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Research Note

High-pressure in situ Mössbauer emission spectroscopy study of the sulfidation of calcined Co–Mo/Al_2O_3 hydrodesulfurization catalysts

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Abstract

The influence of high pressure on the sulfidation of calcined CoMo/Al_2O_3 catalysts, under conditions relevant to industry, was studied by means of Mössbauer emission spectroscopy (MES). The measurements were carried out in a high-pressure Mössbauer in situ reactor, which offers the possibility of studying cobalt-based catalysts under realistic hydrotreatment conditions. Activation at 673 K and 4 MPa results in complete sulfidation of Co that has diffused into the Al_2O_3 support during calcination, the Co–Mo–S structure being the only Co phase present in sulfided industrial CoMo/Al_2O_3 catalysts. On the basis of comparisons with previous MES results on alumina-supported catalysts it is concluded that the calcination treatment retards the sulfidation of the Co atoms to temperatures where MoS_2 particles are already present, favoring Co–Mo–S phase formation.

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

1. Introduction

The limited natural resources press for efficient use. Further, the environmental demand for full introduction of “zero-sulfur” gasoline and diesel fuels [1]—having no more than 10 mg/kg (ppm) sulfur—requires the development of highly active hydrodesulfurization (HDS) catalysts. The mixed sulfides CoMo, NiMo, and NiW are the most used catalysts in industry for hydrotreatment reactions, CoMo catalysts being excellent for HDS [2]. The evolution of the structural models proposed for the active phase of CoMo sulfide catalysts has been summarized in many reviews [2–9]. Making use for the first time of an in situ technique (Mössbauer emission spectroscopy (MES)) for direct measurements of the local structure of “Co sulfide” species in hydrotreating catalysts, Topsøe and co-workers [10,11] introduced the Co–Mo–S model: Co atoms located at the edges of MoS_2 slabs. Wivel et al. [12] related the high activity of CoMo catalysts to the amount of Co present in the Co–Mo–S phase.

By preparing catalysts with different activities and the same MES signal, it was shown that no simple relationship exists between the amount of Co–Mo–S and activity [13,14]. Later, MES and extended X-ray absorption fine structure (EXAFS) measurements allowed Crajé et al. [15–18] to improve the Co–Mo–S model by showing that the Co sulfide species that are located at the MoS_2 edges differ in particle size and/or ordering. It was concluded that the Co sulfide particles in the Co–Mo–S phase, containing only one Co atom, exhibit the largest quadrupole splitting (QS) value, while larger Co sulfide species exhibit smaller QS values [19]. For high Co/Mo ratios, after sulfidation at higher temperatures, crystalline Co_9S_8 formation occurs and the contact synergy model [20] may apply.

Although there is much evidence that the Co–Mo–S structural model applies for model catalysts under model conditions, there is little evidence that it applies for industrially activated catalysts under real industrial conditions. For example, it was found that calcination treatment of a CoMo/Al_2O_3 catalyst led to a strong interaction between the Co species and the alumina support. This interaction hampers the sulfidation of the Co species during sulfidation at ambient pressure [18].

Because important changes in catalyst structure may occur after variations in reaction conditions [21,37], it is important to perform characterization studies under temperature and pressure conditions relevant to industrial catalysis [22]. In the present work, we report the first in situ high-pressure

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MES study of the sulfidation of calcined CoMo/Al_2O_3 catalysts.

2. Experimental

2.1. Catalyst preparation

Two CoMo catalysts were prepared by pore-volume impregnation using 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) as support material. Aqueous solutions of cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ (Merck p.a.) and ammonium heptamolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Merck, 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 MES measurements. After introduction of both Mo and Co, the catalysts were dried in static air at 383 K for 16 h and subsequently heated up to 673 K in 5 h and calcined at this temperature for 24 h in static air. The two CoMo/Al_2O_3 catalysts contained 7 wt% Mo, with a high promoter-loading catalyst having 2.25 wt% Co, denoted as Co(2.25)Mo(7)/Al_2O_3, and a low promoter-loading catalyst having 0.04 wt% Co, denoted as Co(0.04)Mo(7)/Al_2O_3. The catalyst loadings are given relative to the support material and are calculated from the impregnation solutions. The samples were sulfided in a flow of 60 $cm^3\,min^{-1}$ 10% H_2S/H_2 mixture at 4 MPa in a high-pressure Mössbauer in situ reactor, similar to the reactor described in detail in [23]. This reactor offers the possibility of studying the catalysts under realistic synthesis conditions. The applied sulfidation treatment is denoted (S, x MPa, y K, z h), indicating that during the experiment the catalyst is linearly heated to y K at x MPa in 1 h and kept at that temperature for z h.

2.2. MES measurements

The 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 corresponding to the absorber moving toward the source. The spectra were analyzed using a Lorentzian fitting procedure as described in [19].

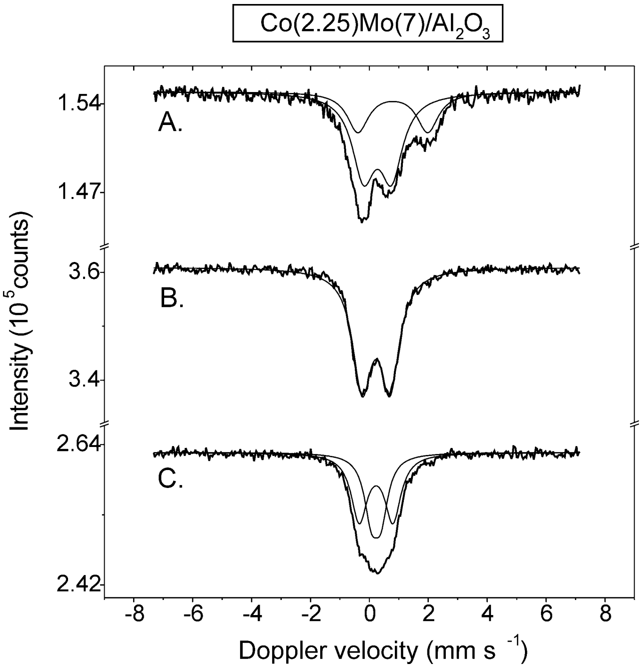

Fig. 1. MES spectra obtained at 300 K with Co(2.25)Mo(7)/Al_2O_3. (A) Fresh catalyst; (B) S, 4 MPa, 673 K, 1 h; (C) S, 4 MPa, 673 K, 4 h. The broad doublet of Co:Al_2O_3 disappeared after high-pressure sulfidation, spectrum B showing only the Co–Mo–S doublet presence. The small QS doublet of sintered Co_9S_8 is observed in spectrum C after 4 h treatment.

3. Results and discussion

The Mössbauer spectra of the sulfided Co(2.25)Mo(7)/Al_2O_3 catalyst are presented in Fig. 1 and the resulting MES parameters are listed in Table 1.

Table 1
MES parameters of Co(2.25)Mo(7)/Al_2O_3 catalyst after sulfidation treatment

T_s (K)	P (MPa)	IS[a] ($mm\,s^{-1}$)	QS[b] ($mm\,s^{-1}$)	Γ[c] ($mm\,s^{-1}$)	A[d] (%)	IS ($mm\,s^{-1}$)	QS ($mm\,s^{-1}$)	Γ ($mm\,s^{-1}$)	A (%)	IS ($mm\,s^{-1}$)	QS ($mm\,s^{-1}$)	Γ ($mm\,s^{-1}$)	A (%)
			Co oxide				Co sulfide				High-spin 2+		
Fresh		0.275	0.946	0.935	67.7	–	–	–	–	0.796	2.371	0.882	32.3
673	4	–	–	–	–	0.224	0.943	0.783	100	–	–	–	–
							Co sulfide				Co_9S_8		
673[e]	4	–	–	–	–	0.227	1.141	0.663	57.6	0.229	0.322	0.577	42.4

[a] Isomer shift: ±0.03 $mm\,s^{-1}$.
[b] Quadrupole splitting: ±0.03 $mm\,s^{-1}$.
[c] Linewidth: ±0.05 $mm\,s^{-1}$.
[d] Spectral contribution: ±5%.
[e] Treatment at 673 K for 4 h.

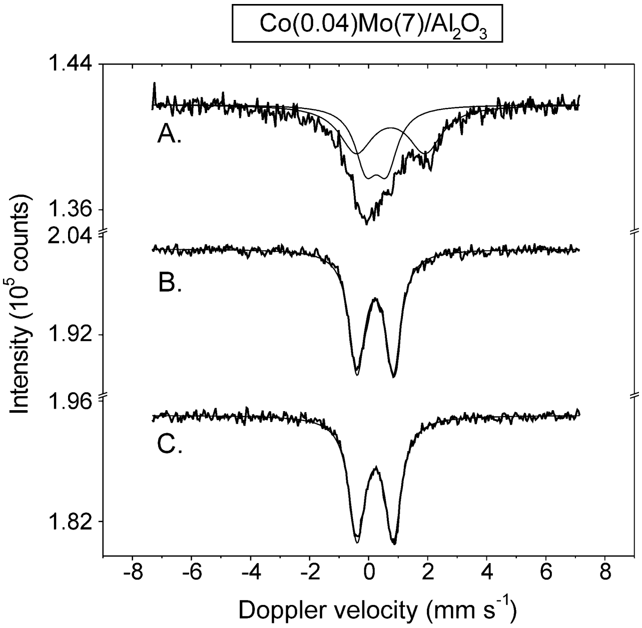

Fig. 2. MES spectra obtained at 300 K with Co(0.04)Mo(7)/Al$_2$O$_3$. (A) Fresh catalyst; (B) S, 4 MPa, 673 K, 1 h; (C) S, 4 MPa, 673 K, 4 h. Only the Co–Mo–S doublet is present in the spectrum of the sulfided catalyst; 4 h treatment does not change the spectrum.

The spectrum of the fresh catalyst consists of one quadrupole doublet indicating a low-spin 2+ or a 3+ phase and a second contribution consistent with Co^{2+} in the high-spin state [24]. After stepwise sulfidation of the catalyst in the H$_2$S/H$_2$ gas mixture up to 673 K at 4 MPa, the high-spin 2+ spectral contribution disappeared in favor of a doublet with IS of 0.22 mm s^{-1} and QS of 0.94 mm s^{-1}. This doublet is assigned to a Co–Mo–S species.

After 4 h treatment at 673 K and 4 MPa, Co-sulfide species sintering is observed. The QS value of 0.32 mm s^{-1} for the new-formed doublet is larger than the QS value of 0.26 mm s^{-1} for crystalline Co$_9$S$_8$ [11], and this doublet is assigned to a dispersed Co$_9$S$_8$-like species [19].

The spectrum of the fresh Co(0.04)Mo(7)/Al$_2$O$_3$ catalyst shows features similar to those of the Co(2.25)Mo(7)/Al$_2$O$_3$ catalyst. On stepwise sulfidation of the Co(0.04)Mo(7)/Al$_2$O$_3$ catalyst up to 673 K at 4 MPa, the high-spin 2+ spectral contribution disappears completely from the spectrum and 4 h treatment under the same conditions does not change the spectrum further (see Fig. 2 and Table 2). The resulting doublet has an IS value of 0.22 mm s^{-1} and a QS value of 1.22 mm s^{-1}, parameters that are characteristic of Co–Mo–S.

Clearly, during sulfidation of the calcined CoMo/Al$_2$O$_3$ catalysts at 4 MPa, the interaction between Co and Al$_2$O$_3$ (characterized by a high-spin 2+ doublet) can be broken and all Co forms Co–Mo–S during a stepwise sulfidation up to 673 K.

The Co$_9$S$_8$-like doublet is not observed in the spectrum of the sulfided Co(0.04)Mo(7)/Al$_2$O$_3$ since the Co$_9$S$_8$ segregation is shifted to higher temperatures with decreasing Co content [25]. The observed increase in QS value of the Co–Mo–S doublet with decreasing Co loading is explained in terms of changing particle size of the Co sulfide species [19]. As the MoS$_2$ edge dispersion is decreasing after activation, an increase in Co loading will result in increased Co sulfide particle size and smaller QS value. The same trends were first explained by Crajé et al. [18,19] in MES studies of the uncalcined catalysts.

In previous MES studies on the sulfidation of Al$_2$O$_3$-supported CoMo catalysts at ambient pressure, it was found that Co in the uncalcined catalysts can be sulfided to Co–Mo–S completely. However, in the MES spectra of the calcined CoMo/Al$_2$O$_3$ catalysts sulfided at atmospheric pressure, the high-spin 2+ subspectrum of Co diffused in the Al$_2$O$_3$ support (Co:Al$_2$O$_3$) was always present [10,18]. For the first time in the MES studies of calcined CoMo/Al$_2$O$_3$ catalysts, we are able to show that, following treatment at 673 K and 4 MPa, Co in the calcined catalysts becomes completely sulfided. Upon high-pressure activation of the catalysts, the Co atoms exit the subsurface positions of the alumina lattice attaching to the edges of the MoS$_2$ crystallites.

The doublet in both Co(2.25)Mo(7)/Al$_2$O$_3$ and Co(0.04)Mo(7)/Al$_2$O$_3$ catalysts, with an IS value of about 0.22 mm s^{-1} and QS values of 0.94 and 1.22 mm s^{-1}, respectively, clearly reveals a Co–Mo–S structure defined by the suggested MES parameters: IS = 0.22 mm s^{-1} and QS = 1.0–1.3 mm s^{-1} [26]. So, it can be concluded that the Co–Mo–S phase is the only Co phase present in these calcined CoMo/Al$_2$O$_3$ catalysts sulfided under conditions relevant to industry.

Several studies have shown that the interaction of promotor atoms with the alumina increases with increasing calcination temperature [27], the amount of tetrahedrally coordi-

Table 2
MES parameters of Co(0.04)Mo(7)/Al$_2$O$_3$ catalyst after sulfidation treatment

T_S (K)	P (MPa)	IS (mm s^{-1})	QS (mm s^{-1})	Γ (mm s^{-1})	A (%)	IS (mm s^{-1})	QS (mm s^{-1})	Γ (mm s^{-1})	A (%)	IS (mm s^{-1})	QS (mm s^{-1})	Γ (mm s^{-1})	A (%)
		Co oxide				Co sulfide				High-spin 2+			
Fresh		0.261	0.696	0.90[a]	45.3	–	–	–	–	0.746	2.338	1.375	54.7
673	4	–	–	–	–	0.219	1.227	0.640	98.7	1.053	2.184	0.131	1.3
673[b]	4	–	–	–	–	0.219	1.223	0.662	100	–	–	–	–

[a] Fixed during fit.

[b] Treatment at 673 K for 4 h.

nated Co growing at the expense of octahedrally coordinated Co [28]. The conclusion that the fraction of Co atoms that can be sulfided decreases as the calcination temperature is increased [29,30] was drawn on the basis of investigations performed at atmospheric pressure and it is not applicable to catalysts activated under real industrial conditions.

Also, the conclusion that calcination temperatures higher than 500–550 °C will generally result in catalysts with poorer performance [2] should now be reconsidered. Calcination treatment retards sulfidation of the Co atoms to temperatures where MoS_2 particles are already present, favoring Co–Mo–S phase formation. Presumably higher calcination temperatures will result in catalysts with more Co–Mo–S phase and, thus, better performance after activation under industrial conditions than previously believed. Binding of oxidic Co and Mo precursors during calcination may also increase the sulfidation temperature of Co [31].

From activity comparison studies [32,33] it was found that high-temperature sulfidation treatment may induce transformation of the Co–Mo–S phase from an incompletely sulfided Type I phase to a highly active Type II Co–Mo–S, where all Mo–O–Al linkages with the alumina support are completely sulfided. The use of complexing agents, which retard sulfidation of the Co atoms until complete Mo sulfidation [34,35] and decrease Mo–support interactions [36], can also lead to Type II Co–Mo–S phase formation.

By increasing the calcination temperature and the temperature of the high-pressure activation of the catalysts, we suggest that highly active, high-temperature Type II Co–Mo–S phases can be formed and, at the same time, Co_9S_8-like structure segregation avoided. Future investigations will deal with this assumption.

4. Conclusion

The high-pressure sulfidation of calcined $CoMo/Al_2O_3$ catalysts in H_2S/H_2 gas mixture at 673 K was studied by MES. Calcination treatment retards sulfidation of the Co species to temperatures where most of the Mo is probably sulfided, allowing Co sulfide particles to attach to the edges of MoS_2.

We have been able to show that after activation of the calcined $CoMo/Al_2O_3$ catalysts at 673 K and 4 MPa, the $Co:Al_2O_3$ becomes completely sulfided, all promoter atoms ending up in the desired Co–Mo–S phase; the Co–Mo–S model is well suited for industrial catalysts.

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