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Sulfur Exchange Studies on a Mo/Al_2O_3 Catalyst

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A relatively simple technique was developed to assess catalyst sulfur exchange using nonradioactive hydrogen sulfide-34. Exchange of catalyst sulfur on a Mo/Al_2O_3 catalyst with $H_2{}^{34}S$ was carried out at several temperatures. The extent of exchange was determined by a subsequent temperature-programmed oxidation, measuring the amounts of regular and heavy SO_2 evolved. Exchange occurred very rapidly at each temperature studied. The extent of exchange increased with temperature up to a limiting value at the highest temperature investigated (530°C). The limiting value was ascribed to exchange of sulfur at edge sites of the MoS_2 slabs. Smaller values of exchange at lower temperatures were attributed to different bonding strengths of the edge sulfur atoms.

INTRODUCTION

A number of sulfur-exchange studies over sulfided molybdenum catalysts using $H_2{}^{35}S$ have been reported in the literature (1–6). These studies generally showed that more than one type of sulfur bonding exists, as evidenced by different rates and extents of exchange with time and temperature. Dissociative adsorption of H_2S and the presence of SH groups on the surface of the catalyst were implied in some of these studies.

Because of the specialized equipment needed and the complexity of the analysis using radioactive sulfur-35, the present study was undertaken to establish whether useful information could be obtained using a nonradioactive sulfur species namely, sulfur-34. The objective of the study was to determine if differences in reactivity of S atoms in MoS_2 supported on alumina could be detected by measuring the exchange of the catalyst S with the heavier S isotope via reaction with H_2S using a mass spectrometer to monitor the different H_2S species. The experiment envisioned reacting the catalyst, which had been sulfided with regular H_2S, with heavy H_2S, and measuring the regular H_2S evolved by mass spectrometry. It turned out that quantitative measurement of H_2S was not sufficiently accurate, due to a varying background in the mass spectrometer. Therefore, after exchange, temperature-programmed oxidation was used to determine the amount of exchange which had occurred.

EXPERIMENTAL

The catalyst, consisting of 9.6% Mo/γ-alumina, was prepared by incipient wetness impregnation of 1/20″ cylindrical extrudates with a surface area of 220 m^2/g, using ammomium paramolybdate. After drying for 6 hr, it was calcined at 500°C, for 2 hr.

Because of the high cost of obtaining sulfur-34 in the form of H_2S required for the experiments, H_2S^* (where S^* signifies the heavy isotope) was prepared from elemental sulfur-34 by the following procedure: (1) reacting sulfur-34 with iron to form FeS, (2) reacting the FeS with acid solution to form H_2S, and (3) collecting the H_2S in a suitable vessel. The sulfur-34, obtained from Icon Services, Inc., had an isotopic purity of 90%.

The procedure which was developed came from a number of trial runs with regular sulfur, and consisted of the following steps:

(1) mix 2 g of sulfur with about 7 g of iron filings in a test tube and heat over a Bunsen burner;

(2) grind up thoroughly the iron sulfide obtained;

(3) place the ground iron sulfide in a flash and add a small amount of water;

(4) with stirring, slowly drop in a 4 *M* solution of nitric acid until no further reaction of the FeS occurs, as evidenced by a clear solution. (The iron left will continue to react with the acid, producing H_2.)

(5) A stream of H_2 is passed through the flask containing the FeS to carry over the H_2S^* formed.

(6) This stream is first passed though a trap immersed in a salt–ice mixture (about −10°C) to remove most of the water which is carried over with the H_2S, followed by a stainless-steel vessel in a liquid-N_2 trap to collect the H_2S^*.

(7) When reaction of FeS had ceased, the steel vessel was closed and removed from the liquid-N_2 bath, and hooked onto the reactor system.

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The reactor system was the same as that used in previous TPO studies (7, 8). Approximately 0.3 g of crushed (20–30 mesh) catalyst was presulfided at 450°C for 30 min using a high purity gas mixture of 3% $H_2S/30\%H_2$/argon. After sulfiding, the temperature was lowered to the desired temperature in the sulfide stream. A flow of H_2S^* plus H_2/Ar to approximate the same composition as used in the presulfiding mixture was then passed over the catalyst until no further reaction occurred, as evidenced by the constancy of the H_2S and H_2S^* profiles in the mass spectrometer. The flow was switched to He and the temperature raised to 450°C and held for 2 hr. For the exchange experiment at 530°C, the catalyst was sulfided at this temperature for 2 hr, and then switched to the H_2S^* mixture. After exchange, the catalyst was purged in He at temperature for two hours to remove any adsorbed H_2S. Finally, the temperature was lowered to below 50°C for the start of the TPO run.

Temperature-programmed oxidation was carried out on the exchanged catalyst in order to measure the relative amounts of normal and heavy S in the sample, as SO_2 area measurements. A 50 cm^3/min flow of 20% O_2/Ar, at a heating rate of 5°C/min up to 650–700°C was used. The effluent gas stream was monitored for off species by means of the mass spectrometer. Further details are given elsewhere (7).

RESULTS

1. Sulfur Exchange Reaction

The exchange of catalyst S with S* (^{34}S) was monitored by following the change in concentrations of H_2S (mass 34) and H_2S^* (mass 36). Profiles of these species for exchange at 278°C are shown in Fig. 1. A rapid rise followed by a slower decay is observed in the mass-34 peak, signifying evolution of H_2S from the catalyst. A mirror image occurs for mass 36, showing a concomitant loss of H_2S^* from the feed stream due to incorporation in the catalyst. Similar results were obtained in the other exchange runs. Due to a high baseline relative to the changes, and to variations in the baseline with time, it was not possible to determine areas from these profiles to determine the extent of exchange.

2. TPO of Exchanged Catalysts

In order to determine the amount of S which had been exchanged, masses 64 (SO_2) and 66 (S^*O_2) were recorded during TPO. Figure 2 displays a plot of masses 64 and 66 versus temperature for the exchange run at 382°C. Two ranges of oxidation are evident, the lower temperature region (I) representing the majority of the sulfur removal, and a high-temperature region (II). In temperature region I, it can be seen that the mass-66 profile peaks about 25°C before that of mass 64. In contrast, little difference in the peak maximum temperature is observed for the higher temperature region II. Similar results were obtained for catalysts exchanged at other temperatures.

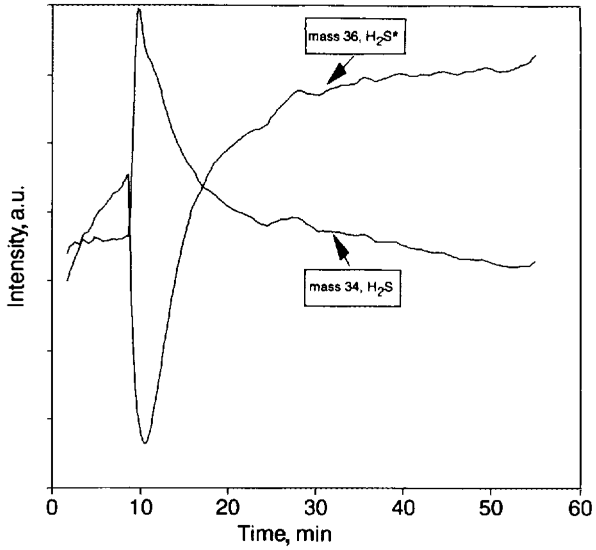


FIG. 1. Sulfur exchange at 278°C.

3. S Exchange versus Temperature

The sulfur exchange experiments were carried out at several temperatures between 160 and 530°C. Higher temperatures were not employed in order to avoid the possibility of sintering of the MoS_2 phase. The results of these

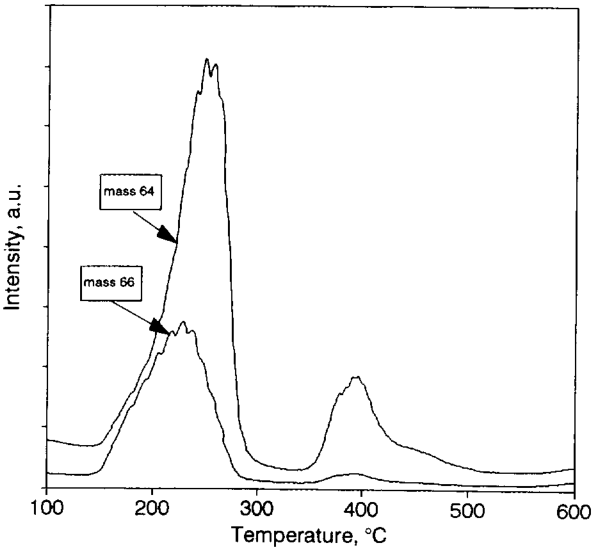


FIG. 2. TPO of catalyst exchanged at 382°C.

TABLE 1

Results of Exchange Runs

Exchange T (°C)	Fract. (I) exchanged	Fract. (II) exchanged	Fract. (II) of total
161	0.17	0.16	0.20
278	0.23	0.13	0.19
351[a]	0.29	0.18	0.22
382	0.27	0.19	0.23
439	0.42	0.21	0.23
530	0.40	0.22	0.24

[a] Without H_2 during exchange.

runs are presented in Table 1, which gives the fraction exchanged [mass 66/mass (66 + 64)] for both temperature regions. Table 1, column 4, gives the fraction of sulfur as oxidized in temperature region II to the total sulfur in temperature regions I + II. The ratio of $^{34}SO_2/^{32}SO_2$ was consistent within 5%, whereas total S recovered for the Mo catalyst varied between the samples with a relative deviation of about 10%. The maximum temperature for the low-temperature peak is reproduced within 5°C. The fractions of S exchanged for each region are plotted versus temperature in Fig. 3. Sulfur exchange in the low-temperature region I was considerably more than in the high-temperature region II. Also, exchange in region I showed a greater increase with temperature. Of significance, the fraction exchanged reached a maximum at about 450°C.

4. *Exchange with Pure H_2S^**

One run was made using the H_2S^* in Ar, without H_2 present, to see the effect of the presence of H_2 on the extent of exchange. The pertinent profiles for this exchange experiment done at 350°C are shown in Fig. 4. A sharp evolution of H_2 occurred upon introduction of the heavy H_2S^* in the Ar stream. At the same time, exchange of H_2S took place. The rate of exchange did not appear to be different from that of the previous runs with H_2 present. The TPO data for this run are given in Table 1, and the extent of exchange shown in the plot of Fig. 3. The exchange in region I was slightly higher, but probably within experimental reproducibility, than the comparable data with H_2 present. For region II the results were essentially the same as before. Therefore, it is evident that the presence of H_2 did not affect the exchange reaction to any noticable degree.

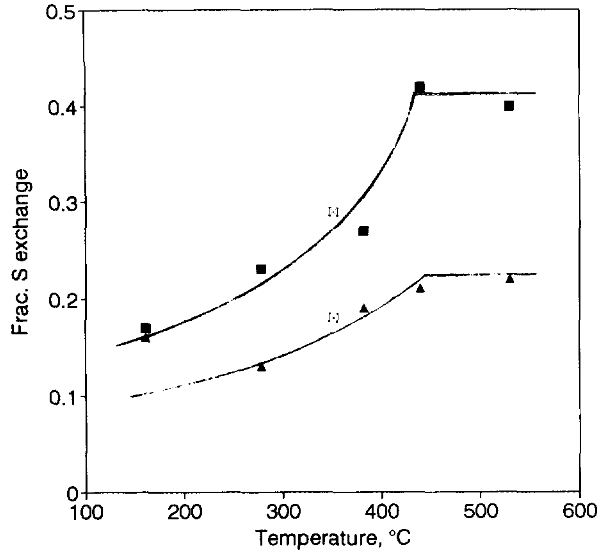


FIG. 3. Fraction S exchange vs. temperature. Symbols: (■) region I, (▲) region II, and (☒) without H_2 present.

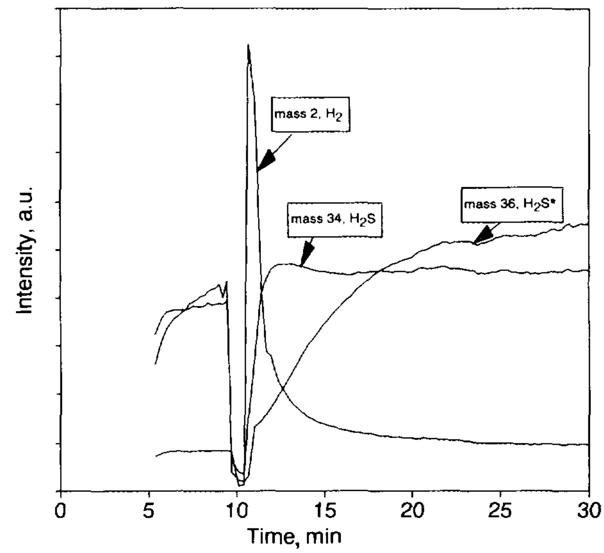


FIG. 4. Sulfur exchange at 351°C without H_2 present.

DISCUSSION

1. *S Exchange in Low-Temperature Region I*

The temperature difference in the two TPO mass profiles of region I indicates that the S* which had been exchanged oxidized faster than the S which remained in the catalyst. It may therefore be surmised that the S* is located at readily accessible surface positions on the MoS_2 phase. However, there is significant overlap of the two profiles (Fig. 2), indicating that not all of the S* is removed before the S is oxidized. This signifies preferred oxidation at certain reactive sites, rather than uniform (random) oxidation. As a consequence, after removal of the outer S* atoms, the underlying S atoms undergo rapid oxidation before, or concurrently with, oxidation of the other, less active S* atoms.

Although Fig. 2 clearly shows differences in the SO_2 profiles, no such difference had been observed in previous

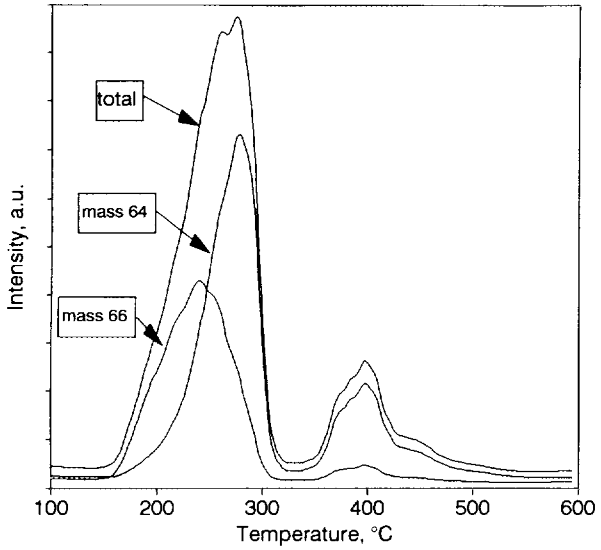


FIG. 5. Total SO$_2$ calculated from exchange experiment at 439°C.

TPO experiments on regularly sulfided catalysts (7). The reason is that due to the overlap of the profiles, only one SO$_2$ peak is observed. This is evident in Fig. 5, showing a TPO experiment of the catalyst exchanged at 439°C, where the two experimental SO$_2$ peaks are summed to give the total calculated SO$_2$ evolved. Ignoring the spikes in the profiles, it can be seen that the total SO$_2$ profile fails to distinguish between the two SO$_2$ profiles obtained in the TPO of the exchanged catalyst. Therefore, the exchange technique used here is able to distinguish two different reactivities (bond strengths) of S atoms, whereas the normal TPO cannot. A TPO on the unexchanged sulfided catalyst at a heating rate of 2°C still failed to give resolution of two peaks.

2. S Exchange in High-Temperature Region II

The situation is apparently different for the high-temperature region II, in that both S and S* appeared to oxidize concurrently. This would seem to indicate that the S* is randomly distributed in this MoS$_2$(II) phase, implying that all of the S atoms are equally accessible to exchange. A possible explanation is that due to the high temperature, the oxidation proceeds so rapidly that both S and S* are oxidized simultaneously. Also, due to the lower amount of this phase, the peaks are not very well developed and it is difficult to determine the peak maxima.

The presence of the high-temperature SO$_2$ peak on the Mo catalyst was unexpected, as it had not been reported in the literature (9, 10), and we had not seen it in the TPO of a Mo sample run earlier (7). Since the fraction of sulfur in temperature region II is nearly constant, as shown in Table 1, we find that the reproducibility is clearly demonstrated. A difference in the present Mo sample and the previous one is that the former was prepared at a high pH, while the latter was prepared at a low pH. According to the literature (11), high pH favors the presence of singular tetrahedral Mo species in solution, whereas low pH favors polyoxide Mo species. Thus, it is possible that on calcination some small amount of Mo will be strongly attached to the alumina, the rest in a more weakly attached Mo polyoxide form. Upon sulfiding, the Mo polyoxide forms MoS$_2$ slabs. However, the strongly attached Mo may be more difficult to sulfide and may only undergo partial sulfiding due to strong bonding of the Mo oxide to the alumina. This latter form would be expected to be more resistant to oxidation (region II), as well as to S exchange, as observed. Also, if this phase exists as very small domains of only a few Mo atoms, then all the S atoms would be essentially available for exchange and not show any S exchange preference.

*3. S Exchange with Pure H$_2$S**

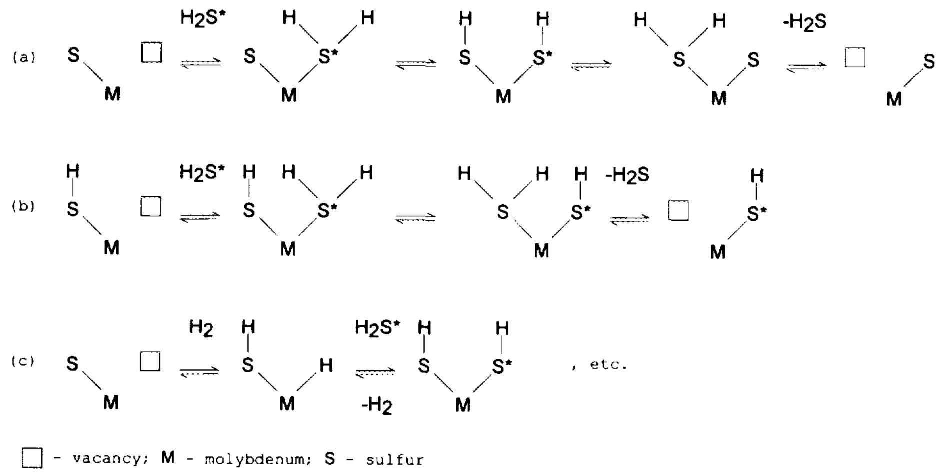
This experiment was designed to establish whether the presence of H$_2$ has an influence on the extent of S exchange. The results showed no essential difference whether H$_2$ was present or not. An interesting additional result obtained was the evolution of H$_2$ upon introduction of the H$_2$S (Fig. 4), indicating that H$_2$S adsorption displaced H$_2$ from the same site.

4. S-Exchange Reactions

It is now generally accepted that the MoS$_2$ slabs contain sulfur anion vacancies located at the edge of the MoS$_2$ slabs (12). A basic premise is that exchange of H$_2$S must occur via adsorption at these vacancies. Two possible reaction mechanisms are depicted in Scheme I involving (a) a S–V pair and (b) a SH–V pair (V is a vacancy site). The second sequence is more probable, as much evidence exists for the presence of SH on sulfided Catalysts (13, 14). In fact, the displacement of H$_2$ by H$_2$S when H$_2$ was absent (Fig. 4) demonstrates that strongly attached H is present. At least a part of this H must be associated with vacancies. A possible reaction of H$_2$ with a vacancy during sulfiding is shown in Scheme Ic. Thus, the exchange reactions of Schemes Ia and Ib would probably be accompanied by displacement of H from the vacancy. This indicates that the adsorption strength of H$_2$S is stronger than that of the H adsorbed on the vacancy site.

5. Extent of S Exchange

a. Total exchange. Sulfur exchange showed a constant line-out value at a temperature above about 450°C. However, this value (about 40% exchange) does not represent complete exchange of the S in the catalyst, which should be about 90% (the original sulfur sample was 90% ^{34}S). Since edge S atoms are the most reactive (15), the limiting



SCHEME I. Possible mechanisms for S exchange. Side view of a part of an edge of a MoS_2 slab. The molybdenum is located behind the plane of the sulfur.

extent of S exchange obtained should represent the fraction of S at the edges. The average fraction of S at the edges would then be about 0.41/0.90 or 0.46 edge S/total S. Assuming hexagonal slabs and a stochiometry of 2S/Mo, Table 2 gives calculated fractions of edge S/total S for slabs of various sizes consistent with ranges of slab sizes quoted in the literature (16–18). The smallest and largest entries represent slab lengths of about 1.2 and 3.5 nm, respectively. The experimental exchange result appears to agree well with a model of the smaller slab size.

The above analysis assumes no top S atoms have exchanged. Shabtai *et al.* (19) have recently proposed a special "V" site, consisting of one edge or corner vacancy and one or two basal plane vacancies to explain their results on the stereochemistry of aromatic hydrogenation.

TABLE 2

Sulfur Exchange at Edge Positions for Hexagonal MoS_2 Slabs[a]

	Mo in slab				
	12	27	48	75	108
Total possible S positions in slab	38	74	122	182	254
Total S for MoS_2	24	54	96	150	216
Vacancies[b]	14	20	26	32	38
Possible S positions at edge	24	36	48	60	72
Actual edge S atoms	10	16	22	28	34
Fraction edge S atoms exchangeable[c]	0.42	0.30	0.23	0.19	0.16

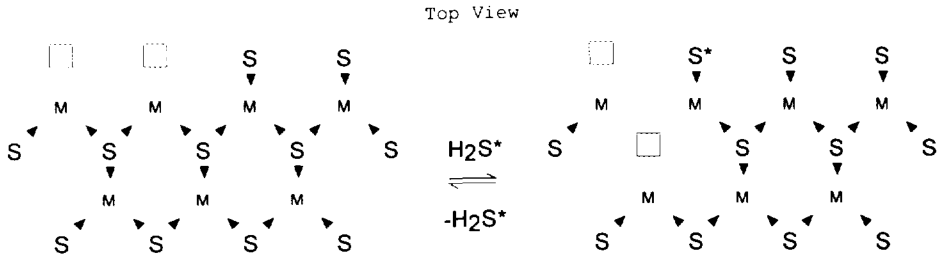
[a] Assumes hexagonal slabs of equal sides, and MoS_2 stoichiometry.
[b] Assumes all vacancies are at edge positions.
[c] Actual edge S atoms/total S atoms.

It is possible that some top S atoms adjacent to an edge vacancy might undergo exchange, although top S atoms are relatively inert (20). This could occur if the adjacent top S atom contains an H atom, so that during exchange, it could be removed as H_2S, leaving a vacancy in the top site, as illustrated in Scheme II. In fact, Wright *et al.* (13) have suggested that hydrogen dissociation occurs on edge S atoms, the hydrogen atoms subsequently moving to top S sites. Hydrogen–deuterium exchange studies (21) have indicated that a high fraction of S atoms contains hydrogen. Note that in this case, the fraction of S exchanged would be greater than that predicted for edge sites only, and thus be in accord with a somewhat larger slab size.

b. Partial exchange. At temperatures below 450°C, only partial exchange of the edge S atoms occurred. This indicates that there are some S atoms at the edge which are less strongly attached than others, e.g., terminal S bonded to one Mo versus bridged S bonded to two Mo atoms (22).

From molecular orbital calculations, Diez and Jubert (23) estimated that S atoms are first removed from corner sites at relatively mild conditions (25–225°C). With an increase in temperature, edge S atoms are then removed (225–525°C), and finally basal plane S atoms (>525°C).

Scheme III depicts a possible mechanism leading to partial exchange. The important point here is the relative strength of the residual S* or HS* (from adsorbed H_2S^*) vs the bond strength of the adjacent S or HS. If the latter is too strong, then H_2S^* will desorb rather than exchange. Thus, at low temperature, exchange would be limited to the weakest bonded S atoms. As temperature is raised, moderately strongly bonded S will begin to participate in exchange. Unfortunately, the results obtained in the exchange experiments did not show any breaks in the exchange–temperature plot (Fig. 3), which would indicate



SCHEME II. Possible exchange of top S site to form a "V" site. Top view of a part of a MoS_2 slab. The molybdenum is situated below the plane of the sulfur.

a specific fraction of the weaker S sites. It may be that a continuous distribution of S atom bonding strengths is present.

6. *On Vacancy Migration*

The H_2S exchange mechanism, an envisioned in Scheme I, involves a movement of vacancies (and countermovement of edge S atoms), since in order for exchange to take place, an adjacent edge S atom must be removed as H_2S. The exchange experiments showed that initial exchange was very fast. Startsev *et al.* (5) reported that the exchange rate was one to two orders of magnitude greater than the rate of hydrogenation of butadiene. Under typical hydroprocessing conditions, in the presence of H_2S, a rapid adsorption/desorption of H_2S will take place, leading to a rapid interchange of vacancies and edge S atoms. Thus, the vacancies under reaction conditions will not be fixed, but will be mobile, and a different distribution of vacancies can be expected from one instant to another. This migration could lead to combinations of single and multiple vacancy centers, which at one instant would be favorable to adsorption of a given reactant molecule requiring a certain adsorption site configuration, and not favorable at another instant. Thus, this vacancy mobility assures that, on a statistical basis, a reactant molecule will encounter a suitable vacancy center for reaction.

It should be mentioned that although H_2S exchange requires the presence of vacancies, the extent of exchange is not directly related to the number of vacancies present, but rather to the degree of susceptibility of the S atoms to exchange. How the latter is related to the number of vacancies, which presumably are related to catalytic activity, is not known at present.

CONCLUSIONS

The S-exchange reaction using heavy H_2S, in conjunction with a subsequent TPO, was found to be a useful method to determine S-bonding species in sulfided catalysts.

Sulfur exchange was very rapid under typical hydroprocessing conditions. A limiting S exchange was obtained at about 450°C, which represented about 40% of the total S in the catalyst. The exchanged S is most likely to be located at the edges of the MoS_2 slabs. At lower temperatures, less S exchanged, implying a distribution of S bond strengths present at the slab edges.

Gas-phase hydrogen did not appear to participate in the S-exchange process. In fact, some chemisorbed hydrogen is displaced by H_2S adsorption. At least some of the adsorbed H_2 is located on vacancies.

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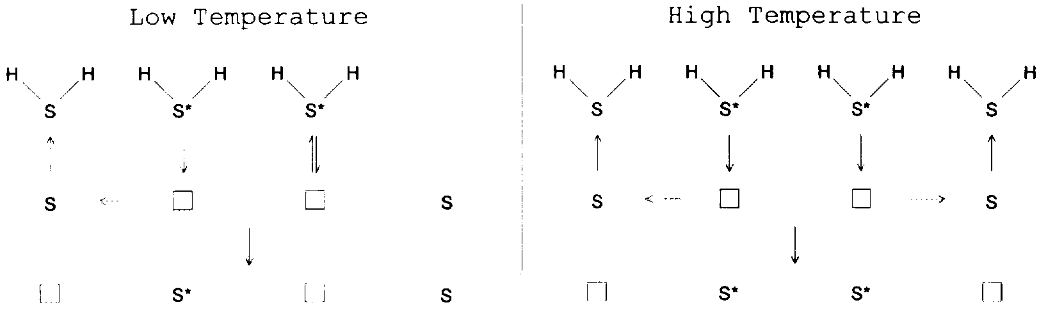

SCHEME III. S exchange vs temperature. Side view as in Scheme I.

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