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High-pressure sulfidation of a calcined $CoMo/Al_2O_3$ hydrodesulfurization catalyst

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Abstract

The influence of the pressure during the sulfidation on the structure and activity of a calcined $CoMo/Al_2O_3$ catalyst was studied by Mössbauer emission spectroscopy (MES), extended X-ray absorption fine structure (EXAFS), transmission electron microscopy (TEM) and dibenzothiophene hydrodesulfurization (HDS) activity measurements. Sulfidation at elevated pressure (4 MPa) leads to a much higher HDS activity than upon 0.1 MPa sulfidation. Similarly, the HDS activity increases when after 0.1 MPa sulfidation (673 K) the sulfidation pressure is increased to 4 MPa. The average slab size (~2.8 nm) and stacking degree (~1.4) do not depend on the sulfidation pressure. EXAFS data point to a higher rate of Co and Mo sulfidation at elevated pressure. Although this leads to a somewhat more aggregated form of Co-sulfide particles at intermediate temperatures compared to the case of 0.1 MPa sulfidation, redispersion takes place to small Co-sulfide species on the MoS_2 edges. The spectroscopic data of such stepwise sulfided series support the supposition that sulfidation at 4 MPa leads to a Type II Co–Mo–S phase whereas 0.1 MPa sulfidation results in a less active Type I phase. In addition, upon direct high-pressure sulfidation all Co atoms end up in the Co–Mo–S phase, whereas atmospheric pressure sulfidation leaves a small fraction of Co in close interaction with the support.

Keywords: Hydrodesulfurization; Mössbauer emission spectroscopy; High-pressure; Sulfide catalysts; Co–Mo–S

1. Introduction

The development of improved hydrodesulfurization (HDS) catalysts is essential in order to meet the new environmental legislation requirement for cleaner fuels, having a maximum sulfur content of 10 ppm [1]. Mixed CoMo and NiMo sulfides supported on Al_2O_3 are the most important HDS catalysts. Major progress in our understanding of the synergy between Co and Mo has been the development of the Co–Mo–S model. Amongst others, *in situ* Mössbauer emission spectroscopy (MES) has been instrumental to develop a structural model for CoMo sulfide catalysts, i.e. the Co–Mo–S phase, in which Co atoms are located at the edges of MoS_2 slabs [2–4]. Recently, we performed the very first high-pressure *in situ* MES study of the sulfidation of CoMo catalysts [5,6], confirming the applicability of the Co–Mo–S structural model under industrial-like conditions.

The initial Co–Mo–S model was refined by Crajé et al. [7–9], after identical MES spectra observed in Co and CoMo catalysts indicated that no simple relation exists between the amount of Co–Mo–S and the activity [10,11]. Combined MES and extended X-ray absorption fine structure (EXAFS) studies showed that Co-sulfide species at the MoS_2 edges differ in particle size and/or ordering. Co-sulfide species in the Co–Mo–S phase exhibit a high quadrupole splitting (Q.S.) value, while smaller Q.S. values point to the presence of larger Co sulfide species [12].

Because important changes in the catalyst structure may occur as a function of the reaction conditions [13,14], it is important to characterize the structure of the catalyst under temperature and pressure conditions relevant to industrial practice [15]. In a systematic manner, we follow the formation and evolution of the active phase as a function of temperature and pressure. Although the MES spectra of the Co-sulfide species in Co and CoMo catalysts can be indistinguishable, we should be able to identify a sulfidation pattern that characteristically occurs when the Co–Mo–S structures are formed. In the same time we examine the

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sulfidability of the Co atoms under conditions closer to industrial practice than those used in earlier studies performed under atmospheric pressure conditions [12]. Our previous results obtained with an identical catalyst sulfided directly at high-pressure [5,6] have shown that activation at 673 K and 4 MPa results in the complete sulfidation of Co ions that have diffused into the Al_2O_3 support during the calcination treatment.

Besides MES, the catalysts were characterized using extended X-ray absorption fine structure (EXAFS) to obtain information about the local environments around Co and Mo during sulfidation. The catalytic activity was evaluated by dibenzothiophene (DBT) HDS reaction tests. Complementary information about the influence of the size and morphology of the active structures on the activity was derived from transmission electron microscopy (TEM).

2. Experimental

2.1. Catalyst preparation and sulfidation

$CoMo/Al_2O_3$ was prepared by pore-volume impregnation of γ-Al_2O_3 (Ketjen 001-1.5E, BET surface area 271 $m^2\ g^{-1}$, pore volume 0.7 $ml\ g^{-1}$, particle size 0.5–0.85 mm). Aqueous solutions of cobalt nitrate $Co(NO_3)_2{\cdot}6H_2O$ (Merk p.a.) and ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Merk, min. 99.9%) were used in a two-step impregnation procedure, Mo being introduced first. About 50 MBq ^{57}Co as an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ was added to the Co-containing impregnation solution, for the MES measurements.

The resulting $CoMo/Al_2O_3$ catalyst contained 7 wt.% Mo and 2.25 wt.% Co and it is denoted as $Co(2.25)Mo(7)/Al_2O_3$. After preparation, the catalyst was dried in static air at 383 K for 16 h. Subsequently the catalyst was calcined at 673 K for 24 h in static air. The calcination temperature is indicated as a postfix.

Prior to Mössbauer spectroscopic measurements the catalyst was sulfided in a flow of 60 $cm^3\ min^{-1}$ of a mixture of 10 vol.% H_2S in H_2 at pressures between 0.1 MPa and 4 MPa in a high-pressure Mössbauer *in situ* cell, earlier described in detail [16]. This cell offers the possibility to study catalysts under high-pressure conditions. The sulfidation procedure is denoted by the suffix (S, x MPa, y K), indicating heating of the catalyst in the sulfidation mixture to y K at x MPa in 1 h and keeping the catalyst at this temperature for 1 h.

2.2. MES, EXAFS, TEM and DBT HDS measurements and analysis

All MES spectra were recorded at room temperature and at the sulfiding pressure, using a constant acceleration spectrometer in a triangular mode with a moving single-line $K_4Fe(CN)_6{\cdot}3H_2O$ absorber enriched in ^{57}Fe. The velocity scale was calibrated with a ^{57}Co:Rh source and a sodium nitroprusside (SNP) absorber. Zero velocity corresponds to the peak position of the $K_4Fe(CN)_6{\cdot}3H_2O$ absorber measured with the ^{57}Co:Rh source; positive velocities correspond to the absorber moving toward the source. The spectra were analyzed with a Lorentzian fitting procedure as described in [12].

X-ray absorption spectra at the Co K-edge (7.709 keV) and the Mo K-edge (20 keV) were obtained at the Dutch-Belgian Beamline (DUBBLE) of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The electron energy and ring current were 6 GeV and 150–200 mA, respectively. Catalysts were stepwise sulfided in stainless-steel tubular reactors that were subsequently flushed with Ar and opened in a glove box. Self-supporting wafers of the sulfided catalysts were pressed inside the glove box and brought in an environmental cell. The thickness of the wafer was chosen to give an absorbance (μx) of about 2.5 in the Mo K-edge region to ensure an optimal signal-to-noise ratio. Because of the low Co concentration in the catalyst, the absorbance for the Co K-edge measurements was about 3. Three scans of each sample were recorded in transmission mode. The XDAP program (version 2.2.2 [17]) was used for data manipulation and data analysis. Standard procedures for background removal, normalization and fitting procedure were employed [18–20].

TEM measurements were performed at the National Center for High Resolution Electron Microscopy at Delft University of Technology, Delft. The micrographs were obtained using a Philips CM30T electron microscope equipped with a field emission gun operated at 300 keV [13]. Samples were prepared by mounting a few drops of a suspension of ground catalyst in n-hexane on a microgrid carbon polymer supported on a Au grid (400 mesh). For the TEM measurements, the samples sulfided for EXAFS measurements were used. After preparation, the samples were transferred to glass ampoules in a glove box. At least 10 micrographs were taken of each sample and the mean slab length and the stacking degree were determined by manually measuring at least 300 slabs per sample in three representative images.

Medium-pressure gas-phase dibenzothiophene (DBT) HDS measurements were performed in a stainless-steel reactor. DBT dissolved in n-decane (1.0 wt.% DBT) was fed by an HPLC pump at a rate of 0.1 $cm^3\ min^{-1}$ into a hydrogen stream of 0.5 $dm^3\ min^{-1}$ (final DBT concentration 200 ppm [21]). The reactor was loaded with about 20 mg of catalyst, diluted with 5 g SiC to obtain a catalyst bed height of about 3 cm. Prior to activity measurements, the catalyst was activated at the desired pressure in a flow of 60 $cm^3\ min^{-1}$ of a mixture of 10 vol.% H_2S in H_2, whilst heating to 673 K at a rate of 6 $K\ min^{-1}$ followed by an isothermal period of 1 h. Subsequently, the reactant feed was passed over the catalyst at a total pressure of 3 MPa. Typically, 8 h were allowed at each reaction condition for the catalyst to stabilize. Gaseous products were analyzed by on-line gas chromatography (HP 5890, CP-Sil-5CB, FID). For the calculation of the rate constant (k_{HDS}) first-order kinetics in DBT were assumed.

3. Results

Mössbauer spectra of $Co(2.25)Mo(7)/Al_2O_3$ in the fresh state, after temperature-programmed atmospheric-pressure sulfidation up to 673 K and after subsequent sulfidation at pressures of 1, 2, 3 and 4 MPa at the final temperature are presented in Figs. 1 and 2. The corresponding MES fit

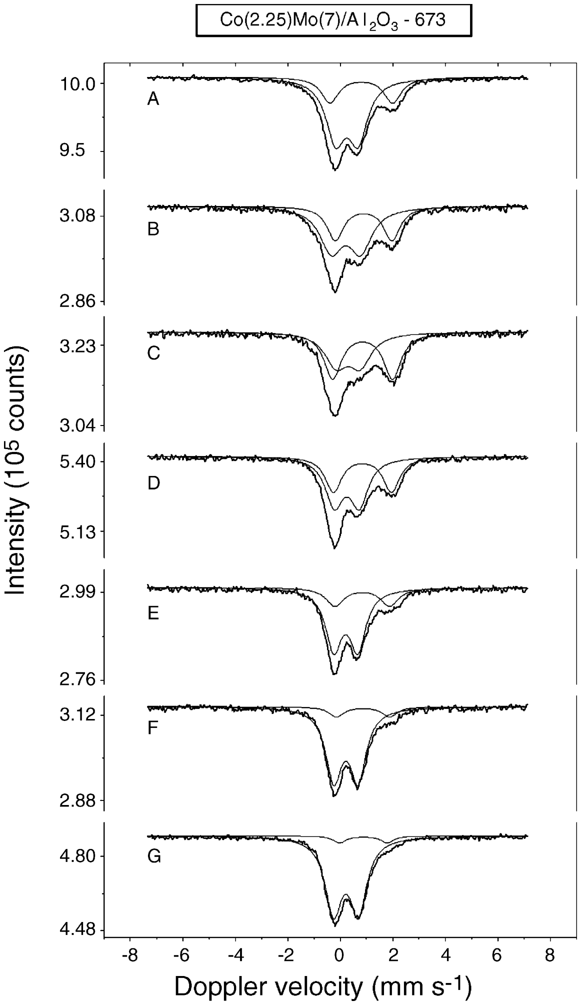

Fig. 1. MES spectra obtained at 300 K with Co(2.25)Mo(7)/Al_2O_3-673 after various successive sulfidation steps. (A) Fresh catalyst; (B) Ar, 393 K; (C) S, 0.1 MPa, 300 K; (D) S, 0.1 MPa, 373 K; (E) S, 0.1 MPa, 473 K; (F) S, 0.1 MPa, 573 K; (G) S, 0.1 MPa, 673 K.

parameters are collected in Table 1a. For comparison, the MES fit parameters obtained after stepwise sulfidation at 4 MPa [5,6] are also given (Table 1b).

The spectrum of the fresh catalyst consists of one quadrupole doublet indicating a low-spin Co 2+ or a 3+ phase and a second contribution consistent with Co^{2+} in the high-spin state [22]. The doublet with an isomer shift (I.S.) value of 0.27 mm s^{-1} and a Q.S. of 0.86 mm s^{-1} is assigned to a ^{57}Co-oxide species. The high-spin 2+ contribution observed in the MES spectra is assigned mainly to Co diffused in the Al_2O_3 support (Co:Al_2O_3) during the calcination treatment. The formation of an intermediate oxygen-containing species during sulfidation, having the same high-spin 2+ doublet – most probably a Co-sulfate type phase – was reported before [8].

To observe the influence of water removal on the high spin 2+ contribution in the fresh catalyst, the sample was dried in an Ar flow at 393 K for 2 h. This treatment resulted in a clear increase of the high spin 2+ contribution. The removal of water results in an increased interaction of such Co species with the support [12]. The high-spin 2+ contribution increases strongly after exposing the catalyst to the sulfidation mixture at 300 K. Increasing the sulfidation temperature results in a continuous decrease of this contribution, although it does not completely disappear after sulfidation at 673 K and 0.1 MPa.

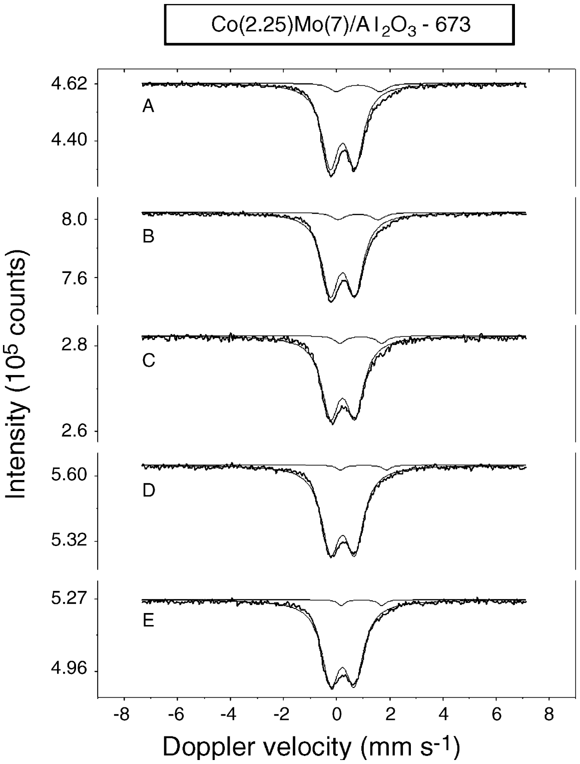

Fig. 2. MES spectra obtained at 300 K with Co(2.25)Mo(7)/Al_2O_3-673 after various successive sulfidation steps. (A) S, 0.1 MPa, 673 K, repeated; (B) S, 1 MPa, 673 K; (C) S, 2 MPa, 673 K; (D) S, 3 MPa, 673 K; (E) S, 4 MPa, 673 K.

The Q.S. values of the Co-sulfide doublet at intermediate temperatures (Q.S. = 0.95–0.99 mm s^{-1}) are somewhat larger than the values previously obtained with an identical catalyst sulfided directly at high-pressure [5,6]. The Q.S. values decrease during sulfidation from 1.10 mm s^{-1} at 300 K to 0.92 mm s^{-1} at 473 K. A further increase of the sulfidation temperature up to 673 K at 0.1 MPa results in a small increase of the quadrupole splitting. A successive treatment at 673 K and 0.1 MPa showed that prolonged activation under these conditions does not have any influence on the Mössbauer spectra. During the subsequent treatments at elevated pressures, a slight decrease in the Q.S. value of the Co-sulfide doublet is observed. The high-spin 2+ contribution is still present after sulfidation at 673 K and 4 MPa.

The fit results of the Mo K-edge EXAFS measurements of Co(2.25)Mo(7)/Al_2O_3-673 as a function of sulfidation temperature at atmospheric and elevated (4 MPa) pressures are collected in Table 2. The spectrum of the sample sulfided at 473 K and 4 MPa was fitted by two contributions, i.e. a Mo–S contribution at 2.47 Å and a Mo–Mo contribution at 2.72 Å. The Mo–S distance of 2.47 Å is larger than the interatomic Mo–S distance in crystalline MoS_2 (2.41 Å), whereas the Mo–Mo distance is smaller than the typical distance of 3.16 Å in MoS_2 [23]. A relatively high Mo–S coordination number (6.2) is found under these conditions.

Table 1a

MES parameters of Co(2.25)Mo(7)/Al_2O_3-673 after sulfidation treatment

T_s (K)	P (MPa)	I.S. (mm s^{-1}) “Co-oxide”	Q.S. (mm s^{-1})	Γ (mm s^{-1})	A (%)	I.S. (mm s^{-1}) “Co-sulfide”	Q.S. (mm s^{-1})	Γ (mm s^{-1})	A (%)	I.S. (mm s^{-1}) “High-spin 2+”	Q.S. (mm s^{-1})	Γ (mm s^{-1})	A (%)
Fresh		0.27	0.86	0.90	71.8					0.82	2.39	0.80	28.2
Ar-393		0.24	1.11	1.06	62.8					0.90	2.15	0.77	37.2
300	0.1					0.20	1.10	0.75[b]	37.7	0.93	2.10	0.89	62.3
373	0.1					0.24	0.99	0.75[b]	54.8	0.89	2.12	0.83	45.2
473	0.1					0.23	0.92	0.75	74.6	0.86	2.08	0.83	25.4
573	0.1					0.24	0.93	0.75	87.8	0.89	2.04	0.72	12.2
673	0.1					0.24	0.95	0.78	91.4	0.90	1.81	0.60	8.6
673[a]	0.1					0.23	0.95	0.77	92.9	0.82	1.65	0.65	7.1
673	1					0.23	0.94	0.78	93	0.81	1.50	0.61	7
673	2					0.23	0.92	0.81	93.1	0.88	1.55	0.60[b]	6.9
673	3					0.23	0.91	0.83	95.8	0.96	1.70	0.60[b]	4.2
673	4					0.23	0.90	0.83	96.2	0.92	1.54	0.60[b]	3.8

[a] Repeated treatment at 673 K and 0.1 MPa.

[b] Fixed during fit.

Table 1b

MES parameters of Co(2.25)Mo(7)/Al_2O_3-673 after direct high-pressure sulfidation

T_s (K)	P (MPa)	I.S. (mm s^{-1}) “Co-oxide”	Q.S. (mm s^{-1})	Γ (mm s^{-1})	A (%)	I.S. (mm s^{-1}) “Co-sulfide”	Q.S. (mm s^{-1})	Γ (mm s^{-1})	A (%)	I.S. (mm s^{-1}) “High-spin 2+”	Q.S. (mm s^{-1})	(Γ) mm s^{-1}	A (%)
Fresh		0.28	0.95	0.94	67.7					0.80	2.37	0.88	32.3
300	0.1					0.22	1.12	0.80	51.2	0.94	2.15	0.78	48.8
300	4					0.26	0.89	0.83	54.2	0.85	2.20	0.79	45.8
373	4					0.26	0.85	0.76	66.2	0.83	2.21	0.84	33.8
473	4					0.26	0.84	0.74	86.8	0.79	2.28	0.70	13.2
573	4					0.22	0.93	0.73	94.2	0.90	1.81	0.51	5.8
673	4					0.22	0.94	0.78	100				

Table 2
Mo K-edge EXAFS parameters of Co(2.25)Mo(7)/Al_2O_3-673 after different sulfidation treatments

Treatment	N	R (Å)	$\Delta\sigma^2$ (Å^2 × 10^{-3})	ΔE_0 (eV)	N	R (Å)	$\Delta\sigma^2$ (Å^2 × 10^{-3})	ΔE_0 (eV)	N	R (Å)	$\Delta\sigma^2$ (Å^2 × 10^{-3})	ΔE_0 (eV)
	Mo–S				Mo–Mo				Mo–Co			
S, 4 MPa, 473 K	6.2	2.47	5.3	1.3	1.9	2.72	6.2	7.9				
S, 4 MPa, 573 K	4.8	2.41	2.5	1.7	2.3	3.15	5.4	4.3	0.8	2.76	9.8	9.8
S, 4 MPa, 673 K	5.6	2.41	1.6	2.1	3.4	3.16	3.7	2.5	0.9	2.75	9.5	7.9
S, 0.1 MPa, 473 K	3.2	2.41	7.3	0	1.0	3.10	9.7	9.3				
S, 0.1 MPa, 573 K	4.0	2.41	3.5	0.7	1.8	3.13	5.8	8.5	0.6	2.78	9.5	5.3
S, 0.1 MPa, 673 K	5.0	2.41	1.8	0.1	3.2	3.16	3.9	0.8	0.7	2.73	9.9	9.5
S, 0.1 MPa + S, 4 MPa, 673 K	5.4	2.41	1.6	1.5	3.4	3.16	3.6	2.2	0.8	2.74	9.9	9.1

After increasing the sulfidation temperature to 573 K and 673 K, the Mo–S and Mo–Mo interatomic distances agree well with the structural parameters of bulk MoS_2, while the observed coordination numbers are lower than those of MoS_2 ($N_{Mo–S} = 6$, $N_{Mo–Mo} = 6$), indicating the presence of dispersed MoS_2 particles. In contrast, sulfidation at atmospheric pressure results in the presence of species with structural parameters close to those of MoS_2 at all intermediate temperatures. The catalyst activated at 673 K and 4 MPa has a slightly higher Mo–S coordination number than the sample sulfided at 0.1 MPa. The Mo–Mo coordination numbers and the corresponding Debye-Waller factors are very similar for all catalysts sulfided at 673 K. In all spectra of catalysts sulfided above 473 K, inclusion of a Mo–Co contribution was found to be relevant at distances ranging from 2.74 Å and 2.78 Å.

The Co K-edge EXAFS fit parameters of sulfided Co(2.25)Mo(7)/Al_2O_3-673 are summarized in Table 3. The spectra obtained after sulfidation at 300 K and 373 K at elevated pressure could be fitted with a Co–S contribution at a distance of about 2.21 Å and two Co–Co contributions at 2.43–2.49 Å and 3.35 Å. These distances are smaller than the corresponding Co–Co distances in bulk Co_9S_8 (2.51 Å and 3.51 Å, respectively) [24,27]. After increasing the sulfidation temperature to 673 K, both Co–Co distances increase to the values reported for Co_9S_8. A Co–Mo contribution at 2.8 Å was fitted in the spectra measured after treatment at 573 K and 673 K. After sulfidation at 673 K and 4 MPa, the Co–S coordination number increases to 6.1, pointing to a six-fold sulfur coordination by the Co atoms.

The Co EXAFS parameters for CoMo/Al_2O_3 (S, 0.1 MPa, 673 K) show somewhat different Co–Co coordination distances (2.6 Å and 3.41 Å) from those obtained after high-pressure sulfidation. The Co–Mo coordination number after atmospheric pressure sulfidation was 0.6 in contrast to the value of 1.2 found upon sulfidation at 4 MPa. Notably, subsequent sulfidation at 4 MPa of atmospheric pressure sulfided CoMo/Al_2O_3 resulted in an increase of the Co–Mo coordination number ($N_{Co–Mo} = 0.9$).

Fig. 3 shows representative TEM micrographs of Co(2.25)Mo(7)/Al_2O_3-673 sulfided at 673 K and various pressures. The micrographs show the well-known MoS_2 slab-like structure. The average slab length and the stacking degree of the three catalysts are summarized in Table 4. The slabs appear to be better defined when the catalyst is sulfided at 4 MPa, indicating increased crystallinity after treatment at higher pressure. This is evidenced by the more frequent presence of a second direction of d-spacings (ordered lines that are visible in a direction perpendicular to the length direction of the slabs). The average slab length as well as the stacking degree does not vary significantly for the three treatments.

The DBT HDS activities of Co(2.25)Mo(7)/Al_2O_3-673 sulfided at 673 K as a function of sulfidation pressure are shown in Table 5. The rate constant (k_{HDS}) is given after a reaction time of 8 h. Clearly, the sulfidation pressure has a very strong influence on the DBT HDS activity of CoMo/Al_2O_3: the activity of the catalyst sulfided at 4 MPa is about 2.5 times higher than for the sample sulfided under atmospheric

Table 3
Co K-edge EXAFS parameters of Co(2.25)Mo(7)/Al_2O_3-673 after different sulfidation treatments

Treatment	N	R (Å)	$\Delta\sigma^2$ (Å^2 × 10^{-3})	ΔE_0 (eV)	N	R (Å)	$\Delta\sigma^2$ (Å^2 × 10^{-3})	ΔE_0 (eV)	N	R (Å)	$\Delta\sigma^2$ (Å^2 × 10^{-3})	ΔE_0 (eV)	N	R (Å)	$\Delta\sigma^2$ (Å^2 × 10^{-3})	ΔE_0 (eV)
	Co–S				Co–Co (1)				Co–Mo				Co–Co (2)			
S, 4 MPa, 300 K	5.3	2.22	4.6	2.6	1.4	2.46	9.8	5.9					0.5	3.35	9.8	4.6
S, 4 MPa, 373 K	5.4	2.21	4.4	2.9	1.3	2.49	9.5	0.1					0.8	3.35	9.3	5.2
S, 4 MPa, 473 K	5.6	2.21	4.0	2.5	1.5	2.51	9.7	−3.6					1.0	3.42	9.4	−1.9
S, 4 MPa, 573 K	5.5	2.22	2.9	0.7	0.6	2.51	9.6	−8.9	0.9	2.80	7.4	0.1	0.6	3.48	7.1	−9.9
S, 4 MPa, 673 K	6.1	2.21	3.5	−0.3	0.6	2.51	9.2	−9.6	1.2	2.80	8.6	−0.8	1.1	3.48	10.1	−10
S, 0.1 MPa, 300 K	4.9	2.22	5.7	5.9	1.7	2.43	9.7	8.4					1.3	3.25	11.0	10.0
S, 0.1 MPa, 373 K	5.3	2.22	5.2	2.4	1.8	2.44	9.2	4.7					1.6	3.24	10.7	9.1
S, 0.1 MPa, 473 K	5.4	2.21	4.0	1.0	0.6	2.55	1.3	−10.0					0.9	3.31	10.4	9.6
S, 0.1 MPa, 573 K	5.2	2.22	3.9	1.8	0.8	2.51	9.3	1.6	0.3	2.80	9.2	−7.7	0.7	3.44	10.4	−2.7
S, 0.1 MPa, 673 K	5.6	2.22	2.6	−1.7	0.6	2.6	1.5	−8.9	0.6	2.80	9.2	−9.2	0.4	3.41	4.1	−9.5
S, 0.1 MPa + S, 4 MPa, 673 K	5.7	2.22	2.8	−1.9	0.6	2.6	0.7	−8.5	0.9	2.80	6.2	−8.9	0.3	3.41	3.8	−9.8

conditions. A very similar result was obtained after extending the sulfidation at 4 MPa of an atmospheric pressure sulfided catalyst. Also, a catalyst stepwise sulfided at 4 MPa, thus mimicking the sulfidation procedure of the MES experiments, showed a much higher activity than catalyst sulfided at 0.1 MPa.

4. Discussion

Sulfidation of calcined CoMo/Al_2O_3 already starts after room-temperature exposure to the sulfidation mixture. The doublet with an I.S. value of 0.20 mm s^{-1} and a Q.S. value of 1.10 mm s^{-1} is assigned to a Co-sulfide phase. Clearly, increasing the sulfidation pressure and temperature causes changes in the shape of the MES spectra. The Q.S. of the Co-sulfide doublet decreases to 0.92 mm s^{-1} after atmospheric pressure sulfidation at 373 K and 473 K, indicating an increase in the particle size of the Co-sulfide species. Almost no change in the Q.S. value is observed when increasing the temperature from 473 K to 573 K (Table 1a).

A significant increase in the Q.S. value (from 0.84 mm s^{-1} to 0.93 mm s^{-1}), pointing to a larger decrease in particle size of the Co-sulfide species, takes place in the sample treated directly at high-pressure (Table 1b). This can be understood in terms of redispersion of the larger Co-sulfide particles, obtained after the more complete sulfidation at 4 MPa, over the edges of newly formed MoS_2 crystallites. A similar redispersion model has been put forward for NiS_x particles in NiW catalysts [34]. This effect is less observable at atmospheric pressure because of the smaller Co-sulfide particles formed under those conditions. The doublets obtained after sulfidation at 673 K and different pressures with I.S. values of 0.23 and 0.24 mm s^{-1} and Q.S. values of 0.90 and 0.95 mm s^{-1}, are characteristic for Co–Mo–S species [12]. The Mössbauer results indicate that the Co–Mo–S structures are intact upon sulfidation at 673 K under both atmospheric and high-pressure conditions.

As can be seen in Fig. 1, the Co:Al_2O_3 contribution remains in the MES spectra of the sample treated at atmospheric pressure. Even, after subsequent increase of the sulfidation pressure (Fig. 2), Co(2.25)Mo(7)/Al_2O_3-673 shows the presence of a small high-spin 2+ contribution. This contrasts the result upon direct high-pressure sulfidation (Table 1b) where it was found that these Co species can be fully sulfided. Seemingly, when these Co ions in strong interaction with the support are not sulfided at low temperature by applying a high sulfidation pressure, they cannot be sulfided at higher temperatures even when the sulfidation pressure is increased at 673 K.

The Co K-edge EXAFS fit results for Co(2.25)Mo(7)/Al_2O_3-673 (Table 3) show that the Co atoms are sulfided already after exposure to the H_2S/H_2 gas mixture at room temperature. The resulting Co-S coordination distances are similar to the values reported for Co_9S_8 [8,27,28]. The two Co–Co contributions at 2.51 Å and at 3.48 Å of the catalysts sulfided at high pressure are closer to the corresponding distances in Co_9S_8 compared to the catalyst sulfided first at atmospheric pressure, in which coordination distances at 2.6 and 3.41 Å are found. This

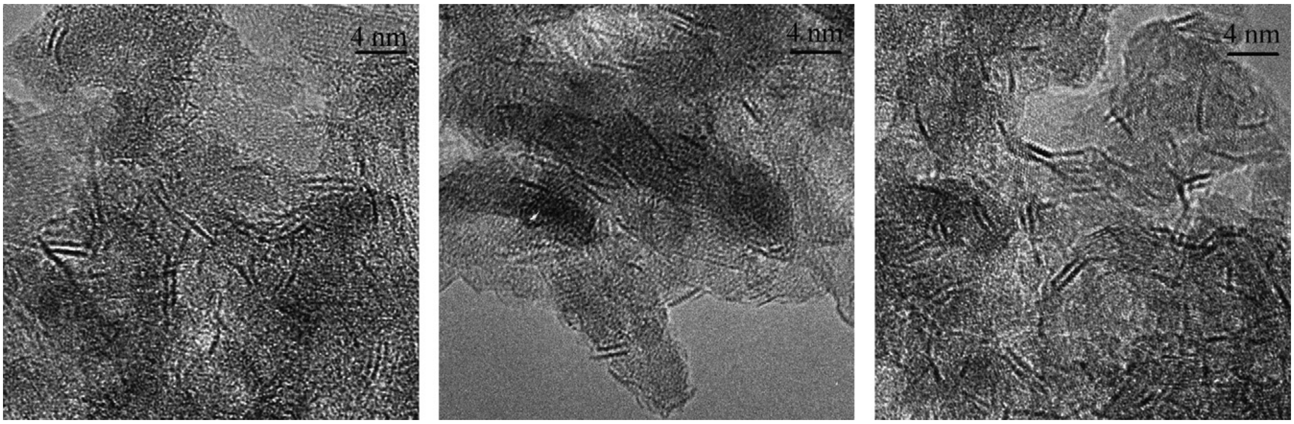

Fig. 3. TEM images of Co(2.25)Mo(7)/Al_2O_3-673 after various sulfidation treatments. Left: S, 4 MPa, 673 K; middle: S, 0.1 MPa, 673 K; right: S, 0.1 MPa, 673 K + S, 4 MPa, 673 K.

confirms the formation of larger Co-sulfide species upon high-pressure activation as a result of the higher rate of Co sulfidation under these conditions.

The Co–S coordination numbers increase both during atmospheric and high-pressure sulfidation. A coordination number of about 6 is obtained at a sulfidation temperature of 673 K. This forms an indication that no large amounts of Co_9S_8 are present at this stage. Also the relatively small Co–Co coordination numbers support such conclusion. Similar results were obtained for CoMo/C [8] and NiMo/SiO_2 catalysts [29]. The formation of an intermediate sulfided species, with very disordered Co–S structures and coordination distances and numbers different from those of crystalline cobalt sulfide systems, was proposed. These special structures are formed as soon as the catalysts are sulfided and only after activation at 573 and 673 K the Co atoms will participate in the Co–Mo–S species or form Co_9S_8. The stronger redispersion of the Co-sulfide particles after direct high-pressure sulfidation at 573 K is confirmed by the significant decrease in the Co–Co contribution from $N_{Co–Co} = 1.5$ (after treatment at 473 K) to $N_{Co–Co} = 0.6$ (Table 3). No decrease of the Co–Co coordination number at 573 K was observed for the sample treated under atmospheric pressure conditions.

The EXAFS data analyses of the catalysts sulfided at 573 K and 0.1 and 4 MPa (Table 3) reveal the presence of a Co–Mo contribution at 2.8 Å, in good agreement with the previously reported values [8,30]. This is in line with the conclusion that Co–Mo–S structures are formed at this temperature. Higher Co–Mo coordination numbers were found for the catalysts activated at 4 MPa. This trend points in direction of Type II Co–Mo–S phase formation upon increasing sulfidation pressure. The Co species become better defined upon sulfidation at higher pressure.

The Mo EXAFS fit results for Co(2.25)Mo(7)/Al_2O_3-673 sulfided directly at high pressure (Table 2) reveal the presence of a large Mo–S coordination number ($N_{Mo–S} = 6.2$), in combination with a short Mo–Mo distance (2.72 Å), after treatment at 473 K. Previous EXAFS studies attributed these contributions to a MoS_3-like intermediate species [25,31,32]. After increasing the sulfidation temperature to 573 K and 673 K, the Mo–S and Mo–Mo interatomic distances are in agreement with the structural parameters of MoS_2 crystallites. The sample sulfided at atmospheric pressure shows the presence of MoS_2-like species at all intermediate temperatures. A lower Mo–S coordination number ($N_{Mo–S} = 5.0$) is obtained after treatment at 673 K and 0.1 MPa, indicating that the MoS_2 edges are not completely saturated with sulfur, probably due to the presence of some Mo–O–Al linkages of Mo atoms with the alumina support or at least incomplete sulfur coordination [26]. This agrees with the definition of the Type I Co–Mo–S phase, which typically forms under these sulfidation conditions. Contributions from Mo–Co coordination are also observed starting from sulfidation at 573 K, although the Mo–Co coordination numbers are slightly smaller compared to those of the catalyst sulfided at 4 MPa. This trend was also observed in the Co EXAFS fit results.

After sulfidation at 673 K and 4 MPa, the Mo–S and Mo–Mo coordination numbers have increased compared to atmospheric pressure sulfidation, indicating an accelerated Mo sulfidation under high-pressure conditions. The resulting

Table 4
Slab length and stacking degree of Co(2.25)Mo(7)/Al_2O_3-673 after different sulfidation treatments

Treatment	Average slab length (nm)	Average stacking
S, 4 MPa, 673 K	2.7	1.4
S, 0.1 MPa, 673 K	2.8	1.3
S, 0.1 MPa, 673 K + S, 4 MPa, 673 K	2.9	1.4

Table 5
DBT HDS activities of Co(2.25)Mo(7)/Al_2O_3-673 after different sulfidation treatments

Treatment	k_{HDS} (mol DBT $Kg_{catalyst}^{-1}$ s^{-1}) × 10^{-3}
S, 4 MPa, 673 K	3.0
S, 0.1 MPa, 673 K	1.2
S, 0.1 MPa, 673 K + S, 4 MPa, 673 K	2.9
S, 4 MPa, 373 K + S, 4 MPa, 473 K + S, 4 MPa, 573 K + S, 4 MPa, 673 K	2.5

Mo–Mo Debye-Waller factors are slightly smaller that that of the catalyst sulfided under atmospheric pressure conditions, pointing to a higher static order. All this data suggest the formation of the Type II Co–Mo–S phase upon high-pressure activation of the catalysts.

The TEM micrographs of Co(2.25)Mo(7)/Al_2O_3-673 sulfided at 673 K and different pressures (Fig. 3) do not show significant differences in the dispersion or the morphology of MoS_2 slabs. This result is different from the one of Kooyman et al. [13], who found an increase in the slab length after 1 MPa sulfidation compared to sulfidation at ambient pressure for a commercial CoMo/Al_2O_3 catalyst. Slabs appear to be better defined when the catalyst is sulfided also at elevated pressure. This would indicate a better crystallinity of the MoS_2 phase upon a higher sulfidation pressure.

The DBT HDS data of Co(2.25)Mo(7)/Al_2O_3-673 sulfided at 673 K and different pressures (Table 5) show reaction rate constants that are 2.5 times higher for the samples treated also at 4 MPa compared to the sample that was activated only at atmospheric pressure. This ratio is somewhat higher than the relative activities of the Type I and II Co–Mo–S species observed in gas phase thiophene HDS, where Type II phase was twice as active than Co–Mo–S I [31,33]. The somewhat higher degree of Co sulfidation upon sulfidation at 4 MPa may explain this difference.

The large difference in activity between the catalysts sulfided at atmospheric and elevated (4 MPa) pressures is remarkable, the more since our spectroscopic results including those probing the environments around Co (MES, EXAFS) and Mo (EXAFS) do not probe any significant differences in the final state. However, the stepwise approach taken in this study helps to understand evolution of the Co–Mo–S phase in detail. The higher Co–Mo coordination numbers and the more crystalline MoS_2 slabs for the sample obtained after 4 MPa sulfidation give support for the formation of Type II Co–Mo–S structures.

The finding that sulfidation at elevated pressure leads to predominantly Type II Co–Mo–S formation is an important one. The current state of knowledge is that one requires modified preparation routes, for instance using chelating agents [29,35], to diminish metal-support interactions during catalyst activation so as to arrive at fully sulfided Type II structures with a reasonably high dispersion. Considerable improvements in the performance of commercial CoMo- and NiMo-based hydrotreating catalysts have been attributed to maximization of the amount of Type II phase. Despite widely varying activation procedures in industry, in general catalysts are brought into the sulfided state under elevated pressure conditions. As evidenced in this study, a typical calcined CoMo/Al_2O_3 catalyst, which as expected performs as a Type I catalyst following atmospheric pressure sulfidation, renders a much more active, Type II catalyst upon high-pressure activation, albeit at considerably higher temperatures than generally applied commercially. Nevertheless, this observation warrants a re-evaluation of the previous statements and a closer look at the question to what extent it is possible to preserve Type I Co–Mo–S under industrial sulfidation conditions.

5. Conclusions

The sulfidation of a calcined CoMo/Al_2O_3 catalyst under conditions relevant to industrial practice was studied by MES, EXAFS, TEM and DBT HDS. In essence, all Co atoms end up in Co–Mo–S structures upon activation at atmospheric as well as elevated (4 MPa) pressure. The stepwise sulfidation approach points to higher sulfidation rates of Co and Mo during high-pressure activation. This leads to somewhat more aggregated CoS_x species at intermediate temperatures, followed by redispersion of these species to more dispersed ones, once MoS_2 is formed. The final state of the catalyst after 0.1 MPa or 4 MPa sulfidation is very similar in terms of Q.S. of the Co–Mo–S phase. Nonetheless, the high-pressure sulfided sample has a much higher HDS activity than the sample activated at 0.1 MPa. The difference is due to formation of Type II Co–Mo–S phase at elevated pressures. Spectroscopically, support for this is found in increased Co–Mo coordination numbers and increased crystallinity of the MoS_2 slabs in transmission electron microscopy.

When the catalyst is directly sulfided at 4 MPa, all Co species including those strongly interacting with the alumina support can be sulfided. On the contrary, increasing the sulfidation pressure to 4 MPa subsequent to sulfidation at 673 K and 0.1 MPa leaves part of the Co atoms in strong interaction with alumina. This latter procedure also results in a Type I to Type II Co–Mo–S phase transformation and higher HDS activity. These results suggest that it is difficult to preserve Type I Co–Mo–S structures under industrial sulfidation conditions.

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References

[1] Directive 2003/17/EC of the European Parliament and of the Council on the Quality of Petrol and Diesel Fuels, Brussels, 3 March 2003.
[2] B.S. Clausen, S. Mørup, H. Topsøe, R. Candia, J. Phys. 37 (1976) 249.
[3] H. Topsøe, B.S. Clausen, R. Candia, C. Wivel, S. Mørup, J. Catal. 68 (1981) 433.
[4] C. Wivel, R. Candia, B.S. Clausen, S. Mørup, H. Topsøe, J. Catal. 68 (1981) 453.
[5] A.I. Dugulan, M.W.J. Crajé, G.J. Kearley, J. Catal. 222 (2004) 281–284.
[6] A.I. Dugulan, M.W.J. Crajé, A.R. Overweg, G.J. Kearley, AIP Conf. Proc. 765 (2005) 26.
[7] M.W.J. Crajé, V.H.J. de Beer, A.M. van der Kraan, Appl. Catal. 70 (1991) L7–L13.
[8] M.W.J. Crajé, S.P.A. Louwers, V.H.J. de Beer, R. Prins, A.M. van der Kraan, J. Phys. Chem. 96 (1992) 5445.
[9] M.W.J. Crajé, V.H.J. de Beer, J.A.R. van Veen, A.M. van der Kraan, J. Catal. 143 (1993) 601.
[10] J.A.R. van Veen, E. Gerkema, A.M. van der Kraan, A. Knoester, J. Chem. Soc. Chem. Commun. (1987) 1684.

[11] M.W.J. Crajé, V.H.J. de Beer, J.A.R. van Veen, A.M. van der Kraan, Appl. Catal. A 100 (1993) 97.
[12] M.W.J. Crajé, Ph.D. thesis, Delft University of Technology, Delft, 1992, ISBN 90-73861-08-X.
[13] P.J. Kooyman, J.G. Buglass, H.R. Reinhoudt, A.D. van Langeveld, E.J.M. Hensen, H.W. Zandbergen, J.A.R. van Veen, J. Phys. Chem. B 106 (2002) 11795.
[14] H. Topsøe, Stud. Surf. Sci. Catal. 130 (2000) 1.
[15] H. Topsøe, J. Catal. 216 (2003) 155.
[16] M.W.J. Crajé, A.M. Van Der Kraan, J. van de Loosdrecht, P.J. van Berge, Catal. Today 71 (2002) 369.
[17] J.B.A.D. van Zon, D.C. Koningsberger, H.F.J. van't Blik, D.E. Sayers, J. Chem. Phys. 82 (1985) 5742.
[18] J.W. Cook, D.E. Sayers, J. Appl. Phys. 52 (1981) 5024.
[19] S.M.A.M. Bouwens, R. Prins, V.H.J. de Beer, D.C. Koningsberger, J. Phys. Chem. 94 (1990) 3711.
[20] B.K. Teo, P.A. Lee, J. Am. Chem. Soc. 101 (1979) 2815.
[21] W.R.A.M. Robinson, J.A.R. van Veen, V.H.J. de Beer, R.A. van Santen, Fuel Proc. Technol. 61 (1999) 89.
[22] J.G. Steven, L. Zhe, H. Pollak, V.E. Stevens, R.H. White, J.L. Gibson, Mössbauer Handbook Minerals, Mössbauer Effect Data Center, University of North Carolina, Asheville, 1983.
[23] T.G. Parham, R.P. Merrill, J. Catal. 85 (1984) 295.
[24] S.M.A.M. Bouwens, F.B.M. van Zon, M.P. van Dijk, A.M. van der Kraan, V.H.J. de Beer, J.A.R. van Veen, D.C. Koningsberger, J. Catal. 146 (1994) 375.
[25] R. Cattaneo, T. Weber, T. Shido, R. Prins, J. Catal. 191 (2000) 225.
[26] D. Nicosia, R. Prins, J. Catal. 231 (2005) 259.
[27] S.M.A.M. Bouwens, J.A.R. van Veen, D.C. Koningsberger, V.H.J. de Beer, R. Prins, J. Phys. Chem. 95 (1991) 123.
[28] W. Niemann, B.S. Clausen, H. Topsøe, Catal. Lett. 4 (1990) 355.
[29] L. Medici, R. Prins, J. Catal. 163 (1996) 38.
[30] S.M.A.M. Bouwens, D.C. Koningsberger, V.H.J. de Beer, S.P.A. Louwers, R. Prins, Catal. Lett. 5 (1990) 273.
[31] S.P. Cramer, K.S. Liang, A.J. Jacobson, C.H. Chang, R.R. Chianelli, Inorg. Chem. 23 (1984) 215.
[32] R. Cattaneo, R. Fota, R. Prins, J. Catal. 199 (2001) 318.
[33] J.A.R. van Veen, H.A. Colijn, P.A.J.M. Hendriks, A.J. van Welsenes, Fuel Proc. Technol. 35 (1993) 137.
[34] E.J.M. Hensen, Y. van der Meer, J.A.R. van Veen, J.W. Niemantsverdriet, Appl. Catal. A 322 (2007) 16.
[35] E.J.M. Hensen, V.H.J. de Beer, J.A.R. van Veen, R.A. van Santen, Catal. Lett. 84 (2002) 59.