Catalysis Letters 67 (2000) 81–85

Changes in metal–sulfur bond energy in promoted and unpromoted molybdenum catalysts

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Received 30 March 2000; accepted 19 May 2000

Insight into the changes in the metal–sulfur bond energy in unpromoted and promoted (Co, Ni, or Fe) MoS_2 catalysts is obtained by temperature-programmed reduction (TPR) studies of *in situ* sulfided catalysts. The experiments reveal a significant decrease in the metal–sulfur bond energy for the more active Co–Mo–S and Ni–Mo–S structures as compared to MoS_2. A similar decrease is not observed for the less active Fe–Mo–S structure. The sulfur coordination is directly measured by *in situ* EXAFS and the results support that one of the roles of the promoter atoms is to facilitate vacancy formation. The findings are in accord with recent density functional theory calculations.

Keywords: sulfur bond energy, molybdenum, TPS, TPR, EXAFS, Co–Mo–S, HDS

1. Introduction

The metal–sulfur bond energy is expected to be one of the key parameters in hydrotreating and in particular in hydrodesulfurization (HDS) since it determines the number of sulfur vacancies at given process conditions. In general, the HDS reaction is very complicated involving many different steps [1–4]. Since the generation of vacancies for the subsequent adsorption of sulfur-containing reactants may be the rate-limiting step, correlations may exist between catalytic activity and the metal–sulfur bond energy of different catalyst materials. Generally, metal–sulfur bond energy data are not available for the actual surface structures and different approaches have therefore been taken. For example, it has been proposed that the catalytic activity is related to the heat of formation of the bulk sulfides [5] or to the theoretically estimated metal–sulfur bond energies [4,6], forming the basis for the bond energy model (BEM) [4]. Based on the theoretical calculations for bulk structures, it was predicted that the addition of Co and Ni to MoS_2 should give rise to a lower metal–sulfur bond strength. Byskov et al. [7,8] addressed the above problem by performing self-consistent density functional theory (DFT) calculations on the type of edge structures present in MoS_2-based catalysts. Recent calculations have also verified this [9].

In order to obtain experimental insight into the metal–sulfur bond energies, we have performed temperature-programmed reduction (TPR) studies of *in situ* sulfided alumina-supported catalysts. This technique has been used previously to study bulk sulfides [10,11] and supported model catalysts [12–16]. In the present study, we compare the alumina-supported MoS_2 with the promoted Co–Mo–S, Ni–Mo–S, and Fe–Mo–S structures. In general, the present results are in agreement with DFT calculations [7–9]. The decrease in the average sulfur coordination before and after TPR is further quantified by extended X-ray absorption fine structure (EXAFS).

2. Experimental

The unpromoted and the Co-, Ni-, and Fe-promoted catalysts were prepared by pore filling of η-Al_2O_3 ($\sim$270 m^2/g). 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. A batch of Mo/Al_2O_3 (8.0 wt%) catalyst was prepared by impregnating the alumina with ammonium heptamolybdate and calcining for 2 h at 450 °C. The calcined Mo/Al_2O_3 catalyst was impregnated with either $Co(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, or $Fe(NO_3)_3\cdot 9H_2O$ and subsequently calcined again for 2 h at 450 °C. The Fe/Al_2O_3 catalyst was prepared by impregnating the Al_2O_3 support with $Fe(NO_3)_3\cdot 9H_2O$. Table 1 summarizes the metal loadings. The promoter to Mo mole ratio is rather

Table 1
The metal loading of the catalysts, as determined by chemical analysis.

Sample	Mo loading (mmol/g)	Promoter loading (mmol/g)
Mo/Al_2O_3	0.83	–
$CoMo/Al_2O_3$	0.80	0.34
$NiMo/Al_2O_3$	0.81	0.35
$FeMo/Al_2O_3$	0.81	0.36
Fe/Al_2O_3	–	0.35

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high (∼0.44) in order to diminish the concentration of unpromoted Mo edge sites [1].

The gas stream from the reactor outlet is analyzed online by a Balzers mass spectrometer (GAM 400). The concentrations of H_2, H_2S, H_2O, He, and Ar are calculated using masses 2, 34, 18, 4, and 40, respectively. The catalysts were crushed and sieved to a particle fraction between 300 and 850 μm. In all experiments ca. 0.200 g of the sieved fraction was loaded in a quartz reactor. The temperature was measured by a chromel–alumel thermocouple fixed at the outside of the quartz reactor. The TPS experiments were performed in 2% H_2S/98% Ar. The catalysts were sulfided in a flow of 100 Nml/min for 2 h at room temperature (RT) before the temperature was increased (10 °C/min) to 450 °C where it was kept for 2 h. The sulfided catalysts were cooled to RT in the sulfiding mixture (H_2S/Ar). Subsequent TPR measurements were performed in 1% H_2/99% He with a flow rate of 100 Nml/min. The sulfided catalysts were exposed to the H_2/He gas at RT for 1 h before the temperature was increased (10 °C/min) to 800 °C.

The HDS activity of the unpromoted and Co-, Ni-, and Fe-promoted catalysts has not been measured but their relative activities are expected to be very similar to those reported in [8].

The EXAFS experiments were performed at the RÖMO II experimental station at beamline X1 (HASYLAB). The double Si crystal monochromator (Si(311) for the Mo K-edge and Si(111) for the Co, Ni, and Fe K-edges) was detuned to 60% 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.

3. Results and discussion

Figure 1 shows the TPS patterns for the unpromoted and promoted Mo/Al_2O_3 catalysts. The H_2O production is not shown but in all cases it was correlated with the H_2S consumption, as also observed by, e.g., Arnoldy et al. [17].

From a comparison of the different TPS traces, it is clear that they follow essentially the same pattern: (i) a large H_2S consumption is observed immediately after the catalyst is introduced into the H_2S/Ar flow, (ii) desorption of a small amount of physisorbed H_2S at the start of the temperature ramp, (iii) large H_2S consumption at the start of the heating ramp followed by a slower H_2S consumption extending up to the highest sulfiding temperature used (450 °C). The H_2S consumptions in the different regions have been integrated and are summarized in table 2. Table 2 shows that the RT H_2S consumption for Mo and NiMo is smaller than for CoMo and FeMo. The H_2S consumption during the temperature ramp is largest for the Fe-promoted catalyst, and the total H_2S consumption during the entire TPS follows the trend: Mo < NiMo < CoMo ≪ FeMo. Since the metal loadings are slightly different for the four catalysts, it may be more relevant to compare the ratio of the measured H_2S consumption and the expected H_2S consumption assuming the formation of stoichiometric MoS_2 and promoted sites with a metal to sulfur ratio equal to 1 (X/S = 1, X = Co, Ni, and Fe). An edge stoichiometry with X/S = 1 is supported by recent STM images of atom-resolved MoS_2 slabs [18] and DFT calculations [7,8].

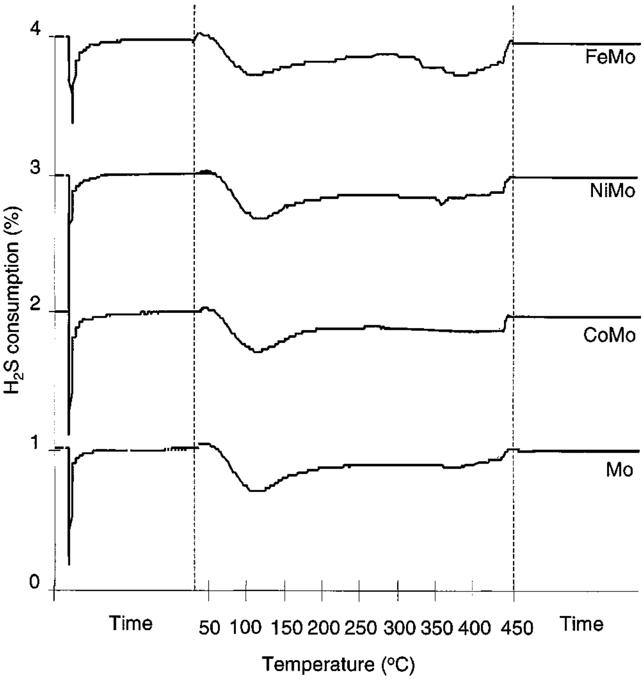

Figure 1. TPS spectra of alumina-supported Mo, CoMo, NiMo, and FeMo. The gas mixture (2% H_2S/98% Ar) is introduced to the catalyst after 10 min and the temperature ramp (10 °C/min to 450 °C) is initiated after 120 min. The H_2S consumption is plotted as a function of time and temperature, respectively.

Table 2
Integrated H_2S consumptions.

Sample	Consumption[a] (mmol/g)			H_2S consumption/ calculated H_2S consumption[b]
	RT H_2S	TPS H_2S	Total H_2S	
Mo/Al_2O_3	0.42	1.52	1.94	1.16
CoMo/Al_2O_3	0.62	1.67	2.29	1.18
NiMo/Al_2O_3	0.44	1.67	2.11	1.07
FeMo/Al_2O_3	0.67	2.17	2.84	1.43

[a] RT H_2S – during room temperature sulfiding, TPS H_2S – during the temperature ramp, and Total H_2S – total consumption.

[b] The ratio of the measured H_2S consumption and the calculated H_2S consumption assuming the formation of stoichiometric MoS_2 and promoted edge sites with stoichiometry of X/S = 1 (X = Co, Ni, and Fe).

In the case of Mo, CoMo, and NiMo, the H_2S consumption is ∼10–20% larger than the expected stoichiometric values. In the case of FeMo, the consumption is approximately 45% larger than the expected stoichiometric value which may indicate that the edge structure of the

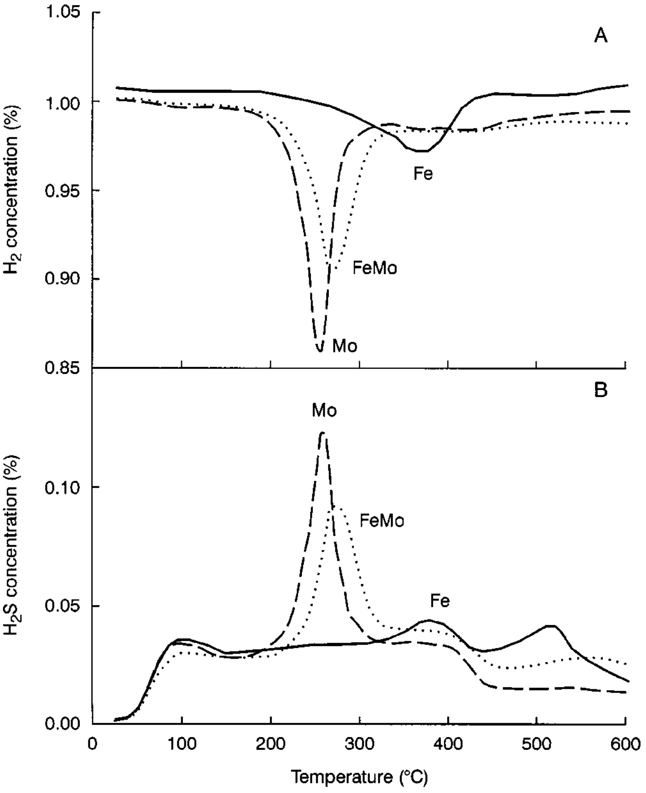

Figure 2. Hydrogen consumption (A) and H_2S production (B) during TPR in 1% H_2/99% He of sulfided alumina-supported Mo, Fe, and FeMo catalysts.

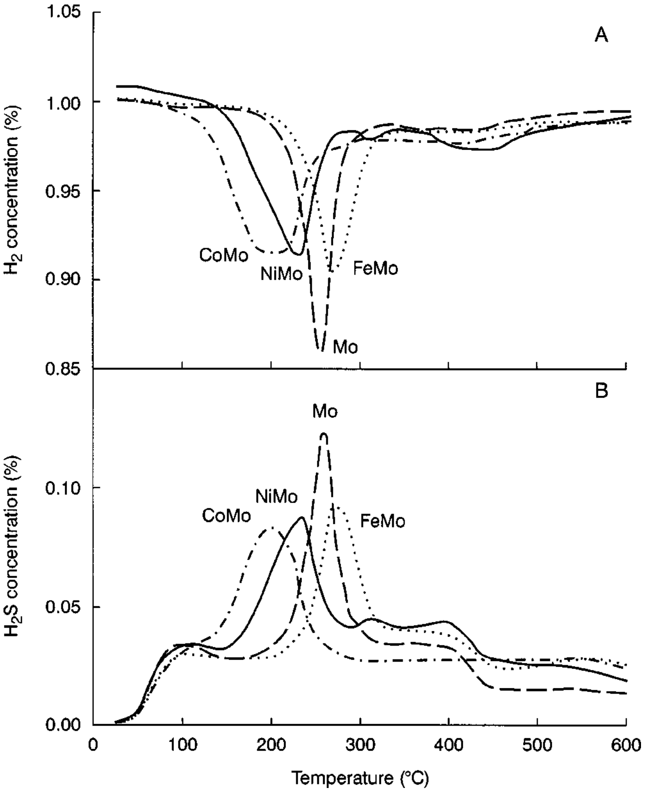

Figure 3. Hydrogen consumption (A) and H_2S production (B) during TPR in 1% H_2/99% He of sulfided alumina-supported Mo, CoMo, NiMo, and FeMo catalysts.

Fe–Mo–S catalyst is different compared to the analogous Ni–Mo–S and Co–Mo–S structures or that FeS_2 is formed. Some FeS_2 may be expected due to the quite high Fe/Mo atomic ratio (0.44). Nevertheless, the TPR spectrum of the sulfided Fe-promoted Mo catalyst (Fe–Mo–S) is significantly different from a simple superposition of the TPR spectra of the separate sulfide phases (i.e., $FeS_2 + MoS_2$), as revealed from figure 2 (A) and (B). The sulfided Fe catalyst shows a clear well-separated high-temperature H_2 consumption around 380 °C which is absent in the TPR spectra of the Fe–Mo–S catalyst. In accordance with the TPR results, infrared spectroscopy using NO as probe molecule also indicates that the Fe-promoted Mo catalyst contain mainly the Fe–Mo–S phase [19].

The H_2 consumptions and H_2S productions during TPR of the sulfided catalysts are shown in figure 3 (A) and (B), respectively. For both the H_2 consumption and the H_2S production, the position of the peak maxima/minima depends on the type of promoter. The addition of Ni and Co causes a significant downward shift (25 and 47 °C, respectively) in the peak position relative to the temperature position (256 °C) of the unpromoted MoS_2 phase. In contrast, the addition of Fe is observed to cause a small upward shift (8 °C) relative to the temperature position of the unpromoted MoS_2 catalyst. The different peak positions are summarized in table 3. The lower TPR peak temperatures for Co- and Ni-promoted catalysts suggest a smaller sulfur binding energy as compared to unpromoted MoS_2.

Table 3

Integrated H_2 consumptions and H_2S productions during TPR in 1% H_2/ 99% He.

Sample	H_2 consumption (mmol/g)	H_2S production (mmol/g)	Temperature position of peak max/min[a] (°C)
Mo/Al_2O_3	0.18	0.42	256
$CoMo/Al_2O_3$	0.31	0.45	209
$NiMo/Al_2O_3$	0.38	0.49	231
$FeMo/Al_2O_3$	0.22	0.45	264

[a] The temperature position of the TPR peak maxima/minima (max/min).

The number of sulfur vacancies formed during TPR can be estimated from the integrated H_2 consumptions and H_2S productions (see table 3). The H_2 consumption is observed to be lower than the amount of produced H_2S. This can be explained by the observation that a small amount of physisorbed H_2S will desorb from the alumina surface when a temperature ramp is initiated. The loss of two terminal Mo–S–H groups due to sintering of two smaller MoS_2 slabs ($–Mo_{slab,1}–S–H + –Mo_{slab,2}–S–H \rightarrow –Mo_{slab,1+2}–S–Mo_{slab,1+2}– + H_2S$) or the re-combination of two neighboring S–H groups within the same slab ($2Mo_{slab,1}–S–H \rightarrow –Mo_{slab,1}–S–Mo_{slab,1}– + H_2S$) may also give rise to H_2S evolution without H_2 consumption. The small H_2S desorption peak at ∼100 °C, which is not correlated with H_2 consumption, may be associated with physisorbed H_2S. The H_2S evolution above 450 °C may be associated with sintering or re-combination of S–H groups since the catalysts

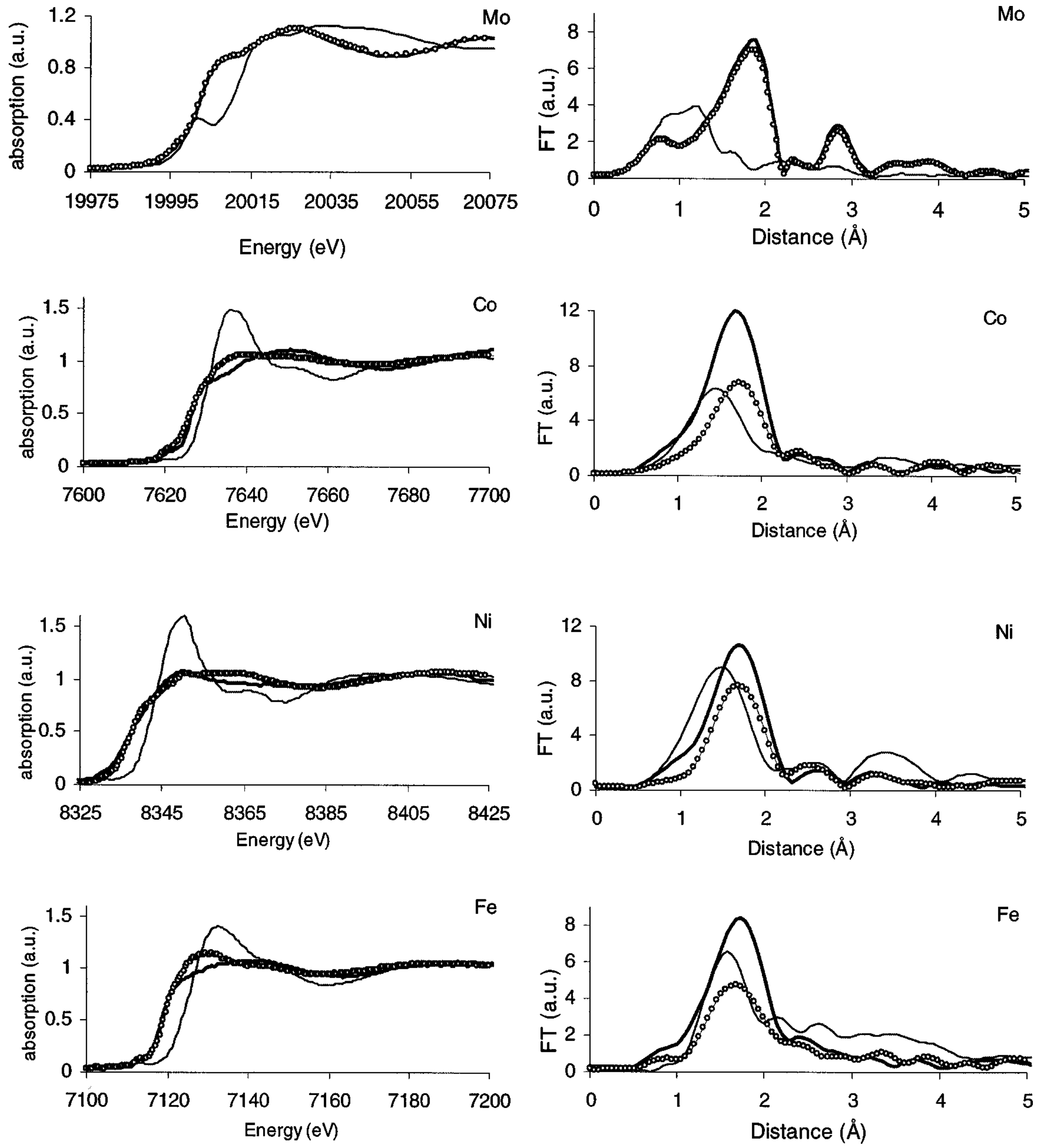

Figure 4. XANES spectra (left) showing the K-edge absorption spectra of alumina-supported Mo, CoMo, NiMo, and FeMo catalysts recorded at RT in the oxidic state (thin line), after sulfiding at 450 °C (thick line) and after TPR to 600 °C (open circles). The corresponding k^1-weighted Fourier transforms are shown on the right.

have only been sulfided to 450 °C prior to TPR. The H_2 consumption during TPR increases according to: MoS_2 (0.18 mmol/g) $<$ Fe–Mo–S (0.22 mmol/g) $<$ Co–Mo–S (0.31 mmol/g) $<$ Ni–Mo–S (0.38 mmol/g). The H_2 consumptions indicate that the number of vacancies which can be formed during TPR of unpromoted MoS_2 and in Fe–Mo–S, is approximately the same. For Co–Mo–S and Ni–Mo–S, the number of sulfur vacancies formed during TPR appears to be higher with an average vacancy to promoter ratio close to one. It is interesting that the difference between the H_2 consumption and the H_2S production is around 0.12 mmol/g for the Co- and Ni-promoted catalysts. For the unpromoted MoS_2 and the Fe-promoted catalyst, the difference between the H_2 consumption and the H_2S production is twice as large (0.24 mmol/g). This may point to either a higher –S–H concentration in the Fe–Mo–S phase and the unpromoted MoS_2 phase, or alternatively, to more unpromoted edge sites in the case of the Fe–Mo–S catalyst since the TPR of the Fe–Mo–S phase is very similar to that of the unpromoted MoS_2 phase.

The present TPR results are in accord with measured HDS activities [1,8], and with self-consistent DFT calculations of Byskov et al. [7,8] showing that the promotional effect of the Co–Mo–S and Ni–Mo–S phases is caused by partial filling of the antibonding states resulting in weaker metal–sulfur bond energies. For the Fe–Mo–S phase, we observed an increase in the metal–sulfur bond energy relative to the unpromoted MoS_2 phase. This is also in accord with the DFT calculations showing that the antibonding state in the Fe–Mo–S phase is empty (above the Fermi level) resulting in a stronger metal–sulfur bond energy. These findings nicely explain the observation [1,8] that iron is a poor promoter for the HDS reaction over Mo/Al_2O_3 catalysts. Indeed, iron appears to inhibit the sulfur vacancy formation in the Fe–Mo–S phase as compared to the unpromoted MoS_2 phase.

Figure 4 (left panel) shows the X-ray absorption near edge structures (XANES) for the Mo K-edge in the unpromoted Mo/Al_2O_3 catalyst and the K-edges of the promoter atoms in the promoted catalysts. The spectra show the catalysts in the oxidic state, after sulfiding in H_2S/Ar at 450 °C, and after TPR in hydrogen to 600 °C. Generally, the energy position of the absorption edges is shifted towards lower energies upon sulfiding. For Mo, the characteristic pre-peak ascribed to a 1s–4d atomic transition is absent after sulfiding. For the promoter atoms, the characteristic white-line signifying Co, Ni, and Fe in oxidic surroundings is also absent after sulfiding. Figure 4 (right panel) shows the corresponding k^1-weighted Fourier transforms. It is seen that the nearest neighbor peak is shifting towards larger distances upon sulfiding. Furthermore, it is observed that the intensity of the peak ascribed to nearest neighbor sulfur is decreasing as a result of sulfur removal during TPR. The change in the average sulfur coordination numbers is much larger for the promoter atoms compared to the Mo atoms. This is expected since the promoter atoms are primarily atomically dispersed at the edges of the MoS_2 slabs thereby being accessible to hydrogen reduction. For the Mo/Al_2O_3 catalyst, the average Mo–S coordination number is only decreased by 1% upon heating in hydrogen to 600 °C. For the promoted catalysts, the average sulfur coordination number is decreased by 42 (Co), 25 (Ni), and 30% (Fe), respectively. An average decrease in the sulfur coordination number of 30% for the edge-exposed promoter atoms is equivalent to the removal of 1.5 sulfur atom per promoter atom assuming an initial sulfur coordination of 5 [1]. The average H_2 consumption during TPR of the promoted catalysts is approximately 0.30 mmol/g equivalent to the removal of approximately one sulfur atom (as H_2S) per promoter atom. Thus, the removal of one to two sulfur atoms per Co/Ni atom appears to be in accord with both the TPR results and the changes measured in the average sulfur coordination numbers before and after TPR.

4. Conclusion

In the present study it was demonstrated that it is possible to establish a ranking in the sulfur bond energies of alumina-supported catalysts by TPR. The addition of Co or Ni to Mo-based catalysts was observed to cause a decrease in the metal–sulfur bond energy as reflected by a significantly downward shift in the peak temperatures for H_2 consumption and H_2S production during TPR. In contrast, an increase in the peak temperature is observed for the Fe-promoted catalyst. From combined TPR and EXAFS it was found that one to two sulfur atoms are removed per promoter atom during TPR up to 600 °C. The measured ranking of the metal–sulfur bond energies is in accord with recent DFT calculations [7–9].

Acknowledgement

HASYLAB is gratefully acknowledged for offering beamtime at the RÖMO II station and DANSYNC for financial support. We acknowledge Michael Brorson, Claus H. Jacobsen, Eric Törnqvist, and Nan Topsøe for stimulating discussions.

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