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Some Effects of Sulfiding of a $NiMo/Al_2O_3$ Catalyst on Its Activity for Hydrodenitrogenation of Quinoline

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The method of presulfiding of a commercial $NiMo/Al_2O_3$ catalyst has a significant effect on its inherent activity for the hydrodenitrogenation of quinoline (HDN). In addition, during reaction the addition of H_2S increases the HDN rate and its removal decreases it in a reversible manner. The effect of H_2S on the kinetics of a variety of hydrodenitrogenation, hydrodesulfurization, and hydrogenation reactions on molybdenum catalysts can be rationalized in terms of its effect on two kinds of sites, sulfur anion vacancies and Brønsted acids.

It is well known that the method of presulfiding a hydrotreating catalyst such as $NiMo/Al_2O_3$ may have a marked effect on its subsequent activity and commercial catalyst manufacturers prescribe one or more presulfiding procedures for the catalysts they supply that can be readily used on their customer's premises. A deeper understanding of the relationships between presulfiding procedures and catalyst activity is complicated for a variety of reasons: these include the complex nature of sulfided molybdenum catalysts, interactions between the metal components and the support, the effect of processing conditions and feedstock composition on catalyst composition and the fact that the morphology of the sulfided catalyst depends in considerable part on the morphology of the oxide precursor, which in turn depends on catalyst manufacturing procedures. All of these can affect the intrinsic catalyst activity.

It is known that hydrogen sulfide can depress the hydrodesulfurization (HDS) rate of thiophene (*1*, *2*) and of dibenzothiophene (*3*). It also depresses the hydrogenation of 1-butene (*2*) as well as the HDN reaction of *o*-ethylaniline (*4*). However it enhances the HDN reactions of pyridine (*5*, *6*), and of quinoline (*7*) and it also enhances the HDO reaction of dibenzofuran (*8*). Ramachandran and Massoth (*9*) report that it enhances the cracking of hexene, but had no effect on hydrogenation of hexene. In the HDS of thiophene, both the hydrogenolysis and hydrogenation reactions in the overall reaction network are hindered by H_2S; while in the HDS of dibenzothiophene, H_2S depresses hydrogenolysis and leaves hydrogenation essentially intact. In quinoline HDN, the hydrogenolysis reactions are markedly enhanced and hydrogenation reactions somewhat inhibited by H_2S.

It would seem that the catalytic sites facilitating C–S bond breaking in HDS are not the same as those for C–N bond breaking in HDN, and that the catalytic sites facilitating hydrogenation in HDS are not the same sites in HDN. Yet competitive adsorption, for example that observed between thiophene and pyridine (*5*), hints that at least to some extent the same catalytic sites are involved in HDS and HDN reactions.

In the present study samples of a commercial $NiMo/Al_2O_3$ catalyst were subjected to each of three different presulfiding conditions and their subsequent activity was determined for the hydrodenitrogenation of quinoline in the presence or absence of H_2S in the gas phase. We will demon-

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strate that the HDN activity of a sulfided NiMo/Al$_2$O$_3$ catalyst is sensitive to presulfidation conditions and that this inherent degree of activity is maintained for at least several hundred hours throughout variations in subsequent reaction conditions.

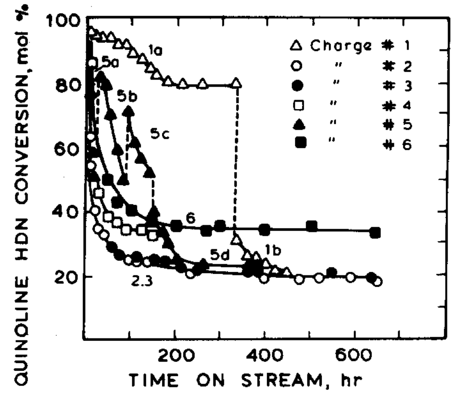

FIG. 1. Activity history of six catalyst charges (see text).

EXPERIMENTAL

Presulfidation methods. The catalyst was a NiMo/Al$_2$O$_3$ (American Cyanamid HDS-3A; 3.3% NiO, 15.0% MoO$_3$, and 1.4% P, on alumina). Three presulfidation methods were employed, similar to the manufacturer's recommendation, but differing in the partial pressure of hydrogen sulfide used and the duration of sulfidation. For method 1, the catalyst was heated to 175°C under a flow of helium. A mixture of 10% H$_2$S in H$_2$ was then passed through the bed at 20 cc/min (STP) and 0.24 MPa for 12 h. The temperature was then increased to 315°C at a rate of 1°C/min and held at 315°C for 1 h. The catalyst was then cooled to 150°C under the H$_2$S–H$_2$ flow and further cooled to room temperature under flow of helium. Method 2 differed from method 1 in that the total pressure of the 10% H$_2$S in H$_2$ mixture was 0.30 MPa instead of 0.24 MPa. Method 3 was like method 1, except that the catalyst was held at 175°C for 24 h instead of 12 h and held at 315°C for 2 h instead of 1 h.

HDN activity. The quinoline HDN reaction was carried out in a trickle-bed reactor which is described elsewhere (*10*). The catalyst charge was either 0.8 or 1.6 g of catalyst averaging 0.2 mm diameter, diluted either 1 : 9 or 1 : 4, respectively, with inert. Catalyst activity was measured by the percent HDN of quinoline observed by a standardized test at 6.9 MPa and 375°C, using 5 wt% quinoline in an inert liquid carrier at a space-time of 269 h g catalyst/mol quinoline, without the presence of added H$_2$S in the gas phase. This test was applied at various times, between which different reaction conditions and other reactants may have been used.

Each of six charges of catalyst were presulfided by one of the three methods and then used for the HDN of quinoline under each of several conditions. Charges 1, 2, 3, and 5 were presulfided by method 1; charge 4 by method 2; and charge 6 by method 3. The activity of charge 2 as measured by the standardized test conditions is representative. It decreased markedly during about the initial 100 h, and then more slowly, arriving at a constant value after about 150 h on stream. This was maintained for at least 650 h, as shown in Fig. 1. During the period between 150 and 650 h a variety of HDN studies were performed. Occasionally the standardized test condition was run to check the activity.

The catalyst was resulfided about every 10 to 15 h as a precaution, although we did not establish that this was necessarily required. This was done with a 10% H$_2$S in H$_2$ mixture at 40 cm^3 (STP)/min and 0.24 MPa total pressure at 350°C for 1 h. The catalyst bed was then cooled as in the presulfiding procedure. After each resulfiding the catalyst bed was also flushed with a mixture of inert carrier and xylene for $\frac{1}{2}$ h to help dissolve any possible accumulated high-molecular-weight material. Charge 3 was a duplicate to charge 2, except that twice the quantity of catalyst was placed in the reactor. The liquid and gas flow rates were corresponding doubled to keep space–time and gas/liquid mole ratios constant. Charge 3 behaved identically to charge 2.

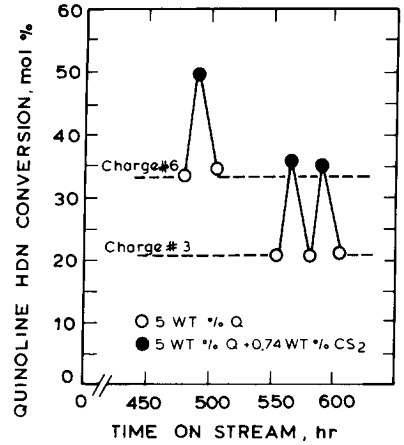

FIG. 2. Presence of H_2S increases HDN of quinoline. 6.9 MPa, 375°C, 269 h g catalyst/mol quinoline.

The steady-state activity of charge 6 under the standardized test conditions was significantly higher than that of charge 3, as shown in Fig. 1. Charge 4 was presulfided by method 2. Although it was run for only 150 h, it clearly had higher activity than charge 2.

Effect of H_2S on HDN reactions. As discussed elsewhere (4, 7), the HDN of quinoline is enhanced by H_2S in the vapor phase, a phenomenon that is reversible and is separate from the effect of H_2S during the initial activation procedure. Addition of 0.74 wt% CS_2 to the liquid feed, to generate H_2S in situ, causes an increase in percent HDN of quinoline but when the CS_2 is removed, the activity drops to its former level. The phenomenon is illustrated in Fig. 2 for data with charge 6 and charge 3, showing that the degree of increase was independent of the method of presulfiding. The inherent activity of each of the two charges was unaffected by the subsequent presence of H_2S in the vapor phase. Evidently the presulfiding procedure using H_2S and H_2 alone is more severe than when the H_2S is present in the presence of nitrogen compounds.

Catalyst deactivation during HDN. Charges 1 and 5 were subjected to different reaction conditions than charges 2 and 3, although all four were presulfided by method 1. Charge 1 was first brought on stream using a feed of 1 wt% quinoline, and a high space–time, 693 h g catalyst/mol quinoline. The rate of deactivation was slower than with 5 wt% quinoline, but it reached a constant activity after 200 h. After 330 h on stream, the standardized test conditions were applied. The percent HDN decreased to a steady value close to that obtained with charge 3, as shown in Fig. 1. Evidently, the initial use of a lower quinoline concentration and higher space–time had no effect on the ultimate activity.

Adding and removing H_2S from the feed and periodic resulfiding by the specified procedure seemed to have no significant effect on the steady-state intrinsic activity as measured by the standardized test. The intrinsic activity is determined only by the initial sulfiding procedure as shown by a run with charge 5 (Fig. 1). It was first on stream under the standardized HDN condition (no added CS_2) for 33 h, during which the percent HDN decreased from 92 to 50% conversion (Fig. 1, curve 5a). It was then resulfided and subjected to the standardized HDN conditions except with 0.74 wt% CS_2 added to the feed. The HDN increased to 83%, dropping to 50% after a total of 85 h (Fig. 1, curve 5b). A second resulfiding then increased conversion to 70% under standardized conditions with CS_2, which further dropped to 52% conversion after another 55 h (total of 140 h) (Fig. 1, curve 5c). Eliminating CS_2 from the feed dropped the activity to 40%. It was then resulfided periodically and its steady-state activity by the standardized test (no CS_2) dropped to a steady-state level (Fig. 1, curve 5d) essentially the same as that of charges 2 and 3 which had been subjected to quite different interim reaction conditions.

RESULTS

The results can be summarized as follows:

(1) Within the three presulfiding procedures used, higher steady-state catalyst activity was achieved by sulfiding at a higher

pressure and/or for a longer duration. This ultimate activity was not affected by variations in the quinoline concentration in the feed, space–time, or presence versus absence of H_2S in the subsequent reaction conditions.

(2) The time required to reach steady-state activity is longer with a lower concentration of quinoline in the feed and at higher space–times.

(3) The steady-state catalyst activity as measured by the standardized test with quinoline is substantially higher in the presence of H_2S than in its absence. This effect is reversible.

DISCUSSION

Presulfidation Procedures

Several papers describe the effect of sulfiding procedures on the sulfur content of catalysts containing molybdenum, including effects of temperature, use of H_2S versus thiophene, prereduction, etc. Most commonly presulfiding is carried out on the MoO_3 precursor under a flow of H_2S and H_2. The resulting structures are controversial, but the reaction may be thought of as a combination of reduction of the molybdenum and replacement of oxygen by sulfur. In fact considerable oxygen may be retained even after severe presulfiding and if cobalt is present, it may be reduced to the metallic state or converted to Co_8S_9 to various degrees.

If MoO_3 is reduced to MoO_2 prior to presulfidation, the MoO_2 cannot be easily transformed into MoS_2 even at a temperature as high as 800°C (*11*). Thus care must be taken not to expose the oxide form of the catalyst to hydrogen at high temperature. Though we suspect that our $NiMo/Al_2O_3$ did not undergo complete sulfidation under the method 1 presulfiding procedure, the catalyst did not show an increase in activity with reaction time. This suggests that no further transformation of an oxide form to sulfide form occurred when CS_2 was present during reaction. Three studies, summarized in Table 1, give representative results on effects of various presulfiding conditions and subsequent treatments on the S/Mo atomic ratio.

Presulfiding a MoO_3/Al_2O_3 catalyst with H_2S–H_2 at 1 atm and 400°C for 2 h, de Beer *et al.* (*12*) reported a S/Mo atomic ratio of 2.04. The catalyst was cooled to room temperature under the H_2S–H_2 flow after sul-

TABLE 1

Effects of Sulfidation Treatment on S/Mo Ratio

Catalyst	Presulfidation condition	Postsulfidation treatment	S/Mo Atomic ratio	Reference
MoO_3 (12 wt%)/ Al_2O_3	H_2S/H_2 (1 : 6), 1 atm 400°C, 2 h	Cool to room temp. in H_2S/H_2, purge under N_2 for 10 min	2.04	de Beer *et al.* (*12*)
	400°C, 2 h	400°C in H_2 (1 atm) for 2 h	1.20	
	300°C, 2 h	Cool to room temp. in H_2S/H_2, purge under N_2 for 10 min	1.78	
CoO (4 wt%) MoO_3 (12 wt%)/Al_2O_3	400°C, 2 h	Cool to room temp. in H_2S/H_2, purge under N_2 for 10 min	2.40	
MoO_3 (8 wt%)/Al_2O_3	H_2S/H_2 (1 : 10), 1 atm, 400°C, 2 h	Under N_2 purge at 400°C for 1 h	1.70 ($MoO_{0.95}S_{1.7}$)	Massoth (*13*)
$CoMo/Al_2O_3$	Thiophene/H_2 (1 : 5) 10 Torr 400°C, 100 min	—	1	Okamoto *et al.* (*14*)

fiding; Massoth (*13*) carried out the sulfiding by the same method but then purged the catalyst under nitrogen at 400°C for 1 h. The resulting S/Mo ratio was 1.70. When de Beer *et al.* further treated their catalyst by H_2 flow at 400°C for 2 h after sulfiding, the S/Mo ratio decreased from 2.04 to 1.20. To purge the catalyst at high temperature under inert gas or treat the catalyst at high temperature under H_2 considerably reduces the S/Mo ratio.

Presulfidation at 300°C for 2 h and cooling under H_2S–H_2 resulted in a S/Mo ratio of 1.78, presumably due to incomplete sulfidation (*12*). Even after presulfiding with H_2S–H_2 at 400°C for 2 h, Massoth (*13*) reported the structure to have the composition $MoO_{0.95}S_{1.7}$. Apparently the period of 2 h is not long enough for a complete replacement of the oxygen even at 400°C; Massoth observed that sulfidation was still taking place, though at a very slow rate, after 2 h treatment.

A very low S/Mo ratio of 1, reported by Okamoto *et al.* (*14*) for one of their studies, clearly resulted from incomplete presulfidation by passing thiophene/H_2 at the very low pressure of 10 Torr. Declerck-Grimee *et al.* (*15*) presulfided their MoO_3/Al_2O_3 catalyst in a flow of H_2S–H_2 (15 : 85) at 1 atm following a long heating program: first heating the catalyst slowly from room temperature to 400°C in 24 h, holding it at 400°C for 24 h, and then cooling to room temperature. XPS measurements showed no residual molybdenum oxide. One concludes that a well sulfided MoO_3/Al_2O_3 catalyst should have a S/Mo ratio near 2. The presence of cobalt in the catalysts may result in a higher S/Mo ratio since some of the sulfur can be combined as cobalt sulfide.

From the above we judge that the three presulfidation methods we used should result in fairly good sulfidation, but we do not know the extent to which oxides were actually converted to sulfides. Since our three methods do result in different catalyst activities, in which a higher activity is produced by a higher partial pressure of hydrogen sulfide or longer sulfiding duration, we conclude that method 2 or 3 provides more complete sulfidation than method 1.

Nonstoichiometry

Molybdenum sulfide catalysts are nonstoichiometric, which causes their composition to be susceptible to the environment. The nature of such nonstoichiometry is not clear, though it must affect the activity of a sulfided catalyst. Many metal oxides at high temperatures have nonstoichiometric phases extending over a considerable composition range. Their structure and thermodynamic properties have been reviewed by Sørenson (*16*). His review emphasizes that nonstoichiometry is observed in oxide systems when metal cations can exist in several oxidation states, and it originates from structure defects. In an oxygen-deficient metal oxide, oxygen vacancies are predominantly formed, while in an oxygen-excess metal oxide, oxygen ions exist in interstitial positions. The composition of such an oxide is a function of oxygen partial pressure and temperature.

This basic picture of a nonstoichiometric metal oxide can be applied to molybdenum disulfide catalysts. Thermodynamic data on bulk phases (*17*) show that molybdenum is not reduced to the metallic form here. A value of P_{H_2S}/P_{H_2} of $\sim 10^{-5}$ at 375°C is sufficient to make MoS_2 the stable phase, which may be compared to a value of this ratio of 0.002 obtained by the presence of 0.74 wt% CS_2 in our feed.

A commercial HDS catalyst is typically composed of CoO in the range of 3–5 wt% and MoO_3 in the range of 12–15 wt%. When such a catalyst is sulfided, the major part of the molybdenum is converted to MoS_2 and CoO is transformed to Co and Co_8S_9 (*15, 18, 19*). Smaller amounts of oxysulfides, polymeric sulfur, and Mo(V) and Mo(VI) may also be present. It has been demonstrated that MoS_2 exists in a two-dimensional form on an alumina support (*19, 20*).

Nonstoichiometry, if it is not a result of incomplete presulfidation, can be achieved easily on such a two-dimensional MoS_2 structure. Both weak MoS_2-support interaction (*15*) and weak Mo–S bonds make structural defects easy to form, either as sulfur vacancies or interstitial sulfur, depending on the environment the catalyst is subjected to. Gachet *et al.* (*21*) labeled catalyst sulfur on a $CoMo/Al_2O_3$ catalyst with the ^{35}S radioisotope and studied its fate during the HDS reaction of dibenzothiophene. Some of the sulfur was shown to be labile and is progressively replaced by the sulfur of dibenzothiophene, while the remainder stayed on the catalyst. Such labile sulfur can contribute to the nonstoichiometry. The presence of cobalt not only disperses molybdenum on the support, but also possibly causes more defects to be present in the MoS_2 structure.

Catalytic activity must be closely related to the nonstoichiometry of a sulfided HDS catalyst. An ESR study of sulfided MoO_3/Al_2O_3 and $NiMo/Al_2O_3$ suggested the existence of surface vacancies on these catalysts (*22, 23*); and an ESR study of sulfided NiW/Al_2O_3 catalyst related hydrogenation of benzene to surface vacancies (*24*).

S/Mo Ratio and HDS Activity

Massoth and Kibby (*25*) demonstrated that activity for HDS of thiophene increased as the S/Mo ratio of their sulfided MoO_3/Al_2O_3 catalyst was decreased from 2 to 1, where this was varied by varying the temperature of sulfiding, at a fixed time. Later Okamoto *et al.* (*26, 27*) also arrived at the same conclusion from studies with a series of catalysts of varying Mo content that were sulfided at the same temperature and time. Figure 3 shows the data of Massoth and Kibby for HDS of thiophene (measured at 343°C) and also the data of Okamoto *et al.* (*26, 27*) (measured at 400°C) where the former data are replotted to put them on the basis of weight of MoO_3, as used by Okamoto *et al.* Though the two studies differed in their analytical techniques and in presulfidation conditions, both show higher HDS activity to correlate with lower S/Mo ratios.

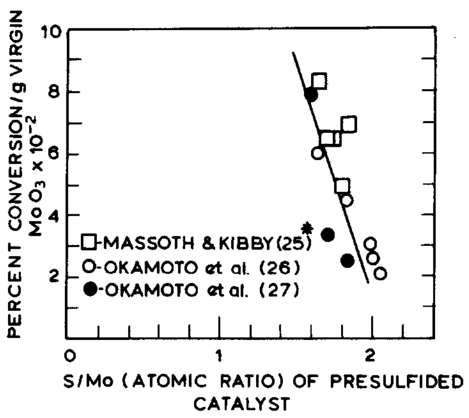

FIG. 3. Presulfidation to produce lower S/Mo ratios on catalyst increases thiophene HDS activity. *Catalyst weight taken to be 250 mg.

The S/Mo ratio after presulfidation is a measure of the degree of completeness of this reaction, but a change in the S/Mo ratio during reaction, especially removal of S by inert gas or hydrogen probably represents largely a different type of alteration of the catalyst structure associated with weakly bonded sulfur. Its effect on reactivity may be interpreted in terms of acidity associated with protons or vacancies associated with removal of sulfur.

Nature of the Active Sites

In order to explain kinetic data for hydrodesulfurization or hydrodenitrogenation, several researchers have found it necessary to postulate the existence of two kinds of catalytic sites on sulfided $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ catalysts. In a detailed study of the thiophene HDS reaction network, Desikan and Amberg (*28*) proposed two kinds of sites to exist on sulfided $CoMo/Al_2O_3$ catalyst: Site I is responsible for olefin hydrogenation and thiophene HDS, and it has strong affinity for thiophene and pyridine; Site II is weakly electrophilic and it facilitates hydrogenolysis of hydrothiophenes (see Discussion). Later Satterfield *et al.* (*5*), studying the simultaneous

HDS of thiophene and HDN of pyridine, proposed that two kinds of catalytic sites exist on a sulfided $CoMo/Al_2O_3$ catalyst: Site I is active for HDS and very sensitive to poisoning by nitrogen bases, Site II is much less active for HDS, and less susceptible to pyridine poisoning.

Recently, in order to explain the effect of hydrogen sulfide on the HDN of quinoline, we also postulated two kinds of catalytic sites to exist on sulfided $NiMo/Al_2O_3$ catalyst (4): Site I is a sulfur vacancy associated with molybdenum while Site II is a Brønsted acid site. We suggest that sulfur vacancies are responsible for hydrogenation and hydrogenolysis reactions, while Brønsted acid sites are responsible for hydrogenolysis only. Adsorption of an H_2S molecule and dissociation can convert a sulfur vacancy to a Brønsted site (H^+) and a sulfhydryl group (SH), but the adsorption is readily reversible if H_2S is removed from the reaction system.

The existence of SH groups on a commercial sulfided $CoMo/Al_2O_3$ catalyst has been recently established by Maternová (*29*) by a technique that involved adsorption of silver ions from a pyridine solution. The sulfhydryl group may also be considered to act as a Brønsted acid. However, the electron affinity of a H^+ site should be stronger than that of an H atom in an SH group. Therefore, H^+ sites should more readily promote reactions involving a carbonium ion mechanism.

The two kinds of catalytic sites proposed in the three studies above parallel each other, and a sum of their characteristics can be invoked to provide a consistent explanation of how H_2S affects HDS, HDN, hydrogenation, and cracking reactions in general. Some of these involve one category of reaction, others involve more than one in the overall process. Hydrogenolysis is defined here as breakage of a single C–S, C–N, or C–O bond. The direct extrusion of sulfur from thiophene is not a simple hydrogenolysis reaction due to the involvement of the aromaticity of the ring; Lipsch and Schuit (*30*) proposed that direct extrusion is facilitated by surface vacancies.

Based on the three studies, the characteristics of the two types of sites can be summarized as follows:

Type I sites: (1) These are sulfur vacancies associated with the molybdenum atom. There may be different types of vacancies on the surface as shown by ESR studies (*22*). Muralidhar *et al.* (*31*) suggest that there are corner vacancy sites having a higher degree of uncoordination than edge vacancy sites.

(2) They can facilitate hydrogenation and dehydrogenation reactions as well as the direct extrusion of sulfur from thiophene. Muralidhar *et al.* propose that the corner sites are active for HDS and edge sites are active for hydrogenation.

(3) They are easily poisoned by nitrogen bases.

(4) There remains the possibility that these sites facilitate hydrogenolysis.

Type II sites: (1) These are Brønsted acid sites, consisting of H^+ on the surface either from a promoter added to the catalyst (e.g., phosphate) or from the dissociation of H_2S on the surface (*4*) or from the support. (The HDS 3-A catalyst used here contains some sulfate and silicate, which are also possible sources of Brønsted acid sites.)

(2) These sites facilitate hydrogenolysis, cracking, and isomerization reactions that involve a carbonium ion mechanism.

(3) They are comparatively less vulnerable to poisoning by nitrogen bases, though it is well known that nitrogen compounds poison the protonic acid centers of cracking catalysts easily.

The above framework can be used to rationalize the competitive adsorption phenomena observed in simultaneous HDS/HDN reactions (5), HDO/HDN reactions (*32*), and simultaneous hydrogenation of tetralin when present with quinoline in the HDN reaction (*4*), as well as a variety of studies of hydrogenation, HDN and HDS as such.

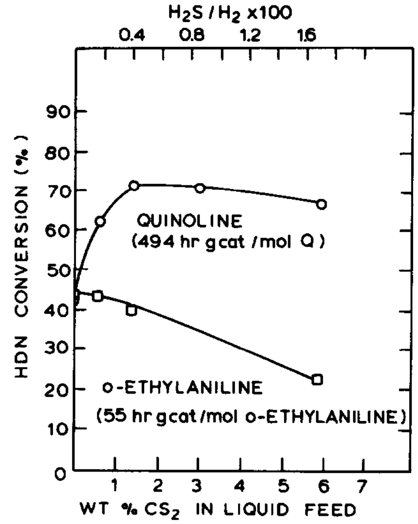

FIG. 4. H_2S increases the HDN of quinoline but inhibits that of *o*-ethylaniline. 6.9 MPa, 375°C.

HDN of Quinoline and o-Ethylaniline

The HDN reaction networks of quinoline and *o*-ethylaniline are described elsewhere (*10, 33, 34*). Both networks involve hydrogenation and hydrogenolysis reactions. With quinoline the heteroring must be hydrogenated before the hydrogenolysis of the C–N bond can occur. Similarly the aromatic ring of *o*-ethylaniline must be hydrogenated prior to hydrogenolysis.

The presence of H_2S accelerates the overall quinoline HDN reaction but inhibits the *o*-ethylaniline HDN reaction over a sulfided $NiMo/Al_2O_3$ catalyst, as shown on Fig. 4. We have shown that within these reaction networks H_2S depresses the hydrogenation and dehydrogenation reactions, but enhances the hydrogenolysis reactions and ring isomerization (*4*). Our interpretation is that the presence of H_2S results in less sulfur vacancies (Type I sites) and more Brønsted acid sites (Type II sites). Two hydrogenolysis reactions in the quinoline HDN reaction network are rate-limiting so the net effect of the presence of H_2S is an enhanced quinoline HDN conversion. However in the HDN reaction network of *o*-ethylaniline, the rate-limiting step is hydrogenation of its aromatic ring, and H_2S therefore reduces the total HDN conversion.

HDS of Thiophene

The thiophene HDS reaction network over a sulfided $CoMo/Al_2O_3$ was studied in detail by Desikan and Amberg (*28*) using feeds of thiophene and tetrahydrothiophene. They proposed the scheme shown in Fig. 5. Sulfur can be removed through two pathways: A and B, A being the major route. In pathway A thiophene undergoes direct extrusion of sulfur to form butadiene, which is rapidly hydrogenated to 1-butene. Thiophene can also be hydrogenated, through pathway B, to tetrahydrothiophene, which undergoes hydrogenolysis to 1-butene.

Owens and Amberg (*35*) observed that H_2S inhibited the hydrogenation of butene and the HDS of thiophene, the latter to a lesser degree. The presence of H_2S had very little effect on *cis–trans* isomerization, double-bond shifts, and butadiene conversion to butene. These phenomena can be rationalized as follows: H_2S decreases sulfur vacancies (Type I sites) and increases Brønsted acid sites (Type II sites) and therefore it depresses the direct extrusion of sulfur and hydrogenation of 1-butene in pathway A, while increasing the hydrogenolysis of tetrahydrothiophene and butanethiol in pathway B. The net effect is that butene hydrogenation is inhibited the most, and thiophene HDS as a whole is in-

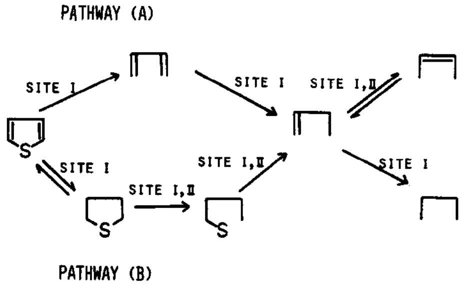

FIG. 5. Thiophene HDS reaction network proposed by Desikan and Amberg (*28*).

hibited less. Hydrogenation of butadiene, double-bond shifting of 1-butene, and *trans–cis* isomerization of 2-butene are always fast and close to thermodynamic equilibrium (*28*) so that H_2S has no significant effect on their rates.

Hydrogenation and Cracking of Hexene

Satterfield and Roberts (*1*) and Lee and Butt (*2*) found that H_2S inhibited butene hydrogenation as well as thiophene HDS. Ramachandran and Massoth (9) observed that similar concentrations of H_2S exerted no effect on hydrogenation of hexene, but a small amount of cracking of hexene occurred that increased linearly with H_2S concentration.

The $CoMo/Al_2O_3$ catalysts used in the three studies had similar compositions, about 3–4% CoO and 10–12% MoO_3. In the first two studies "moderate" presulfidation procedures were used, H_2S–H_2 at 1 atm and 315°C for 3 h for Satterfield and Roberts, H_2 at 400°C for 10 h and thiophene and H_2 for several hours for Lee and Butt. In the third work, a more severe sulfidation was employed. The catalyst was not only presulfided with H_2S–H_2 at 400°C for 2 h, but was also subjected to a feed of benzothiophene, H_2S, H_2, and heptane for 3 weeks to achieve steady state activity before studies with hexene.

Some rates of thiophene HDS, chosen from the first two studies, which have similar reaction conditions, are plotted in Fig. 6a for comparison. The data of the first were obtained at 265°C and 14 Torr thiophene feed, while the data of Lee and Butt were at 275°C and 32 Torr thiophene feed. The rates are converted to the common basis of mol/g min Torr of H_2. In the first study, an average of 694 Torr is taken as the hydrogen partial pressure from the range reported. Though the reaction conditions differ slightly, both "moderately sulfided" catalysts showed comparable reaction rates and inhibition of thiophene HDS by H_2S.

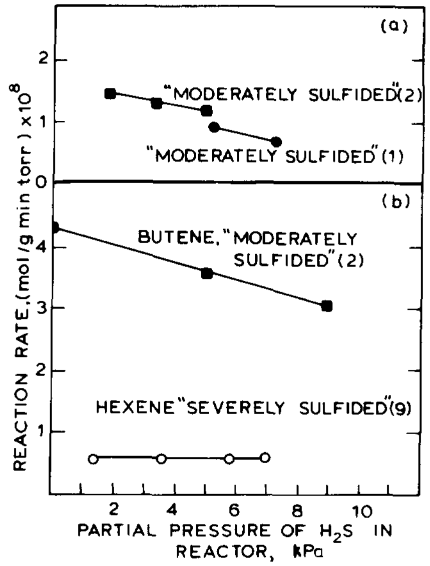

FIG. 6. Effects of H_2S partial pressure on thiophene HDS (6a) and olefin hydrogenation (6b). Total pressure about 1 atm. ●, Satterfield and Roberts (*1*). ■, Lee and Butt (*2*). ○, Ramachandran and Massoth (*9*).

The hydrogenation rate of butene at 300°C by Lee and Butt and that of hexene at 350°C of Ramachandran and Massoth are plotted in Fig. 6b. The "moderately sulfided" catalyst provided a higher rate of butene hydrogenation which however was inhibited by H_2S, while a "severely sulfided" catalyst provided a lower rate of hexene hydrogenation even at a higher temperature and this was not affected by the same concentrations of H_2S used in the other two studies.

Ramachandran and Massoth attributed the hexene cracking to protons formed by the heterolytic dissociation of H_2S. This is parallel to our suggestion that adsorption of a H_2S molecule converts a sulfur vacancy to a Brønsted acid site (H^+) and a SH group on the catalyst surface. A "severely sulfided" catalyst presumably has a high ratio of S/Mo and less sulfur vacancies, so the presence of H_2S would not exert the same degree of influence on the catalyst as in the case of "moderately sulfided" catalyst. A smaller amount of H_2S would be dissociated on sulfur vacancies under reaction conditions. Such a small reduction of sulfur vacancies might not be reflected in the hydrogenation rate, but the generation of a

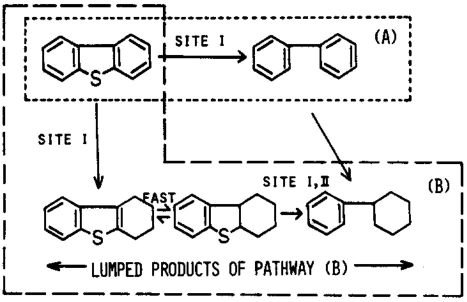

FIG. 7. Dibenzothiophene reaction network proposed by Broderick and Gates (*3*).

small amount of Brønsted acid sites could result in a small portion of the hexene being cracked.

HDS of Dibenzothiophene

Broderick and Gates (*3*) studied the HDS reaction network of dibenzothiophene and found that H_2S depressed hydrogenolysis but left hydrogenation unchanged, which seems contradictory to the findings of thiophene HDS. However their results can be interpreted in terms of the two kinds of catalytic sites we propose as follows.

The two principal pathways that they propose are shown in Fig. 7. In pathway A, dibenzothiophene undergoes direct sulfur extrusion to form biphenyl. In pathway B, dibenzothiophene is hydrogenated to tetrahydrodibenzothiophene and further to hexahydrodibenzothiophene, which in turn will undergo hydrogenolysis to form cyclohexylbenzene. Broderick and Gates found that H_2S inhibited the reaction in pathway A but had no effect on the formation of the lumped products in pathway B. This can be rationalized as follows:

In the presence of H_2S, sulfur vacancies (Type I sites) are decreased, while Brønsted acid sites (Type II sites) are increased. This results in an inhibition for pathway A which requires vacancies as catalytic sites. Since the whole pathway B can be kinetically controlled by hydrogenation as well as hydrogenolysis steps, a simultaneous acceleration of hydrogenolysis and inhibition of hydrogenation can result in no significant change in the rate of formation of the lumped products in pathway B. Simultaneous acceleration of hydrogenolysis and inhibition of hydrogenation resulted in an almost constant quinoline HDN conversion over the range of 2 to 6 wt% CS_2 added to feed, as shown elsewhere (*4*).

HDO of Dibenzofuran

The HDO reaction network of dibenzofuran was studied by Krishnamurthy *et al.* (*8*), who found that the presence of H_2S enhanced the total HDO conversion. This suggests that some rate-limiting steps in dibenzofuran HDO are hydrogenolysis reactions which are accelerated by H_2S. It is interesting to notice that H_2S decreases the HDS conversion of dibenzothiophene, though the two heterocyclic compounds have similar structures except for the nature of the heteroatom.

CONCLUSIONS

Many of the results of the effects of sulfidation and presence or absence of H_2S during reaction in a variety of studies of HDS, HDN, HDO, and hydrogenation reactions on molybdenum catalysts can be interpreted in terms of a few generalizations. A moderate presulfidation procedure provides the greatest HDS activity while complete sulfidation is desired for highest HDN activity. Under reaction conditions the presence of H_2S inhibits any reaction with a rate-limiting step facilitated by surface vacancies, but H_2S enhances any reaction with a rate-limiting step proceeding via Brønsted acid sites. HDS, HDN, and HDO reactions are too complex to be simply categorized as such in considering catalyst activity.

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