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TPS, XPS, and QEXAFS Investigation of the Sulfidation Behavior of Tungsten on Fluorine-Promoted Alumina

Mingyong Sun, Thomas Bürgi, Riccardo Cattaneo, and Roel Prins[1]

Laboratory for Technical Chemistry, Swiss Federal Institute of Technology (ETH), 8092 Zurich, Switzerland

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The sulfidation behavior of alumina-supported W catalysts was investigated by means of temperature-programmed sulfidation, quick extended X-ray adsorption fine structure measurements, and X-ray photoelectron spectroscopy of two series of tungsten catalysts, one made from ammonium metatungstate and the other from ammonium tetrathiotungstate. The effect of the fluorination of the alumina support on the sulfidation behavior of W on these two series of catalysts was also studied. The sulfidation of catalysts prepared with ammonium metatungstate passes through intermediates of W oxysulfides; the sulfided catalysts are mixtures of W oxysulfides and WS_2. After sulfidation at 400°C and atmospheric pressure for 4 h, the degree of sulfidation is only about 50%. Fluorination slightly increases the degree of sulfidation. When ammonium tetrathiotungstate is used as the precursor, fully sulfided catalysts can be obtained. Fluorination accelerates the transformation of WS_3 sulfide to WS_2.

Key Words: **TPS; XPS; quick EXAFS; sulfidation; tungsten; hydrotreating; fluorination.**

1. INTRODUCTION

Among hydrotreating catalysts tungsten-based catalysts are well known for their excellent hydrogenation activity (1, 2). However, alumina-supported tungsten catalysts are very difficult to sulfide due to the strong interaction between the tungsten phase and alumina (3–5). The state of sulfidation is an essential factor in the catalytic performance of hydrotreating catalysts. Catalysts prepared from a sulfidic precursor, which are expected to become fully sulfided, have a much higher activity than those prepared from an oxidic precursor (6). The low sulfidability of classical tungsten catalysts and the profound effect of sulfidability on activity indicate the direction that the search for high-activity tungsten catalysts should take.

The importance of sulfidation for hydrotreating catalysts has stimulated extensive investigations of the sulfidation behavior of tungsten catalysts (3–5, 7–10). The incorporation of phosphorus (11) and fluorine (12) into the alumina support favors the formation of polytungstates, making the supported W phase easier to reduce. It has been claimed that, as a consequence, tungsten is easier to sulfide. Benitez *et al.* observed that the fluorination of alumina increases the proportion of WS_2 crystallites, which can be viewed by transmission electron microscopy (TEM), on one hand (13). X-ray photoelectron spectroscopy (XPS) results, on the other hand, showed that F decreased the sulfidability of the tungsten catalyst (14). TEM and XPS are surface-sensitive techniques probing a few surface layers of a catalyst. Temperature-programmed sulfidation (TPS) and quick extended X-ray absorption fine structure (QEXAFS) proved to be powerful techniques in investigating the sulfidation behavior of hydrotreating catalysts (4, 15, 16). In the present work, a systematic investigation of the effects of F on the sulfidation of alumina-supported tungsten catalysts was performed by means of TPS, XPS, and QEXAFS.

2. EXPERIMENTAL

Catalyst Preparation

Catalysts were prepared by means of the incipient wetness impregnation method. Pellets γ-Al_2O_3 (Condea, surface area 228 m^2/g, pore volume 0.49 ml/g) were milled and sieved to a particle size of 0.05 to 0.1 mm. Fluorided alumina (Al_2O_3F) was prepared by impregnating γ-Al_2O_3 with a 0.8 M aqueous solution of ammonium fluoride, followed by drying at 120°C for 4 h and calcination at 500°C for 4 h. The resulting fluoride content was 1 wt%. To obtain WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts, the Al_2O_3 and Al_2O_3F were impregnated with a 0.07 M aqueous solution of ammonium metatungstate, followed by drying at 120°C for 4 h and calcination at 500°C for 4 h.

Fully sulfided catalysts were prepared from ammonium tetrathiotungstate ($(NH_4)_2WS_4$, ATT), which was synthesized according to the procedure described by Ramanathan and Weller (17). ATT/Al_2O_3 and ATT/Al_2O_3F catalysts were prepared by impregnating the dried Al_2O_3 and Al_2O_3F with a 0.83 M *N*,*N*-dimethylformamide solution of ATT under protection of argon. After impregnation, ATT/Al_2O_3

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[1] To whom correspondence should be addressed. Fax: 41-1-6321162. E-mail: prins@tech.chem.ethz.ch.

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and ATT/Al$_2$O$_3$F were dried at room temperature in a vacuum desiccator. The tungsten loading of all the catalysts was 10 wt%.

TPS Measurements

The technique and equipment used for TPS measurements were developed and used extensively by Moulijn and co-workers (4, 5, 8). The catalysts were sulfided in a quartz reactor with a mixture of H_2S, H_2, and Ar (3, 25, and 72 vol%, respectively) at a total flow rate of 0.12 mol/h. Since the sulfidation temperature of the catalysts used in the hydrodenitrogenation of toluidine was 400°C (6), one of the aims of this study was to determine the degree of sulfidation at 400°C. To determine the amount of W sulfided at this temperature, a period of 4 h of isothermal sulfidation at 400°C was added to the usual continuous temperature program during TPS. After 0.5 h at room temperature, the samples were heated to 400°C (10°C/min) and kept at this temperature for 4 h. After 4 h of isothermal sulfidation at 400°C, the temperature was increased to 1000°C, and the sample was kept at this temperature for 1 h to complete sulfidation. The changes in the concentration of H_2 and H_2S were recorded with a thermal conductivity detector and an UV detector, respectively.

XPS Measurements

The samples were first sulfided under the conditions that were used for the activity tests (400°C, 1.5 MPa, 4 h) (6). Then, the sulfided samples were kept under protection of Ar. Before the XPS measurements, the samples were ground and pressed onto a stainless steel sample holder in air; the holder was immediately mounted onto the XPS machine. The time of exposure of the sample to air was less than 3 min. Ng and Hercules (3) found no change in the W^{4+} XPS signal after their sulfided sample had been exposed to air for 2 days, indicating that WS_2 is stable in air.

The XPS measurements were performed at room temperature using a Leybold Heraeus LHS11 apparatus equipped with a Mg source (1253.6 eV) and operating at 240 W. The spectrometer energy scale was calibrated using the Au($f_{7/2}$), Ag(3$d_{5/2}$), and Cu(2$p_{3/2}$) lines at 84.2, 367.9, and 932.4 eV, respectively. Spectra were recorded at a constant pass energy of 31.5 eV. Sample charging was compensated using the Al(2p) line of Al_2O_3 at 74.7 eV as an internal standard (18). The background was subtracted according to the method of Shirley (19), and quantification was performed using the sensitivity factors reported by Wagner *et al.* (20). For quantification of the W^{4+} and W^{6+} species, the W(4f) spectrum was deconvoluted by fitting the experimental spectrum to mixed Gaussian–Lorentzian functions with a Lorentzian fraction of 70 to 80%. For the fit, the $I(W(4f_{7/2}))/I(W(4f_{5/2}))$ ratio of the integrated intensities was kept at 4/3.

QEXAFS Measurements

The quick EXAFS measurements were carried out at the X1 (RÖMO II) beamline of HASYLAB (Hamburg, Germany), which was equipped with a monochromator with a pair of Si(111) crystals to measure the W L_{III} edge. The k range used for the analysis of the data was 3 to 14 Å^{-1}. The catalyst samples were pressed into self-supporting wafers and placed in an *in situ* EXAFS cell. After two spectra of the original samples in a He atmosphere were collected, the samples were sulfided *in situ* during data collection. A 60 ml/min stream of 10% H_2S in H_2 flowed through the cell while the sample was heated to 400°C at a rate of 3°C/min. The sample was then kept at 400°C for 30 min. Each EXAFS scan took 6 min, which corresponded to a temperature interval of 18°C during the temperature ramp.

The XDAP program (version 2.2.2) was used to analyse and process the data (16, 21). The pre-edge background was approximated by a modified Victoreen function, and the background was subtracted using a cubic spline routine. The spectra were normalised by the edge jump. The k^3-weighted EXAFS functions were Fourier transformed.

3. RESULTS

TPS Measurements

Figure 1 shows TPS patterns of the WO_3/Al_2O_3, WO_3/Al_2O_3F, ATT/Al$_2$O$_3$, and ATT/Al$_2$O$_3$F catalysts. For each

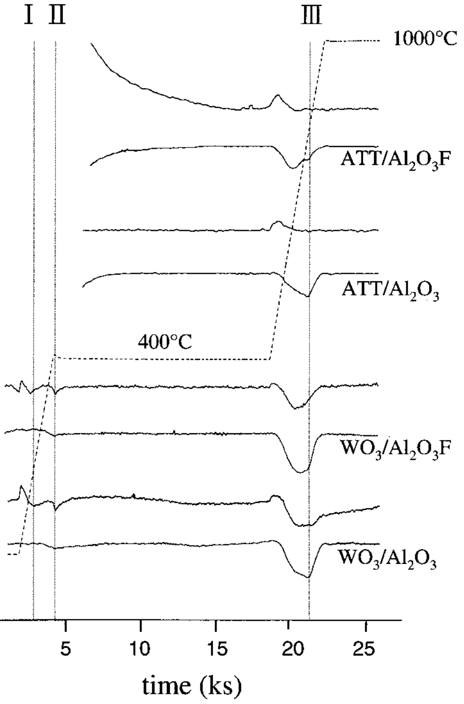

FIG. 1. TPS patterns of the WO_3/Al_2O_3, WO_3/Al_2O_3F, ATT/Al$_2$O$_3$, and ATT/Al$_2$O$_3$F catalysts with isothermal sulfidation at 400°C. The temperature program is indicated by the dashed line.

catalyst, the lower signal represents the change in the H_2 concentration of the effluent stream of the reactor and the upper signal the change in the H_2S signal. Negative peaks correspond to consumption and positive peaks to production of either H_2S or H_2. At the beginning of the temperature program, a small positive H_2S peak was recorded, which is due to the desorption of the adsorbed H_2S. The H_2S may desorb from both the W phase and the Al_2O_3; however, for the convenience of comparison the H_2S desorption is normalized to moles of tungsten on the catalysts. The amount of desorbed H_2S is about 0.15 mol/mol of W for the WO_3/Al_2O_3 catalyst and 0.074 mol/mol of W for the WO_3/Al_2O_3F catalyst. During the course of sulfidation, three H_2S consumption peaks were recorded for the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts (peaks I, II, and III, respectively). The three vertical lines in Fig. 1 indicate the maximum of the peaks for the WO_3/Al_2O_3 catalyst. Since there is no consumption of H_2 corresponding to the first H_2S consumption peak, this peak is due to the formation of W^{6+} oxysulfides by exchange of S for O without reduction of W. The amount of H_2S consumed in this process corresponds to $S/W = 0.13$ for the WO_3/Al_2O_3 catalyst and 0.16 for the WO_3/Al_2O_3F catalyst. The second H_2S uptake process starts at around 320°C for both WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts. The rate of H_2S uptake increases with temperature until the isothermal stage at 400°C. H_2 consumption is observed, which parallels the second H_2S consumption. The ratio of consumed H_2S to H_2 corresponding to peak II is about 5.0 for both WO_3/Al_2O_3 and WO_3/Al_2O_3F (Table 1). During the isothermal period at 400°C, the sulfidation proceeds very slowly, with hardly any changes in H_2 and H_2S concentrations. A further increase in temperature accelerates sulfidation. However, prior to the consumption of H_2S, production of a small amount of H_2S is observed upon increasing the temperature. This indicates that a small amount of H_2S is chemically adsorbed on the catalysts at 400°C, which can be removed by increasing the temperature. H_2S consumption above 400°C is accompanied by H_2 consumption. The amounts of H_2S and H_2 that are consumed in this temperature range are given in Table 1 (peak III); their ratio is 2.0 for the WO_3/Al_2O_3 catalyst and 1.6 for the WO_3/Al_2O_3F catalyst.

TABLE 1

Consumption of H_2S and H_2 in the TPS Measurements

	Peak I mol/mol of W H_2S/H_2	Peak II mol/mol of W H_2S/H_2	Peak III mol/mol of W H_2S/H_2
WO_3/Al_2O_3	0.13/0	0.15/0.03	1.13/0.57
WO_3/Al_2O_3F	0.16/0	0.13/0.03	1.02/0.64
ATT/Al_2O_3			0/0.34
ATT/Al_2O_3F			0/0.19

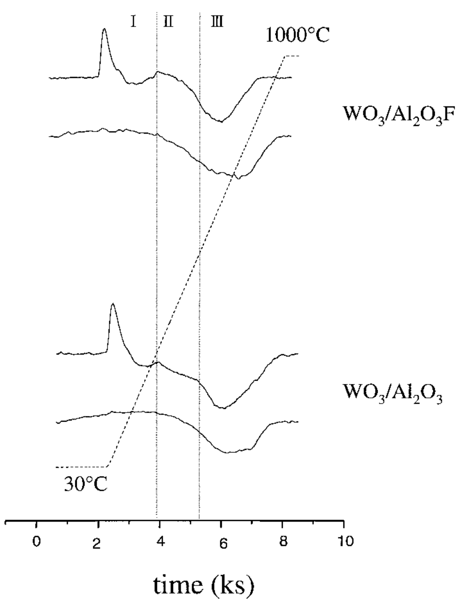

FIG. 2. TPS patterns of the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts without isothermal sulfidation.

For the ATT and ATTF catalysts, the production of a large amount of H_2S (out of recording range), accompanied by the consumption of a large amount of H_2, is observed at the beginning of the temperature program due to the decomposition of ammonium tetrathiotungstate. Both the H_2S and the H_2 signals return to the baseline after 3 h of isothermal treatment at 400°C. When the temperature is increased further, a small amount of H_2S is produced due to the removal of chemically adsorbed H_2S at 400°C, as is the case for the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts. No H_2S consumption was observed, in contrast to H_2 consumption for both catalysts. The H_2 consumption reaches a maximum at around 750°C for the ATT catalyst and at around 650°C for the ATTF. The amounts of the consumed H_2 for the ATT and ATTF catalysts in this temperature range are given in Table 1.

Figure 2 shows the TPS patterns of the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts obtained with a continuous temperature program without the isothermal sulfidation stage. According to the rate of H_2S consumption, the sulfidation process is divided into three stages. The first stage is up to 320°C. At this stage, sulfidation proceeds slowly without H_2 consumption. Above this temperature, the rate of H_2S consumption increases continuously with temperature, and there is a parallel H_2 consumption. Above 520°C, the sulfidation rate is accelerated and a broad maximum in the rate of H_2 and H_2S consumption is observed at about 750 to 800°C. The total amounts of consumed H_2 and H_2S for both catalysts are 1.8 mol of H_2S and 0.94 mol of H_2 per mol of W, which indicates that almost all the W on the catalysts has been converted to WS_2 upon sulfidation at 1000°C.

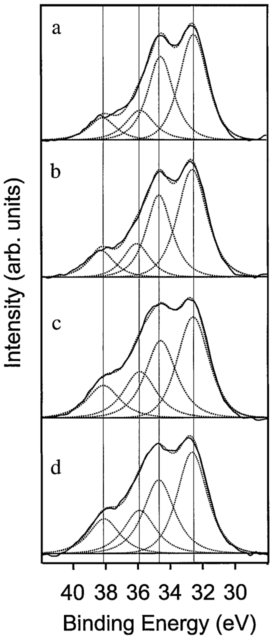

FIG. 3. W(4*f*) XPS of sulfided ATT/Al_2O_3 (a), ATT/Al_2O_3F (b), WO_3/Al_2O_3 (c), and WO_3/Al_2O_3F (d) (sulfided at 400°C and 1.5 MPa for 4 h with 10% H_2S in H_2).

XPS Measurements

Figure 3 shows the W(4*f*) XP spectra of the WO_3/Al_2O_3, WO_3/Al_2O_3F, ATT, and ATTF catalysts sulfided for 4 h at 400°C and 1.5 MPa. Each spectrum consists of two partially overlapping doublets, as indicated by the individual peaks obtained from the fit. Table 2 summarises the surface concentrations of F, S, and W relative to Al. The ratio of W^{4+} to the total amount of W is also given. It should be noted that the $4f_{5/2}$ line of W^{6+} overlaps with the weak $5p_{3/2}$ line of W^{4+}. Consideration of this signal could lead to an increase of the W^{4+} fraction given in Table 2 by at most 5%. The binding energies of the W($4f_{7/2}$) and W($4f_{5/2}$) levels are around 32.6 and 34.6 eV, respectively, for W^{4+} and 35.9 and 38.1 eV, respectively, for W^{6+}. As can be seen from Table 2, the W/Al ratio is a little lower for the ATT samples, whereas fluorination does not affect the W/Al ratio. The fraction of W^{4+} is slightly below 80% for the ATT samples and slightly below 70% for the other two samples. The influence of fluorine on the W^{4+} fraction is only marginal, the W^{4+} fraction being slightly lower for the fluorinated samples. The S/W^{4+} ratio is similar for all four samples and larger than 2, whereas the ratio of S to the total amount of W is close to 2.

TABLE 2

XPS Results of the Sulfided Catalysts

	ATT/Al_2O_3	ATT/Al_2O_3F	WO_3/Al_2O_3	WO_3/Al_2O_3F
F/Al	—	0.087	—	0.093
S/Al	0.046	0.046	0.050	0.047
W/Al	0.021	0.021	0.026	0.027
W^{4+}/W	0.79	0.77	0.69	0.68
S/W	2.19	2.19	1.92	1.74
S/W^{4+}	2.77	2.84	2.79	2.56

Note. Sensitivity factors: Al(2*p*), 0.185; S(2*p*), 0.54; F(1*s*) 1.00; W(4*f*), 2.75.

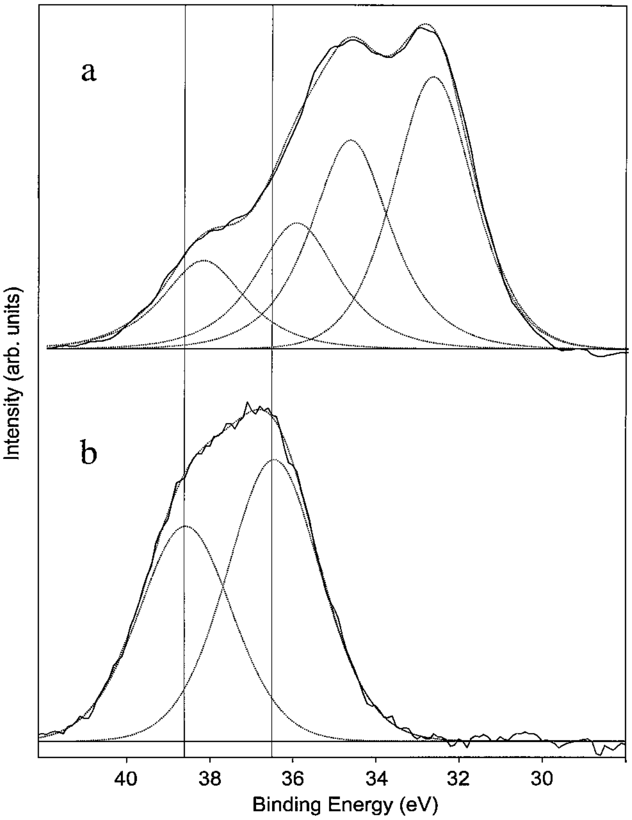

FIG. 4. W(4*f*) XPS of sulfided WO_3/Al_2O_3 (a) and original oxidic WO_3/Al_2O_3 (b).

Figure 4 shows the XP spectra of the WO_3/Al_2O_3 catalyst before and after sulfidation. As indicated by the fit, the W^{6+}(4*f*) binding energy is about 0.4 eV less for the sulfided sample. This implies that at least some of the W^{6+} in the sulfided sample is different from that in the original WO_3/Al_2O_3. For both fluorinated samples the binding energy of the F(1*s*) level is 685.5 eV, which is within the 685.2- to 685.9-eV range reported for F^- on alumina (14). The binding energy of the S(2*p*) level is 162.2 to 162.3 eV for all samples, indicative of S^{2-} and close to the value reported for WS_2 (18).

EXAFS Measurements

Figure 5 presents the Fourier-transformed $\chi(k) \cdot k^3$ W L_{III}-edge QEXAFS spectra of the WO_3/Al_2O_3 catalyst. The first spectrum was collected for the untreated sample, and the others were obtained during its sulfidation. The

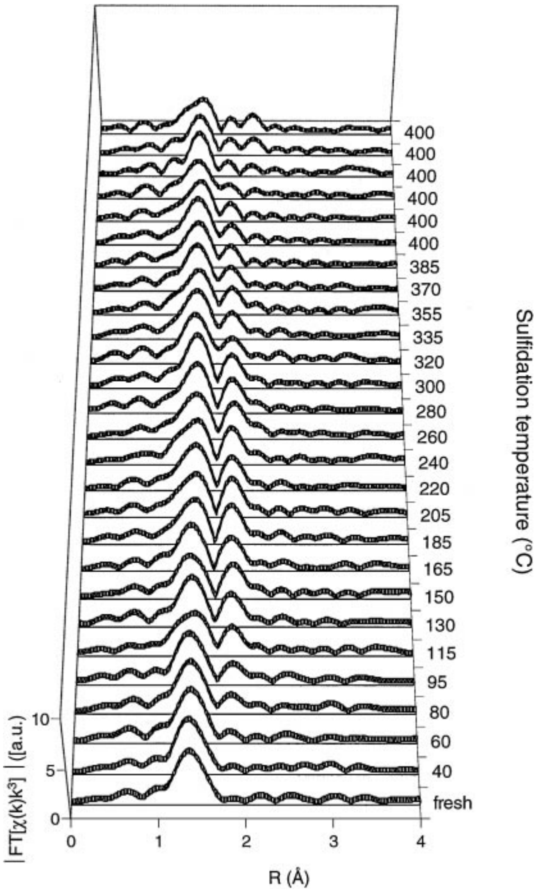

FIG. 5. Fourier transforms of the W L_{III} edge k^3-weighted Quick EXAFS functions measured during the sulfidation of the WO_3/Al_2O_3 catalyst.

numbers next to the spectra denote the average temperatures in °C during the scans. The first spectrum has only one pronounced signal (between 0.8 and 1.7 Å, not phase corrected) due to the W–O contribution. This signal remains even after sulfidation at 400°C for 30 min (the last spectrum). A signal between 1.9 and 2.3 Å (not phase corrected) appears upon sulfidation at 400°C for about 15 min (see the last three spectra). This peak is at the same distance as that in WS_2 (22), and its appearance indicates the formation of WS_2. As well as the W–O and the WS_2 signals, another signal is observed between 1.7 and 2.0 Å (not phase corrected), which appears at about 80°C and increases in intensity with sulfidation temperature until around 300°C and then decreases at higher sulfidation temperatures. This peak is at the same position as the peak observed in the spectrum of the untreated ATT catalyst (Fig. 6) and is attributed to sulfur atoms in the first-coordination sphere of W^{6+}. This reveals that the sulfidation of WO_3/Al_2O_3 to WS_2/Al_2O_3 passes through an intermediate containing W^{6+} and S.

In the series of spectra that were collected during the sulfidation of the ATT catalyst (Fig. 6), the signal due to sulfur around W^{6+} (between 1.7 and 2.0 Å, not phase corrected) decreases with the sulfidation temperature and disappears at around 300°C when the WS_2 signal (between 1.9 and 2.3 Å, not phase corrected) appears. The WS_2 signal increases in intensity with the sulfidation temperature, and it is well developed in the last spectrum, indicating that WS_2 is the major species after 30 min of sulfidation at 400°C. The small shoulder at the shorter distance side of the WS_2 signal is probably due to a W–S coordination in which W remains at a higher oxidation state than W^{4+}. In the last spectrum of the ATT catalyst, there are a few W–W signals around 3.2 Å (not phase corrected) (22), which are not present in the spectra for the WO_3/Al_2O_3 catalyst sulfided at 400°C. From 100 to 370°C, there is a peak at around 1.3 Å (not phase corrected), indicating the formation of W–O bonds. However, no W–O contribution is observed in the spectra of the ATT catalyst sulfided at 400°C, which confirms that a fully sulfided alumina-supported tungsten catalyst can be obtained from the thiotungstate precursor.

The spectra of the F-containing catalysts (Figs. 7 and 8) show a significant difference compared with those of the nonfluorine counterparts. For the WO_3/Al_2O_3F catalyst, the

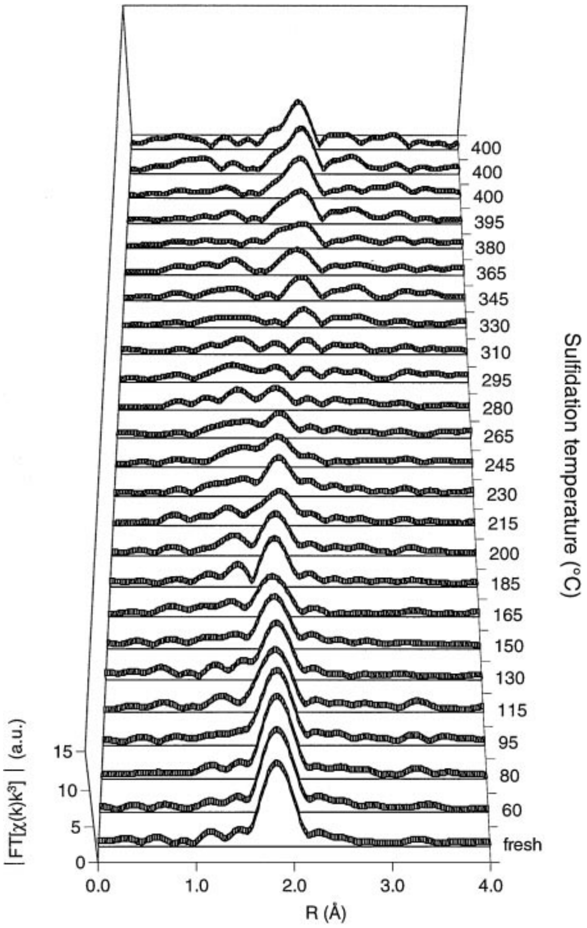

FIG. 6. Fourier transforms of the W L_{III} edge k^3-weighted Quick EXAFS functions measured during the sulfidation of the ATT/Al_2O_3 catalyst.

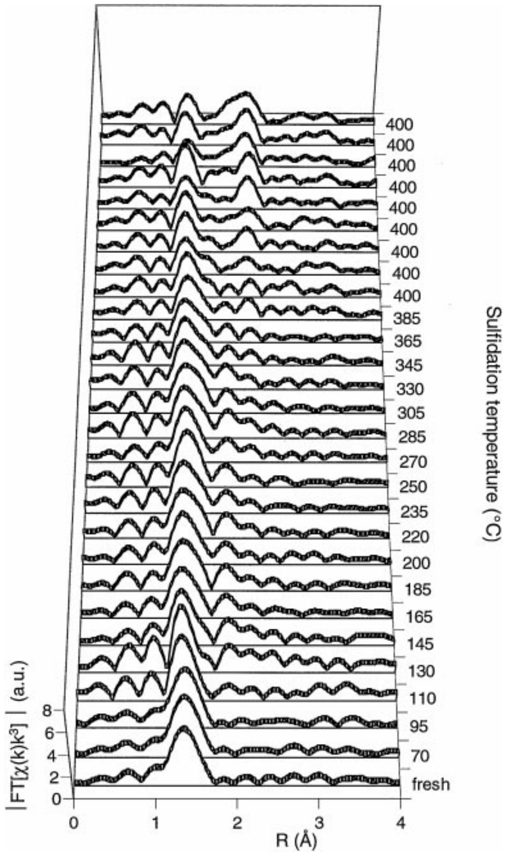

FIG. 7. Fourier transforms of the W L_{III} edge k^3-weighted Quick EXAFS functions measured during the sulfidation of the WO_3/Al_2O_3F catalyst.

W–O contributions decrease more strongly, although they still remain after sulfidation at 400°C for 30 min. The intermediate signal (between 1.7 and 2.0 Å, not phase corrected) is not as significant as that in the spectra of the WO_3/Al_2O_3 catalyst and it is not detectable below 100°C. The WS_2 peak appears earlier and is stronger than that in the spectra of the WO_3/Al_2O_3 catalyst. In the spectra of the WO_3/Al_2O_3F catalyst, the presence of W–W contributions (around 3.2 Å, not phase corrected) are also seen, indicating that F aids the growth of WS_2. Compared with the spectra of ATT, the main difference in the spectra of ATTF is that the WS_2 signal appears much earlier and is much sharper, and it is already observed, even below 200°C. The ATTF sample also shows W–O contributions between 100 and 370°C.

4. DISCUSSION

The TPS, XPS, and QEXAFS results confirm that it is very difficult to complete the sulfidation of alumina-supported tungsten catalysts prepared from oxidic precursors. Sulfidation at 400°C for 4 h results in the partial sulfidation of W because significant amounts of H_2S and H_2 are still required for complete sulfidation at higher temperature (Fig. 1). XPS measurements (Table 2) show that, on the surface of the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts sulfided at 400°C, the fraction of W^{4+} is below 70%. QEXAFS spectra of the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts (Figs. 5 and 7) reveal that there is still a significant amount of oxygen in the first-coordination shell of W after 30 min of sulfidation at 400°C, despite the W–S contributions.

Three major peaks are seen in the QEXAFS spectra of the WO_3/Al_2O_3 catalyst sulfided at 400°C, which are attributed to W^{6+}–O (between 0.8 and 1.7 Å), W^{6+}–S (between 1.7 and 2.0 Å), and W^{4+}–S (between 1.9 and 2.3 Å) contributions. The fact that the S/W^{4+} ratio of normally sulfided catalysts is higher than 2 (Table 2) also indicates that some of the sulfur is in a form other than WS_2. It can be seen in Fig. 4 that the $W^{6+}(4f)$ binding energy is about 0.4 eV lower for the sulfided sample. This means that even though some tungsten remains in the 6+ state after sulfidation at normal conditions (400°C, 4 h), its chemical environment has changed. In general, the binding energy increases with increasing oxidation state, and for a fixed oxidation state it increases with the electronegativity of the ligands. The shift in the $W^{6+}(4f)$ binding energy of the sulfided sample

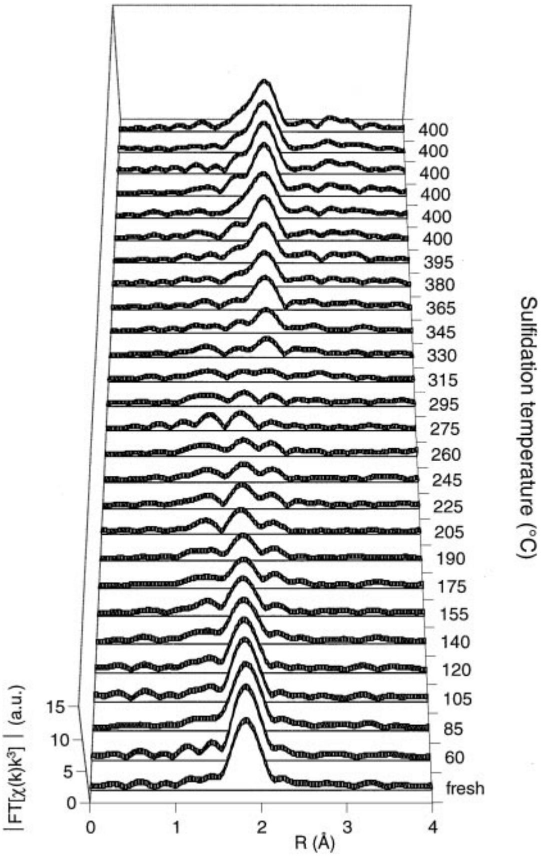

FIG. 8. Fourier transforms of the W L_{III} edge k^3-weighted Quick EXAFS functions measured during the sulfidation of the ATT/Al_2O_3F catalyst.

is due to the replacement of oxygen by sulfur. Therefore, in the WO_3/Al_2O_3 catalyst sulfided at 400°C, there is a mixture of $WO_{3-x}S_x$ and WS_2. If all the W^{4+} ions in the sulfided catalysts are in the form of WS_2, then it can be calculated from the surface concentrations of S, W^{4+}, and W^{6+}, measured by XPS (Table 2), that the W^{6+} and the remaining sulfur on the surface have the following stoichiometry: $WO_{1.2}S_{1.8}$ for the WO_3/Al_2O_3 catalyst and $WO_{1.8}S_{1.2}$ for the WO_3/Al_2O_3F catalyst. The fact that there is less sulfur in the tungsten oxysulfides on the WO_3/Al_2O_3F catalyst sulfided at 400°C is consistent with the fact that no significant W^{6+}–S contribution for the WO_3/Al_2O_3F catalyst sulfided at 400°C was observed in the QEXAFS spectra (Fig. 7). To better understand the structure of the sulfided catalysts, a more detailed investigation is necessary. A classical EXAFS study will enable the quantitative evaluation of the difference between the sulfided catalysts; this will be included in a future study.

From the continuous TPS measurements of the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts (Fig. 2), it was observed that the sulfidation rate increases significantly above 520°C, reaching a maximum at about 750°C, and that sulfidation is completed above 920°C. The degree of sulfidation of W in a catalyst sulfided at 400°C for 4 h cannot be determined from these TPS results. However, it is possible to determine it from the modified TPS measurements, which include a period of 4 h of isothermal sulfidation (Fig. 1). Sulfidation proceeds very slowly below 400°C, with very little consumption of H_2S and H_2 during isothermal sulfidation at 400°C. Thus, it is difficult to accurately determine the amount of H_2S consumed during sulfidation at this temperature. On the other hand, the modified TPS measurements give a well-defined H_2S consumption peak at elevated temperature with a maximum between 750 and 800°C (Fig. 1). Therefore, it is possible to accurately calculate the amount of H_2S consumed above 400°C, which is 1.13 and 1.02 mol of H_2S/mol of W for the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts, respectively. Because sulfidation is completed at 1000°C and transformation of 1 mol of W to WS_2 requires 2 mol of H_2S, the degree of sulfidation after sulfidation at 400°C for 4 h is calculated as

$$\mathrm{SD} = \frac{2 - \mathrm{H_2S(III)}}{2} \times 100\%,$$

where SD is the degree of sulfidation achieved after sulfidation at 400°C for 4 h and $H_2S(III)$ is the amount of H_2S corresponding to peak III in Fig. 1. Thus, the degree of sulfidation is 44% for the WO_3/Al_2O_3 catalyst and 49% for the WO_3/Al_2O_3F catalyst. According to this result, the addition of F slightly improves the degree of sulfidation of W.

The continuous TPS measurements (Fig. 2) show that the total amount of H_2S consumed during sulfidation up to 1000°C is close to 2 mol of H_2S per mol of W. Thus, the sum of H_2S consumed at different periods during the modified TPS measurements (Fig. 1) should be close to 2 mol of H_2S per mol of W. The sum of the amounts of H_2S corresponding to peak I, peak II, and peak III (Table 1) is 1.41 mol of H_2S per mol of W for the WO_3/Al_2O_3 catalyst and 1.31 mol of H_2S per mol of W for the WO_3/Al_2O_3F catalyst. Therefore, the amount of H_2S consumed at 400° during isothermal sulfidation should be 0.59 mol of H_2S per mol of W for the WO_3/Al_2O_3 catalyst and 0.69 mol of H_2S per mol of W for the WO_3/Al_2O_3F catalyst. This result suggests that fluorination accelerates the isothermal sulfidation at 400°C and that isothermal sulfidation contributes about 70% to the total degree of sulfidation achieved after sulfidation at 400°C for 4 h.

Sulfidability has also been defined as the fraction of W^{4+} (W^{4+}/W) measured by XPS (3, 14). Table 2 gives this sulfidability of the four catalysts after sulfidation at 400°C, 1.5 MPa for 4 h. The sulfidability of the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts measured by XPS is higher (69 and 68%, respectively) than that derived from TPS measurements (44 and 49%, respectively). This discrepancy is attributed to differences in the experimental methods and sulfiding conditions. XPS can only measure the concentration of W on the catalyst surface, while TPS reflects the sulfidation behavior of the bulk. The samples used in the XPS measurements were sulfided at 400°C and 1.5 MPa, which are the conditions used in the activity test (6), while TPS measurements were performed at atmospheric pressure. According to the XPS definition, adding F slightly decreases the sulfidability of W. A similar result was observed by Benitez *et al.* (14). This result seems to contradict the results derived from TPS and QEXAFS measurements. After sulfidation at 400°C for 30 min, the F-containing sample has a more pronounced WS_2 QEXAFS signal (Fig. 7) than the sample without fluorine (Fig. 5). Considering that XPS is a surface-sensitive technique, the smaller fraction of W^{4+} in the WO_3/Al_2O_3F sample compared to that of the WO_3/Al_2O_3 sample can be attributed to the poor dispersion of WS_2. In the QEXAFS spectra of the F-containing sample that was sulfided at 400°C, a W–W contribution was observed (Fig. 7) while there did not seem to be a W–W contribution in the spectra of the sample without fluorine, which was sulfided at 400°C (Fig. 5). This means that the fluorination contributes to the increase in the diameter of the WS_2 particles or that the WS_2 structure on the WO_3/Al_2O_3F catalyst is better defined than that on the WO_3/Al_2O_3 catalyst. This observation is consistent with the HRTEM observation by Benitez *et al.* that fluorination favors the formation of larger WS_2 crystals and higher stacking (13).

The W^{4+} fraction on the surface of the sulfided ATT and ATTF samples is 79 and 77%, respectively. Although no H_2S consumption was observed in the TPS measurements of the ATT and ATTF catalysts (Fig. 1), H_2 consumption above 400°C was recorded for both catalysts. The maximum of the H_2 consumption peak for the ATT catalyst is between 750 and 800°, as is also the case for the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts. This indicates that there is still some W at high oxidation states (5+ or 6+) on the ATT catalyst after sulfidation at 400°C, although it is in a sulfided state. The XPS and TPS results are in good agreement on this point. H_2 consumption reaches a maximum at a lower temperature (about 650°C) on the ATTF catalyst. This indicates that the W species, other than WS_2 on the ATTF catalyst, is also affected by F and that F makes it easier to transform this W species to WS_2 during sulfidation at higher temperature.

Walton and Hibble studied the thermal decomposition of $(NH_4)_2WS_4$ in dry nitrogen (23). They observed that when the temperature was increased at 1°C/min, the crystalline starting material had decayed completely by 180°C and that there were no sharp XRD features until 315°C when poorly crystalline WS_2 features appeared. The QEXAFS spectra of the ATT catalyst (Fig. 6) show that the alumina-supported $(NH_4)_2WS_4$ decomposes completely at around 300°C and that, at the same time, the WS_2-like structure forms. For the ATTF catalyst, WS_2 appears at a temperature lower than 200°C, although the decomposition is still complete only at about 300°C. This means that F accelerates the transformation of $(NH_4)WS_4$ to WS_2 (Fig. 8). During the decomposition of the supported $(NH_4)_2WS_4$ some kind of W–O coordination forms between 100 and 370°C (Figs. 6 and 8). This is probably due to a reaction of W species with the alumina hydroxyl groups. Nevertheless, the QEXAFS spectra show that WS_2 is the major species and that there is no W–O coordination on the ATT and ATTF catalysts sulfided at 400°C. We, therefore, conclude that this W–O linkage is not as strong as that in the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts and that it can be transformed to W–S coordination in the presence of H_2S and H_2 at 400°C.

Furthermore, the W–W signal is more pronounced in the spectra of the ATT and ATTF catalysts sulfided at 400°C than in the spectra of the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts. This means either that the size of the WS_2 particles is larger or that the WS_2 structure is better developed on the ATT and ATTF catalysts than on the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts sulfided at 400°C. Ramirez *et al.* observed that the WS_2 structures in their NiW catalysts prepared from thiosalt had a higher stacking than the catalysts prepared from the oxysalt and that fluorination of the alumina support resulted in larger crystallites (24). They also found that the fraction of the tungsten atoms in the WS_2 structures observed on the catalyst made from thiosalt was about 83%, larger than the fraction of 46% for the catalyst made from oxysalt.

Reinhoudt *et al.* observed that, depending on the calcination temperature, surface species of different sizes are formed. A high calcination temperature favored the formation of small subnanometer and nanometer particles but not the formation of WS_2 slabs (25). This is because high-temperature calcination aids the formation of W–O–Al linkages (4). In the case of our catalysts, WO_3/Al_2O_3 and WO_3/Al_2O_3F were calcined at 500°C; the calcination step was omitted for the ATT and ATTF catalysts. Consequently, the weaker interaction of the W species with the alumina leads to the formation of larger WS_2 particles in the ATT and ATTF catalysts. The effect of fluorination on the particle size of WS_2 can also be interpreted by assuming that fluorination weakens the interaction of the W species and the alumina. The hydroxyl groups on the alumina are replaced by F^- anions, and this reduces the possibility of the formation of linkages between the W species and the alumina. Therefore, the W species on the fluorinated alumina have less interaction with the support, and the final WS_2 particles have a higher stacking and a larger particle size.

Sulfidation of WO_3/Al_2O_3 and WO_3/Al_2O_3F passes through three stages (Fig. 2). In the first stage the H_2S consumption does not have a corresponding H_2 consumption. This is due to the exchange of S from H_2S with the terminal oxygen of the W species on the catalysts, which can be expressed by the following equation:

$$WO_3 + xH_2S \rightarrow WO_{3-x}S_x + xH_2O. \quad [1]$$

It was reported that the surface of a WO_3/Al_2O_3 catalyst with a loading below 15% WO_3 consists exclusively of tetrahedrally coordinated WO_4^{2-} interaction species (26). Since the W–S distance in $WO_{3-x}S_x$ is the same as that in the untreated ATT catalyst (Figs. 5 and 6), the W–S coordination in $WO_{3-x}S_x$ should have a similar W=S structure as that in $(NH_4)WS_4$. Therefore, Eq. [1] might apply as shown in Fig. 9.

In the QEXAFS spectra of the WO_3/Al_2O_3 catalyst, the intermediate signal (between 1.7 and 2.0 Å, Fig. 5) appears at about 80°C, and its intensity increases with sulfidation temperature until around 300°C when it decreases. At the second stage of the sulfidation of the WO_3/Al_2O_3 catalyst, H_2S consumption is paralleled by H_2 consumption (Fig. 2). These two observations indicate that another process starts at about 300°C, which can be expressed as

$$WO_{3-x}S_x + H_2 + (2-x)H_2S \rightarrow WS_2 + (3-x)H_2O. \quad [2]$$

Sulfidation is usually carried out at 400°C or below. When the temperature was halted at 400°C, the sulfidation rate decreased (cf. Figs. 1 and 2). During the 400°C isothermal sulfidation period, sulfidation proceeded at such a low rate that hardly any consumption of H_2S or H_2 was detected

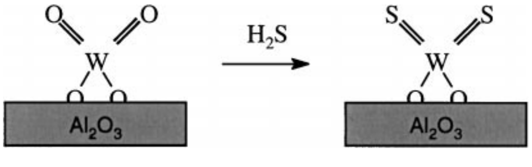

FIG. 9. Scheme of the exchange of S of H_2S with O of the W species on the catalyst surface.

(Figs. 1 and 2), although the WS_2 structure was developing (Figs. 5 and 7). After the temperature was increased, sulfidation accelerated again. It is very possible that some of the tungsten species on the catalyst surface can only be sulfided at elevated temperature and not through extended sulfidation at low temperature.

In the first step (Eq. [1]) no H_2 is consumed, and in the second step (Eq. [2]) the ratio of consumed H_2S to H_2 should be lower than 2. However, the ratio of the consumed H_2S to H_2 between 320 and 400°C is much higher than 2, which means that, in this temperature range, the above two reactions of the formation and transformation of $WO_{3-x}S_x$ take place simultaneously and that the former still predominates. Between 400 and 1000°C, the ratio of consumed H_2S to H_2 is close to 2, indicating that the second step becomes dominant and that the amount of $WO_{3-x}S_x$ intermediate is not significant. Once it forms, it immediately reacts further to WS_2, as if sulfidation goes directly from WO_3 to WS_2. The sum of the above two equations gives the equation for the overall sulfidation process:

$$WO_3 + 2H_2S + H_2 = WS_2 + 3H_2O. \qquad [3]$$

This is probably due to the decrease in the amount of exchangeable oxygen in WO_3; thus, the relative rate of the first step decreases. It is also possible that the second step has a higher activation energy and that its rate increases faster with temperature than the rate of the first step. Another possibility is that the sulfidation of the refractory species, which can only be sulfided at elevated temperatures, follows a different mechanism during its sulfidation and does not pass through the $WO_{3-x}S_x$ intermediate.

The fluorination of the alumina support affects the sulfidation process. QEXAFS spectra collected during the sulfidation of the WO_3/Al_2O_3 and WO_3/Al_2O_3F catalysts show that the intermediate signal of the non-fluorinated WO_3/Al_2O_3 sample is much stronger than that of the WO_3/Al_2O_3F sample. The WS_2 signal is stronger and appears earlier in the spectra of the WO_3/Al_2O_3F catalyst. The WS_2 signal does not show up clearly in the spectra of the WO_3/Al_2O_3 catalyst until sulfidation at 400°C for about 15 min (Fig. 5), while it appears at around 345°C in the spectra of the WO_3/Al_2O_3F catalyst (Fig. 7).

On the surface of fluorinated alumina, there are fewer hydroxyl groups and less possibility of the formation of W–O–Al linkages. Salvati *et al.* found that, for a loading of WO_3 above 15%, new Raman bands corresponding to WO_3 appeared, while at lower loading, WO_4^{2-} was the only species (26). When most surface hydroxyl groups are occupied, the additional tungsten apparently forms WO_3-like species. The QEXAFS spectra of a WO_3/Al_2O_3 catalyst with a 20% WO_3 loading (not shown) do not clearly show the intermediate signal either. This suggests that, on the F-occupied surface, the W precursor forms amorphous WO_3-like species. Such an effect of fluorination is depicted in Fig. 10. That F accelerates the transformation of the intermediate to WS_2 and leaves less time for the formation of a well-defined W^{6+}–S coordination is also a plausible explanation for the less pronounced intermediate signal in the spectra of the WO_3/Al_2O_3F catalyst.

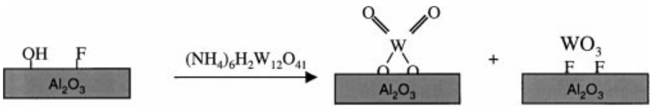

FIG. 10. Scheme of the fluorine effect on the surface W species.

5. CONCLUSIONS

TPS and QEXAFS techniques enabled us to follow the sulfidation of tungsten on alumina-supported catalysts *in situ*. Combined with XPS measurements, which reveal the surface composition of sulfided samples, this gave us a clear picture of the sulfidation behavior of alumina-supported tungsten catalysts. Classically prepared alumina-supported tungsten catalysts are very difficult to sulfide. Under normal conditions (400°C, 4 h), only about 44% sulfidation occurs. Sulfidation of WO_3/Al_2O_3 to WS_2/Al_2O_3 passes through W^{6+} oxysulfide intermediates. The classically sulfided catalyst is actually a mixture of W^{6+} oxysulfides and WS_2. It is possible to obtain a fully sulfided catalyst when ammonium tetrathiotungstate is the precursor. Fluorination of the alumina support prior to tungsten impregnation slightly increases the sulfidability of WO_3/Al_2O_3 (from 44 to 49%) and favors the formation of larger particles of WS_2. The fluorination also aids the transformation of W^{6+} sulfides and oxysulfides to WS_2.

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