Combined TPS, XPS, EXAFS, and NO-TPD study of the sulfiding of Mo/Al_2O_3

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The sulfiding of Mo/Al_2O_3 in H_2S/Ar versus in H_2S/H_2 has been studied by temperature-programmed sulfiding (TPS), X-ray photon electron spectroscopy (XPS), extended X-ray absorption fine structure (EXAFS), and temperature-programmed desorption of NO (NO-TPD). All the applied techniques agree on the sulfur content in the sulfided catalysts and the findings are in accord with a model for the H_2S production reaction. The nucleation and growth of well-ordered MoS_2 clusters are probed by XPS during sulfiding with and without the presence of hydrogen. The resulting dispersion of the MoS_2 phase is evaluated on the basis of XPS, EXAFS, and NO-TPD, and is found to be highest when the sulfiding occurs in the presence of hydrogen.

KEY WORDS: hydrotreating; molybdenum; MoS_2; TPS; XPS; EXAFS; NO-TPD

1. Introduction

The activation process of molybdenum- and tungsten-based hydrotreating catalysts has been studied extensively for several decades (for a review, see, e.g., [1–3]). However, a detailed atomic-scale model of the sulfiding mechanism, i.e., the transformation of MoO_3-like clusters into MoS_2, is still lacking. In order to elucidate the sulfiding mechanism we have performed combined temperature-programmed sulfiding (TPS), X-ray photon electron spectroscopy (XPS), and extended X-ray absorption fine structure (EXAFS) on an unpromoted molybdenum catalyst supported on alumina. Both TPS and EXAFS are well established *in situ* techniques in the field of catalyst characterization [1], whereas XPS experiments on non-conducting porous catalysts are non-trivial and cannot be performed *in situ*. The latter has traditionally been overcome by studying conducting model systems prepared in high pressure cells interfaced on ultrahigh vacuum (UHV) systems, as illustrated by, e.g., Niemantsverdriet and coworkers [4,5]. We have adapted an alternative experimental procedure, where the positive charging of the non-conducting catalyst is counter-balanced by bombarding the sample with a constant electron flux supplied by a filament positioned near the sample.

In the present paper we will discuss the sulfiding mechanism of a Mo/Al_2O_3 catalyst upon sulfiding in 2% H_2S/98% Ar and in 2% H_2S/98% H_2, respectively, as probed by a combination of TPS, XPS, EXAFS, and NO-TPD. It will be illustrated that charge-compensated XPS may be a powerful surface sensitive technique, giving complementary information on the activation mechanism of hydrotreating catalysts. We will address important aspects such as the H_2S production reaction, the total sulfur consumption, and the total sulfur content of catalysts sulfided with and without hydrogen being present. The onset temperature for the nucleation and growth of well-ordered MoS_2 clusters in H_2S/Ar and in H_2S/H_2 gaseous environment will be probed by XPS, and the resulting MoS_2 dispersion will be evaluated by EXAFS and NO-TPD.

2. Experimental

The unpromoted Mo/Al_2O_3 catalyst was prepared by impregnating η-Al_2O_3 ($\sim$270 m^2/g) with ammonium heptamolybdate and subsequently calcining for 2 h at 450 °C. According to European continental and American (ALCOA) nomenclature, the cubic transitional alumina is called eta, while the (slightly) tetragonal form is called gamma. However, the British authors call them gamma and delta, respectively. The Mo load of the catalyst was 12 wt%, which is close to a complete monolayer [8]. Assuming Mo is present in MoO_3-like surroundings, 12 wt% Mo corresponds to Mo per 30 Å^2. The Mo/Al_2O_3 catalyst was crushed and sieved to a particle size distribution between 300 and 850 μm.

The TPS experiments were performed in a quartz microreactor setup coupled online to a Balzers mass spectrometer (GAM 400). The concentration of H_2, H_2S, H_2O, and Ar is calculated from the intensities at masses 2, 34, 18, and 40, respectively. The TPS experiments were performed in 2% H_2S/98% Ar or in 2% H_2S/98% H_2 gas mixtures, using 0.2 g catalyst. The catalysts were sulfided in a flow of

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100 Nml/min for 2 h at room temperature (RT) before the temperature was increased (10 °C/min) to 450 °C, where the catalysts were sulfided for 2 h. The NO-TPD measurements were performed after H_2S/Ar or H_2S/H_2 sulfiding according to the following procedure. After sulfiding the catalysts were cooled to RT in the sulfiding mixture, i.e., in 2% H_2S/98% Ar or in 2% H_2S/98% H_2. Subsequently, the catalysts were heated in 100% hydrogen to 500 °C (10 °C/min) where the temperature was held for 4 h. The flow was changed to 100% He after 2 h and the samples were flushed for additionally 2 h before cooling in He to RT. NO was adsorbed for 30 min at RT from a mixture of 3800 ppm NO in Ar. Finally, the flow was switched back to He, and the NO-TPD was recorded with 10 °C/min after flushing for 1 h in order to remove the weakly bound NO species. All applied gas flows during the NO-TPD procedure were 100 Nml/min.

The EXAFS experiments were performed at the RÖMO II experimental station at beamline X1 (HASYLAB, Hamburg). The double Si(311) crystal monochromator was detuned to 70% intensity to minimize the presence of higher harmonics. The measurements were all carried out in transmission mode, using three optimized ion chambers. The energy calibration was obtained from the absorption edge of a reference sample measured simultaneously with the catalysts. All spectra were recorded at RT. Standard EXAFS procedures were used to extract the EXAFS data from the measured absorption spectrum [9,10].

The XPS experiments were carried out at beamline 5 at the synchrotron radiation source ASTRID at Institute for Storage Ring Facilities (ISA), University of Aarhus, employing a Zeiss SX700 plane grating monochromator with a 200 μm slit. The energy distribution curves (EDC) were obtained with a VG CLAM2 electron spectrometer running at 40 eV pass energy with a 4 mm slit. The combined resolution (full width at half-maximum (FWHM)) of the monochromator and the spectrometer was measured to be 1.7 eV [11]. The core-level measurements were obtained at normal emission with a photon energy of 406 eV in order to avoid overlap of the Mo 3d, Al 2p, S 2p, and O 2s XPS peaks with Auger lines. Without charge compensation the intense X-ray beam introduces surface potentials in the non-conducting Mo/Al_2O_3 catalysts, causing BE shifts of more than 100 eV as well as severe distortions of the XPS peaks. These effects were reduced by bombarding the sample with a constant electron flux supplied by a small high-emission filament placed at zero potential near the sample. With optimum filament current the charging of the sample was still of the order of 10 eV. The energy calibration was fixed by setting the Al 2p of Al_2O_3 to 74.7 eV. The Mo/Al_2O_3 samples for the XPS measurements were sulfided *ex situ* in 2% H_2S/98% H_2 or in 2% H_2S/98% Ar according to the following recipe. The samples were sulfided for 2 h at RT followed by a temperature ramp (10 °C/min) to the temperature, *T*, where they were sulfided for approximately 20 h (T = RT, 100, 200, 300, and 450 °C). After sulfiding the samples were cooled to RT in the sulfiding mixture and passivated in 2% O_2/98% He before they were exposed to air. The sulfided samples were subsequently pressed into small pellets and outgassed gently ($T_{\mathrm{outgasssing}} < T_{\mathrm{sulfiding}}$) under vacuum in a load lock system before they were introduced into the UHV chamber. The outgassing temperature was ~175 °C, except for the samples sulfided at RT, and 100 °C where the outgassing temperature was RT and ~75 °C, respectively. Following the above-mentioned procedure, the base pressure of the UHV chamber was always below 1×10^{-9} mbar. All spectra were recorded repeatedly in order to determine any temporal changing of the samples during the XPS measurements. The XPS spectra have been background subtracted and integrated according to standard XPS procedures.[1]

The S $2p_{3/2}$ binding energies (BE) of various types of sulfur species have recently been summarized by Smart et al. [6]. The BE of sulphide S^{2-}, disulphide S_2^{2-}, polysulfide S_n^{2-}, and sulfur S_n^0 species have progressively higher values as the sulfur species are getting more oxidized, i.e.: S^{2-} (160.1–161.2 eV), S_2^{2-} (162.1–162.6 eV), S_n^{2-} (161.9–163.2 eV), and S_n^0 (163.0–164.2 eV). However, due to the full width at half-maximum (FWHM) of the XPS peaks in the present studies, it is not possible to resolve the different sulfur species. The BE [7] of the Mo doublet ($3d_{5/2}$ and $3d_{3/2}$) is 232.6 eV ($3d_{5/2}$) in MoO_3 and 229.0 eV ($3d_{5/2}$) for MoS_2. The BE of $2p_{3/2}$ in MoS_2 is 161.7 eV.

3. Results and discussion

Figure 1 shows the H_2S concentration during TPS in 2% H_2S/98% Ar and 2% H_2S/98% H_2, respectively. From the TPS traces, it is evident that when the sulfiding is performed in the presence of hydrogen, a very sharp H_2S production reaction occurs at ~240 °C. The integrated H_2S consumption is 2.68 mmol/g when sulfiding in 2% H_2S/98% H_2 and 3.02 mmol/g when sulfiding in 2% H_2S/98% Ar. Since the sulfiding of MoO_3 into MoS_2 involves the reduction of Mo^{+VI} to Mo^{+IV}, we suggest to attribute the H_2S production reaction to the hydrogenation of elementary sulfur (S^0) formed during the reduction of Mo, i.e,

$$Mo^{+VI}O_3 + 3H_2S^{-II} \rightarrow Mo^{+IV}S_2 + 3H_2O + S^0 \quad (1)$$

$$S^0 + H_2 \rightarrow H_2S^{-II} \quad (2)$$

The sulfiding reaction (1) progresses with and without the presence of hydrogen, whereas the H_2S production reaction (2) is obviously only relevant in the presence of hydrogen. This sulfiding mechanism is parallel to that proposed by Moulijn et al. [12]. In accordance with the above-mentioned reactions, evaporation and subsequent condensation of yellow sulfur at the cold reactor outlet is only observed when the catalyst is sulfided in the absence of hydrogen. In contrast, when hydrogen is present, the elementary sulfur is hydrogenated before reaching the evaporation temperature. The evaporation of sulfur is initiated above approximately 360 °C, which can be observed through the condensation of

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[1] Standard XPS analysis including linear background subtraction and peak fitting.

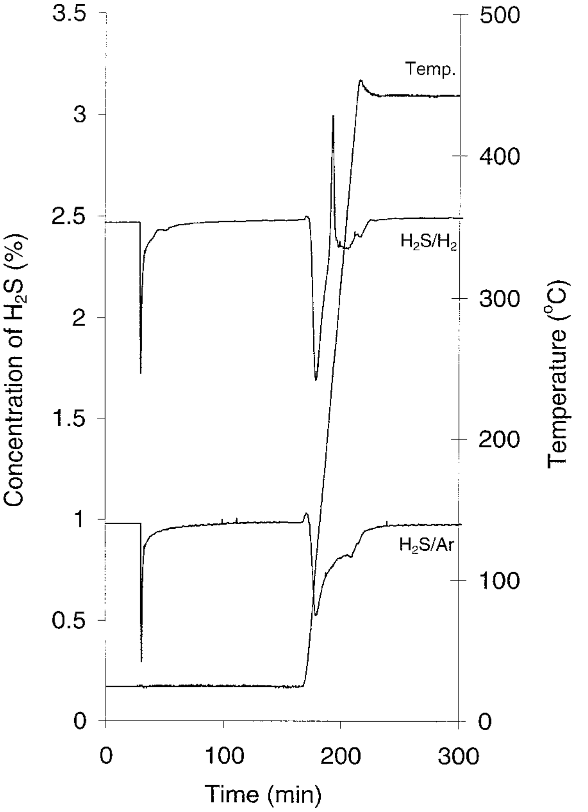

Figure 1. Temperature-programmed sulfiding of Mo/Al_2O_3 in 2% H_2S/98% H_2 and in 2% H_2S/98% Ar, respectively.

yellow sulfur crystals at the colder reactor outlet when sulfiding in the absence of hydrogen (S_n is observed to evaporate at ~120 °C in UHV [13]). The H_2S production reaction will be discussed in detail elsewhere [14]. Since H_2S is only produced when sulfiding in the presence of hydrogen, the integrated H_2S consumption is expected to be larger when sulfiding in the absence of hydrogen. This is in accord with the measured H_2S consumptions during TPS. Based on the above considerations, the total sulfur content in the samples is not dependent on whether hydrogen is present or not as long as the sulfiding temperature is below the onset temperature for the H_2S production reaction (reaction (2) is initiated at ~240 °C). Beyond this temperature the sulfur content of the H_2S/Ar-sulfided catalyst should be larger than in the catalysts sulfided in H_2S/H_2 due to the removal of S^0 by the reaction with hydrogen (reaction (2)). At even higher temperatures the sulfur content of the catalysts sulfided in H_2S/Ar and H_2S/H_2 should approach each other again due to the evaporation of S^0. Figure 2 shows the sulfur concentration as a function of the sulfiding temperature in the two series of catalysts prepared for the XPS measurements. The sulfur content (in wt%) was measured by conventional sulfur analysis. Clearly, the total sulfur content follows the trend discussed above.

In the following we will address the XPS results. Figure 3 (a) and (b) shows the XPS peaks for Mo 3d and S 2p for the catalysts sulfided *ex situ* in H_2S/Ar and H_2S/H_2, respectively, at different temperatures. The XPS signals have been integrated by applying conventional software (see also [11]). Although the XPS peaks are rather broad, a clear shift in the Mo 3d XPS peaks towards lower binding energies is observed as the sulfiding temperature is increased (figure 3(a)). This is in accord with the well-known [7] shift in BE when going from MoO_3 (232.6 eV ($3d_{5/2}$)) to MoS_2 (229.0 eV ($3d_{5/2}$)). Figure 3(b) illustrates that the S 2p XPS peaks show states close to that of MoS_2 and oxidized sulfur. The latter is formed upon exposing the sulfided samples to air. The sulfiding of MoO_3 into well-ordered MoS_2 is associated with significant agglomeration of the Mo phase, causing the regeneration of bare alumina [16]. It is therefore expected that the Al 2p signal would change as a function of the sulfiding temperature. The observation of this change may not be trivial because the chemical composition of the sample changes as a consequence of the progressing sulfiding. The total sulfur 2p XPS signal is, however, expected to be related to the Mo phase, and thus, the integrated sulfur 2p XPS signal normalized to the integrated Mo signal will be proportional to the total concentration of sulfur in the surface layer (~10 Å) of the porous catalysts. Figure 4 shows the normalized sulfur XPS area $((\sum \text{S 2p})/(\sum \text{Mo 3d}))$ plotted as a function of the sulfiding temperature for H_2S/Ar and H_2S/H_2, respectively. The amount of sulfur measured by the surface sensitive XPS technique follows the same trend as discussed above. Figure 5 shows the concentration of sulfur probed by the surface sensitive XPS technique $((\sum \text{S 2p})/(\sum \text{Mo 3d}))$ as a function of the average bulk content of sulfur. Clearly there is a good agreement between the average bulk content and the sulfur concentration evaluated by the surface sensitive XPS method. An indication of the nucleation and growth of Mo into well-ordered MoS_2 may be obtained from the Mo XPS signal relative to the XPS signal from the support $((\sum \text{Mo 3d})/(\sum \text{Al 2p}))$, since a restructuring of the "MoS" phase into well-ordered MoS_2 will result in a lower dispersion (smaller Mo signal) and more vacant Al_2O_3 (higher Al signal). Figure 6 shows the Mo XPS signal relative to the XPS signal from the Al_2O_3 support. In the case where the sulfiding is performed in H_2S/Ar, it is seen that the growth of the MoS_2 phase is significant above 200 °C, where the $(\sum \text{Mo 3d})/(\sum \text{Al 2p})$ ratio starts to decrease. In contrast, when the sulfiding is per-

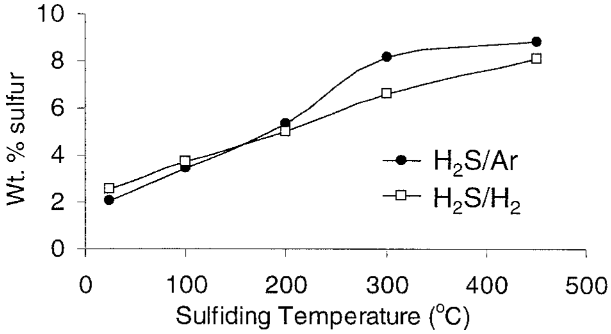

Figure 2. Total sulfur content in Mo/Al_2O_3 sulfided in 2% H_2S/98% Ar and in 2% H_2S/98% H_2 at different temperatures. The sulfided catalysts are similar to those used in the XPS experiments.

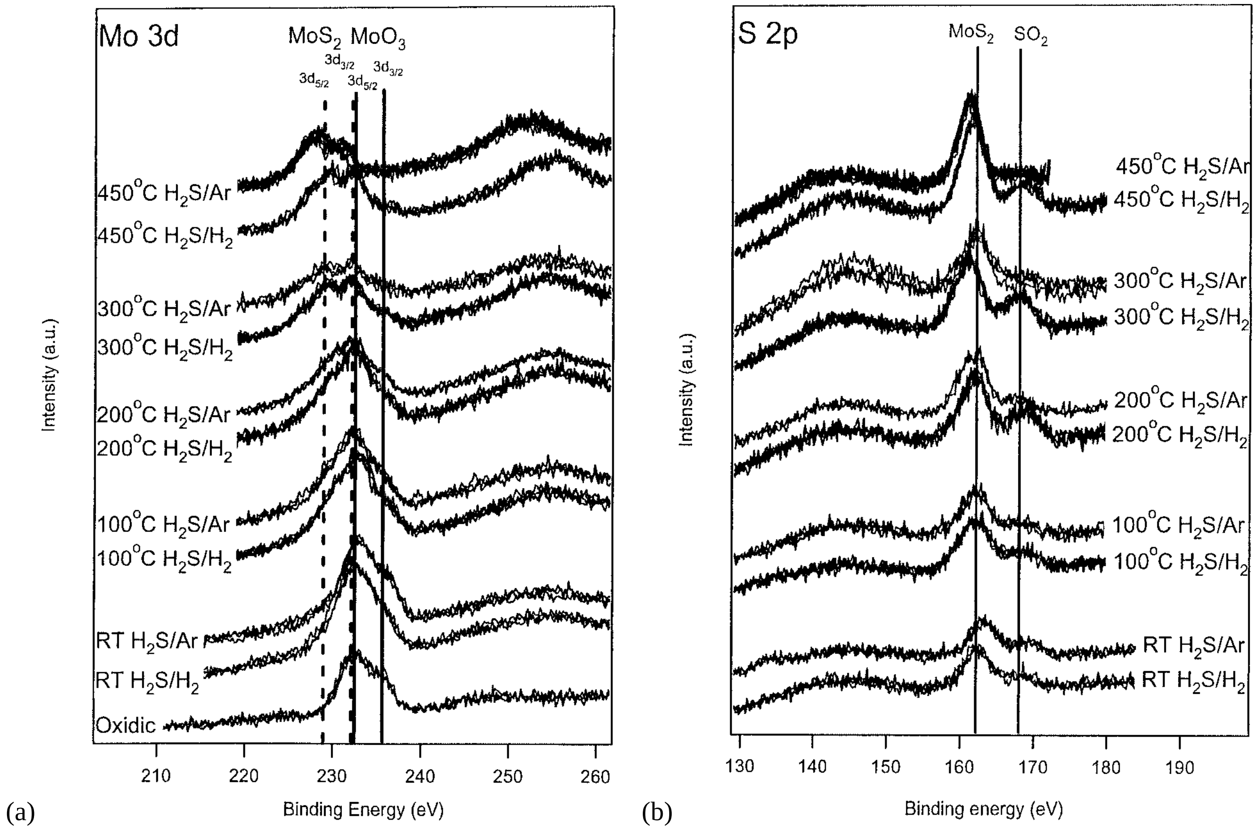

Figure 3. XPS spectra showing the photonemission intensity (a.u.) in the BE range around Mo 3d (a) and S 2p (b). The vertical lines indicate the positions of the MoO_3 and MoS_2 in (a), and MoS_2 and SO_2 (b), respectively.

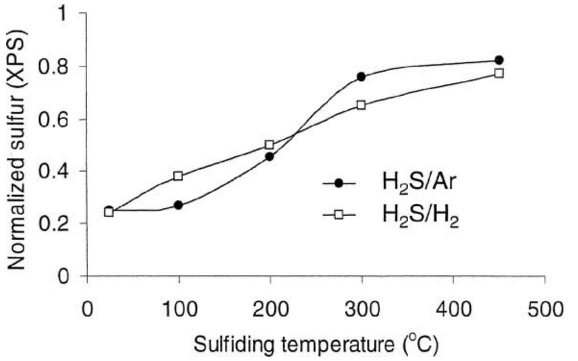

Figure 4. XPS sulfur content $((\sum \text{S 2p})/(\sum \text{Mo 3d}))$ plotted as a function of the sulfiding temperature when sulfiding *ex situ* in 2% H_2S/98% Ar and 2% H_2S/98% H_2, respectively.

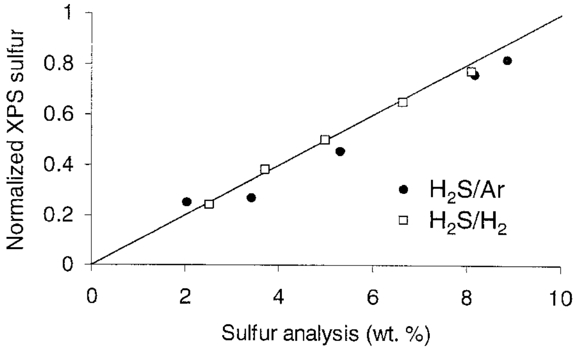

Figure 5. The normalized XPS sulfur concentration $((\sum \text{S 2p})/(\sum \text{Mo 3d}))$ plotted as a function of the bulk content of sulfur, as measured by conventional sulfur analysis.

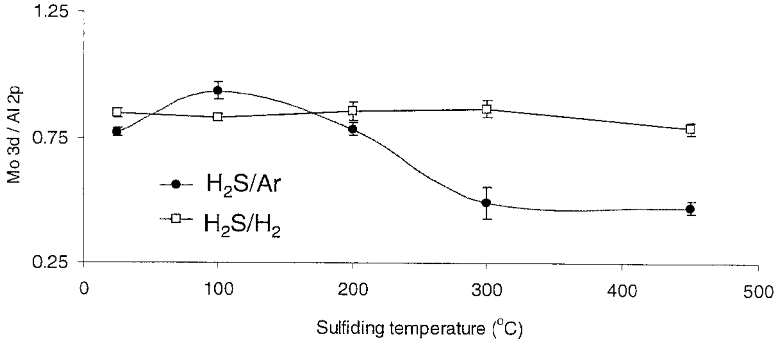

Figure 6. The Mo XPS signal relative to the XPS signal from the support $((\sum \text{Mo 3d})/(\sum \text{Al 2p}))$ as a function of the sulfiding temperature.

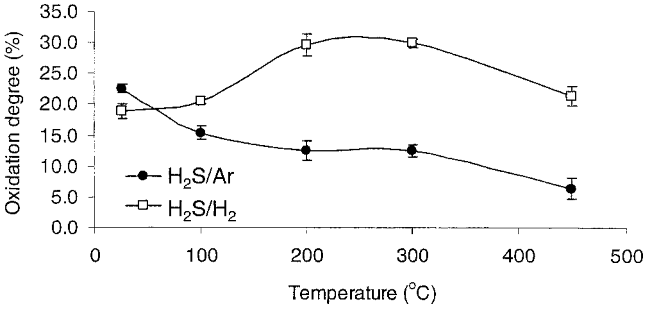

Figure 7. The percentage of oxidized sulfur ((S 2p "SO_2")/($\sum$ S 2p)) as a function of the sulfiding temperature.

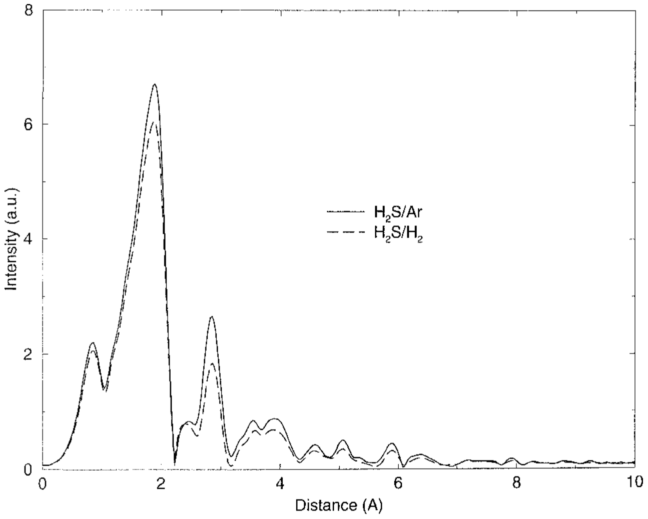

Figure 8. Fourier transform of the Mo K absorption edge after sulfiding in 2% H_2S/98% H_2 and 2% H_2S/98% Ar, respectively. The spectra are recorded at RT.

formed in H_2S/H_2 a restructuring of the Mo–S phase is not observed. Thus, it is tempting to suggest that the dispersion of the MoS_2 phase on the Al_2O_3 surface is highest when the sulfiding is performed in H_2S/H_2 compared to in H_2S/Ar.

Figure 3(b) clearly reveals that a substantial amount of sulfur has been re-oxidized when the sulfided samples were exposed to air prior to the XPS investigations. The percentage of oxidized sulfur can be further quantified by plotting the area of the "SO_x" XPS peak (at ~168 eV) relative to the total sulfur XPS area ((S 2p "SO_2")/($\sum$ S 2p)). Figure 7 shows this quantity as a function of the sulfiding temperature, when sulfiding in H_2S/H_2 and H_2S/Ar, respectively. A large amount of the sulfur is clearly found as oxidized sulfur (10–30%). It is, however, interesting to note that the H_2S/Ar phase is much less oxidized, which may again indicate that the MoS_2 phase is less well-dispersed when sulfided in the absence of hydrogen. (A highly dispersed MoS_2 structure is expected to be more reactive towards oxygen.)

We will now address the EXAFS results. Figure 8 shows the Fourier transform of the Mo K absorption edge after sulfiding in H_2S/H_2 and H_2S/Ar, respectively. The peak arising from sulfur atoms in the first coordination sphere around the Mo atoms is largest when sulfiding occurs in the absence of hydrogen. This is due to the influence of the sulfur vacancy formation reaction (3), giving a higher density of sulfur vacancies, and hence, a lower sulfur coordination number when sulfiding in the presence of hydrogen. The peak at 2.8 Å (not phase corrected) is due to nearest neighbor Mo atoms, and thus, a fingerprint of the average MoS_2 cluster size. Detail fitting with bulk MoS_2 ($N_{Mo} = 6$) gives molybdenum (N_{Mo}) coordination numbers of $N_{Mo} = 4.8$ when sulfiding in H_2S/Ar. Sulfiding in H_2S/H_2 gives a molybdenum coordination number of $N_{Mo} = 3.4$, i.e., an increase of a factor 1.4 when sulfiding in the absence of hydrogen. Thus, EXAFS shows a smaller average MoS_2 cluster size when sulfiding in H_2S/H_2 as compared to H_2S/Ar. This is in accordance with the re-oxidation results discussed above.

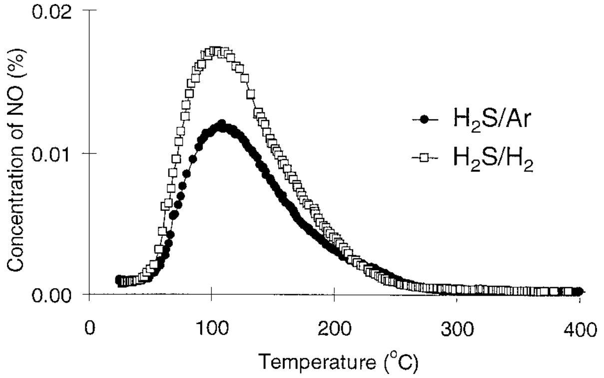

Figure 9. NO-TPD after sulfiding in H_2S/Ar or H_2S/H_2, respectively. The sulfided catalysts were treated in H_2 and He prior to NO adsorption (see text).

Before applying *in situ* NO-TPD as a probe method for determining the relative dispersion of MoS_2 clusters generated when sulfiding with and without hydrogen, it is important to facilitate the same density of coordinated unsaturated sites (CUS). Clearly, the density of sulfur vacancies (CUS) depends critically on the H_2S/H_2 ratio of the sulfiding mixture through the equation

$$\text{Mo–S} + H_2 \rightarrow H_2S + \text{Mo–}* \qquad (3)$$

where $*$ indicates the formation of a sulfur vacancy, i.e., an active site in the HDS reaction (1). The dependence of the density of sulfur vacancies on the H_2S/H_2 ratio of the sulfiding mixture is clearly seen in figure 8, where the intensity of the sulfur peak is lowest (highest density of sulfur vacancies) when sulfided in the presence of hydrogen. A recent TPR study [15] of H_2S/Ar-sulfided promoted and unpromoted MoS_2-based catalysts shows that sulfur vacancies are formed at 260 °C over alumina-supported MoS_2 in diluted hydrogen. Heating in pure hydrogen to 500 °C should therefore be adequate to facilitate the same density of sulfur vacancies. Introducing a He flush at 500 °C prior to NO adsorption ensures the removal of adsorbed hydrogen. Figure 9 shows the resulting NO-TPD from which it is evident that the NO-TPD area is significantly larger (a factor of 1.4) when sulfiding in H_2S/H_2 (0.037 mmol/g) as compared to sulfiding in H_2S/Ar (0.026 mmol/g). Thus, NO-TPD, EXAFS, and XPS indicate a higher dispersion when the catalyst is sulfided in H_2S/H_2 as compared to in H_2S/Ar.

4. Conclusion

We have shown that there is a correlation between the H_2S consumption and the sulfur content of sulfided MoO_3/Al_2O_3 measured by TPS, XPS, and conventional sulfur analysis. The sulfur content is highest when sulfiding in H_2S/Ar since, in this case, a H_2S production reaction is absent. The formation and subsequent growth of MoS_2 were probed by XPS, and it was suggested that the MoS_2 clusters formed when sulfiding in H_2S/Ar are much larger than those obtained when sulfiding in H_2S/H_2. The higher dispersion when sulfiding in the presence of hydrogen was proved by both EXAFS and NO-TPD. EXAFS reveals that the Mo coordination number is lowered by a factor of ∼1.4, whereas the NO-TPD area increases by a factor of ∼1.4 when sulfided in the presence of hydrogen.

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