

Deuterium Tracer Studies on Hydrotreating Catalysts—Isotopic Exchange between Hydrogen and Hydrogen Sulfide on Sulfided NiMo/Al₂O₃

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The H–D isotopic exchange between H₂ and D₂ and between H₂ (D₂) and D₂S (H₂S) was studied at 80°C in a recycling reactor under a pressure of 2 bar in the presence of a sulfided NiMo/Al₂O₃ catalyst and by means of gas chromatography. From the H₂–D₂ exchange an amount of three exchangeable surface hydrogen atoms retained by the catalyst per Mo atom was estimated after sulfiding the catalyst by 10% H₂S in H₂ at 400°C and sweeping it by helium at 80°C. H–D isotope exchange occurred between H₂(D₂) and D₂S(H₂S). As expected under the reaction conditions, H₂S(D₂S) did not produce H₂(D₂). The isotope exchange between H₂ and D₂ was about six times faster than the exchange between H₂(D₂) and D₂S(H₂S). However, it was shown that H₂S competed with H₂ for adsorption: H₂S inhibited the exchange between H₂ and D₂. It is proposed that H₂(D₂) and H₂S(D₂S) dissociate heterolytically on the same sites, involving both a sulfur vacancy and a sulfur atom. Furthermore, it is suggested that the isotope exchange could occur by dissociation of both reactants on one single center provided that this center possesses at least two coordinative unsaturations. © 1997 Academic Press

INTRODUCTION

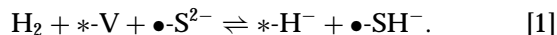
Hydrodesulfurization and hydrodenitrogenation are industrially very important reactions, generally occurring on sulfided CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts in the presence of hydrogen and hydrogen sulfide. These reactions involve various steps including hydrogenation and carbon–heteroatom bond cleavages (1–6). To identify the mechanism of these reactions, the processes of adsorption and of activation of hydrogen and hydrogen sulfide must be well understood. For instance, HDS tracer experiments (³⁵S and ³H), carried out by Isagulyants and co-workers (7), showed that surface SH groups were involved in the formation of H₂S, but the origin of the hydrogen related to this process is not clear.

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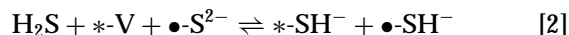
Indeed, several proposals have been made concerning the origin and the mode of activation of the hydrogen involved in hydrotreating reactions (8–19). Delmon (11) suggested that hydrogen atoms, resulting from the dissociation of dihydrogen on specific centers of CoMo/Al₂O₃ catalysts (Co₉S₈ phase), would spill over to hydrogenation centers located on the MoS₂ phase. However, the active phase (and MoS₂ itself) is capable of activating molecular hydrogen, and hence the question of the involvement of surface sulfur atoms in this process arises.

Two hypotheses concerning the adsorption and dissociation of molecular hydrogen on a sulfide phase can be considered:

First, heterolytic dissociation could occur on dual sites (17, 18) constituted by a vacancy and a sulfur atom

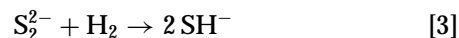


Actually, theoretical studies (20) have shown that this is possible on MoS₂ edge sites. It can be observed that the heterolytic dissociation of H₂S leading to two SH groups (21–26) is generally supposed to occur on the same type of sites. This can be expressed as (17, 18)



It is clear that, if the dissociation of H₂ and of H₂S occurs as described in Eqs. [1] and [2], it can be expected (on the basis of microscopic reversibility) that the exchange of H atoms between these two reactants is possible.

The second hypothesis is the dissociation of H₂ on S₂²⁻ species (13) as follows:



which can be considered as a homolytic process.

As pointed out by Polz *et al.* (15) and more recently by Topsoe *et al.* (27), it is rather difficult to discriminate between these two possibilities.

Another point to be considered is that of H_2S as a possible source of hydrogen. It has been shown that H_2S decomposed in the presence of sulfide catalysts such as MoS_2 (28–31), but for this to occur a temperature of at least 400°C was necessary (29). Nevertheless, to account for the effect of the molar ratio hydrogen sulfide/hydrogen on pyridine hydrogenolysis, Hanlon (14) proposed an equilibrium reaction between H_2S and surface vacancies on the catalyst, H_2 and elemental sulfur ($\text{H}_2\text{S} + \square \rightleftharpoons \square\text{-S} + \text{H}_2$). On the other hand, it is known that sulfur vacancies can be created by the reverse reaction (32 and references therein).

The study on sulfide catalysts of the isotope exchange between H_2 and D_2 and more particularly between $\text{H}_2(\text{D}_2)$ and D_2S (H_2S) should bring new insights into the mechanism of dissociation of H_2 and the possible interaction between H_2 and H_2S . Indeed, deuterium tracer experiments (8–10, 12) indicated that there may be an interaction between H_2 and H_2S on MoS_2 catalysts and that the hydrogen of SH groups could be active in hydrogenation reactions, i.e., that sulfur atoms could act as catalytic centers for the dissociation of molecular hydrogen. In a preliminary work we reported that a H–D exchange also occurred in the presence of a presulfided $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst between H_2 and D_2S (19), which was interpreted as indicating the heterolytic cleavage of H_2 . Actually, experiments conducted with bulk MoS_2 indicated that hydrogen atoms from H_2S could be incorporated into butenes formed by the hydrogenation of butadiene (12). The hypothesis that SH groups may be the source of hydrogen during a catalytic cycle was also suggested by Topsoe and Topsoe (16), who assumed that these groups could be generated by the reduction of molybdenum atoms by H_2 which would give H^+ interacting with a sulfide ion. The existence and origin of sulfhydryl groups on the surface of hydrotreating catalysts has been the subject of numerous studies and speculations (16 and references therein). Until recently they have been mainly considered as the source of the protonic acidity needed in the C–heteroatom bond cleavages or as possible nucleophilic species in the same reactions (4, 6, 33–35). Their possible involvement in hydrogenation reactions adds to the importance of the role played by these sulfhydryl groups.

In this paper we report on the deuterium isotopic exchange between H_2 and D_2 , D_2 and H_2S , H_2 and D_2S on a presulfided $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst and on the alumina support.

The aim of the work is to develop a tool which may make it possible to measure and compare the rates of the above reactions in order to obtain information on the mode of dissociation of the reactants and on the catalytic centers on which this dissociation occurs. Moreover, H_2/D_2 isotopic exchange will give access to the amount of preadsorbed hydrogen under conditions which, in principle, do not modify the state of the catalyst at a given temperature. To make ac-

curate kinetic measurements, the experiments were carried out at a low temperature compared to that of hydrotreating. Nevertheless, the method will, in future, provide a convenient means of investigating the effect of the support and of promoters on the activation of hydrogen.

EXPERIMENTAL

Chemicals and Procedure

The $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst contained 2.9 wt% NiO and 12.5 wt% MoO_3 deposited on alumina ($240\text{ m}^2 \cdot \text{g}^{-1}$). It was sulfided *in situ* in a flow of H_2 (90%) and H_2S (10%) at 400°C for 15 h under atmospheric pressure.

H_2 (Air Liquide), D_2 (Eurisotop), H_2S (Air Liquide), and D_2S (Isotec) were of 99.95, 99.8, ≥ 99.7 , and 98% purity, respectively.

The reaction was carried out in a 72-cm³ recycling reactor (Fig. 1). After sulfidation, the catalyst (0.250 or 0.050 g) was cooled to the reaction temperature (80°C) and swept with helium (1 bar), the diluting gas. The reactant mixture (H_2 plus D_2 , or H_2 plus D_2S , or D_2 plus H_2S ; 0.5 bar of each component) was then introduced into the reactor. The recycling pump (Masterflex) was started and adjusted so as to obtain a flow rate of $6\text{ dm}^3 \cdot \text{h}^{-1}$. The calibration by gas chromatography of the amounts of H_2 and D_2 , as a function of the pressure in the reactor, made it possible to determine the exact composition of the starting reaction mixture, samples (0.05 cm^3) of which were automatically extracted using a six-port switching valve (Valco) and analyzed by gas chromatography. To prevent hydrogen sulfide from damaging the column and the detector of the chromatograph, a short column containing a $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst in its oxide form was inserted between the switching valve and the analytical column.

No pressure variation was detected during any of the experiments, except for a slight drop due to sampling by gas chromatography. It was also verified that the total surface area of the chromatographic peaks did not change significantly. This means that no significant amount of gaseous material (e.g., H_2S), unable to be detected analytically, was desorbed from the catalyst.

The reaction mixture $\text{H}_2\text{-HD-D}_2$ was analyzed by gas chromatography (36, 37) using a column of Al_2O_3 impregnated with MnCl_2 to ensure an *ortho/para*-hydrogen equilibrium. This column was maintained at -196°C in liquid nitrogen and was connected to a short column of CuO which allowed the transformation of H_2 into H_2O , D_2 into D_2O and HD into HDO at 350°C , so as to improve the sensitivity of the thermal conductivity detection (Fig. 2). Helium was the carrier gas. The apparatus employed was a Varian 3400 gas chromatograph. Unfortunately, it was not possible to analyze the deuterium distribution in H_2S with this equipment.

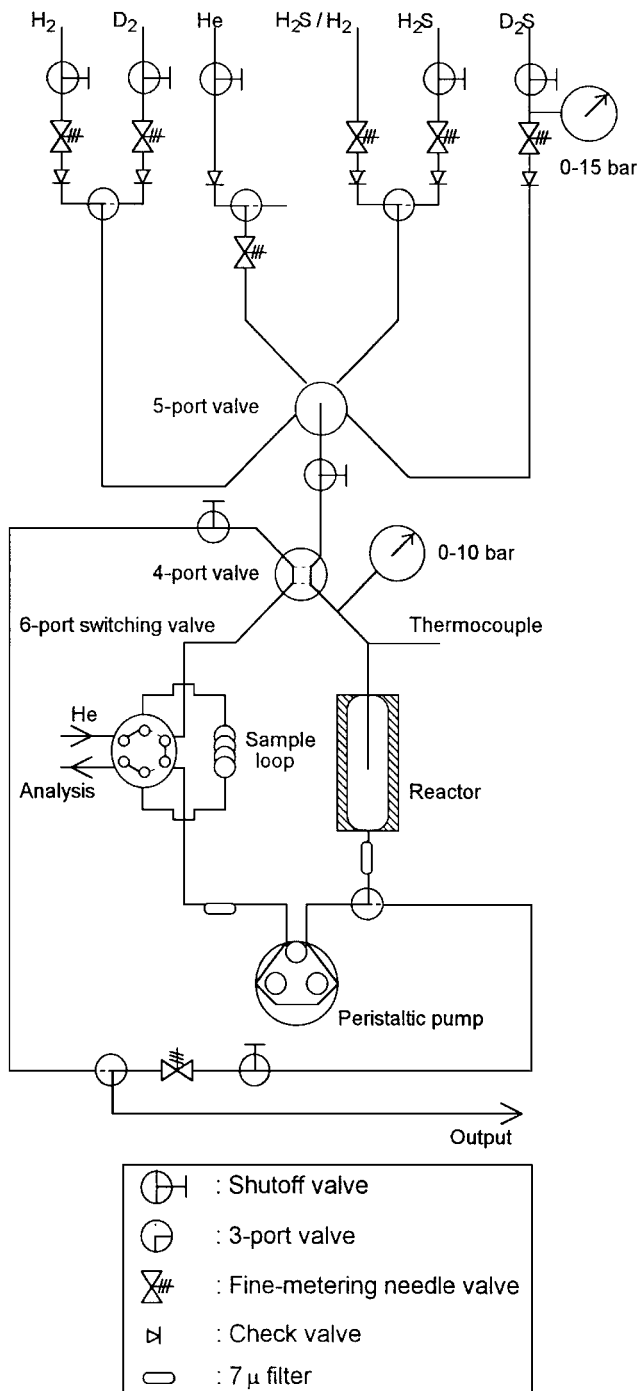


FIG. 1. Schematic diagram of the apparatus.

The rate of formation of the various "hydrogen" species (H_2 , D_2 or HD) is given by

$$r(\text{mol} \cdot \text{s}^{-1} \cdot \text{g}^{-1}) = \frac{P \cdot V}{R \cdot T} \cdot \frac{1}{m} \cdot \frac{dx}{dt},$$

where P is the partial pressure of hydrogen (Pa), V is the volume of the reactor (m^3), R is the gas constant

($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is the reaction temperature (K), m is the weight of catalyst (g), x is the molar fraction of the "hydrogen" species, t is the reaction time (s), and dx/dt is the slope of the curve representing the mol fraction of the species versus reaction time (at reaction time equal to zero).

Titration of the Amount of Exchangeable H on the Catalyst

The exposure of the catalyst to D_2 or to the H_2 - D_2 reaction mixture allows an estimation of the number of surface hydrogen species present after sulfidation and cooling of the catalyst to the reaction temperature. If we assume that the HD scrambling equilibrium is obtained at the end of a precise experiment, we can estimate this amount (or at least the amount incorporated into the reactants during the experiment) by considering that this hydrogen is distributed equally in the gas phase and on the surface of the catalyst.

If we consider

— $n^\circ H$, $n^\circ H(g)$, $n^\circ D(g)$, and $n^\circ H(\text{ads})$: the mol numbers of H (total), of H in the gas phase, of D in the gas phase, and of H in the adsorbed phase at time zero, respectively;

— nH , $nH(g)$, and $nH(\text{ads})$: the mol numbers of H (total), of H in the gas phase, and of H in the adsorbed phase at the end of the experiment (time t), respectively;

— $nH_2(g)$ and $nHD(g)$: the mol numbers of H_2 and of HD in the gas phase at time t ,

with $nH(g) = 2nH_2(g) + nHD(g)$ then the following balance equations result:

$$\text{at time } t = 0: n^\circ H = n^\circ H(g) + n^\circ H(\text{ads})$$

$$\text{at time } t \text{ (equilibrium mixture): } nH = nH(g) + nH(\text{ads})$$

$$\text{with } n^\circ H = nH.$$

If we assume that the percentage (mol) of H (H%) is the same in the gas phase and in the adsorbed phase at the end of the reaction, we can calculate $n^\circ H(\text{ads})$ as

$$H\% = \frac{nH(g) \times 10^2}{n^\circ H(g) + n^\circ D(g)} = \frac{nH(\text{ads}) \times 10^2}{n^\circ H(\text{ads})}$$

then

$$n^\circ H(\text{ads}) = \frac{H\% \times 10^{-2} \cdot (n^\circ H(g) + n^\circ D(g)) - n^\circ H(g)}{1 - H\% \times 10^{-2}},$$

which simplifies into

$$n^\circ H(\text{ads}) = \frac{H\%}{10^2 - H\%} \cdot n^\circ D(g) - n^\circ H(g).$$

RESULTS

A series of experiments was carried out on sulfided $NiMo/Al_2O_3$ and on the sulfided alumina support (Experiments 1–8 and Experiments 9 and 10, respectively; Tables 1 and 2).

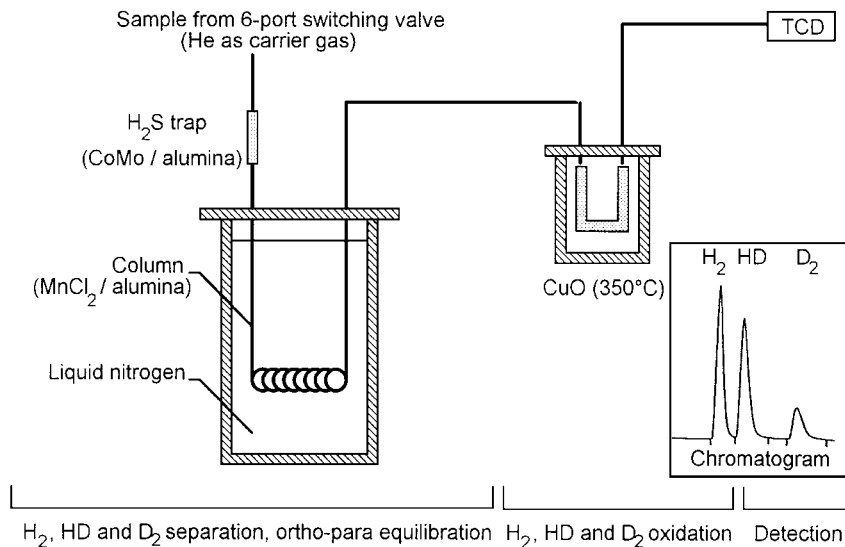


FIG. 2. Gas chromatographic analysis of the H_2 /HD/ D_2 mixture and typical chromatogram.

No reaction between H_2 and D_2 was detected in the absence of a catalyst (reactor filled with glass beads). This proved, too, that the H_2S trap before the chromatographic column was inactive during the reaction.

TABLE 1
H-D Isotopic Exchange Reactions

Expt.	Reactants (partial pressure, bar)	Rate of formation ($10^{-7} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}^{-1}$)		
		H_2	HD	D_2
$\text{NiMo}/\text{Al}_2\text{O}_3$				
1	H_2/D_2 (0.50)/(0.50)	—	19.8	—
2	$\text{H}_2\text{S}/\text{D}_2$ (0.49)/(0.48)	0.6	3.3	—
3	H_2/D_2 (0.40)/(0.42)	—	18.3	—
4	$\text{H}_2/\text{D}_2/\text{H}_2\text{S}$ (0.40)/(0.41)/(0.20)	—	2.8	—
5	$\text{D}_2\text{S}/\text{H}_2$ (0.48)/(0.50)	—	2.9	0.4
6	D_2 (0.49)	0.30	8.4	—
7	D_2S (0.5) then $\text{H}_2/\text{D}_2\text{S}$ (0.40)/(0.40)	—	1.8	0.4
8	D_2S (0.49) then helium then H_2 (0.39)	—	4.5	0.04
Al_2O_3				
9	H_2/D_2 (0.50)/(0.50)	—	0.10	—
10	$\text{H}_2\text{S}/\text{D}_2$ (0.50)/(0.50)	—	0.06	—

Note. Reaction rates at 80°C in a recycling reactor.

Reactions on Sulfided $\text{NiMo}/\text{Al}_2\text{O}_3$

H_2 - D_2 . H-D isotopic exchange between H_2 and D_2 occurred very readily under our experimental conditions (Table 1, Experiment 1). Total H-D scrambling was obtained after about 3 h (Fig. 3). Moreover, the H-D balance in the equilibrium mixture showed that there was a hydrogen uptake from the sulfided $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst ($n\text{H}$, Table 2). More H_2 than expected was formed. This corresponded to about three exchangeable H-atoms per molybdenum atom of the catalyst (Table 2).

H_2S - D_2 . Although the HD scrambling equilibrium was not obtained in this case (Fig. 4), the H uptake from both the catalyst and the H_2S introduced was much higher (Experiment 2, Table 2) than the H uptake from the catalyst in the

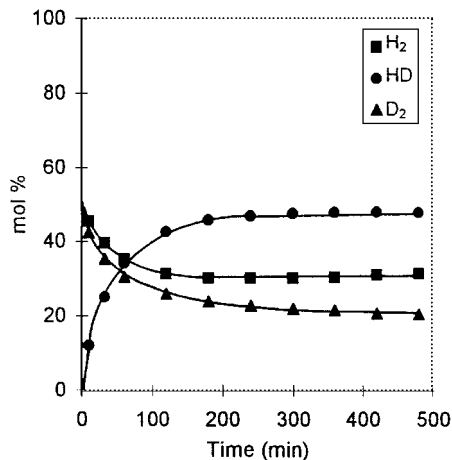


FIG. 3. H-D isotopic exchange between H_2 (0.50 bar) and D_2 (0.50 bar) over sulfided $\text{NiMo}-\text{Al}_2\text{O}_3$ (250 mg). Recycling reactor, 80°C .

TABLE 2
H-D Isotopic Exchange Reaction

Expt.	Reactants (partial pressure, bar)	Product distribution (%) after 7-8 h				H/D concentration in the dihydrogen phase (%)				<i>n</i> H adsorbed (mol) ^a	<i>n</i> H/ <i>n</i> Mo	<i>n</i> H or <i>n</i> D incorporated in hydrogen phase (mol) after 7-8 h
		H ₂	HD	D ₂	Reactants		Products					
					H	D	H	D				
NiMo/Al ₂ O ₃												
1	H ₂ /D ₂ (0.50)/(0.50)	31.5	47.9	20.6	50	50	55.5	44.5	6.0 × 10 ⁻⁴	2.8	—	
2	H ₂ S/D ₂ (0.49)/(0.48)	24.6	41.9	33.5	0	100	45.5	54.5			H: 10.7 × 10 ⁻⁴	
3	H ₂ /D ₂ (0.40)/(0.42)	35.8	35.1	29.1	48.8	51.2	53.4	46.6				
4	H ₂ /D ₂ /H ₂ S (0.40)/(0.41)/(0.20)	49.7	12.3	38.0	50	50	55.8	44.2				
5	D ₂ S/H ₂ (0.48)/(0.50)	50.2	39.6	10.2	100	0	70.0	30.0			D: 7.4 × 10 ⁻⁴	
6	D ₂ (0.49)	5.9	35.2	58.8	0	100	23.5	76.5	6.4 × 10 ⁻⁴	3.0	H: 5.6 × 10 ⁻⁴	
7	D ₂ S (0.5) then H ₂ /D ₂ S (0.40)/(0.40)	54.2	36.1	9.7	100	0	72.2	27.8			D: 5.4 × 10 ⁻⁴	
8	D ₂ S (0.49) then helium then H ₂ (0.39)	77.3	20.9	1.8	100	0	87.8	12.2			D: 2.3 × 10 ⁻⁴	
Al ₂ O ₃												
9	H ₂ /D ₂ (0.50)/(0.50)	48.1	2.5	49.4	50	50	49.4	50.6			—	
10	H ₂ S/D ₂ (0.50)/(0.50)	0	3.3	96.7	0	100	1.6	98.4			H: 0.4 × 10 ⁻⁴	

Note. 80°C, recycling reactor. Isotope distribution.

^a On 250 mg catalyst.

H₂-D₂ experiment (Experiment 1, Table 2). This means that a H-D isotopic exchange occurred between H₂S and D₂. However, HD formation was slower by a factor of 6 compared to Experiment 1 (Table 1). The reaction also led to

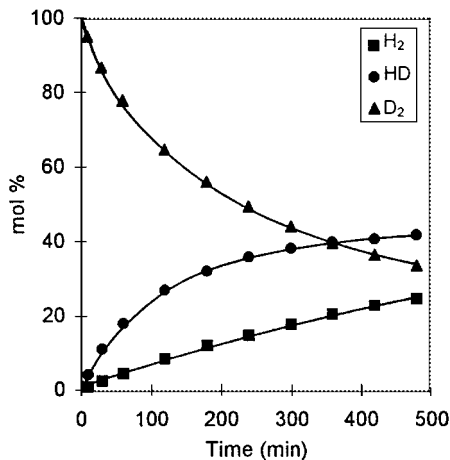


FIG. 4. H-D isotopic exchange between H₂S (0.49 bar) and D₂ (0.48 bar) over sulfided NiMo-Al₂O₃ (250 mg). Recycling reactor, 80°C.

H₂. Both HD and H₂ appeared as primary products (Fig. 4), but the formation of HD was faster than that of H₂ (Table 1) by about a factor of 5.5.

Effect of H₂S on H₂-D₂ isotopic exchange. Figure 5a shows the effect of H₂S on the H-D isotopic exchange between H₂ and D₂. The experiments were conducted with a smaller amount of catalyst (50 mg) so as to measure the initial rates more precisely. As shown in Table 1 (Experiment 3), the initial rate in the absence of H₂S in the reaction mixture was approximately the same as in Experiment 1, but it was smaller by a factor of about 6.5 in its presence (Experiment 4). This was confirmed by an experiment where H₂S was added during the reaction (Fig. 5b). This experiment clearly showed that the introduction of H₂S caused a significant decrease in the rate of HD formation. This observation is in accordance with previous experiments by Wilson *et al.* on bulk MoS₂ and WS₂ (8).

D₂S-H₂. Both HD and D₂ appeared as primary products (Fig. 6). However, the formation of HD was faster than the formation of D₂ (Experiment 5, Table 1) by a factor of about 7. Compared to the H₂S-D₂ experiment

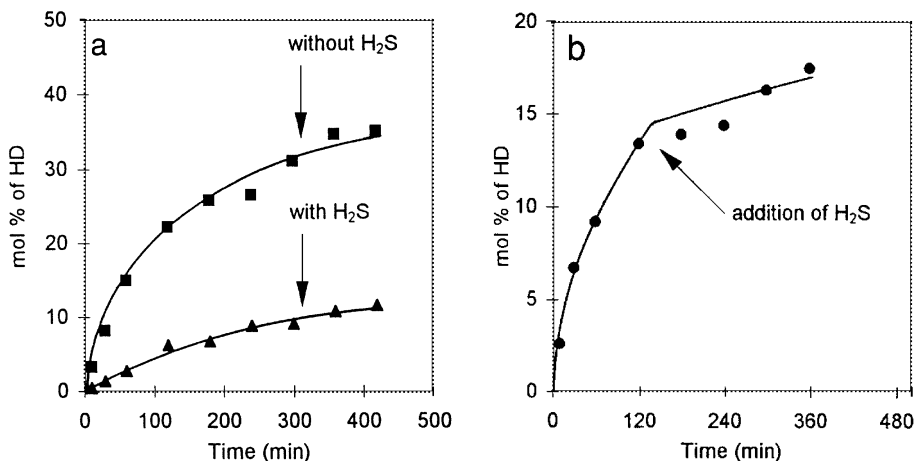


FIG. 5. (a) Effect of H₂S (0.2 bar) on the H-D isotopic exchange between H₂ (0.40 bar) and D₂ (0.42 bar). Sulfided NiMo-Al₂O₃, 50 mg; recycling reactor, 80°C. (b) H-D isotopic exchange between H₂ (0.40 bar) and D₂ (0.41 bar). Effect of H₂S (0.2 bar) added in the course of the reaction. Sulfided NiMo-Al₂O₃, 50 mg; recycling reactor, 80°C.

(Experiment 2), the rate of formation of HD was practically the same (Table 1), but the amount of D₂ was slightly lower than the amount of H₂ in the preceding case (compare Figs. 4 and 6). As in Experiment 2, the HD scrambling equilibrium between D₂S and H₂ was not obtained: there was a considerable excess of H₂ at the end of the experiment.

D₂. Figure 7 shows the results obtained when only D₂ was introduced onto the catalyst which had been previously sulfided by the H₂/H₂S mixture. HD formation occurred at an initial rate which was lower by a factor of about 2 than the rate of HD formation in Experiment 1 (Experiment 6, Table 1). The uptake of hydrogen from the catalyst corresponded approximately to the uptake obtained in Experiment 1 (*n*H, Table 2).

D₂S. When only D₂S was introduced onto the presulfided catalyst, no (or very little) H₂ (or D₂) was detected in the gas phase. However, when H₂ was added (after elimination of part of the helium and D₂S so as to reproduce the conditions of Experiment 5), HD and D₂ appeared as in Experiment 5. Figure 8 shows the results of a complementary experiment in which pure D₂S remained in contact with the catalyst and was then swept by helium before the introduction of H₂. As can be seen in Fig. 8, HD appeared (as soon as H₂ was introduced) at a rate (Experiment 8, Table 1) which was significantly higher than in the previous case (Experiment 7) and not much lower than that for the HD obtained when pure D₂ was introduced onto the presulfided catalyst (Fig. 7, Experiment 6). This means that there was H-D exchange between D₂S and H species retained on the catalyst after sulfidation occurred. This experiment confirms that

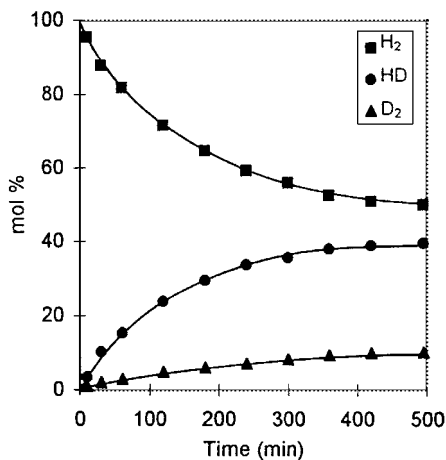


FIG. 6. H-D isotopic exchange between H₂ (0.50 bar) and D₂S (0.48 bar) over sulfided NiMo-Al₂O₃ (250 mg). Recycling reactor, 80°C.

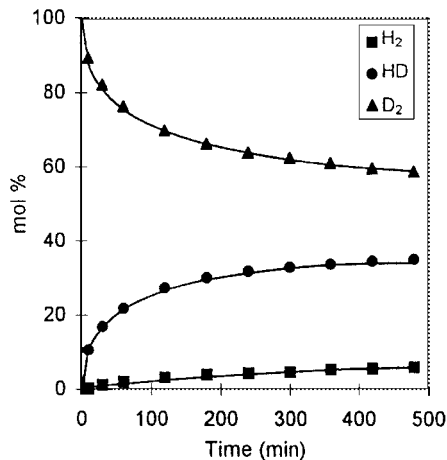


FIG. 7. Transformation of D₂ (0.49 bar) over sulfided NiMo-Al₂O₃ (250 mg). Recycling reactor, 80°C.

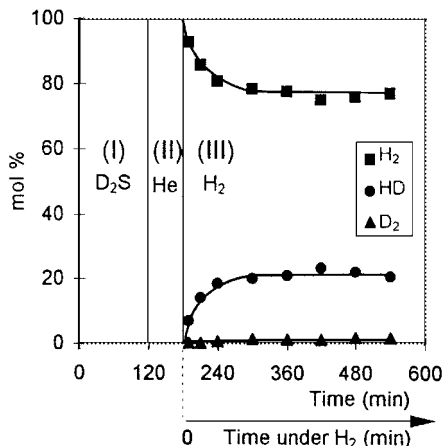


FIG. 8. Reaction of D_2S (I, D_2S , 0.49 bar; helium; 1.5 bar) followed by helium flow (II, 1 h) and addition of H_2 (III, H_2 , 0.39 bar; helium, 1.6 bar). Sulfided $NiMo-Al_2O_3$, 250 mg; recycling reactor, $80^\circ C$.

D_2S slows down the rate of HD formation, as shown in Experiment 4.

Reactions on Sulfided Alumina

H-D isotopic exchange between H_2 and D_2 occurred on alumina sulfided under the same conditions as $NiMo/Al_2O_3$. However, it was much slower than with sulfided $NiMo/Al_2O_3$. The initial rate of HD formation was lower by about a factor of 200 (Experiment 9, Table 1). Less than 3% of HD was formed after 8 h of reaction.

The HD exchange between H_2S and D_2 was also very limited. About 3.3% HD was formed after an 8-h reaction. The rate of HD formation was about the same as above (Experiment 10, Table 1).

DISCUSSION

H uptake from the catalyst. The content of "hydrogen" obtained in the H_2 - D_2 experiment (Experiment 1, Table 2) shows that a significant quantity of surface exchangeable H existed on the catalyst presulfided by H_2 - H_2S . This was confirmed by the experiment with D_2 only (Experiment 6, Table 2). Both experiments gave roughly the same figures concerning the amount of exchangeable hydrogen retained by the catalyst. This corresponds to about 3H atoms per Mo atom on the catalyst. This value is much greater than those found by TPD experiments (38 and references therein) or by H_2 uptake experiments (15 and references therein, 39, 40).

The difference may be due to the contribution of the support. We are presently performing experiments to quantify this contribution under our experimental conditions. According to the model of Peri (41), the number of H atoms on alumina after treatment at $500^\circ C$ could be as high as $15 \cdot 10^{-4} \text{ mol} \cdot \text{g}^{-1}$, which corresponds to 60–75% of the amount we detected through H_2/D_2 exchange (20

$24 \cdot 10^{-4} \text{ mol} \cdot \text{g}^{-1}$). Even if the introduction of the active phase and the treatment with the H_2 - H_2S sulfiding mixture can modify the amount of H on the support, its contribution to the exchange can be very significant.

The direct exchange between D_2 from the gas phase and the support is very slow, as shown by the experiment carried out with the alumina support itself (Experiment 9). However, if it is assumed that D atoms from SD groups on the active phase can migrate to the support and exchange with H atoms from its OH groups, the unexpectedly high value of the H/Mo ratio can be explained. That H from the support may exchange with D_2 in the gas phase through the active phase is not surprising, since it is well known (15, 38, 42) that hydrogen "spillover" from the support can occur on supported sulfide catalysts and that this hydrogen can be involved in hydrogenation reactions (42). The H/Mo value found is not very far from the maximum value obtained by Jalowiecki *et al.* (42) who measured the quantity of "active hydrogen" on MoS_2 and MoS_2/Al_2O_3 by hydrogenation at $150^\circ C$ of isoprene. However, this may be a coincidence, since their sample was treated under hydrogen at high temperature ($700^\circ C$). Moreover, these authors detected no active hydrogen with their technique on samples treated under H_2/H_2S and which were not reduced afterward under pure hydrogen, indicating that the active hydrogen they detected was not necessarily the same as that involved in hydrotreatment reactions on nonreduced sulfided catalysts.

The pretreatment procedure can also cause significant differences in the surface state of the catalyst. In the TPD experiments reported in the literature, the samples were generally prerduced, which could bring about a considerable decrease in the amount of reversible hydrogen on the catalyst (38, 39), while in TPR or H_2 uptake experiments the samples were either flushed under inert gas at the sulfiding temperature or evacuated (14, 40), which may have eliminated some of the SH groups present after sulfiding. These procedures may also explain, at least in part, why the H/Mo ratio was lower than in our experiments.

Moreover, TPR (or H_2 uptake) experiments obviously do not give the same information as H_2 - D_2 isotopic exchange. In particular, TPR does not take into account preexisting hydrogen on the catalyst, whereas the H_2 - D_2 experiments which we carried out should, in principle, give access to all of the available hydrogen remaining adsorbed after sulfidation and exposure of the catalyst to the sulfiding mixture at the reaction temperature.

H-D exchange between H_2 (D_2) and D_2S (H_2S). HD was apparently obtained as a primary product from the mixtures H_2S/D_2 and D_2S/H_2 (Figs. 4 and 6). H_2 (Fig. 4) and D_2 (Fig. 6) seem to be formed by an independent route. On the other hand, it can be seen (Experiment 2, Table 2) that the amount of H incorporated into D_2 is greater (by a factor of 2) than that of the "exchangeable hydrogen" remaining on the catalyst after sulfidation by the H_2/H_2S mixture as estimated

either from the H₂/D₂ experiment (Experiment 1) or from the D₂ experiment (Experiment 6). This shows that there is an exchange of H(D) atoms between H₂(D₂) and D₂S(H₂S) through a process which will be discussed later.

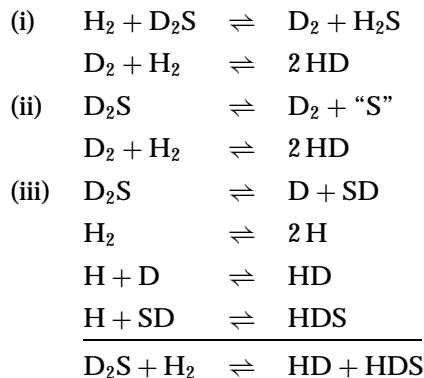
As will be seen, the direct formation of D₂ in the experiment D₂S + H₂ (Experiment 5 and Fig. 6) or of H₂ in the experiment H₂S + D₂ (Experiment 2 and Fig. 4) is difficult to conceive based on mechanistic processes unless a direct diatomic exchange, such as D₂ + H₂S ⇌ H₂ + D₂S, exists as suggested by Katsumoto *et al.* (9). Another possibility is that the isotopic exchange between D₂S in the gas phase and the SH groups of the sulfide phase (or possibly the OH groups of the support), with H–D scrambling over the surface, is fast compared to the exchange with H₂ of the gas phase. Unfortunately, we were unable to measure the isotopic distribution in H₂S with our equipment which would obviously help to clarify this point.

The contribution of hydrogen from the support may also explain why the rate of D₂ formation given by D₂S + H₂ was lower than that of H₂ given by H₂S + D₂. The exchange of D₂S with the OH groups of the support can lead to a “loss” of D atoms. If this exchange is fast enough, some D₂ will appear in the “hydrogen” of the gas phase, which will be lower than that of H₂ in the case of H₂S + D₂.

Occurrence of H₂S (D₂S) decomposition into H₂(D₂) plus S. As expected (28–31), D₂S did not decompose into D₂ + S (Fig. 8) when no H₂ was added to the reaction mixture. At least no D₂ was detected in the gas phase. Taking into account that the concentration of H₂ at equilibrium with H₂S and S at the reaction temperature should be less than 10^{−3} mol% (28), this is not surprising. Nevertheless, small quantities of hydrogen could be formed by a reaction between H₂S and surface vacancies as proposed by Hanlon (14), but it is clear that we cannot expect large amounts of H₂(D₂) to be formed from pure H₂S(D₂S) at this temperature. However, the formation of HD and the direct formation of D₂ seemed to occur when H₂ was added. This means that the presence of molecular hydrogen is necessary to displace H₂, D₂, or HD from the surface (to help H₂, D₂, or HD desorption). When, after sulfidation, the catalyst was cooled to the reaction temperature (80°C) and then swept over by helium at this temperature (as indicated in the experimental procedure), all the H₂ that could desorb through adsorption–desorption equilibration desorbed and was eliminated by the helium stream. Consequently, the desorption of HD and D₂ into the gas phase, after the introduction of pure D₂S at this temperature, could occur only if the adsorption-desorption equilibrium of “hydrogen” was modified, which could only be so if H₂ was introduced (see last part of the experiment reported in Fig. 8), because D₂S did not decompose into D₂ + S. This is in accordance with the results obtained by Barbour and Campbell (12), who found that D-atoms from D₂S were incorporated into hydrocarbons (butenes formed from butadiene) directly from

the adsorbed state provided that gas phase hydrogen was present.

Mechanism of H–D exchange between H₂(D₂) and D₂S(H₂S). Ignoring, for the moment, the modes of dissociation of both H₂ and H₂S, which we shall consider later, three possible reaction schemes for the formation of HD can be examined, for instance, in the case of the H₂–D₂S experiment:



Schemes (i) and (ii) imply that HD is a secondary product of the reaction, which was, in fact, not the case. As described above, the decomposition of D₂S into D₂ + S is quite unlikely so that Scheme (ii) can be rejected. Therefore, Scheme (iii) is the one which probably explains best the direct formation of HD. However, since apparently D₂ (or H₂) were also primary products in the case of H₂–D₂S (or D₂–H₂S) exchange, we cannot exclude the possibility of the coexistence of Schemes (iii) and (i), although the mechanism of a diatomic exchange of H₂ with D₂S (9) is still difficult to understand. In fact, as indicated above, the rapid H–D exchange between H₂S(D₂S) and the “hydrogen” of the active phase (and support) could also explain the apparent direct formation of D₂ and H₂ from the H₂–D₂S and D₂–H₂S mixtures, respectively.

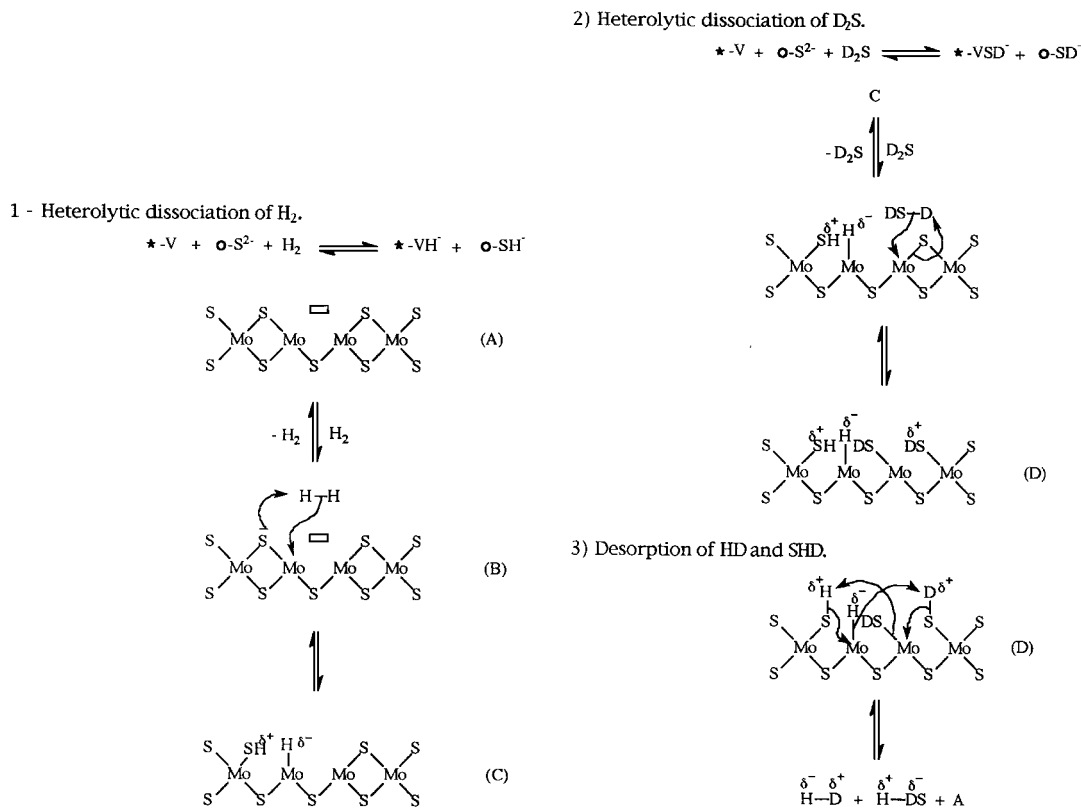
The fact that the H–D exchange between H₂ and D₂ was faster by a factor of 6 to 7 than between H₂(D₂) and D₂S(H₂S) could be interpreted as follows:

(a) the existence of two different modes of dissociation for H₂(D₂), homolytic and heterolytic, which we could not distinguish from each other. The former would lead to a rapid isotope exchange between H₂ and D₂, while the latter would lead to a slower isotope exchange with D₂S(H₂S);

(b) the dissociation mode of H₂ is unique (for instance, both reactants dissociate heterolytically), but the rate-limiting step for the isotope exchange between H₂(D₂) and D₂S(H₂S) is the dissociation of the latter;

(c) H₂(D₂) dissociation is, to a certain extent, inhibited by the presence of D₂S(H₂S).

Some of our results suggest that H₂S(D₂S) rapidly dissociates and undergoes H–D exchange with the surface SH groups; hypothesis (b) therefore seems unlikely. Moreover,



SCHEME 1. Elementary steps in the H-D exchange between H₂ and D₂S on dual sites (17, 18) through heterolytic dissociation. (The scheme represents the edge of a MoS₂ slab. Each Mo atom should be coordinated to six sulfur atoms except when it is coordinatively unsaturated. Similarly, for the sake of clarity, preexisting H atoms at the edge of the MoS₂ slab are not represented.)

considering the results of Experiments 3 and 4 and of the experiment shown in Fig. 5b, it is clear that H₂S (or D₂S) inhibits the H₂-D₂ isotopic exchange. This means that the third hypothesis seems to account, to a large extent, for the difference in rates of the two reactions. Therefore, we assume that both reactants dissociate in the same way on the same catalytic centers, which is the simplest explanation of the isotope exchange.

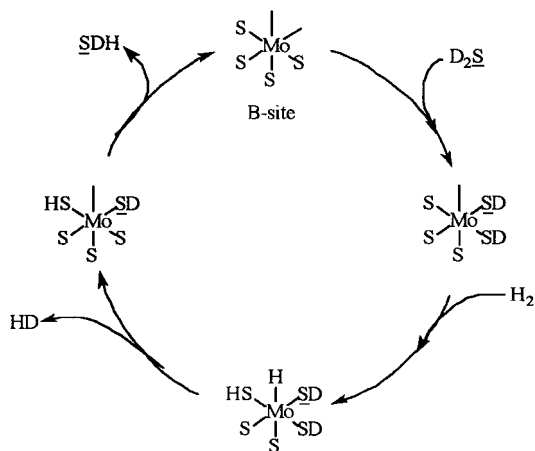
As suggested by Polz *et al.* (15), the homolytic dissociation of H₂ on S₂²⁻ centers was considered. However, the dissociation of H₂S on the same centers is not possible. For the isotope exchange between H₂ and D₂S to occur, we must assume that the adsorption of H₂ according to Eq. [3] and of D₂S according to Eq. [2] lead to the same SH species. Although this hypothesis cannot be disregarded completely, it seems more likely that both reactants dissociate heterolytically. The heterolytic dissociation of H₂S on MoS₂ type catalysts is widely accepted (21-26). Moreover, the literature (20) suggests that H₂ can dissociate heterolytically into H⁺ and H⁻. Under these conditions, H-D exchange between H₂ and H₂S is possible if a hydride ion issuing from H₂ can recombine with a proton issuing from H₂S (Scheme 1). This can occur readily, since it is likely considered that H species are mobile on the catalyst surface (39). Nevertheless, the exchange could occur on isolated centers provided that these

centers possess enough coordinative unsaturations to allow the dissociation of both reactants. At least two coordinative unsaturations would be necessary, corresponding to category B (two unsaturations) or C (three unsaturations) according to Siegel's model for active centers (43). These sites were also labeled ²M and ³M respectively (44). They were supposed to be present at the edges or corners of MoS₂ slabs, as proposed by Tanaka and Okuhara (45) and by Kasztelan *et al.* (46), and were assumed to be the centers for the isotopic exchange of ethene and for H₂-D₂ equilibration on MoS₂ by Tanaka and co-workers (45, 47). The isotope exchange involving the heterolytic dissociation of both H₂ and D₂S on such centers can be described as in Scheme 2. Partially reduced centers, such as BH or CH sites (43), formed during sulfidation may also be involved (Scheme 3).

It is also interesting that such centers may be the source of nucleophilic species (SH⁻), which could, for instance, explain C-N bond cleavages in HDN reactions (4, 33-35).

CONCLUSIONS

H exchange between H₂ and H₂S was shown, in particular, by the experiments conducted with H₂ and D₂S. Since the catalyst was presulfided by a mixture of H₂ and H₂S, the

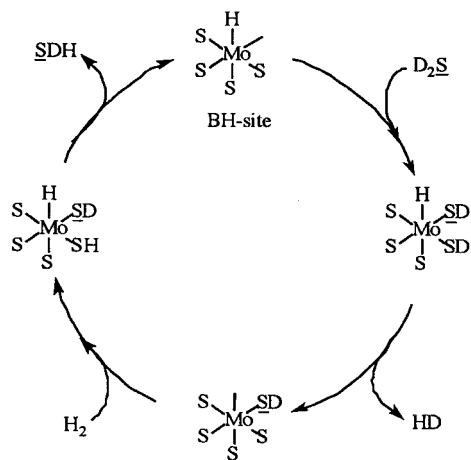


SCHEME 2. Isotopic exchange between D_2S and H_2 on B-sites (43).

D atoms incorporated into H_2 could only originate from D_2S . (The reverse would not be true in the case of the D_2/H_2S experiments.)

The existence of this exchange reaction between the two reactants and the fact that H_2S inhibits the isotope exchange between H_2 and D_2 seem to indicate there is a common mode of dissociation which would occur on the same catalytic centers. Since it is generally accepted that H_2S dissociates heterolytically on dual sites involving a vacancy and a sulfur atom located at the edges of MoS_2 slabs it can be concluded that H_2 dissociates on the same type of sites.

$H_2S(D_2S)$ does not dissociate to give $H_2(D_2)$ under our reaction conditions. It is, therefore, supposed that the exchange occurs through dissociation of both reactants and recombination in the adsorbed phase of the various species. This exchange could occur through dissociation on discrete centers and migration of H(D) atoms on the surface. Some of our results seem to indicate that $H_2S(D_2S)$ dissociation and H-D scrambling on the surface are fast compared with the exchange with $D_2(H_2)$. It is suggested however, that the



SCHEME 3. Isotopic exchange between D_2S and H_2 on BH-sites (43).

exchange may also occur on single centers such as B sites or BH sites, as proposed by Siegel (43).

The experiments made it possible to evaluate the amount of exchangeable "H" retained by the catalyst under our reaction conditions. This corresponded to about 3H atoms per Mo atom. This value is much greater than those generally obtained by TPD or TPR experiments. The difference can be attributed, at least in part, to the contribution of hydrogen from the support. Experiments are being undertaken to verify this point. Moreover the samples used in this study were not evacuated nor reduced after sulfidation which may explain why a large number of SH groups may be present on the surface and undergo H-D exchange.

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