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Deuterium Tracer Studies on Hydrotreating Catalysts. 2. Contribution of the Hydrogen of the Alumina Support to H-D Exchange

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H-D isotopic exchange between H_2 and D_2 was carried out at 80°C in a recycling reactor under a pressure of 2 bar over unsupported MoS_2 as well as on alumina supported Mo or NiMo sulfide catalysts. H_2-D_2 experiments carried out over a commercial NiMo/Al_2O_3 catalyst, to which were mixed different amounts of the alumina support, and over a series of Mo/Al_2O_3 catalysts containing different amounts of Mo (4.4 to 14.8 wt%) showed that part of the exchangeable hydrogen detected by isotopic dilution came from the added alumina or from the support. This amount of hydrogen on the alumina was estimated for each series, to be respectively 22.1×10^{-4} and 17.8×10^{-4} mol $H \cdot g^{-1}$. Since under the same conditions H-D exchange between H_2 and D_2 did not occur at an appreciable rate on the alumina alone, it is concluded that hydrogen atoms from structural hydroxyl groups of the alumina or from hydroxyl groups resulting from the dissociation of H_2S were able to migrate from grain to grain and to exchange with H_2 (D_2) dissociated on the sulfide active phase. The hydrogen atoms supposedly migrate as protons by jumping from oxygen to oxygen atoms on the alumina surface or are conveyed through the gas phase by H_2S (the "shuttle molecule") which can adsorb dissociatively both on the alumina support and on the active phase. D_2 adsorption followed by FTIR under similar conditions confirmed that the presence of the sulfide phase was necessary, under the conditions of the experiments, to make the isotopic exchange between H_2 (D_2) in the gas phase and the hydroxyls of the alumina possible. OD bands were difficult to detect on sulfided alumina alone, even after 5 h of exposure to D_2, whereas a strong OD band appeared very rapidly on sulfided NiMo/Al_2O_3. These results are considered as being in favour of a heterolytic splitting of H_2 on sulfide catalysts. © 1998 Academic Press

INTRODUCTION

It has been known for a long time that the isotopic exchange between H_2 and D_2 (or the isotopic dilution in D_2) makes it possible to measure the amount of hydrogen present on oxides (1) or metals (2, 3). The method was also applied to sulfides (4–6) and supported sulfides (7–9). However, in the case of supported sulfides the amount of hydrogen of the solid measured by this method was much greater than on bulk sulfides, this being in accordance with the results obtained by other methods (5, 8, 10–12). In our previous work, for instance, we found H/Mo atomic ratios as high as 3 (9) for NiMo/Al_2O_3, a value in fact within the range of those reported by Sundberg *et al.* (1.6 to 3.8) (8). This was attributed to a contribution of hydrogen of the support, despite the fact that under the same conditions of pretreatment and reaction (9) the isotopic exchange between H_2 and D_2 was much slower on the alumina support alone than on the supported sulfide catalyst. Therefore, it can be supposed that the hydrogen of the gas phase can exchange atoms with the support through a process similar to the spillover described for instance for Pt/zeolite catalysts (13) or for Rh/Al_2O_3 (14).

The aim of this work was to demonstrate the contribution of the support to the amount of catalyst hydrogen which can be exchanged with gas phase hydrogen and to determine quantitatively this contribution. For this purpose, the amount of exchangeable hydrogen was measured using H_2-D_2 equilibration on various catalysts:

—a MoS_2 unsupported catalyst;
—physical mixtures of alumina and of a NiMo/Al_2O_3 commercial catalyst;
—a series of MoS_2 supported catalysts with different Mo loadings and containing MoS_2 slabs with lengths in the range 20 to 30 Å (15).

On the other hand, the dissociation of D_2 on sulfided alumina alone and on an alumina-supported sulfide catalyst was followed by FTIR spectroscopy.

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EXPERIMENTAL

Catalysts

The $NiMo/Al_2O_3$ commercial catalyst contained 2.9 wt% NiO and 12.5 wt% MoO_3 deposited on alumina ($230\ m^2 \cdot g^{-1}$).

The $NiMo/Al_2O_3 + Al_2O_3$ physical mixtures were obtained by mixing Al_2O_3 (γ-Al_2O_3, Rhône-Poulenc, $230\ m^2 \cdot g^{-1}$, 0.25–0.315 mm) with the commercial catalyst (particles with the same size).

The Mo/Al_2O_3 catalysts (Table 1) were obtained by impregnation (pore-filling method) with a solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$, $4H_2O$, Merck) of a γ-Al_2O_3 support (Rhône-Poulenc; 1.2 mm extrudates; BET surface area: $230\ m^2 \cdot g^{-1}$; pore volume: $0.75\ cm^3 \cdot g^{-1}$). The samples were dried overnight at 120°C and calcined at 500°C for 2 h in air.

The MoS_2 unsupported catalyst was obtained by decomposition of ammonium tetrathiomolybdate, $(NH_4)_2MoS_4$ (15). $(NH_4)_2MoS_4$ was prepared by addition of H_2S to a solution of ammonium heptamolybdate (50 g) in ammonium hydroxyde (500 cm^3, 33 wt% NH_3) and water (150 cm^3) (16, 17). The colorless solution became red after the addition of H_2S. After cooling at 0°C, the $(NH_4)_2MoS_4$ crystals were separated by filtration, dried at room temperature for 8 h under vacuum and stored under argon. The decomposition of $(NH_4)_2MoS_4$ into bulk molybdenum sulfide was carried out according to a procedure adapted from the literature (18, 19). $(NH_4)_2MoS_4$ was heated for 1 h at 350°C (heating rate $15°C \cdot min^{-1}$) in flowing hydrogen ($4\ liters \cdot h^{-1}$). After the hydrogen treatment, the sample was cooled down to room temperature, flushed with argon for 10 min, evacuated at 2×10^{-4} mbar and sealed in a glass tube. Its BET surface area was $55\ m^2 \cdot g^{-1}$.

Chemicals

H_2 (Air Liquide) and D_2 (Eurisotop) were respectively of 99.95 and 99.8% purity.

Apparatus and Procedure

Isotopic exchange between H_2 and D_2. The reaction was carried out at 80°C in a 72 cm^3 recycling reactor. The catalyst was presulfided *in situ* with a flow of H_2 (90%) and H_2S (10%) at 400°C for 15 h. The procedure was the same for all the samples including bulk MoS_2. After sulfidation, the catalyst was cooled down to the reaction temperature (80°C) and treated under a helium flow (1 bar), the diluting gas. The reactant (H_2 plus D_2; 0.5 bar of each) was introduced into the reactor and the recycling pump was started.

TABLE 1

Characteristics of the Mo/Al_2O_3 Catalysts (15)

Mo (wt%)	BET surface area ($m^2 . g^{-1}$)	L (Å, ±2)	N (±0.2)	M
4.4	225	21	1.1	43
9.8	208	25	1.2	58
14.8	185	27	1.1	67

Note. L is mean length from TEM pictures; N is mean number of layers in MoS_2 slabs; M is mean number of Mo ions in MoS_2 slabs.

The $H_2/HD/D_2$ reaction mixture was analyzed by gas chromatography (20, 21) using a column of alumina impregnated with $MnCl_2$ and maintained at −196°C. The amount of exchangeable hydrogen on the catalyst was calculated by assuming that the H-D scrambling equilibrium was obtained at the end of the experiments and that H and D atoms were equally distributed in the gas phase and on the catalyst. All the details concerning the apparatus and procedure as well as the calculations have been published elsewhere (9).

Dissociation of D_2 followed by FTIR spectroscopy. Two activation procedures (**1** and **2**) were used to evaluate the effect of traces of water (which could be adsorbed on the sample during the prolonged contact with D_2) in the IR cell. In procedure **1**, a disc of catalyst ($5 \times 10^{-3}\ g \cdot cm^{-2}$) was evacuated by heating at the rate of $10°C \cdot min^{-1}$, up to 400°C. Sulfidation was carried out under static conditions by three treatments with 80 torr H_2-H_2S (15 vol%) at 400°C, the first for 1 h, the second for 15 h, and the third for 2 h. Each treatment was followed by an evacuation for 20 min at 400°C. In procedure **2**, a disc of alumina was introduced into the cell. This second disc was located outside the IR beam but activated under the same conditions as the sample which was analyzed. Sulfidation procedure **1** was employed, except that after the final evacuation, 10 torr of argon was introduced and evacuated after 10 min with the discs at 400°C. The introduction of argon, which was repeated twice, made it possible to improve on the removal of the water formed during the sulfidation step and which could be adsorbed on the walls of the cell. The second disc of alumina was used to trap the remaining traces of water. In the two cases, after the last evacuation ($P < 5 \times 10^{-6}$ torr), the temperature was lowered under vacuum. When it reached 80°C, D_2 (100 torr) was introduced in the cell after a cryogenic purification and the sample maintained at this temperature. The possible dissociation of D_2 was followed by IR spectroscopy for 5 h. The spectra were recorded at room temperature with a Fourier Transform Magna IR spectrometer from Nicolet with a resolution of 4 cm^{-1}.

RESULTS

H_2-D_2 Experiments

$NiMo/Al_2O_3 + Al_2O_3$ physically mixed catalysts. The reaction between H_2 and D_2 was carried out on sulfided mixtures of a $NiMo/Al_2O_3$ commercial catalyst and alumina. The amount of the $NiMo/Al_2O_3$ component in the

TABLE 2

Isotopic Exchange between H_2 and D_2 (Equimolar Mixture) over Presulfided NiMo/Al_2O_3 + Al_2O_3 Physical Mixtures

NiMo/ Al_2O_3 (g)	Al_2O_3 (g)	rate of HD formation (10^{-7} mol · s^{-1} · g^{-1})[a]	nH adsorbed 10^{-4} mol	nH adsorbed 10^{-4} mol · g^{-1}[a]	H/Mo
0.375	0	19.0	9.2	24.5	2.8
0.375	0.125	17.3	9.6	25.6	2.9
0.375	0.250	16.5	13.7	36.5	4.2
0.375	0.500	15.8	19.6	52.3	6.0

Note. Recycling reactor, 80°C.

[a] Per gram of NiMo/Al_2O_3.

mixtures was kept constant and the amount of alumina was increased. The H-D scrambling equilibrium was obtained in about 3 h. The rate of formation of HD could be deduced from the slope of the curve representing the formation of this species at reaction time zero and the amount of exchangeable hydrogen present on the catalyst could be calculated from the isotope distribution (9). Table 2 gives the results obtained when the amount of alumina added to 0.375 g of NiMo/Al_2O_3 was increased from zero to 0.5 g. It can be seen that the rate of formation of HD decreased slightly as the amount of alumina added increased. Conversely, the amount of exchangeable hydrogen, hence the H/Mo atomic ratio, increased significantly.

Mo/Al_2O_3 catalysts. In order to determine the contribution of the alumina support to the amount of exchangeable hydrogen, a series of Mo/Al_2O_3 catalysts with different Mo contents were studied. These samples were shown to contain MoS_2 slabs with a mean length determined by TEM varying between 20 and 30 Å (Table 1). The size of the samples was chosen so as to keep the same amount of molybdenum for all the H_2-D_2 exchange experiments. As shown in Table 3, the turnover frequency, calculated on the basis of the total number of Mo atoms in the sample, was practically the same for all the samples while the amount of exchangeable hydrogen per gram of catalyst; hence, the H/Mo atomic ratio decreased when the Mo concentration increased.

TABLE 3

Isotopic Exchange between H_2 and D_2 (Equimolar Mixture) over Presulfided Mo/Al_2O_3

Sample (g)	Mo (wt%)	Rate of HD formation (10^{-4} mol · s^{-1} · (Mo-Atom)$^{-1}$)	nH adsorbed (10^{-4} mol · g^{-1})	H/Mo
0.9	4.4	31.0	17.1	3.7
0.4	9.8	30.9	16.7	1.6
0.27	14.8	32.1	15.3	1.0

Note. Recycling reactor, 80°C.

Bulk MoS_2 catalyst. The reaction of an equimolar mixture of H_2 and D_2 was carried out on 250 mg of unsupported MoS_2. The isotope distribution equilibrium was obtained in about 1 h. The initial rate of reaction was 47.8×10^{-7} mol HD · s^{-1} · g^{-1}, which means 7.7×10^{-4} mol HD · s^{-1} · (Mo Atom)$^{-1}$. The amount of exchangeable hydrogen which could be deduced from the isotope distribution at equilibrium was of 14.8×10^{-4} mol · g^{-1}. This corresponded to a H/Mo atomic ratio of 0.24 if we consider the total amount of Mo present in the sample.

Dissociation of D_2 Followed by FTIR

With the alumina activated according to procedure **1** (Fig. 1), the D_2 introduction led to the disappearance of part of the ν(OH) bands and to a concomitant appearance of disturbed hydroxyl group vibrations. In the lower wavenumber range, a broad band at 1625 cm^{-1} (characteristic of the presence of H_2O), the intensity of which increased with time was observed. A disturbance of bands due to some residual surface carbonate species (1564 and 1480 cm^{-1}) also occurred.

As could be expected from the more severe conditions used for activation **2**, no bands corresponding to water were detected. The disturbance of the alumina surface was much reduced even after 5 h. Only a small decrease of the hydroxyl group bands and the appearance of two weak ν(OD) bands at 2780 and 2725 cm^{-1} were noted. The band at 2780 cm^{-1} indicated the presence of isolated OD species. OD species were also formed on alumina

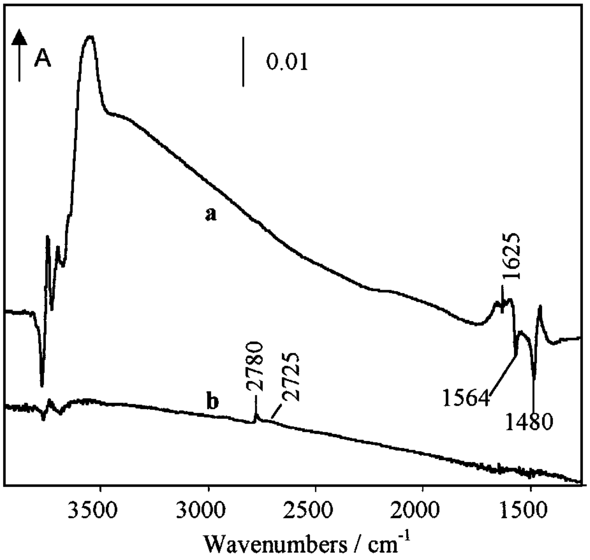

FIG. 1. Effect of D_2 on alumina activated according to procedure **1** (a) or to procedure **2** (b). Difference of spectra recorded between 0 and 5 h of contact.

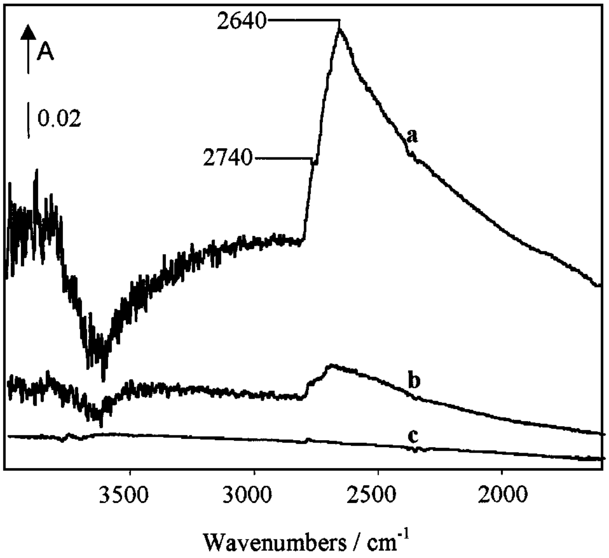

FIG. 2. Difference of spectra between 0 and 5 h of contact with D_2: (a) $NiMo/Al_2O_3$, activation procedure **1**; (b) $NiMo/Al_2O_3$, activation procedure **2**; (c) Al_2O_3, activation procedure **2**.

activated according to procedure **1** but as for OH groups, these species were disturbed by adsorbed water and the corresponding bands became very broad.

On $NiMo/Al_2O_3$ (Fig. 2), despite the weak ratio signal-to-noise in the range of the vibrations of the hydroxyl groups, consumption of these groups could be detected. Moreover, in the region of the lower wavenumbers, we noted a disappearance of water initially present on the surface and the appearance of D_2O (1210 cm^{-1}) for the catalyst activated by procedure **1**. But the most striking difference with the alumina spectra was the formation of a broad ν(OD) band at ~2640 cm^{-1} whose intensity after 5 h of contact with D_2 was greater after activation procedure **1** (Fig. 2a) than after procedure **2** (Fig. 2b). As shown above, very weak bands were detected in this region with the alumina (Fig. 2c). When activation procedure **2** was used for $NiMo/Al_2O_3$, neither bands relative to H_2O or D_2O were present, whereas there was a lower decrease in intensity of the bands corresponding to the alumina hydroxyl groups. The comparison between the results obtained with the two activation procedures (Fig. 3) shows that when traces of H_2O were present the number of OD species was greater and their formation was faster. In another experiment, we also characterized the effect of the presence of H_2S traces. The number of OD species as well as the consumption of OH groups suddenly increased, when H_2S was introduced after 100 min of D_2 contact with the $NiMo/Al_2O_3$ activated under the conditions of procedure **2**.

DISCUSSION

In our previous work on the isotopic exchange between H_2 and D_2 and between H_2 (D_2) and D_2S (H_2S) over a sulfided $NiMo/Al_2O_3$ catalyst we showed that the reaction was much faster on the supported NiMo catalyst than on its support, both of which had been presulfided under the same conditions (9). Compared to the amount that was reported for unsupported sulfides (4, 6, 10, 11, 16, 22–29) the large unexpected amount of exchangeable hydrogen found on the $NiMo/Al_2O_3$ catalyst (corresponding to a H/Mo atomic ratio around 3) was suspected of being due, at least in part, to an involvement of the hydrogen present on the support. Considering that the exchange with the support alone was very slow, we conclude that the hydrogen of the support can be exchanged at an appreciable rate through a process similar to the hydrogen spillover proposed for supported transition metals (13, 14) only if the active phase is present. The other possible reason for the differences in the amounts of exchangeable hydrogen could obviously be the difference in the pretreatment procedures.

We can notice indeed that the value of the H/Mo atomic ratio found with the unsupported MoS_2 catalyst lies within the range of the values found by other methods, although it is rather close to the highest values reported (16, 22, 23, 26). The reason for this high value is probably that our sample was not evacuated after sulfidation but simply treated under flowing helium at the reaction temperature.

The FTIR results obtained with alumina show that the disturbance of the surface in the hydroxyl region observed after the activation procedure **1** was not related to the presence of D_2 but to the adsorption of water present in the cell since there was almost no disturbance after the activation procedure **2**. The formation of a small number of OD species indicates that the dissociation of D_2 at 80°C on the sites of alumina was very slow.

On the other hand, the FTIR experiments confirm the contribution of the hydrogen of the support (in the case

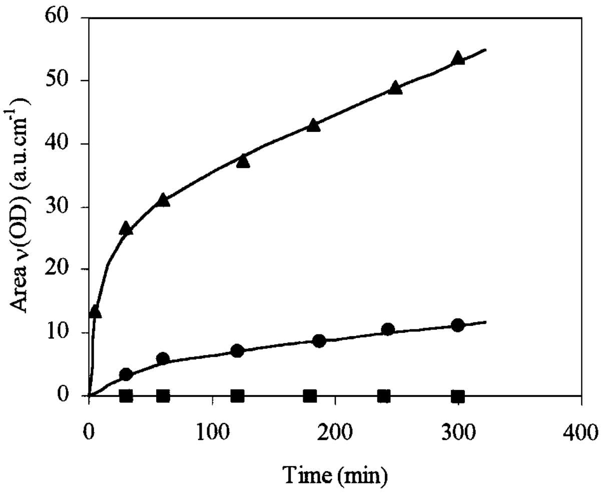

FIG. 3. Effect of the activation conditions on the interaction with D_2. Variation versus time of the area of the ν(OD) band (2640 cm^{-1}): (▲) $NiMo/Al_2O_3$, activation procedure **1**; (●) $NiMo/Al_2O_3$, activation procedure **2**; (■) Al_2O_3, activation procedure **2**.

of NiMo/Al_2O_3 catalysts) to the exchange with the deuterium in the gas phase. They prove also that the presence of the active phase is necessary for this exchange to occur. While OD bands were difficult to detect on pure sulfided alumina even after 5 h contact with D_2 at 80°C, such bands were easy to detect on sulfided NiMo/Al_2O_3 after a few minutes of exposure to D_2. Moreover, the FTIR results show that the disappearance of OH groups accompanied the formation of OD species. This indicates that deuterium species resulting from the dissociation of D_2 on the active phase can easily migrate (spill over) to alumina to form OD groups while H species, initially present on the support as OH groups, can follow the reverse route and desorb from the active phase as HD. This is in accordance with the picture given by Stumbo *et al.* for the creation of acid sites on hydrocracking catalysts (30, 31) and is (together with the H-D exchange between H_2 and D_2S (9)) another indication in favour of a heterolytic dissociation of H_2 on sulfide catalysts. The exchange of D_2 with the "hydrogen" of alumina can therefore be explained by supposing that a deuteron issuing from the dissociation of D_2 on the active phase is transferred to the alumina support where it substitutes for the hydrogen of a hydroxyl group which is, in turn, transferred to the active phase, where it combines with a D atom having a hydride character (adsorbed on a coordinatively unsaturated Mo atom) and desorbs as HD.

It should be mentioned, however (see Fig. 2 and 3), that the number of deuterated species transferred to the support depends on the presence of traces of water. Figure 4 shows the effect of the activation conditions on the bands in the hydroxyl region, before and after 5 h of contact with D_2. Although the amounts of OH groups initially present on the two samples were similar, the intensity of the ν(OH) bands decreased significantly after exposure to D_2 with the activation procedure **1** (see the direct spectra in Fig. 4, B1 compared to A1 and the difference spectrum in Fig. 2a), whereas no noticeable change in the intensity was perceived with the activation procedure **2** (see the direct spectra in Fig. 4, B2 compared to A2 and the difference spectrum in Fig. 2b). Consequently, H_2O does not act only as a provider of OH groups but also as a co-catalyst for the exchange of the H atoms of OH groups with D_2. This acceleration effect can be related to several factors. The higher hydroxylation degree of alumina could increase proton mobility, as well as proton transfer from the support to the sulfided phase. Another possibility for the exchange of H(D) atoms between OH groups of alumina and dissociated D_2 is that H_2O could serve as a "shuttle molecule" to convey H(D) atoms between the support and the active phase. H_2-D_2 exchange measurements were carried out in a reactor in which, if there was no water, there were certainly traces of H_2S. Hence, H_2S could play the same role as water. According to this picture, H_2S could exchange H atoms with hydroxyl groups of the support (either structural OH groups or OH groups resulting from the adsorption of H_2S during the sulfiding procedure (32)), then adsorb on the active phase and exchange H atoms with those of dissociated $D_2(H_2)$ and vice versa (Scheme 1). A similar process involving H_2O, instead of H_2S, was considered to give a possible explanation for the deuteration of hydroxyl groups of silica in the presence of Pt/Al_2O_3 (33). Hence H_2S can help the exchange of H(D) atoms between D_2 and the hydroxyl groups of the support despite the fact that it can also (especially if in large amounts) inhibit the dissociation of D_2 (H_2) on the active phase (9).

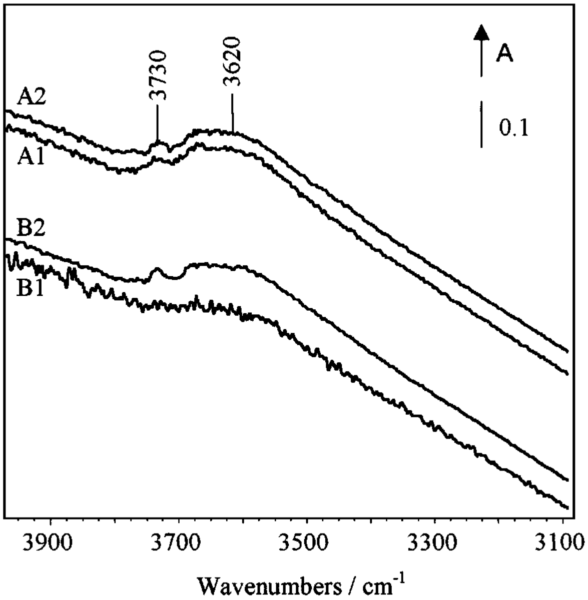

FIG. 4. Comparison between the IR spectra (direct) in the hydroxyl range for the NiMo/Al_2O_3 catalyst activated under procedure **1** and procedure **2**, before (A) and after 5 h (B) of contact with D_2.

(a) *On the active phase:*

$$\begin{aligned}
&D_{2(gas)} + Mo\square + MoS^{2-} &&\rightarrow MoD^- + MoS^{2-}D^+\\
&H_2S + Mo\square + MoS^{2-} &&\rightarrow MoSH^- + MoS^{2-}H^+\\
&MoSH^- + MoS^{2-}D^+ &&\rightarrow Mo\square + MoS^{2-} + HDS_{(gas)}
\end{aligned}$$

(b) *On the support:*

$$\begin{aligned}
&HDS_{(gas)} + Al\square + AlO^{2-} &&\rightarrow AlSH^- + AlO^{2-}D^+\\
&AlSH^- + AlO^{2-}H_s^+ &&\rightarrow Al\square + AlO^{2-} + HH_sS_{(gas)}
\end{aligned}$$

(c) *On the active phase:*

$$\begin{aligned}
&HH_sS_{(gas)} + Mo\square + MoS^{2-} &&\rightarrow MoSH^- + MoS^{2-}H_s^+\\
&MoD^- + MoS^{2-}H_s^+ &&\rightarrow Mo\square + MoS^{2-} + DH_{s(gas)}
\end{aligned}$$

SCHEME 1. H transfer between the support and the active phase using H_2S as "shuttle molecule." For briefness the scheme shows only the steps leading to the exchange of $H_2(D_2)$ from the gas phase and the hydroxyls of the support. H_s is the hydrogen atom of the support.

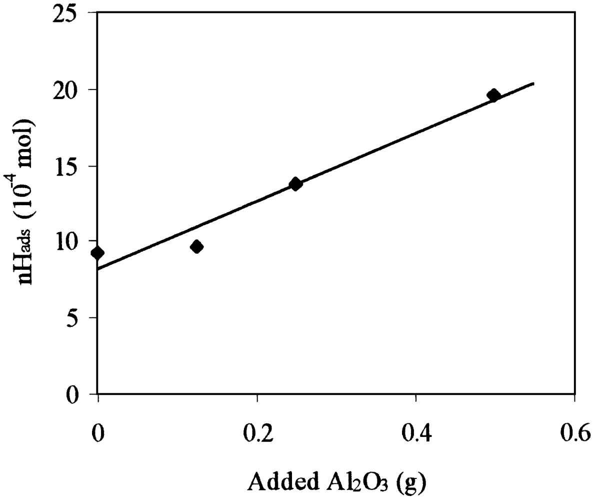

FIG. 5. H-D isotopic exchange between H_2 and D_2 (equimolar mixtures) on physically mixed sulfided NiMo/Al_2O_3 (0.375 g) and Al_2O_3. Effect of added Al_2O_3 on the amount of exchangeable hydrogen (nH_{ads}).

The quantification of the amount of hydrogen issuing from the added alumina or from the support can be obtained respectively from the experiments carried out with physical mixtures of alumina plus NiMo/Al_2O_3 (Table 2) and from the experiments with the series of Mo/Al_2O_3 catalysts (Table 3). By representing the amount of exchangeable hydrogen present on the physical mixtures (nH adsorbed, Table 2) as a function of added alumina (Fig. 5) we obtain a straight line, the slope of which gives the amount of exchangeable hydrogen per gram of added alumina (22.1×10^{-4} mol $H \cdot g^{-1}$) which, compared to the amount of exchangeable hydrogen on the supported NiMo/Al_2O_3 catalyst (24.5×10^{-4} mol $H \cdot g^{-1}$), shows that the amount of exchangeable hydrogen present on the active phase was around 2.4×10^{-4} mol $H \cdot g^{-1}$ (about 10% of the total amount present on the supported catalyst). Hence, we can conclude that a large fraction of the hydrogen which was incorporated into the gas phase H_2-D_2 mixture came from the alumina added to the samples. As indicated in the preceding discussion, the isotopic exchange between H_2 and D_2 on pure alumina being very slow means that in the case of supported and mixed catalysts the exchange of hydrogen atoms of the support with the D_2 of the gas phase occurs via the active phase with migration of the atomic species (protons and deuterons) either directly or through the process described in Scheme 1. The present experiments with physically mixed catalysts (particles of 0.25 to 0.315 mm) indicate that if the process occurs by migration of dissociated species, these species (protons and deuterons) can even migrate from grain to grain. It can be noticed that as shown in Scheme 1 this migration is quite feasible with H_2S as the “shuttle molecule” for the transportation of the H or D species.

As can be seen in Table 3, the amount of exchangeable H per gram of supported Mo/Al_2O_3 decreases slightly when the concentration of molybdenum increases. This could be due to a certain coverage of the alumina by the active phase even in the sulfided state. If we plot the amount of exchangeable H obtained with the various samples versus the weight of alumina in each sample (Fig. 6) we obtain also a straight line. The amount of molybdenum per sample was kept constant in these experiments; hence, if we assume that the degree of sulfidation of the active phase was the same for all the samples and that the slight difference in size of the MoS_2 slabs did not affect significantly the amount of exchangeable hydrogen on the sulfide particle, the slope and the ordinate of the straight line at the origin would give respectively the number of H atoms per gram of the alumina support and the number of H atoms on the active phase. The slope gives a value (17.8×10^{-4} mol $H \cdot (g\text{-}Al_2O_3)^{-1}$) which is significantly lower than in the previous case. Unfortunately the amount of molybdenum present in the samples (4.1×10^{-4} mol) was too small to ensure an accurate determination of the amount of exchangeable hydrogen on the active phase. If this amount were the same as on unsupported MoS_2, it should be around 1×10^{-4} mol H.

As for the alumina support, the value which was found with the series of physically mixed samples (22.1×10^{-4} mol $H \cdot g^{-1}$) corresponds to about 5.8×10^{14} $H \cdot cm^{-2}$. This value is around twice those reported by Hall and Lutinski (2), 2.8×10^{14} $OH \cdot cm^{-2}$, or by Peri (34), 3.5×10^{14} $OH \cdot cm^{-2}$. This can be attributed to the sulfiding treatment and we can assume that about 10^{-3} mol H per gram of alumina corresponds to adsorbed H_2S. This is not surprising, considering the fact that, as shown by various authors (35, 36), H_2S is strongly adsorbed on alumina. Valyon and Hall have indeed reported that upon sulfiding extra OH groups were formed on the alumina support (32). Actually, the amount of H on the alumina which they deduced from the data published

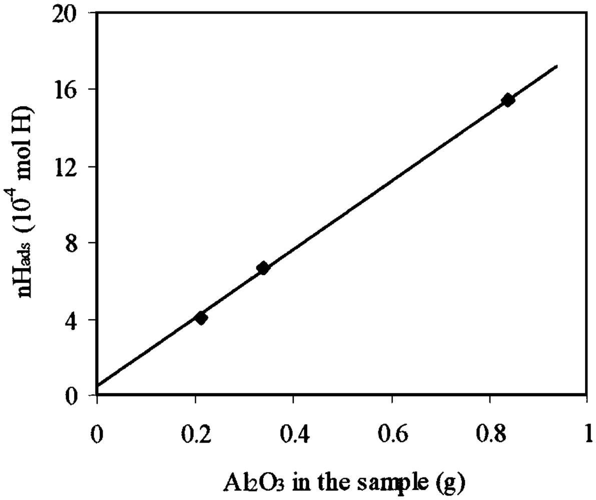

FIG. 6. H-D isotopic exchange between H_2 and D_2 (equimolar mixtures) on Mo/Al_2O_3 catalysts. Effect of Al_2O_3 content of the samples on the amount of exchangeable hydrogen (nH_{ads}).

by Massoth (7) (17.1×10^{-4} mol · g^{-1}) is very close to the one we find for the series of Mo/Al_2O_3 catalysts (17.8×10^{-4} mol · g^{-1}).

The rate of HD formation per Mo-atom is lower with the unsupported catalyst, probably because the proportion of exposed molybdenum atoms is smaller than with the supported catalysts. Concerning the supported catalysts, the rate of HD formation decreases slightly when the amount of alumina added to NiMo/Al_2O_3 increases (Table 2). As we have seen, alumina seems to adsorb a significant amount of H_2S which as we know inhibits the H-D exchange between H_2 and D_2 on NiMo/Al_2O_3 (9). Added alumina could therefore lead to a decrease in the rate of HD formation by contributing to increasing the concentration of H_2S in the catalyst. However, such a phenomenon did not occur with the series of Mo/Al_2O_3 catalysts (Table 3). The turnover number for HD formation was approximately the same with the three catalysts. Therefore, another explanation could be that the necessary migration from grain to grain would contribute to reduce the overall rate of isotopic exchange between H_2 and D_2, this effect being all the more pronounced than the amount of alumina in the mixed catalyst is greater.

On the other hand, if we compare the results obtained with the commercial NiMo/Al_2O_3 catalyst with those obtained with the Mo/Al_2O_3 catalyst which contains approximately the same amount of molybdenum (9.8 instead of 8.3 wt%) we can notice that there is little influence (if any) of nickel on the rate of HD formation (as well as on the amount of exchangeable H). Actually, the rate of HD formation per Mo-atom is even lower with the commercial catalyst (22×10^{-4} mol · s^{-1}) than with the Mo/Al_2O_3 catalyst (Table 3) while the amount of exchangeable H is slightly higher. This, of course, needs to be verified with catalysts containing various amounts of promoter, obtained by the same procedure of preparation, which is currently being carried out with a series of NiMo and CoMo catalysts pretreated under various conditions. However, our result is not surprising if we consider that the promoting effect observed in hydrotreating reactions like hydrodesulfurization, is related to the activation of the organic molecule (37) rather than to the dissociation of H_2 or to the amount of available hydrogen on the catalyst.

CONCLUSION

As we suspected from previous experiments (9), FTIR experiments confirmed that hydrogen from the gas phase can exchange atoms with hydroxyl groups of the support and that under our reaction conditions this exchange is possible at an appreciable rate only via the sulfide phase. This exchange (as well as the hydrogen isotopic exchange between H_2 and H_2S (9 and references therein)) is in favour of the heterolytic dissociation of H_2 on sulfide catalysts.

Two different sets of experiments on NiMo/Al_2O_3 mixed with alumina and on Mo/Al_2O_3 made it possible to evaluate the contribution of the support to the amount of exchangeable hydrogen measured through isotopic dilution. Under our mild experimental conditions (2 bar, 80°C), the amount of exchangeable hydrogen found on the support was very significant, compared to the amount on the active phase, which represents less than about 10% of the total amount. The alumina support (more than the bulk of MoS_2) constitutes an actual reservoir for hydrogen (presumably as adsorbed H_2S) which is mobile under the mild conditions employed in this work, hence, under hydrotreating conditions.

The hydrogen atoms of the support are supposed to migrate as protons, jumping from oxygen atom to oxygen atom or to be conveyed between the support and the active phase by H_2S, the "shuttle molecule."

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