

Kinetics and Mechanism of Catalytic Hydrodesulfurization of Gas Oil: Adsorption and Hydrogenation of the Sulfur Compounds

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Sulfur compounds contained in gas oil were adsorbed on hydrodesulfurization catalysts containing Ni and Mo, or one of these metals, at temperatures between 420 and 650 K and pressures of 20 MPa. In runs performed with a limited amount of gas oil and excess adsorbent during 4 h, the extent of sulfur removal increases with the temperature and is determined by the rate of adsorption of the slowly adsorbed species. Some of the compounds adsorbed at low temperatures are desorbed at higher temperatures without decomposition and formation of H₂S, but when the temperature is raised further they are desorbed with the formation of H₂S. The nickel in the Ni-Mo catalyst does not promote the adsorption of the sulfur compounds but it inhibits cracking and other hydrocarbon reactions. © 1987 Academic Press, Inc.

INTRODUCTION

The mechanism of catalytic reactions is often deduced from studies of the reaction steps, namely adsorption and desorption of reactants and products, and interactions at the surface. An attempt is made in the present paper to apply this approach to the hydrodesulfurization of gas oil, considering primarily the adsorption step. Gas oils contain a large number of sulfur compounds with widely different properties, and it is not possible to determine the adsorption properties of the individual compounds. Nevertheless, sulfur adsorption can be characterized by treating the sulfur compounds jointly as a single population with properties such as energy of adsorption, energy of activation for adsorption, and rate constants which are given by distributions rather than by single values. This approach is useful as compared with the approach based on the study of model compounds, since the reaction parameters in HDS are more likely to reflect properties related to the heterogeneity of the reactant rather than properties of any individual sulfur compound.

Adsorption in energetically homogeneous systems (well-defined adsorbate and uniform surface) is generally characterized by measuring the equilibrium adsorption, $q_{eq}(c)$ at various constant temperatures, and the kinetics, $q(t)$ at various constant values of c and T , where q and q_{eq} are respectively the amounts taken up at time t and at equilibrium, T is the temperature, and c is the concentration in the fluid phase. There are, however, difficulties in applying this treatment to energetically heterogeneous systems (heterogeneous adsorbate and uniform surface or homogeneous adsorbate and nonuniform surface). In this case the uptake at large t is not necessarily the equilibrium one and the uptake at small t is not dictated by the kinetics only. At any given time there are rapid adsorption processes which have already attained equilibrium and slower processes which are still going on and the observed uptake is a sum of equilibrium and nonequilibrium uptakes.

In spite of these difficulties studies of adsorption in such heterogeneous systems have been performed and have led to useful results (1-3). The heterogeneous systems that have been most intensively studied are

those in which the adsorbate is well defined and the surface nonuniform, e.g., adsorption of pure gases on industrial catalysts. It was found convenient in these cases to plot the data as "isochrones" q_t , amount adsorbed at given constant time t_c , against temperature. (These plots are often loosely termed "equilibrium isobars.") For simple cases the isochrone has a maximum: q_t increases with T at low T , because the temperature dependence of the rate dominates, and it decreases at high T because the temperature dependence of the equilibrium uptake dominates. In more complex cases, e.g., more than one mode of adsorption or desorption, or discontinuities in the distribution of the adsorption properties, the plot may have minima and more than one maximum. The general form of the $q_t(T)$ plot varies little with t_c if t_c is large enough so that dq/dt at t_c is relatively small. The $q_t(T)$ plot reflects the heterogeneity of the system and analysis of its parts often gives useful information concerning modes of adsorption and desorption.

We assumed in the present work that adsorption of a heterogeneous adsorbate is comparable to adsorption of a homogeneous adsorbate on a heterogeneous surface, viz., plots of $q_t(T)$ can be used for characterizing the adsorption of sulfur compounds in gas oil and for investigating adsorption properties. We have found it convenient to refer to the amount of sulfur remaining in the oil S_A noting that $(S_{A_0} - S_A)$ is proportional to q_t , where S_{A_0} is the sulfur content in the untreated feed.

EXPERIMENTAL

Basis of Measurements

The adsorption was measured on catalysts in oxide form without previous sulfidation. Measurements were made in the range of temperature from 423 to 643 K, i.e., a range comprising that at which industrial reactions are usually performed and extending below by about 150 K. The oil was kept under pressure during the experi-

ments; this was necessary in order to maintain a liquid phase at the high temperatures used. Data concerning the disappearance of sulfur, obtained in the present experiments, do not represent the net adsorption capacity of the catalyst for the sulfur compounds; they represent the difference between the adsorbabilities of these compounds and that of the sulfur-free hydrocarbons which act as solvent.

Measurements were also performed in the presence of hydrogen, i.e., under conditions at which hydrodesulfurization takes place.

Catalysts

Measurements were performed on a catalyst containing nickel and molybdenum oxides supported on alumina (Ni-Mo-Al), and on catalysts containing only one of these active metals; a sample of alumina support that did not contain either of the active components was also tested. The same alumina was used as support in all the catalysts.

The composition of the catalysts tested and the specific surface areas are given in Table 1.

Gas Oil

We chose for this investigation a heavy gas oil fraction likely to be partially desulfurized under the conditions of the runs. It originated from a Middle Eastern crude, and had a sulfur content of 1.5% by weight. Distillation analysis and sulfur content of the cuts are given in Table 2.

TABLE I

Composition and Surface Area of the Catalysts

| Catalyst designation | Ni-Mo-Al | Mo-Al | Ni-Al | Al |
|---|----------|-------|-------|-----|
| MoO ₃ (wt%) | 15.6 | 15.6 | 0 | 0 |
| NiO (wt%) | 3.0 | 0 | 3.3 | 0 |
| Al ₂ O ₃ (wt%) | 81.4 | 84.4 | 96.7 | 100 |
| Specific area (m ² /g · cat.) | 238 | 243 | 272 | 246 |
| Specific area (m ² /g alumina) | 292 | 288 | 281 | 246 |

Apparatus and Experimental Procedure

Adsorption of the sulfur compounds was performed in a static process. The apparatus used was an autoclave with an internal volume of 20 cm³. Known weights of oil and catalyst were introduced, and weight ratios gas oil to catalyst were generally between 1.2 and 1.6. Air was carefully displaced by nitrogen at 20 MPa. The autoclave was subsequently heated to the desired adsorption temperature and maintained at that temperature for the desired period of time. At the end of the run it was rapidly cooled, and the oil was separated and analyzed for its sulfur content. The autoclave and its contents needed 2 to 3 ks to reach the high temperatures at which adsorption was measured; the adsorption times reported are the times measured from the moment the oil and the catalyst were placed in contact, and include the heating time.

For runs under hydrogen, a vessel containing oxygen-free hydrogen at a pressure of 20 MPa was connected to the autoclave throughout the run. A few two-stage experiments (see caption of Fig. 2) were also performed, e.g., reaction at constant temperature in the presence of nitrogen or hydrogen followed by purging and adsorption in the presence of the same gas or the other gas at another constant temperature. Sulfur analysis was performed at the end of the last stage.

RESULTS AND DISCUSSION

Sulfur Removal as a Function of Time and Temperature

The results for runs under isothermal conditions and equal periods of 14.5 ks are given in Fig. 1. They are depicted as plots of S_A , the percentage of sulfur in the gas oil at the end of the run, against the run temperature T . Figure 1a refers to runs performed with the catalysts Ni-Mo-Al and Mo-Al, and Fig. 1b to runs with the catalyst Ni-Al. In measurements using pure alumina support, no detectable

TABLE 2

| Cut no. | 1 | 2 | 3 | 4 | 5 |
|------------------------------|---------|---------|---------|---------|------|
| Distillation range (K) | 453-593 | 593-621 | 621-651 | 651-663 | >663 |
| Weight percent cut to total | 19.4 | 19.9 | 20.2 | 20.3 | 20.2 |
| Weight percent sulfur to cut | 1.00 | 1.53 | 1.50 | 1.56 | 1.53 |

changes of the sulfur content of the gas oil were obtained.

Plots of the ratio $S_A : S_{A_0}$, against time t are given in Fig. 2. Figure 2a refers to the catalyst Ni-Mo-Al at 588 and 623 K, and Fig. 2b to the catalyst Ni-Al at 588 K. The graphs contain data already depicted in Fig. 1 and data for runs under other conditions, namely times different from 14 ks and two-stage experiments.

Heterogeneity of the Adsorbate

The isochrones for adsorption in the absence of hydrogen (Fig. 1) have a complex form; they have a horizontal part at low temperatures followed as temperature increases by a descending part, an ascending part, and a second descending part. These features are shared by the plots for the three catalysts investigated, but the slopes and the positions of the maxima and minima differ.

Complex adsorption plots are assumed to be associated with heterogeneity, and in the present case we expect heterogeneity of the adsorbate (a group of compounds with different adsorption properties) and heterogeneity of the adsorbent (sites with different adsorption energies and different activation energies for adsorption). Interpretation of the experimental results is considerably simplified if one can show that one of the two above-mentioned heterogeneities is predominant, and therefore mainly reflected by the data. The following considerations indicate that heterogeneity of the adsorbate can be assumed to be predominant.

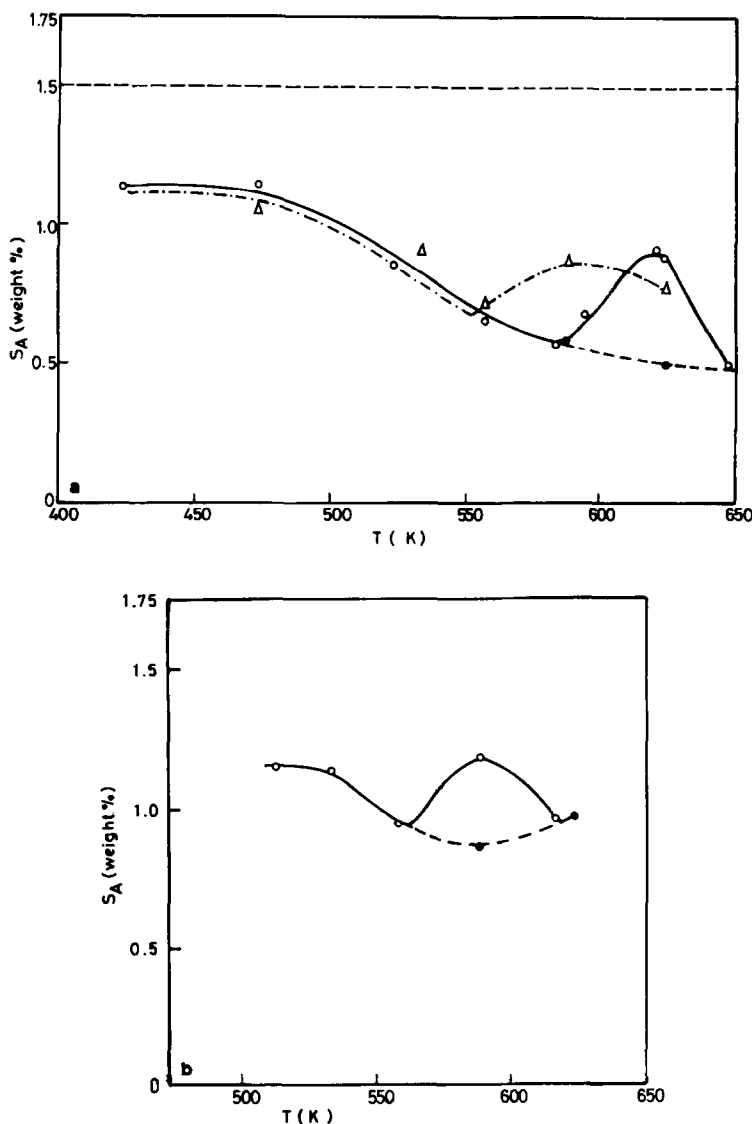


FIG. 1. Adsorption and hydrodesulfurization. Plots of S_A against temperature. (a) (\circ) Ni-Mo-Al catalyst, runs under nitrogen; (\bullet) Ni-Mo-Al catalyst, runs under hydrogen; (Δ) Mo-Al catalyst, runs under nitrogen. (b) (\circ) Ni-Al catalyst, runs under nitrogen; (\bullet) Ni-Al catalyst, runs under hydrogen.

(a) Selective adsorption of the sulfur compounds is a property of the molybdenum oxide or nickel oxide present in the catalyst and not a property of the alumina support. (There is no sulfur removal in experiments with pure support.) The surface associated with these metals could be heterogeneous (nonuniformity of the activation energy for adsorption of sulfur com-

pounds); however, it seems unlikely that the site energy distributions for the two metals should be similar and produce isochrones of the same general form.

(b) In the descending part of the isochrones, e.g., at 588 K for Ni-Mo-Al catalyst (Fig. 1), the concentrations of residual sulfur in experiments in the presence of hydrogen and in the absence of hydrogen

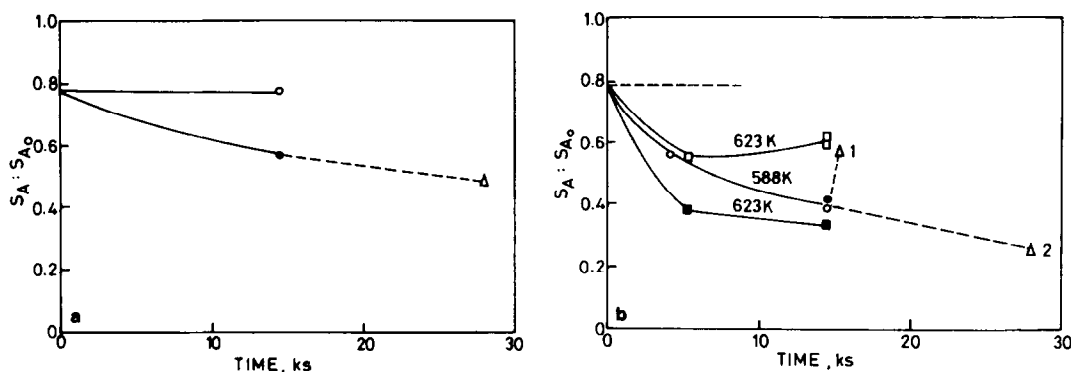


FIG. 2. Plots of S_A/S_{A_0} against time. (a) Ni-Mo-Al catalyst. (○) $T = 588$ K, nitrogen; (●) $T = 588$ K, hydrogen; (□) $T = 623$ K, nitrogen; (■) $T = 623$ K, hydrogen; (△1) $T = 588$ K, $t = 14.5$ ks, nitrogen, followed by $T = 623$ K, $t = 0.9$ ks, nitrogen; (△2) $T = 588$ K, $t = 14.5$ ks, hydrogen, followed by $T = 623$ K, $t = 14.5$ ks, nitrogen. (b) Ni-Al catalyst. (○) $T = 588$ K, nitrogen; (●) $T = 588$ K, hydrogen; (△) $T = 588$ K, $t = 14.5$ ks, hydrogen, followed by $T = 588$ K, $t = 14.5$ ks, nitrogen. (Compounds of type 1 are adsorbed instantaneously.)

are the same. It is presumable that hydrogenation ensures depletion of the adsorbing surface, and the fact that some compounds are not adsorbed although empty sites are present indicates that their rate of adsorption is slow at the test temperature, i.e., the effect of temperature reflects the heterogeneity of the adsorbate. (The assumption that hydrogenation cleared up the surface from adsorbed sulfur compounds is based on the fact that the time allowed for this process was large, of the order of 10^4 s. Hydrodesulfurization in industrial processes is performed at significantly smaller residence times of the order of 10^3 s.)

(c) The two points referring to adsorption in nitrogen by the Ni-Mo-Al catalyst at 623 K during 14.5 ks (Figs. 1 and 2) are the results of two experiments in which two different gas oil-to-catalyst ratios were used, viz., 0.72 and 1.43. The percentages of sulfur in the gas oil found are close, 0.92 and 0.89. However, if the data are used for calculating the amounts of sulfur taken up by the catalyst one obtains results that differ significantly, namely 0.42 and 0.87 g sulfur/100 g catalyst, respectively. This can be explained by assuming that the adsorbing surface was in excess and with a sufficient supply of low activation energy

sites, heterogeneity of the surface cannot determine the results.

Two Types of Sulfur Compounds

The low T descending part in the plots in Fig. 1 (e.g., from 480 to 580 K for Ni-Mo-Al) corresponds to a range of temperatures at which uptake increases with temperature presumably because of an increase in the adsorption rate. The fact that this part is preceded by a horizontal one indicates a discontinuity in the adsorption properties of the adsorbates. The oil contains sulfur compounds with low activation energy for adsorption (type 1) which are completely adsorbed at low temperature, and there is no additional adsorption until the temperature is raised to 480 K. At this temperature and at higher ones the adsorption of other compounds with a higher activation energy of adsorption (type 2) becomes noticeable. The fact that the horizontal part of the graph lies at the same height in the plots referring to the three different catalysts ($S_A \approx 1.15$) confirms the assumption of two distinct types of compounds. One can estimate that the compounds of type 1 account for about 23% of the sulfur.

As there is a wide difference between the temperature at which type 1 compounds are

totally adsorbed and the temperature at which compounds of type 2 start to be taken up, and no signs of desorption in that range (horizontal plot), we may assume that type 1 compounds are strongly sorbed.

The activation energy for adsorption of type 2 compounds is lower in catalysts containing Mo. On Ni-Al catalysts adsorption of these compounds becomes measurable only at temperatures above 530 K, and on Mo-Al and Ni-Mo-Al catalysts it is already detectable at about 450 K. In runs at 550 K the sulfur content is 0.95 when the adsorbent is Ni-Al and 0.7 when the adsorbent is either Mo-Al or Ni-Mo-Al.

Experiments aimed at finding out whether there is a correlation between the adsorption properties of the sulfur compounds and their distribution in narrow boiling cuts were also performed. The cuts defined in Table 2 were submitted to adsorption on Ni-Mo-Al catalyst at 583 K. The results show that there is no significant difference between adsorbabilities of the sulfur compounds in cuts with different boiling points. This suggests that the observed differences in adsorption properties of the sulfur compounds are not strongly related to their molecular weight; they probably reflect differences in the chemical nature of the sulfur-containing groups.

Desorption and Cleavage of the Sulfur Compounds

The presence of an ascending region in the isochrones for adsorption in nitrogen implies that some of the sulfur compounds adsorbed at lower temperatures are desorbed when the temperature is sufficiently raised. The fact that the desorbed sulfur is found in the liquid phase indicates that this desorption is not accompanied by complete removal of the sulfur from the hydrocarbon; however, partial cleavage of the organic sulfur compound is not excluded. It also follows that at least some sulfur compounds are adsorbed without destructive decomposition in agreement with deductions based on IR spectroscopy (4).

Information concerning the extent of desorption and the nature of the compounds desorbed can be gained by comparing these results with those of runs performed in the presence of hydrogen. S_A for both procedures coincide at any point in the descending part of the plots, e.g., at 588 K for Ni-Mo-Al (Fig. 1a), but there is no ascending region in the plots for adsorption in the presence of hydrogen. S_A at 623 K is slightly lower than S_A at 588 K and the line joining these points seems to be the natural prolongation of the descending part of the plot; i.e., adsorption of compounds of type 2 continues smoothly and uninterruptedly in the presence of hydrogen. Similar observations can be made with respect to the plots in Fig. 1b. These results do not imply that the presence of hydrogen hinders the desorption of the sulfur compounds. The desorption takes place with more complete cleavage of the sulfur compounds, i.e., with formation of H_2S which does not reenter into the liquid phase.

One may assume that the ascending regions for the runs performed in nitrogen are the result of two opposite processes taking place simultaneously; these are the adsorption of compounds of type 2 with a high activation energy for adsorption, and the desorption of other compounds previously adsorbed at lower temperature. The net percentage of sulfur attributable to desorption is given for any temperature by the difference between the heights of the curves for adsorption in nitrogen and in hydrogen at that temperature. For the Ni-Mo-Al catalyst it is 0.4% at the maximum of the plot (623 K). For the Ni-Al catalyst it is 0.3% at the maximum (588 K). These figures are close to those corresponding to compounds of type 1.

A series of experiments depicted in Fig. 2 shows that the destructive desorption of the sulfur compounds induced by hydrogen takes place at temperatures lower than those required for nondestructive desorption in the absence of hydrogen. Adsorption at 588 K during 14.5 ks gives the

same results in the absence and in the presence of hydrogen; however, the results obtained with further heating differ. Point 1 refers to adsorption in nitrogen at 588 K during 14.5 ks, followed by heating in nitrogen at 623 K during 0.9 ks; this indicates that further heating produces desorption; i.e., adsorption was not destructive. The final sulfur concentration is slightly lower than that in one-stage adsorption at 623 K and 14.5 ks. Point 2 refers to adsorption in hydrogen at 588 K during 14.5 ks followed by heating in nitrogen at 623 K during 14.5 ks. It shows that further heating produces further adsorption; i.e., adsorbed sulfur compounds were already destroyed at the first stage of the experiment at $T < 588$ in the presence of hydrogen.

Hydrodesulfurization with Intrinsic Hydrogen

The presence of a second descending region in the isochrones at $T > 633$ K for Ni–Mo–Al and at $T > 593$ K for Mo–Al and Ni–Al indicates the occurrence of a high temperature process of sulfur removal. The second descending region is not the continuation of the first descending region displaced to higher S_A ; i.e., it does not represent continuation of adsorption of compounds of type 2 after desorption of lower activation energy compounds has ended. It indicates that the compounds that have desorbed into the liquid phase are removed again. This is confirmed by the fact that measurements in that range of temperature give the same results whether performed in the presence or in the absence of hydrogen, in contrast to what happens at the ascending range (see S_A at $T = 623$ in Fig. 1b).

It is unlikely that disappearance of sulfur compounds at higher temperatures indicates resumption of the adsorption process. It is presumably the result of H_2S formation using hydrogen intrinsically contained in the oil and liberated by processes such as cracking, olefin formation, and aromatization. It is known that these reactions

take place to varying extents in the temperature range under consideration and that they are accompanied by desulfurization. In the present work signs of cracking, such as a decrease in the amount of oil, and coke formation, were observed, especially with Mo–Al catalyst.

It is probable that the desorption that takes place in the ascending region is also related to the liberation of the intrinsic hydrogen, and that the ascending region and the following descending region are coupled and represent two stages of the same process. We may assume that separation of sulfur from the catalyst surface is the result of a hydrogenation process in both cases. At low hydrogen concentrations the sulfur detached from the surface remains attached to a hydrocarbon group of significant size, while at higher hydrogen concentrations, viz., higher temperatures, it is separated from the hydrocarbons as well as from the surface and evolves as H_2S . If hydrogen from an external source is added, desorption takes place as H_2S over the entire temperature range, and the only changes detectable in the oil are those resulting from further adsorption.

The occurrence of partial hydrogenolysis as an intermediate stage in desulfurization has been postulated, e.g., formation of propylbenzenethiol in desulfurization of methyl-dihydrobenzothiophene (5). The intermediates are not detectable when the reaction is performed in the presence of hydrogen under ordinary conditions because of their reactivity. However, they are likely to survive in adsorption–desorption experiments without added hydrogen as performed here. They are not destroyed if the rate of desorption is rapid as compared with the rate of hydrogen production resulting from dehydrogenation of hydrocarbons.

Adsorption of Sulfur Compounds in Hydrodesulfurization

The adsorption measurements show that at any temperature there is a fraction of the sulfur compounds that is slowly adsorbed

at that temperature. This suggests that adsorption of the sulfur compounds may have limiting effects in hydrodesulfurization and must be taken into account in any mechanisms proposed. The fact that desulfurization often obeys Langmuir–Hinshelwood kinetics (6) does not exclude the possibility of rate limited by adsorption.

Nickel as Promoter in Hydrodesulfurization

One cannot discern any difference between the isochrones for Mo–Al and Ni–Mo–Al up to 550 K (Fig. 1a); i.e., the activation energy for adsorption of the sulfur compounds is remarkably similar in both catalysts. Nickel is not a promoter for the adsorption of the sulfur compounds. The most striking difference in the results for Ni–Mo–Al and Ni–Al catalysts is the fact that the ascending and redescending part of the isochrone occurs at a higher temperature in Ni–Mo–Al than in Ni–Al. This indicates that the hydrocarbon reactions that produce the hydrogen responsible for high temperature desorption and desulfurization are retarded by the presence of nickel. This interpretation is confirmed by the fact that the signs of cracking (formation of coke and tar) were considerably more important in the runs with Mo–Al. At 630 K cracking with this catalyst was so important that adsorption runs could not be performed. Since uncontrolled

dehydrogenation of the hydrocarbon ultimately leads to coke formation and to subsequent deactivation of the catalyst, it follows that attenuation of the dehydrogenation of the hydrocarbon is equivalent to promotion of the hydrodesulfurization.

This view is consistent with the results of Laine *et al.* (7). These authors compared the activities of Mo–Al and Ni–Mo–Al catalysts for the hydrodesulfurization of thiophene and measured the carbon deposition resulting from the cracking of butadiene. They found that the rate of carbon deposition is higher in Mo–Al than in Ni–Mo–Al. They also found that the catalytic activity for hydrodesulfurization is higher with Mo–Al at the beginning of the runs but drops rapidly later and becomes significantly smaller than the catalytic activity with Ni–Mo–Al.

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