 78 (1976).
6. Hagenbach, G., Courty, P., and Delmon, B., *J. Catal.* **31,** 264 (1973); Delmon, B., "The Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 73. Climax Molybdenum Co., Ann Arbor, Mich., 1979.
7. Sonnemans, J., and Mars, P., *J. Catal.* **31,** 209 (1973).
8. Iannibello, A., Marengo, S., Trifiro, F., and Villa, P. L., "Preparation of Catalysts II," p. 65. Elsevier, Amsterdam, 1979.
9. Martinez, N. P., Mitchell, P. C. H., and Chiplunker, P., *J. Less. Common Metals* **54,** 333 (1977).
10. Medema, J., Van Stam, C., De Beer, V. H. J., Konings, A. J. A., and Koningsberger, D. C., *J. Catal.* **53,** 386 (1978).
11. Jeziorowski, H., and Krözinger, H., *J. Phys. Chem.* **83,** 1166 (1979).
12. Wang, L., and Hall, W. K., *J. Catal.* **66,** 251 (1980).
13. De Beer, V. H. J., Bevelander, C., Van Sint Fiet, T. H. M., Werter, P. G. A., and Amberg, C. H., *J. Catal.* **43,** 68 (1976).
14. Massoth, F. E., *J. Catal.* **36,** 164 (1975).
15. Schuit, G. C. A., and Gates, B. C., *AICHE J.* **19,** 417 (1973).
16. Voorhoeve, R. J. H., and Stuiver, J. C. M., *J. Catal.* **23,** 228, 236, 243 (1971).
17. De Beer, V. H. J., Van Sint Fiet, T. H. M., Van Der Steen, G. H. A. M., Zwaga, A. C., and Schuit, G. C. A., *J. Catal.* **35,** 297 (1974).
18. Massoth, F. E., and Kibby, C. L., *J. Catal.* **47,** 300 (1977).
19. Bachelier, J., Duchet, J. C., and Cornet, D., *J. Phys. Chem.* **84,** 1925 (1980).
20. Tauster, S. J., Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **63,** 515 (1980).
21. Tauster, S. J., and Riley, K. L., *J. Catal.* **67,** 250 (1981).
22. Parekh, B. S., and Weller, S. W., *J. Catal.* **47,** 100 (1977).
23. Millman, W. S., and Hall, W. K., *J. Catal.* **59,** 311 (1979).
24. Vyskocil, V., and Tomanova, D., *React. Kinet. Catal. Lett.* **10,** 37 (1979).
25. Ramakrishnan, N. R., and Weller, S. W., *J. Catal.* **67,** 237 (1981).

26. Hall, W. K., and Millman, S. W., "Proc. Intern. Congr. Catalysis, 7th (Tokyo 1980)," p. 1304. Elsevier, Amsterdam, 1981.
27. Giordiano, N., Bart, J. C. J., Vaghi, A., Castellan, A., and Martinotti, G., *J. Catal.* **36,** 81 (1975).
28. Kotera, T., Todo, N., Muramatsu, K., Ogawa, K., Kurita, M., Sato, T., Ogawa, M., and Kabe, T., *Ind. Chem. Eng.* **11,** 752 (1971).
29. Okamoto, Y., Tomioka, H., Katoh, Y., Imanaka, T., and Teranishi, S., *J. Phys. Chem.* **84,** 1833 (1980).
30. Okamoto, Y., Tomioka, H., Imanaka, T., and Teranishi, S., *J. Catal.* **66,** 93 (1980).
31. Kwart, H., Schuit, G. C. A., and Gates, B. C., *J. Catal.* **61,** 128 (1980).
32. Chevrel, R., Potel, M., and Sergent, M., *J. Solid. State Chem.* **34,** 247 (1980).