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An Investigation of the Reduction Behaviour of MoS_2/Al_2O_3 and the Subsequent Detection of Hydrogen on the Surface[1]

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The reduction behaviour of a conventional $MoS_2/\gamma Al_2O_3$ catalyst has been studied using a combination of temperature-programmed reduction, temperature-programmed desorption, X-ray photoelectron spectroscopy, and conventional transmission electron microscopy. The quantity of hydrogen detected on the surface of the catalyst was strongly influenced by the reduction temperature, with a maximum at 700°C (H/Mo = 0.64). Two main hydrogen desorption peaks were detected, a low-temperature desorption peak (300–500°C) and a high-temperature peak (500–800°C), with positions and intensities that depend on the reduction temperature. Reduction in hydrogen at temperatures higher than 600°C was found to induce significant differences in the oxidation state of the molybdenum, with an oxidation number lower than 4 detected by XPS in the catalyst. The onset of the detection of molybdenum in an oxidation state lower than 4 was found to coincide with the maximum in the plot of H/Mo as a function of reduction temperature. Further increases in the reduction temperature resulted in increased quantities of reduced molybdenum and decreased quantities of hydrogen. At reduction temperatures lower than 600°C, the surface contains Mo^{4+}, hydrogen, and sulfur species. As the electroneutrality of the MoS_2 slabs must be respected, these results have been taken as indirect evidence for the presence of a hydridic species on the MoS_2 surface.

INTRODUCTION

The most widely studied catalysts for the hydrotreatment of petroleum feedstocks are the cobalt- and nickel-promoted, alumina-supported molybdenum disulfide systems, Co(Ni)–MoS_2/Al_2O_3 (1–7). Although the activity of the promoted phases has been found to be higher for hydroprocessing reactions such as hydrodesulfurization (HDS) and hydrogenation (HYD), unpromoted MoS_2/Al_2O_3 has been established to be the main crystalline component of the active phase (1, 8, 9) consisting of small slabs (less than 100 Å) of MoS_2 on the alumina support (10–13).

The interaction of hydrogen with MoS_2/Al_2O_3 or unsupported MoS_2 is a complex phenomenon which involves several distinct processes. One process is the interaction of hydrogen with the MoS_2 slabs to effectively alter the S/Mo ratio through the removal of sulfur as H_2S (14–22). Catalyst pretreatment of this nature has been shown to influence various catalytic reactions on unsupported (16, 17) and alumina supported MoS_2 (17, 20–22).

A second process is the adsorption or uptake of hydrogen by the sulfide phase. Several experimental methods have demonstrated the presence of hydrogen on MoS_2-based catalysts such as volumetric H_2 uptake measurements (14), temperature-programmed desorption experiments (15, 16, 18), and inelastic neutron scattering measurements (19).

Temperature-programmed reduction (TPR) has been used as a tool for characterizing supported and unsupported molybdenum catalysts in the sulfided and oxidic states (15, 23, 24). The TPR profiles of unsupported MoS_2 recorded in these different studies were quite different in terms of the number of peaks and the temperatures at which the peaks were observed. The most recent study has shown, in addition to two reduction peaks, a negative peak which the authors attribute to an equilibrium between H_2 and MoS_2 (15). For alumina supported sulfides, the effect of loading has been found to be important with differences in the position, intensity, and shape of the high-temperature reduction peak which makes it difficult to make inferences between samples (23).

Temperature-programmed desorption (TPD) has been used to study sulfide catalysts much less frequently. Most recently, studies of bulk MoS_2 and promoted MoS_2 have been reported (15–18). Of particular interest was the observation that the hydrogen desorption peak is influenced by the reduction temperature (15), a result also reported for a MoS_2/alumina catalyst (25).

In the study of MoS_2-based catalysts, X-ray photoelectron spectroscopy (XPS) has been used primarily to investigate the extent of sulfidation (26), the interaction of molecules such as O_2 with the surface (27), and the effect of promoter ion incorporation into the system (26, 28). Roxlo

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et al. (29) have also shown by XPS the existence of a reduced Mo ion, proposed to be Mo^{3+} in bulk MoS_2 samples.

In the present study we have studied a model MoS_2/Al_2O_3 catalyst by XPS, CTEM, TPR, and H_2-TPD to investigate the effect of reductive pretreatment in hydrogen over a large range of reduction temperature on both the distribution of oxidation states in the alumina-supported MoS_2 slabs and the quantity of the hydrogenic species that are present on the surface.

EXPERIMENTAL

The oxidic catalyst (MoO_3/Al_2O_3) was prepared by impregnating γ-alumina extrudates (Rhône–Poulenc, surface area = 240 $m^2\ g^{-1}$, pore volume 0.56 cm^3/g) with a solution of ammonium heptamolybdate, ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ from Merck) drying at 100°C and calcination for 4 h at 500°C. The loading, measured by X-ray fluorescence, was found to be 10.2 wt% Mo (15.2 wt% MoO_3). All sulfided catalysts were prepared by exposing the oxide catalyst to a 15% H_2S/H_2 mixture (Air Liquide) at 1 atm. The temperature was raised to the desired sulfiding temperature at a rate of 5°C/min and maintained for 2 h. Prior to subsequent reductive treatments, the catalysts were cooled to room temperature in the sulfiding mixture. Sulfur and molybdenum analyses for the sulfided and reduced samples were determined using X-ray fluorescence methods.

For samples to be studied by X-ray photoelectron spectroscopy, reduction in hydrogen was carried out following the sulfidation step. Prepurified hydrogen was passed over the catalyst at a flow rate of 40 ml/min. The temperature was raised at a rate of 15°C/min to the desired temperature, where it was maintained for 2 h. The samples were cooled to room temperature, isolated in the cell by means of two Teflon stopcocks, and transferred to a glove-bag. The glove-bag was pumped and backfilled with purified helium four times before the samples were transferred to sealed containers. The samples for analysis by XPS were transferred to the sample holder under helium and transferred to the spectrometer. Spectra were recorded on a Kratos XSAM 800 spectrometer using an Al $K\alpha$ source (1486.6 eV). Binding energies are reported relative to the Al 2*p* peak of the alumina support (73.2 eV). Extreme care has been taken to avoid contamination, and as reduced Mo species with oxidation numbers lower than 4 have been effectively detected, this procedure is considered to be sufficiently efficient to detect such species that were not detected when the reduced sample has been exposed to air (30).

Samples analyzed by conventional transmission electron microscopy (CTEM) were pretreated in the same manner as described for the XPS measurements, but were transferred to the microscope under *n*-heptane to avoid contact of the surface with air. CTEM images were recorded using a JEOL 100 CX instrument.

For the TPD and TPR experiments, the sulfidations (at 400°C) were carried out *in situ* using a GIRA χ-SORB solid catalyst characterization unit. TPR experiments were carried out at a heating rate of 5°C/min to a maximum temperature of 800 or 1000°C in a mixture of H_2/Ar (5%/95%). An in-line molecular sieve trap was used to remove H_2S from the gas stream in advance of the catharometer. Blank experiments carried out with the support demonstrated that only minor quantities of reducible impurities were present either with or without sulfidation treatment. For the TPD experiments, the reductive pretreatments were carried out in pure H_2 using a temperature ramp of 15°C/min to the desired temperature and maintained for 1 h, or in one case 16 h at that temperature. The samples were then cooled to below the desired purge temperature before the gas flow was switched to pure argon and the temperature was maintained for 1 h. The TPD experiments were carried out between 50 and 900°C using a heating rate of 30°C/min.

RESULTS

Temperature-Programmed Reduction

Figure 1 shows the TPR profiles for the supported Mo/Al_2O_3 catalyst which has been sulfided at various temperatures. Each profile posseses three peaks, one centered at approximately 190°C for each of the sulfidation temperatures and two-high temperature peaks for which the peaks maximum depend on the sulfidation temperature. As the

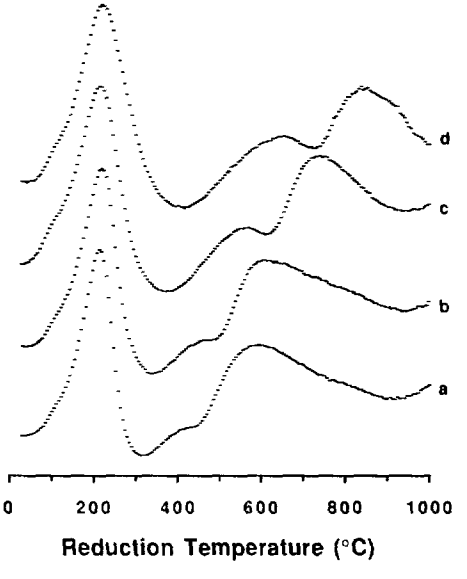

FIG. 1. Temperature programmed reduction profiles for MoS_2/Al_2O_3 samples prepared by sulfiding at various temperatures: (a) 350°C, (b) 400°C, (c) 500°C, and (d) 600°C.

sulfidation temperature was increased, the low-temperature peak broadened, whereas for the high-temperature peaks the peaks maximum were found to shift to higher temperature by about 200°C as the sulfidation temperature was raised from 350 to 600°C.

Immediately following the low-temperature reduction peak, a negative peak (indicating hydrogen desorption from the surface) was observed for each of the four sulfidation conditions that were studied. Additional experiments revealed that this phenomenon was not restricted to the aforementioned experimental conditions. Temperature-programmed reduction profiles measured for a catalyst that had been prepared by sulfiding at 400°C at heating rates of 2.5 and 10°C min^{-1} or using a reducing gas with a composition of 10% H_2 (balance Ar) also showed the presence of the negative peak. This behaviour was similar to that recently reported for an unsupported MoS_2 catalyst (15).

The low-temperature reduction peak is believed to be associated with the removal of sulfur atoms which are present along the edges of the fully saturated MoS_2 slabs following sulfidation. The high-temperature peaks are believed to be associated with the removal of more strongly bonded sulfur atoms, both along the edges of the slabs and from a progressive removal from the basal plane when the temperature is sufficiently high.

The extent or effectiveness of the reduction was investigated by recording a second TPR profile on a sample which had undergone a previous TPR experiment to 800°C. The second profile was featureless except for a small low temperature peak which may have resulted from a small amount of surface reoxidation while the sample was left overnight under flowing argon between the recording of the two profiles (approximately 14 h).

XPS of Alumina-Supported MoS_2

The X-ray photoelectron experiments were performed on catalysts prepared by sulfiding at 400°C. Figure 2a shows the decomposition by curve fitting of the Mo 3*d* envelope for MoS_2/Al_2O_3 prepared by sulfiding at 400°C. The dominant species is the Mo $3d_{5/2}$ and $3d_{3/2}$ doublet of Mo^{4+}. Small quantities of Mo^{5+} and Mo^{6+}, which result from incomplete sulfiding, were also observed, as has often been reported in the literature (26).

A number of MoS_2/Al_2O_3 samples were reduced in hydrogen at different temperatures from 600 to 850°C and subsequently analyzed using XPS. For the sake of clarity only the more significant spectra will be reported in this work (30). Figure 2 shows the Mo 3*d* region of the spectra for the samples which were sulfided at 400°C and subsequently reduced at 700, 800, and 850°C before analysis. Several observations can be made with regard to the overall appearance and characteristics of the spectra.

TABLE 1

Experimental XPS Data for Reduced MoS_2/Al_2O_3 Catalysts

MoS_2/Al_2O_3	Binding energies (eV)				FWHM (eV)
	Mo $3d_{5/2}$	Mo $3d_{3/2}$	S 2*s*	S 2*p*	Mo 3*d*–S 2*s*
Sulfided at 400°C	228.3	231.2	225.6	161.4[a]	5.2
Reduced at 600°C	228.1	231.0	225.7	161.4[a]	5.6
Reduced at 700°C	228.1	231.0	—	161.3[a]	6.0
Reduced at 800°C	227.5	230.8	—	161.2[a]	6.8
Reduced at 850°C	227.1	230.2	—	161.2[a]	6.9
Reduced at 850°C and exposed to air	231.6	234.5	225.7	161.4 + trace 168.9	5.4

[a] Only one peak observed in the B.E. range 155–175 eV.

Binding energies of the peaks of the Mo 3*d* doublet ($3d_{5/2}$ and $3d_{3/2}$) show a progressive displacement or shift to lower energy as the reduction temperature is increased to 800 and 850°C (Table 1). Such a shift towards lower energy, reaching up to 1 eV, clearly indicates that Mo^{4+} ions have been reduced to give Mo ions with oxidation numbers lower than +4. The shift in the binding energies of the experimental peaks is accompanied by changes in the relative intensities of the two peaks as well as an overall increase in the width of the Mo 3*d* band envelope (Table 1).

From the curve fitting of the Mo 3*d* envelope, the band envelope of the samples which were reduced at a temperature higher than 600°C, (Figs. 2b–2d), were most successfully fit following the addition of an Mo 3*d* doublet corresponding to a reduced molybdenum species of oxidation state less than +4. The Mo 3*d* binding energy of the reduced species was found to be shifted by 1 eV to lower energy than for the Mo^{4+} oxidation number. Precise assignment of an oxidation number proved to be difficult as molybdenum oxidation numbers from zero to 4+ have a Mo 3*d* binding energy level within 1 eV (31–33). According to the results of Hercules and co-workers (31, 32) and Stair (33), the value obtained for the Mo $3d_{5/2}$ binding energy of the reduced species found in this work may correspond to Mo^0. However, Roxlo *et al.* (29) have assigned their reduced Mo species to Mo^{3+} for a binding energy shift of 0.8 eV relative to Mo^{4+}. In addition, Brenner and Burwell (34) have shown that reduction to the metallic state of molybdenum oxide on alumina is strongly inhibited by the presence of hydroxyls on the alumina, necessitating the use of dehydroxylated alumina, which cannot be the case after sulfidation. Therefore the additional peak found in this work is viewed as an indication of presence of a reduced molybdenum species with an oxidation number lower than 4+, symbolized by $Mo^{<4+}$.

At a reduction temperature of 600°C, the intensity of the peak of the $Mo^{<4+}$ is very small and within curve-

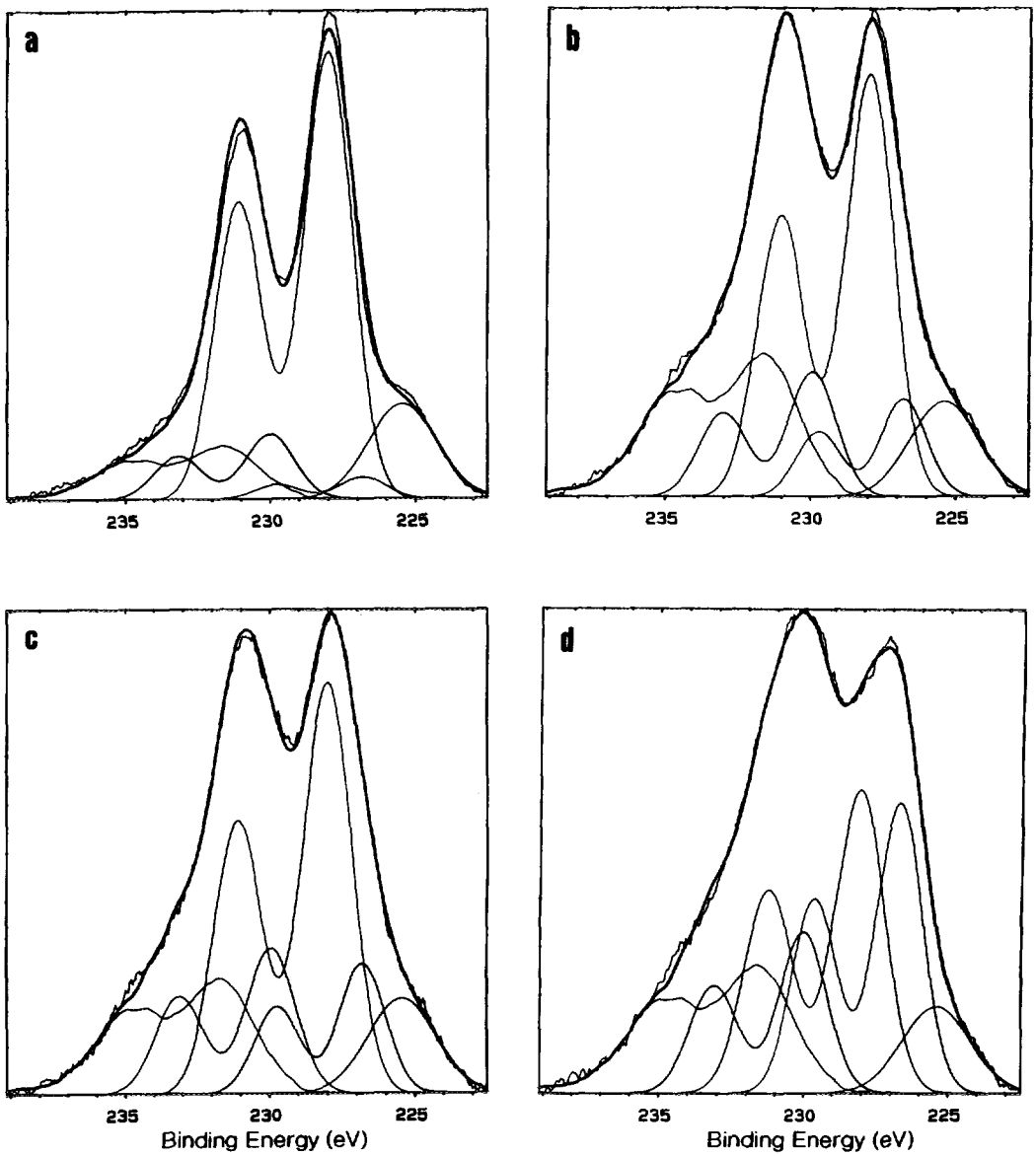

FIG. 2. X-ray photoelectron spectra in the Mo 3*d* region for MoS_2/Al_2O_3 samples prepared by sulfiding at (a) 400°C and subsequently reduced at various temperatures: (b) 700°C, (c) 800°C, and (d) 850°C.

fitting uncertainties. As the reduction temperature was increased, the magnitude of the contribution of the $Mo^{<4+}$ reduced species that was required to optimize the fit to the experimentally measured curves increased. This is reminiscent of the results of Hercules and co-workers (31, 32) for the reduction of the MoO_3/Al_2O_3 system, except that in the present case, significantly higher temperatures are required to effect the reduction of molybdenum, as the starting material, MoS_2, contains mainly Mo^{4+}. It is interesting to note that the increase in the quantity of the $Mo^{<4+}$ reduced species corresponds to a decrease in the quantity of Mo^{4+} used in the curve fitting process (Fig. 3).

It should be noted that this observation does not preclude the existence of reduced Mo under milder reduction conditions, but rather that under these conditions reduced $Mo^{<4+}$ was not detectable using the XPS technique. DeCanio and Storm have recently reported and discussed the detection of reduced Mo as it pertains to their investigations of alkali-promoted MoO_3/Al_2O_3 (35).

The freshly sulfided catalyst showed some evidence for the presence of Mo^{5+} and Mo^{6+} which, as mentioned before, was attributed to incomplete sulfiding (although it appears to be the maximum achievable under the present conditions). For the samples reduced at temperature higher than 600°C, in addition to the reduced Mo species, the samples contained in proportion somewhat larger quantities of Mo^{5+} and Mo^{6+} than did the freshly sulfided sample (Fig. 3). A sample reduced at 850°C and exposed briefly to air (about 2 min) shows drastic changes of the Mo 3*d*–S 2*s* envelope as seen in Table 1. The proportion

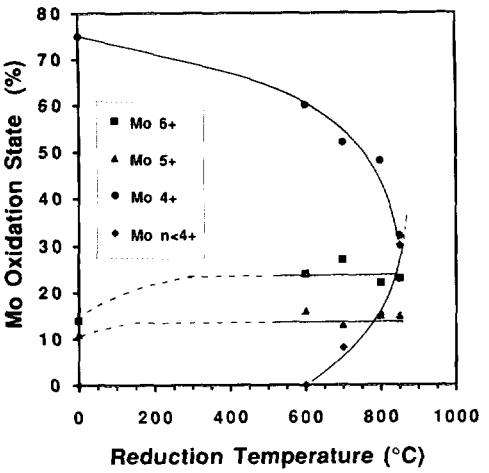

FIG. 3. Distribution of molybdenum oxidation states as a function of reduction temperature for MoS_2/Al_2O_3 prepared by sulfiding at 400°C.

of Mo oxidation number were Mo^{6+} (50%), Mo^{5+} (20%) and Mo^{4+} (30%) with traces of sulfate ions shown by the S 2*p* peak, indicating a large reoxidation of the molybdenum. The increase in the quantity of oxidized molybdenum (oxidation states greater than +4) in samples reduced from 600 to 850°C has been attributed to some reoxidation process that appears to be enhanced by the reductive treatment as shown by Brenner and Burwell for the preparation of metallic molybdenum on alumina from MoO_3/alumina (34). By observing the S 2*p* region, only one peak was detected (Table 1) and assigned to sulfide ion. No detectable sulfate was present on the surface of these catalysts, suggesting that sulfur-deficient exposed molybdenum sites have been reoxidized. All of these observations have also been made for the catalysts that were sulfided at 600°C (30).

Conventional Transmission Electron Microscopy (CTEM) Studies of MoS_2/Al_2O_3

The use of CTEM as an analytical tool for investigating the genesis and morphology of the MoS_2 phase is well documented (10–13). In the present study, CTEM images have been recorded for samples treated at different sulfidation temperatures and different reduction temperatures.

Each of the samples that was studied showed the presence of layered MoS_2 particles on the support following sulfidation at 400, 500, and 600°C. In order to ensure a representative sampling of the catalyst morphology, at least 10 images were recorded per sample and several hundred slabs have been counted and measured. Table 2 shows the average stacking heights and average particle lengths for the samples. Minor differences were observed between the samples. The effect of reducing the sample at 800°C was relatively significant and is large enough to suggest that the slab length has increased by an amount equivalent to the addition of one row of molybdenum atoms. It should also be noted that the present results agree quite well with those found by Portefaix *et al.* for an 11 wt% Mo/Al_2O_3 catalyst sulfided at different temperatures (10).

Temperature-Programmed Desorption Studies

Hydrogen desorption profiles were measured for a series of MoS_2/Al_2O_3 catalysts which had undergone reductive treatment in hydrogen at different temperatures. The same in-line trapping system described for the TPR experiments was used in the TPD experiments to ensure that hydrogen was the only detected species.

Desorption profiles for the sulfided 10.2 wt% Mo/Al_2O_3 catalyst are shown in Fig. 4 for various reduction conditions between 100 and 850°C. In Fig. 4, it can be seen that the reduction temperature affects not only the temperature at which the peaks are observed, but also the peak intensities.

Two main peaks are detected and for clarity, the lower (300–500°C) and higher (500–800°C) temperature peaks will be denoted as Peak I and Peak II, respectively. For the reduction temperature of 100°C, Peak I at ≈270°C is most intense. A peak at ≈500°C (Peak II) is also present as well as a broad band at about 750°C. As the reduction temperature is increased, the features of the peak envelope change gradually. The first thing to note is that the temperature of the peak maximum for Peak I increases gradually to a maximum of 400°C as the reduction temperature increases to 800°C. By contrast, Peak II, centred at 500°C following a reduction at 100°C, remains virtually stationary until a reduction temperature of 400°C is reached. As the reduction temperature is further increased, a monotonic increase in the temperature of the peak maximum for Peak II was observed to a maximum of 880°C for the sample reduced at 800°C.

In addition to the variation in the temperatures of the peak maxima, the intensities of the two peaks were also found to vary. Following an initial increase from 100 to 200°C, the height of peak I subsequently decreases over the remainder of the range of reduction temperatures. The observed behaviour for Peak II is much different as the peak height was found to increase steadily as the reduction

TABLE 2

Stacking Heights and Average Slab Sizes for MoS_2 Supported on Alumina as Determined from Conventional Transmission Electron Microscopy Measurements

Catalyst treatment	Stacking height	Slab length (Å)
Sulfided at 400°C	2.4	38
Sulfided at 400°C/reduced at 400°C	2.0	32
Sulfided at 400°C/reduced at 800°C	1.5	41

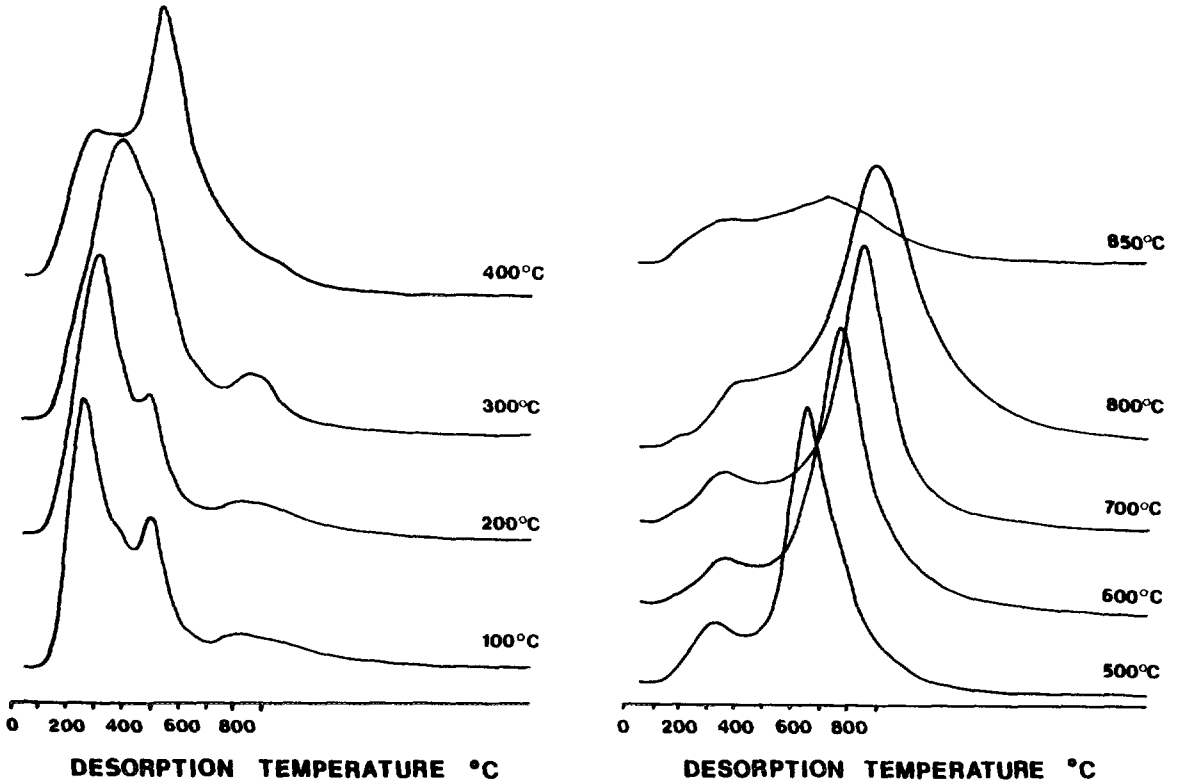

FIG. 4. Temperature-programmed desorption profiles for MoS_2/Al_2O_3 samples prepared by sulfiding at 400°C and subsequently reduced at various temperatures from 100 to 850°C.

temperature increased up to 700–800°C. For the catalysts reduced at 800 and 850°C, the peak height decreased sharply, indicating a loss of surface hydrogen.

In Fig. 5, the quantity of hydrogen detected in the TPD experiments is plotted as the quantity of hydrogen per molybdenum atom (H/Mo) as a function of the reduction temperature. A maximum of H/Mo = 0.64 is found for a reduction temperature of 700°C. Then the amount of desorbed hydrogen decrease sharply to reach a H/Mo = 0.27 at 850°C. The sulfur content of reduced samples have been measured after the TPD experiments and the S/Mo ratio have been computed. Note that after sulfidation only 75% of the total molybdenum content has been sulfided, as shown in Fig. 3, hence the S/Mo ratio of the sulfided phase is underestimated. In Fig. 5, a continuous decrease of the S/Mo ratio is found when the reduction temperature increases with an accelerated decrease for reduction temperatures higher than 600°C, showing that sulfur is removed from the catalyst whereas the hydrogen content increases.

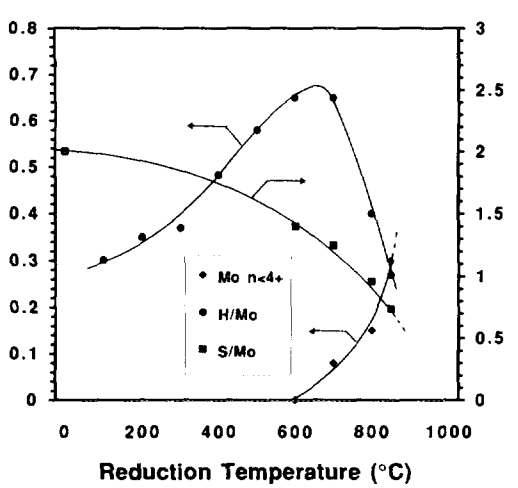

FIG. 5. Plot of S/Mo ratio, H/Mo ratio, and fraction of reduced molybdenum as a function of the reduction temperature for MoS_2/Al_2O_3 prepared by sulfiding at 400°C.

DISCUSSION

The results of the present study indicate that reductive treatment in hydrogen mainly affects the chemical nature of alumina supported MoS_2 whereas the morphological changes are minimal. In particular, it is shown that hydrogen is present on the surface of the MoS_2/Al_2O_3 catalyst as has been demonstrated previously (15–19) and that reduced Mo with an oxidation number lower than 4+ becomes apparent only for reduction temperature higher than 600°C.

In order to address the relationship between XPS and

TPD result, Fig. 5 has been prepared which shows the variation in the S/Mo ratio, the H/Mo ratio, and the quantity of reduced Mo, all as a function of the reduction temperature.

The quantity of hydrogen that can be desorbed from the surface depends strongly on the reduction conditions employed in the pretreatment. In this work a maximum H/Mo = 0.64 is obtained for a reduction temperature of 700–800°C. For a reduction of 500°C for 1 h, we found H/Mo = 0.57, a slightly higher value than the H/Mo = 0.47 determined by Komatsu and Hall (16) from isobars of hydrogen measured on a sulfided MoS_2/Al_2O_3 sample which has not been reduced but heated up to 500°C. Using isoprene as an hydrogen titrating agent, Jalowiecki *et al.* (36) found a similar behaviour for the H/Mo ratio versus reduction temperature but with a maximum value of 1.65. In this latter study, the reduction conditions were more severe with a duration of 12 h in pure hydrogen. To check the effect of the reducing time, the amount of hydrogen desorbed from the MoS_2/Al_2O_3 sample reduced at 700°C for 16 h was determined and found to be 3.6×10^{-4} mol H_2/g (H/Mo = 0.67) compared to 3.45×10^{-4} mol H_2/g (H/Mo = 0.64) for reduction at 700°C for 1 h. In addition, no differences in the shape of the TPD profile were observed. While there is no apparent explanation for this discrepancy, it can be noted that both the hydrogen uptake measurements of Komatsu and Hall and the TPD measurements in this work have the advantage of having no interfering carbonaceous species.

The results of the XPS measurements reported in this study have shown that for the sulfided catalyst there was no evidence for the presence of molybdenum in oxidation states lower than +4 immediately following the sulfidation process. This is not surprising since it is expected that the edge planes of the MoS_2 slabs will be completely saturated with $-SH^-$ groups (S/Mo = 2) under these conditions and that the molybdenum will be in the +4 oxidation state (37). Figure 1b corroborates this point, as the onset of the second reduction peak occurs at approximately 600°C. The low-temperature peak in the TPR profiles is believed to be associated with the removal of nonstoichiometric edge sulfur (23). In accord with Moulijn and co-workers (23), it is believed that this process occurs without reduction of the Mo^{4+} centres, but will be accompanied by the adsorption of hydrogen species.

At reduction temperatures lower than 700°C, no reduction of the Mo^{4+} was observed, but hydrogen species are present in large amounts (H/Mo > 0.3) on the surface and some sulfur has been removed in sufficient quantities (S/Mo change from 2 to 1.4) to require a lowering of the oxidation number of Mo in order to maintain electrostatic neutrality on the slabs. Since reduction of the metal centre does not take place, the charge on the slab must be balanced by a second negatively charged species such as the hydride ion. Assuming that the H_2S formation from the removal of the SH^- groups occurs via a heterolytic mechanism according to

$$*\text{–}SH^- + *\text{–}SH^- \rightarrow *\text{–}S^{2-} + *\text{–}V + H_2S, \qquad [1]$$

with $*\text{–}V$ an empty site, the presence of H^- is readily accounted for if the gaseous hydrogen dissociates heterolytically to produce a H^+ and a H^- according to

$$H_2 + *\text{–}S^{2-} + *\text{–}V \rightarrow *\text{–}SH^- + *\text{–}H^-. \qquad [2]$$

Then SH^- groups along the edge planes can recombined to generate H_2S according to reaction [1]. Hence a process which can be represented by the formal reaction resulting from the sum of reactions [1] and [2],

$$H_2 + *\text{–}SH_e^- \rightarrow *\text{–}H_e^- + H_2S, \qquad [3]$$

with the subscript e standing for edge species. The heterolytic recombination of H_2 from H^- and SH^- (reverse of reaction [2]) is correlated with the low temperature Peak I in the TPD profiles. The decrease in the height of Peak I correlates with a decrease in the number of SH^- groups along the edge planes (decrease of S/Mo) and the increase in the number of hydride ions forming a "surface hydride," i.e., each SH^- group initially present on the surface will be replaced by an H^- according to reaction [3].

The recent ^1H NMR studies of hydrogen on unsupported RuS_2 support this interpretation of heterolytic adsorption mechanism (38). Following a mild reductive treatment, two resonances were observed which were assigned to an acidic proton ($\hat{I}$ = 5.1 ppm) and the hydride ion ($\hat{I}$ = −7.4 ppm). Following a more severe reductive treatment, the downfield peak disappears while the hydride peak remains. This correlates well with our interpretation that a heterolytic process occurs on the MoS_2 surface, both in the low and high temperature regions.

Mo^{4+} ions begin to be reduced at reduction temperatures greater than 700°C (Fig. 5) and in parallel a sharp decrease in the H/Mo ratio is observed. Concomitantly, the S/Mo ratio falls below 1, which indicates that the removal of the edge sulfur is complete and that some removal of sulfur from the basal plane region of the slab has taken place (21, 37). It can be proposed that this reduction correspond to a recombination of two hydride ions according to

$$*\text{–}H^- + *\text{–}H^- \rightarrow 2\,*\text{–}V + H_2 + 2e^- \qquad [4]$$

to form gaseous H_2 and the release of two electrons. The high-temperature Peak II is attributed to this hydrogen desorption.

Thus it is proposed that the reduction by hydrogen of MoS_2 is not a direct process with removal of sulfur in the form H_2S and reduction of Mo ions but that an intermedi-

ary surface hydride state is formed which decomposes at high temperature to generate the reduced Mo ions. The two-step process described above is likely to be too simplified, in particular in the low desorption temperature range where fine structure in the desorption profile seems to exist. Work is in progress to attempt to provide a better description of hydrogen desorption in the low temperature range.

Finally, it is worth pointing out that MoS_2 on alumina appears difficult to reduce significantly. The fact that a high reduction temperature was required to detect some reduction may indicate that at temperatures normally used in hydroprocessing reactions (less than 420°C) only Mo^{4+} is present on the surface. It is not excluded, however, that very low concentrations of $Mo^{<4+}$ ions exist that may have an important catalytic role.

CONCLUSION

The present study has employed a number of surface characterization techniques including TPR, TPD, and XPS to study the distribution of molybdenum oxidation states and the quantity of hydrogen on the MoS_2/Al_2O_3 surface. Temperature-programmed desorption profiles demonstrated that total quantity of hydrogen desorbed from the surface of MoS_2/Al_2O_3 as well as changes in the relative magnitudes of the desorption peaks and the temperatures at which they were observed were sensitive to the temperature of reductive treatment in hydrogen.

When X-ray photoelectron spectroscopy was used, a reduced Mo ($< +4$) was detected only for high-temperature reduction of the catalyst (700°C and greater). The correlation between the H/Mo ratio, the S/Mo ratio, and the quantity of reduced molybdenum as a function of reduction temperature leads to the suggestion that hydride ions generated by heterolytic dissociation are present on the surface. The low-temperature hydrogen desorption peak is assigned to heterolytic recombination of hydrogen, whereas the high-temperature hydrogen desorption peak is assigned to hydride recombination with concomittent reduction of surface Mo^{4+} ions.

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