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Promotion of highly loaded MoS_2/Al_2O_3 hydrodesulfurization catalysts prepared in aqueous solution

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Abstract

A procedure for the preparation and promotion of highly loaded MoS_2/Al_2O_3 catalysts (21 wt% Mo) obtained in aqueous solution by the reduction of $(NH_4)_2MoS_4$ with N_2H_4 in the presence of Al_2O_3 was studied. Treating the freshly prepared material with acetone results in the formation of carbon species (ca. 1 wt% C) that make it possible to maintain a high dispersion of the MoS_2 particles. Several Co-promoted MoS_2/Al_2O_3 catalysts were prepared with different methods and Co precursors. Refluxing with $Co(acac)_2 \cdot 2H_2O$ dissolved in organic solvent proved to be the most efficient method for promoting highly loaded carbon-stabilized MoS_2/Al_2O_3. The catalysts obtained can be used directly in the thiophene hydrodesulfurization reaction without any additional sulfidation, and they exhibit a much higher activity than a commercial reference catalyst. An EXAFS study revealed that the acetylacetonate precursor is decomposed during the refluxing treatment and gives new species in which Co is surrounded by sulfur instead of oxygen. The formation of a highly dispersed CoMoS phase was observed after further thiophene hydrodesulfurization reaction.

Keywords: Hydrodesulfurization; Supported catalysts; Cobalt acetylacetonate; Molybdenum disulfide

1. Introduction

Many different approaches have been proposed to eliminate sulfur-containing molecules from petroleum feedstocks in a more efficient way and to meet the forthcoming severe restrictions on the sulfur concentration in fuels [1–3]. Some of these approaches are based on novel processes such as adsorption and biodesulfurization, whereas others are based on the improvement of current hydrotreatment (HDT) technology. Utilization of more active catalysts, because of their much lower investment costs, may be the most attractive solution for petroleum refiners. This approach is applicable at least in the short- and middle-term perspective as long as complete sulfur elimination (ultimate desulfurization) will not be required. Such a demand for more active HDT catalysts generated an unprecedented research activity in recent years [1–3]. These studies made it possible not only to achieve a more complete understanding of the reaction mechanism, but also to make a breakthrough in creating more active catalysts. Despite some interesting results concerning the catalytic activity of new phases such as carbides [4] or phosphides [5,6], the classic sulfide-based formulations appear to be the most promising in responding to the challenge. The emergence of much more active catalysts, such as NEBULA (jointly developed by Exxon Mobil, Akzo Nobel, and Nippon Ketjen) [7] or SMART (Chevron and Grace Davison) [8], illustrates the fact that MoS_2-based materials, although they have been known for about 70 years, still have a great potential.

These studies have shown in particular that one of the ways to improve MoS_2-based catalysts could be to increase the active phase loading or to use bulk sulfides. However,

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a high dispersion of active phase cannot be achieved in these cases by sulfidation of conventional oxide precursors, and other approaches should be used to create small sulfide particles and to maintain their stability under HDT conditions. One of the possible approaches is the use of Mo precursors containing some organic counterpart. Carbonaceous species formed through decomposition of these organic counterparts during the sulfidation of the catalyst precursors, dispersed well over the sulfide particles, may prevent MoS_2 slabs from sintering [9–11]. The efficiency of such an approach is well illustrated by the fact that pure MoS_2 cannot be prepared with BET surface areas exceeding 60–70 m^2/g, whereas materials that contain some carbon exhibit stable surface areas attaining 300–400 m^2/g and have a considerably higher catalytic activity than pure MoS_2 [10].

If properly promoted with Co or Ni, such highly loaded supported or bulk Mo sulfides might show an excellent performance in HDS. However, the use of $Co(NO_3)_2 \cdot 6H_2O$ as a Co source leads to a promoting effect that is considerably lower than the one observed for conventional alumina-supported MoS_2 [12]. It would therefore be interesting to use other precursors and preparation methods, such as chemical vapor deposition of $Co(CO)_3NO$ [13,14] or impregnation with Co acetylacetonate [15], which have already shown their efficiency in promoting supported MoS_2.

In our previous work we found that reduction of ammonium tetrathiomolybdate $(NH_4)_2MoS_4$ by hydrazine in aqueous solution in the presence of alumina particles leads to the formation of highly dispersed MoS_2 supported on Al_2O_3 [16]. The catalysts prepared in this way showed an increase in catalytic activity with Mo loading up to 22 wt% Mo, in contrast to the usual oxide precursor route, for which the activity stabilizes after 12 wt% Mo. We tried to optimize the preparation of both MoS_2/Al_2O_3 and promoted materials with the described approaches. It was found that their catalytic activity can be further increased by a mild treatment in acetone, resulting in the formation of carbon species that stabilize the sulfide particles. We have also developed a new procedure for promoting these systems, which is more efficient than the pore volume impregnation conventionally used for $Co(Ni)MoS_2/Al_2O_3$ hydrotreating catalysts.

2. Experimental

2.1. Catalyst preparation

High-purity starting materials were obtained from Sigma-Aldrich. Ammonium tetrathiomolybdate, $(NH_4)MoS_4$, was obtained by the addition at ambient temperature of 15 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ to 200 mL of a 20 wt% solution of $(NH_4)_2S$. The precipitated red crystals were thoroughly washed with ethanol, dried, and stored under nitrogen.

The MoS_2/Al_2O_3 samples were prepared with a procedure similar to that described in our previous work [16]. Typically, 1.8 mL (0.036 mol) of $N_2H_4 \cdot H_2O$ was dissolved in 30 mL of water, and concentrated HCl was added to the solution to obtain pH 7.8. A solution of 2.32 g (0.009 mol) of $(NH_4)_2MoS_4$ in 70 mL of water was then mixed with the hydrazine solution and the volume was adjusted to 120 mL. After we added 2 g of γ-Al_2O_3 (Procatalyse, $S_{BET} = 230\ m^2/g$, $V_P = 0.6\ cm^3/g$), the mixture was heated at 95 °C for 2 h with stirring. Then the vessel was quickly cooled to room temperature. The suspension was treated with 300 mL of acetone for 1 h and filtered and thoroughly washed with 500 mL of acetone. Carbon-free samples were obtained without any acetone treatment, and these were washed with water. In both cases (with or without acetone treatment), after washing the solids were dried for 12 h under N_2 flow at 100 °C and then sulfided in a 15 vol% H_2S/H_2 flow at 350 °C for 2 h. The carbon-containing sample is referred to here as C–MoS_2/Al_2O_3.

To promote the prepared samples with Co, several procedures were used. For dry impregnation with $Co(NO_3)_2 \cdot 6H_2O$, the salt was dissolved in the appropriate amount of water, and the solid was thoroughly mixed with the solution and kept in a closed vessel for 6 h at room temperature. To achieve the promotion of the catalysts in the presence of a chelating agent, the diammonium salt of ethylenediaminetetraacetic acid (EDTA) was used (EDTA/Co = 1:1). First the complexing agent was dissolved in concentrated NH_3, then $Co(NO_3)_2 \cdot 6H_2O$ was added. After the complete dissolution of the Co precursor, the solution was used for the pore volume impregnation of MoS_2/Al_2O_3. The samples obtained from these preparations were dried under N_2 at room temperature and resulfided under the same conditions as the initial MoS_2/Al_2O_3 material.

To promote the samples with Co acetylacetonate, two methods were used: the equilibrium adsorption method and refluxing. For *refluxing*, the required amount of acetylacetonate complex (Co/Mo atomic ratio = 0.4) was dissolved in a minimum amount of methanol, then MoS_2/Al_2O_3 was added and the suspension was heated at boiling temperature (65 °C) for 4 h. Afterward, the solid was recovered by filtration and dried under N_2 at room temperature. For the samples prepared by *equilibrium adsorption*, a similar procedure was used, but instead of being refluxed, the samples were stirred at room temperature for 48 h.

2.2. Catalyst characterization

The metal content in the synthesized solids was determined, after dissolution in a HNO_3/H_2SO_4 mixture, by plasma-coupled atomic emission spectroscopy (AES-ICP). The sulfur and carbon contents were measured with a Strohlein Instruments CS-MAT 5500 analyzer.

The EXAFS measurements were performed at the Laboratoire d'Utilisation du Rayonnement Electromagnétique (LURE, Orsay, France), on the XAS 13 spectrometer with a Ge (400) monochromator. The measurements were carried out in transmission mode at the Co K edge (7709 eV), at ambient temperature, with a 2 eV step and 2 s per point. The sample thickness was chosen to give an absorption edge step of about 1.0 near the edge region. Phase shifts and backscattering amplitudes were obtained from FEFF calculations made for cobalt oxide (CoO) and sulfide (Co_9S_8). The EXAFS data were treated with VIPER [17] and FEFF [18] programs. The curve fitting was done in R and k space. Coordination numbers (N), interatomic distances (R), Debye–Waller parameters (σ^2), and energy shifts (ΔE_0) were used as fitting variables.

Infrared spectra were recorded on a Bruker Vector 22 FT-IR spectrometer at 2 cm^{-1} resolution with KBr discs. NMR spectra of carbon-containing MoS_2/Al_2O_3 samples (^{13}C CP MAS) were measured on a Bruker DSX 400 spectrometer. Frequencies of 100.63 MHz (^{13}C) and 400.17 MHz (^1H) were used. The sample was spun at 5 kHz, and the spectra were taken after a pulse of 6 µs and a 3 ms contact time. The interval between successive scans was 4 s. ^{13}C chemical shifts are referenced to tetramethylsilane, which was used as an external standard.

Catalytic activities were measured for thiophene hydrodesulfurization at atmospheric pressure in a fixed-bed flow microreactor. In the chosen temperature range, 280–320 °C, the thiophene conversion was about 30% under the conditions used (50 ml/min gas flow, 50–60 mg of catalyst), and the plug-flow reactor model was used to calculate the rate constant:

$$k = \frac{F}{mC} \ln \frac{1}{1-x},$$

where k is a pseudo-first-order rate constant ($m^3/(g\,s)$), F is the thiophene molar flow (mol/s), m is the catalyst mass (g), C is the thiophene molar concentration (mol/m^3), and x is the conversion determined after 15 h time on stream.

N_2 adsorption and desorption isotherms were measured with a Micromeritics ASAP 2010 instrument. Pore size distributions of the samples in the mesopore domain were calculated from the isotherms by the Barrett–Joyner–Hallenda (BJH) method with the software provided with the apparatus.

3. Results and discussion

3.1. Nonpromoted MoS_2/Al_2O_3 samples

In our previous work [19] we found that unsupported MoS_2 prepared by reduction of an aqueous solution of $(NH_4)_2MoS_4$ with N_2H_4 and washed with acetone shows a high surface area. A detailed analysis of these solids dried under N_2 at 100 °C revealed that they contained ca. 5 wt% carbon. A similar phenomenon was observed when such a treatment with acetone was applied to supported molybdenum sulfide, as shown in Table 1. HRTEM micrographs show that despite the high loading of MoS_2 (21 wt% Mo) and sulfiding treatment at 350 °C, the particles of the sulfide remained well dispersed (Fig. 1). A rigorous determination of the particle size distribution is not possible in this case because of strong interpenetration of the MoS_2 layers, but the image is characteristic of poorly stacked ($n = 2$–4) and highly disordered molybdenum disulfide.

Table 1
Composition, textural and catalytic properties of Al_2O_3 and MoS_2/Al_2O_3 specimens

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Rate constant of thiophene HDS at 300 °C (10^{-8} $m^3/(g\,s)$)	Mo (wt%)	C (wt%)
Al_2O_3	230	0.60	–	–	–
MoS_2/Al_2O_3	193	0.26	42	21.5	–
C–MoS_2/Al_2O_3	196	0.23	65	21.2	1.2

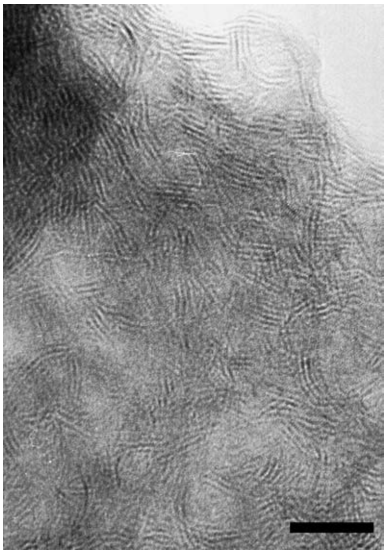

Fig. 1. High resolution TEM image of C–MoS_2/Al_2O_3 (scale bar—10 nm).

Adsorption isotherms of Al_2O_3 and MoS_2/Al_2O_3 samples (Fig. 2a) are typical of mesoporous solids (Type IV). As follows from the BJH analysis of the adsorption part of the isotherms (Fig. 2b), the pore size distribution becomes larger and the mean pore diameter decreases from about 100 Å for Al_2O_3 to 40 Å for MoS_2/Al_2O_3. Surface area and pore volume of the material decrease considerably after the deposition of molybdenum sulfide (Table 1). The volume occupied by MoS_2 itself (ca. 0.07 ml/g) cannot explain the observed loss of pore volume, so some pores are blocked by the deposited particles. As the loading used greatly exceeds that corresponding to the monolayer capacity of Al_2O_3 ($\sim$ 12 wt% Mo), MoS_2 particles should form aggregates with a substantial surface area and therefore make some contribution to the value of S_{BET}. This explains why the BET surface area is decreased to a lesser extent than the pore volume after the alumina is loaded with MoS_2 (Table 1).

The carbon-free sample exhibits a lower catalytic activity than C–MoS_2/Al_2O_3 (Table 1). As the catalytically active sites are located on the edges of MoS_2, this difference

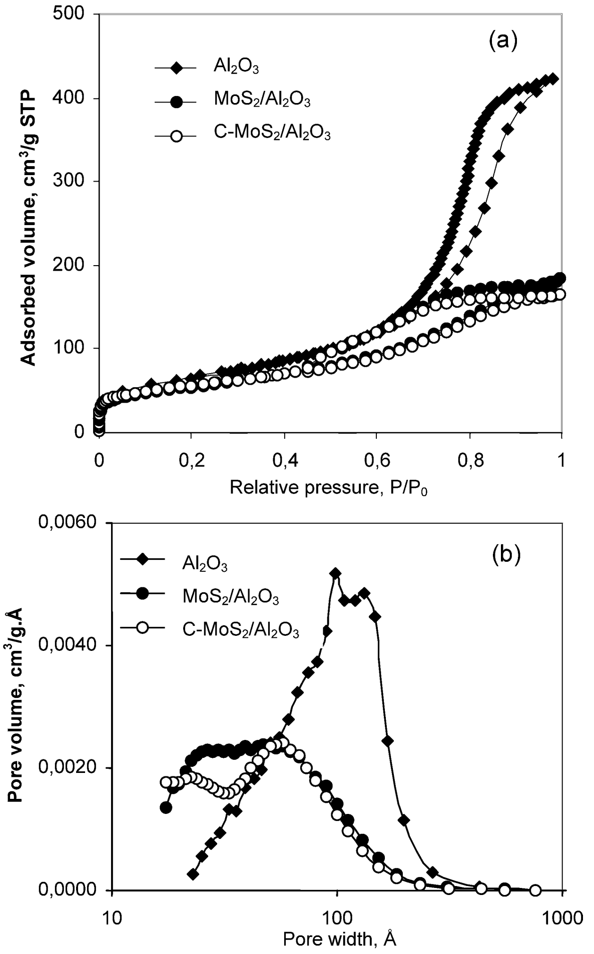

Fig. 2. Textural properties of Al_2O_3 and MoS_2/Al_2O_3 samples: N_2 adsorption–desorption isotherms (a), BJH pore volume distribution (b).

means that in C–MoS_2/Al_2O_3 the sulfide particles contain relatively more edges. The carbon species apparently prevent the lateral growth of the MoS_2 particles during sulfidation. Unfortunately, the interpenetration of the MoS_2 layers did not allow us to confirm a smaller diameter of the MoS_2 slabs in the TEM pictures. Such a difference in the morphology is not reflected by the measured BET surface areas because the surface area of the edges is low.

To elucidate the nature of the reactions resulting in the formation of residual carbon species, we measured the ^{13}C NMR CP MAS spectrum of the sample before sulfidation (i.e., after drying at 100 °C) (Fig. 3). Along with a strong peak at 25 ppm corresponding to hydrocarbon moieties, a weaker signal was observed at 53 ppm, which can be attributed to aliphatic carbon atoms bonded to sulfur [20]. These organosulfur compounds, which are not eliminated upon drying, result from polythioacetone, a product of spontaneous polymerization of thioacetone [21–23]. The formation of the latter is indicated by the reddish color of the washing solution after the addition of acetone (thioacetone has a red color [22]). Moreover, if this solution is evaporated the residue formed is a malodorous, glossy film whose formation was observed after the spontaneous polymerization of thioacetone under ambient conditions [23]. Because of their high molecular weight, the organosulfur polymeric compounds are not desorbed during sulfidation but decomposed, yielding carbonaceous species that prevent MoS_2 particles from sintering.

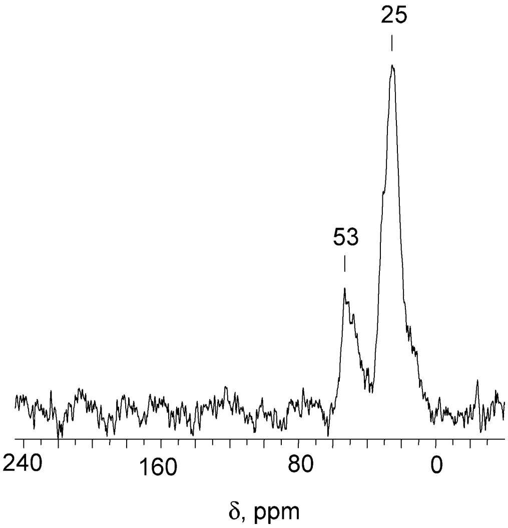

Fig. 3. ^{13}C CP MAS NMR spectrum of the C–MoS_2/Al_2O_3 sample before sulfidation.

3.2. *Promotion of MoS_2/Al_2O_3 catalysts*

It was previously observed that the introduction of a promoter into a presulfided MoS_2-based catalyst might be more efficient than classical co-impregnation of oxide precursors followed by sulfidation [13–15]. This effect was explained by a more facile formation of the mixed CoMoS phase on the preformed MoS_2 particles. Generally, in a mixed Co–Mo supported oxide, the group VIII metal has a tendency to be sulfided before molybdenum and to form isolated sulfide particles not included in the active CoMoS phase. Thus, to increase the amount of catalytically useful Co–Mo sulfide, either sulfidation of cobalt should be retarded or that of molybdenum accelerated. Such a leveling of the sulfidation rates of Co and Mo species was suggested to play a key role in improving the catalytic activity in the presence of chelating agents [24,25].

A more active, carbon-containing MoS_2/Al_2O_3 sample (C–MoS_2/Al_2O_3) was chosen for promotion, and different procedures were tried to study the influence of the nature of the Co precursor and operational conditions on the catalytic activity of $CoMoS/Al_2O_3$ catalysts. The methods used for cobalt introduction and the values of the catalytic activity obtained are summarized in Table 2 (the promotion coefficient is calculated by dividing the activity of the promoted sample by that of C–MoS_2/Al_2O_3).

It can be seen that using an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ as a Co source for promotion leads to the lowest catalytic activity. The main reason for such a low synergetic effect is a reaction between molybdenum sulfide and

Table 2
Preparation, composition and catalytic activity of the Co-promoted C–MoS_2/Al_2O_3 samples

	Promotion procedure	Rate constant of thiophene HDS at 300 °C (10^{-8} $m^3/(g\,s)$)	Co/Mo ratio	Promotion coefficient
	Pore volume impregnation followed by sulfidation			
1	$Co(NO_3)_2 \cdot 6H_2O$	351	0.40	5.4
2	$Co(NO_3)_2 \cdot 6H_2O + EDTA$	395	0.40	6.1
	Equilibrium adsorption			
3	$Co(acac)_2 \cdot 2H_2O$	474	0.17	7.3
4	$Co(acac)_2$	438	0.15	6.7
5	$Co(acac)_3$	389	0.08	6.0
	Reflux			
6	$Co(acac)_2 \cdot 2H_2O$	543	0.16	8.4
7	$Co(acac)_2$	462	0.15	7.1
8	$Co(acac)_3$	451	0.11	6.9
9	Commercial reference catalyst (HR306) 8.3 wt% Mo, 2.2 wt% Co	176	0.43	

cobalt nitrate, which was indicated by the formation of NO_2 (detected by its brown color and characteristic odor) during impregnation. This can be explained by the fact that NO_3^- anions in a moderately acid aqueous solution (due to a partial hydrolysis of Co^{2+}) can oxidize molybdenum sulfide under ambient conditions. To verify this possibility, a solution of $Co(NO_3)_2 \cdot 6H_2O$ was stirred with MoS_2 and then filtered and evaporated under nitrogen. The fact that $CoSO_4 \cdot 7H_2O$, which contains a product of sulfide oxidation (SO_4^{2-}), was found in the XRD pattern of the residue clearly proves that such a reaction occurs. It will certainly modify the structure of the most reactive MoS_2 edge sites containing superficial –SH and S_2^{2-} moieties and consequently will influence the whole impregnation process. A similar phenomenon, replacement of sulfur by oxygen in the local environment of tungsten, was observed when alumina-supported $(NH_4)WS_4$ was impregnated with $Ni(NO_3)_2 \cdot 6H_2O$ [26]. Use of cobalt nitrate, together with a chelating agent, EDTA, which retards Co sulfidation, increases the activity somewhat, but the promotion coefficient remains lower than that obtained with $Co(acac)_2 \cdot 2H_2O$ as precursor (see below).

In an attempt to decrease the chemical impact of the cobalt precursor on the presulfided molybdenum phase, we used cobalt acetylacetonate, which had been found earlier to be a good promoter precursor for carbon-supported MoS_2 [15]. The exact nature of the compound used in that work was not indicated; therefore we searched first the most appropriate Co acetylacetonate from the three compounds commercially available: $Co(acac)_2$, $Co(acac)_2 \cdot 2H_2O$, and $Co(acac)_3$. As none of these acetylacetonates are sufficiently soluble in organic solvents to allow pore-volume impregnation, equilibrium adsorption in methanol was first applied. It was found that $Co(acac)_2 \cdot 2H_2O$ gives the most active catalysts (Table 2).

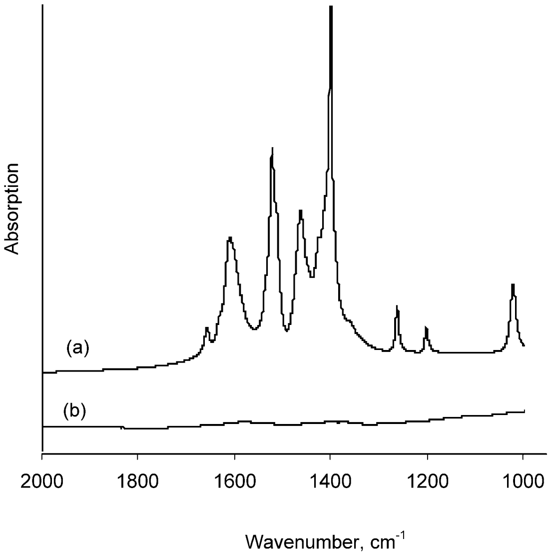

Fig. 4. FTIR spectra of $Co(acac)_2 \cdot 2H_2O$ (a) and the C–MoS_2/Al_2O_3 sample after equilibrium adsorption of $Co(acac)_2 \cdot 2H_2O$ (b).

A more detailed study of the promoted samples revealed that a chemical reaction occurs between $Co(acac)_2 \cdot 2H_2O$ and MoS_2/Al_2O_3 during stirring. A very long contact time between the solution and supported sulfide (48 h) was needed to obtain highly active catalysts, which should not normally be the case if only adsorption is implicated. Furthermore, the FTIR spectrum of the promoted sample does not contain the strong characteristic bands between 1400 and 1650 cm^{-1} observed in the spectrum of the precursor (Fig. 4). To favor this reaction, we refluxed a nonpromoted C–MoS_2/Al_2O_3 sample in a methanol solution of $Co(acac)_2 \cdot 2H_2O$ at the boiling point (65 °C), and we found that the sample obtained shows the highest catalytic activity (Table 2). Moreover, when promotion is done with acetylacetonate, the solids can be used directly in catalytic tests without resulfidation, and we did not observe any increase in activity during the test. This means that the Co species obtained under reflux can easily be transformed into the catalytically active CoMoS phase in the presence of thiophene during heating to 300 °C before the first analysis ($\sim$ 1 h). In contrast, if the samples prepared with $Co(NO_3)_2 \cdot 6H_2O$ (with or without EDTA) are used in the test without being resulfided after impregnation, their activity increases during the test before reaching a pseudostationary state, and it remains much lower than the activity of the sulfided samples.

To elucidate the nature of the cobalt species formed during reflux, the Co K-edge EXAFS spectrum of the sample after promotion was compared with that of the precursor, $Co(acac)_2 \cdot 2H_2O$, and with the spectra of the same sample after catalytic testing and sulfidation (Figs. 5 and 6). It can be seen that the coordination sphere of the Co atoms in the species deposited on the surface of MoS_2/Al_2O_3 differs noticeably from that in acetylacetonate (all peaks at $r > 2$ Å on the FT curves disappear), in accordance with the data of FTIR spectroscopy. Detailed analysis of these spectra (Ta-

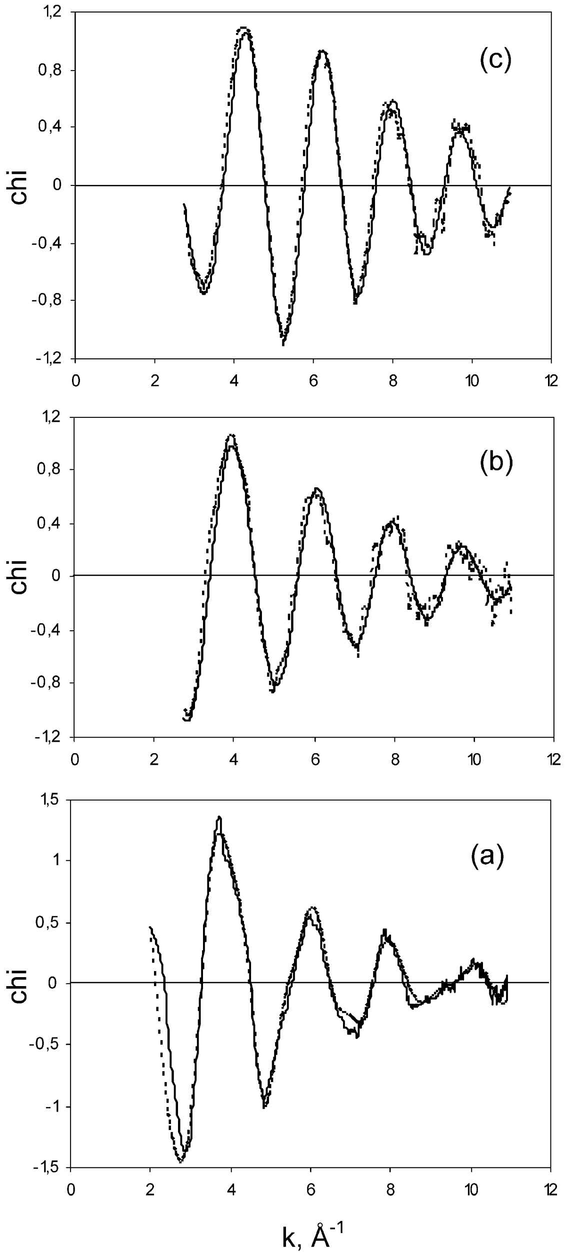

Fig. 5. Co K-edge EXAFS spectra of $Co(acac)_2 \cdot 2H_2O$ (a) and of the $C–MoS_2/Al_2O_3$ sample promoted with $Co(acac)_2 \cdot 2H_2O$: after reflux (b) and after the test (c). Dotted line—experimental data, solid line—fit.

Table 3
EXAFS fit parameters for the Co K absorption edge

	Atom	R (Å)	N	Δσ (Å^2)	ΔE (eV)
$Co(acac)_2 \cdot 2H_2O$	O	2.02	5.3	0.01	−3.6
	Co	4.11	2.0	0.01	1.9
$C–MoS_2/Al_2O_3$ promoted with $Co(acac)_2 \cdot 2H_2O$ (sample 6 from Table 2)					
After reflux	S	2.20	4.2	0.009	−3.5
After the test	S	2.20	3.5	0.008	−2.5
	Mo	2.80	0.7	0.008	−0.5
After sulfidation	S	2.21	3.7	0.007	−4.0
	Mo	2.81	0.7	0.007	−0.4

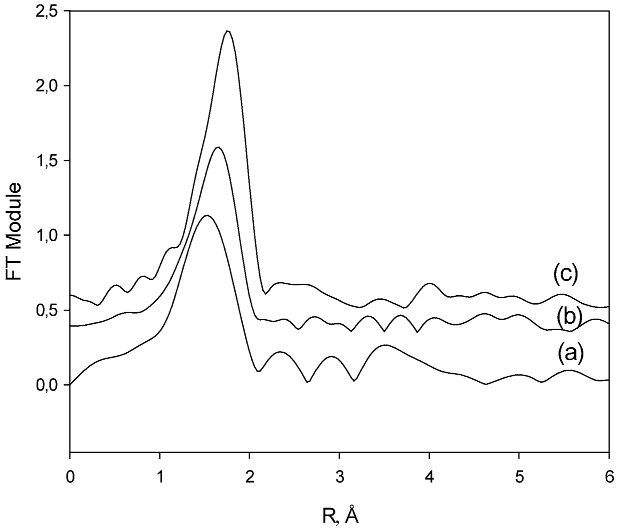

Fig. 6. Fourier transforms of Co K-edge EXAFS spectra of $Co(acac)_2 \cdot 2H_2O$ (a) and of the $C–MoS_2/Al_2O_3$ sample promoted with $Co(acac)_2 \cdot 2H_2O$: after reflux (b) and after the test (c).

ble 3) reveals that already in the refluxed solid, the cobalt atoms are surrounded by sulfur instead of oxygen. No information about a second coordination shell of Co can be extracted from the spectrum, possibly because of a low ordering of the species and/or a large distance to the closest metallic neighbor. The spectra measured after catalytic reaction or sulfidation are similar, and a new peak is observed in the FT curves, corresponding to the existence of a second neighbor (Fig. 6c), which can be fitted as a Mo atom at 2.8 Å, a distance characteristic of the CoMoS phase [27].

These findings suggest that during reflux $Co(acac)_2 \cdot 2H_2O$ interacts with reactive surface groups such as –SH or S_2^{2-}, forming poorly ordered and highly dispersed Co–S species whose exact nature is not fully understood. We would like to stress, however, that these species do not resemble highly dispersed Co_9S_8 or any other cobalt sulfide, as it is well known that these compounds have a low activity in HDS [28]. They can rather be described as isolated Co atoms on the MoS_2 edges. Because of a high degree of dispersion and intimate contact between Co atoms and MoS_2, a mixed CoMoS phase, instead of separate Co sulfide particles, is formed after sulfidation or even during heating before the thiophene HDS test. The fact that acetylacetonates are not simply adsorbed but react with molybdenum sulfide explains the observed higher efficiency of $Co(acac)_2 \cdot 2H_2O$ in comparison with $Co(acac)_3$ and $Co(acac)_2$ (Table 2). In contrast to $Co(acac)_2 \cdot 2H_2O$, both anhydrous complexes have a closed coordination sphere consisting only of chelating ligands, and therefore they are more stable vis-à-vis a decomposition reaction.

The data presented in Table 2 show that the use of $Co(acac)_2 \cdot 2H_2O$ makes it possible to obtain much more active catalysts than pore volume impregnation with $Co(NO_3)_2 \cdot 6H_2O$. We suppose that essentially the same reactions occur during prolonged stirring at room temperature (48 h) and upon reflux at 65 °C. The difference between these two procedures consists of the fact that in contrast to stirring at room temperature, reflux makes it possible to accomplish the reaction of acetylacetonate with MoS_2 in a short time (4 h). Additional experiments confirmed that a further increase in the reflux time did not improve the catalytic activity. In addition to a high catalytic activity, the CoMo catalysts obtained with the use of reactive promotion with $Co(acac)_2 \cdot 2H_2O$ have other particular features. They can be used directly in the HDS reaction without any additional sulfidation, and their improved catalytic performance is achieved with a lower promoter concentration (Table 2), showing that for highly loaded materials, reactive promotion makes it possible to introduce Co atoms in a more efficient way than does impregnation.

4. Conclusions

It has been shown that the stability and catalytic activity of MoS_2/Al_2O_3 (21 wt% Mo) prepared in aqueous solution through the reduction of $(NH_4)MoS_4$ by hydrazine can be considerably improved by a post-reaction treatment in acetone. High-molecular-weight organosulfur compounds formed during this treatment, presumably polythioacetone, are strongly adsorbed to the surface of the MoS_2 particles, limiting the growth of the particles during sulfidation.

A pore volume impregnation of these highly loaded catalysts with $Co(NO_3)_2 \cdot 6H_2O$ does not give a high promotion level. A new procedure, reactive promotion, was therefore developed, which consists of a reflux of the MoS_2/Al_2O_3 sample in a methanol solution of $Co(acac)_2 \cdot 2H_2O$. The EXAFS data showed that after such a treatment the Co atoms appear in a sulfide environment. The catalysts promoted in this way can be directly used in thiophene HDS; the catalytically active CoMoS phase is rapidly formed as the sample is heated to the reaction temperature. This is the first example of a promotion procedure for presulfided MoS_2, which yields Co atoms directly in a sulfide environment, thus making it possible to form the CoMoS phase under very mild conditions. Studies are in progress concerning the application of reactive promotion to highly dispersed *unsupported* MoS_2 catalysts.

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