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Structure and Thiophene Hydrodesulfurization Activity of MoS_2/Al_2O_3 Catalysts

D. I. Kochubei, V. A. Rogov, V. P. Babenko, S. V. Bogdanov, and V. I. Zaikovskii
Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

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Abstract—It was found that, in MoS_2/Al_2O_3 catalysts prepared by exfoliation, the structure of MoS_2 is strongly distorted. The catalytic activities of these catalysts and traditionally prepared catalysts toward the hydrodesulfurization of thiophene were compared. It was established that the stacking dimension of MoS_2 in the catalysts prepared by exfoliation was 200 Å, whereas it was 20 Å in a standard catalyst. It was demonstrated that, although the number of molybdenum atoms in the edge plane per gram of MoS_2 in the catalysts prepared by exfoliation was 10 times smaller than that in the standard catalyst, the activity of these catalysts was close to the activity of the standard catalyst. On this basis, it was suggested that the hydrodesulfurization of thiophene can occur on the basal plane of MoS_2 that has a defect-free structure with a distorted environment of molybdenum.

INTRODUCTION

Oil hydrofining catalysts based on molybdenum disulfide have long been under study because of their widespread use [1, 2]. The structure of the active component, synergism on the addition of a second metal (cobalt or nickel), and the localization site of this metal have been studied intensively. According to universally accepted notions, molybdenum disulfide (MoS_2) nanoparticles constitute the active component, whereas the second metal (cobalt or nickel) occurs at the edge planes of the parent disulfide [3]. The catalytic activity is usually studied in a model reaction of thiophene hydrodesulfurization. There are two main theories of thiophene activation. According to one of them [4], thiophene is adsorbed on nickel or cobalt in the oxidation state 3+ located on the edge planes of the sulfide [5]. Thiophene is activated on adsorption because of charge transfer from thiophene to the metal. The other model [6] assumes the occurrence of point defects like vacancies, positions occupied by sulfur in the basal plate of the disulfide. However, both of the models consider disulfide particles with ideal structures. In the last few years, the support acidity was changed by treating the support with acids (fluorine and phosphorus) or bases (sodium and ammonia) before or after supporting molybdenum disulfide [7–9]. It was found that this treatment somewhat changed the catalytic activity; this change was related to the competitive adsorption of thiophene on surface acid sites. Moreover, the modification of Al_2O_3 surface acidity or the introduction of a second oxide into the catalyst support before supporting molybdenum and cobalt strongly affected the morphology of MoS_2 [10–12]. It was found that a change in the morphology of MoS_2 has no effect on the activity of catalysts; however, it affects the product composition of thiophene hydrodesulfurization.

In 1986, Joensen *et al.* [13] proposed a method for separating MoS_2 into platelets by lithium intercalation between MoS_2 layers using butyllithium. This method was termed exfoliation. After this intercalation, the disulfide was placed in water; because of lithium oxidation, the volume of the interlayer space increased and the disulfide was separated into individual stacks. Thereafter, a stable colloidal suspension was formed in water. The method was used to prepare catalysts for various processes [14–19] including hydrodesulfurization. These catalysts have attracted interest because MoS_2 stacks with different numbers of layers can be prepared using this method. In this case, the catalytic activities of edge planes in the middle of stacks and of the edge planes of surface layers, as well as the activity of the basal plane, can be compared. Such studies were performed for the hydrodesulfurization reactions of various compounds (including dibenzothiophene) with the use of unsupported MoS_2 [16, 17]. It was found that the specific surface area of the disulfide dramatically decreased in the course of reaction, and the catalyst was deactivated. Del Valle *et al.* [17] concluded that the activities of all disulfide edge planes were equal on the condition that steric hindrances were absent. Yang and Frindt [18] changed the number of layers in a stack by varying the pH value of a MoS_2 solution on supporting the disulfide onto Al_2O_3. They found that the catalyst activity in the reaction of thiophene decomposition was independent of the number of layers; however, the distribution of products was changed. In both cases, Yang and Frindt [18] related changes in the product composition to different activities of the edge planes of surface and internal MoS_2 layers in the interaction with secondary products because of steric hindrances.

However, the effect of exfoliation is not restricted by the possibility of obtaining single-layer MoS_2 stacks. In

Table 1. Catalytic activities of MoS_2/Al_2O_3 samples in the hydrodesulfurization of thiophene

Catalyst	MoS_2, wt %	$w \times 10^9$, mol/(s (g MoS_2))
5KB	6.3	1150
21KB	7.6	2800
32KB	5.3	1020
Standard	12.0	1050

many publications [20–22], it was demonstrated that the resulting MoS_2 particle is negatively charged. This charge resulted from the adsorption of lithium ions on the basal plane of the particle. This effect was also retained on the removal of lithium and the adsorption of other reagents, including hydrogen [23], pyridine, and other organic bases. In a study by the intercalation method, it was found that the resulting MoS_2 underwent considerable structural changes. MoS_2 can undergo a structural transition from the standard 2H modification, in which sulfur atoms form a trigonal prism around molybdenum, into the 1T modification with an octahedral sulfur environment of molybdenum [21]. In particular, this effect was observed in the interaction of MoS_2 with hydrogen. Moreover, sulfur and molybdenum atoms were shifted from their crystallographic positions. Various structures were formed depending upon the effect on MoS_2 through the basal plane and upon the charge transferred to it. When a small charge is transferred, structures like charge-density waves are formed with atomic shifts of up to 0.1–0.2 Å [25] with the formation of superstructures with a period of about 30 Å. When greater charges are transferred, molybdenum ion dimers are formed with an Mo–Mo bond length of about 2.8 Å, which is close to the distances in Mo_2S_3. These effects were retained up to 300°C [24, 26].

EXAFS spectroscopy has played an important role in the studies of the active centers of these catalysts. Fundamental structural studies have been performed with the use of this method. However, EXAFS data are not fully consistent with the universally accepted model of the catalyst active center. Underestimated coordination numbers of the sulfur and molybdenum environments of molybdenum atoms, as compared with calculated values, were obtained in almost all the studies performed by this technique [27, 28]. Several attempts to explain this fact were made. First, the underestimated coordination numbers were associated with nonstoichiometry due to the decreased sulfur concentration in the active component. This was supported by Boudart *et al.* [29]; they reported the dependence of coordination numbers derived from EXAFS data for Mo–S on reactant pressures. An increase in the pressure and, correspondingly, in the sulfur amount increased coordination numbers for the Mo–S distance. However, Startsev and Kochubei [30] also observed underestimated coordination numbers in catalysts with a stoichiometric Mo : S ratio. Startsev and Kochubei [30] explained this effect by the methodology of EXAFS spectroscopy, namely, by a high sensitivity of the effective coordination number determined using this technique to the amplitude of atomic thermal vibrations (the Debye–Waller factor). In the proposed model, molybdenum atoms in the outer layer exhibited a much greater Debye factor than that of molybdenum atoms in inner layers. In this case, the outer atoms became undetectable by EXAFS spectroscopy. This assumption resulted in agreement between EXAFS data on the coordination numbers of the active component of pure MoS_2 and commonly accepted values; however, it did not explain why the coordination numbers for Mo–S and Mo–Mo remained unchanged on the addition of a second metal. According to the commonly accepted model, the second metal is located on the edge plane of molybdenum disulfide in an outer layer; thereafter, all molybdenum cations became equivalent and occurred in the inner layers of the active center. This would result in the disappearance of the reason for underestimated coordination numbers. We found [27] that these underestimated coordination numbers can be due to macroscopic distortions in MoS_2, which is a catalyst constituent. In this context, these can be structural distortions like charge-density waves, when local distortions of a molybdenum environment with quasi-periodic repetition are observed.

In this work, we studied the structure and catalytic activity of catalysts prepared by exfoliation in the hydrodesulfurization reaction of thiophene.

EXPERIMENTAL

Catalyst Preparation

The parent MoS_2 was prepared by a solid-phase synthesis from elemental sulfur and molybdenum in accordance with a published procedure [31] and characterized by X-ray diffraction and elemental analysis. The intercalation of lithium was performed by the treatment of 300 mg of MoS_2 with a butyllithium solution (1.6 M) in hexane (Aldrich) for several weeks at room temperature. After the treatment, the resulting $LiMoS_2$ was several times washed with hexane and dried in a flow of argon. An aqueous suspension (1 g/l) was prepared by adding $LiMoS_2$ to water in an argon atmosphere with ultrasonication for 10 min using a UZDN-1 generator. To prepare supported compounds, a support (0.5 g) was added to the suspension. The solution was stirred with a magnetic stirrer for 10 min and then decanted. The sediment was washed with water and dried at 50–100°C. The final drying was performed at 350°C in a flow of argon for 2 h.

A1 γ-Al_2O_3 with a specific surface area of 180 m^2/g was used as the support. Table 1 summarizes data on the molybdenum contents of the tested catalysts.

A catalyst prepared by the conventional method of incipient wetness impregnation [32] using γ-Al_2O_3 and an aqueous $(NH_4)_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$ solution and sulfurized in a flow of H_2S at 400°C for 2 h was used as a reference sample.

Determination of Catalytic Activity

The activity of catalysts in the hydrodesulfurization reaction of thiophene was determined in a flow setup at 400°C and a hydrogen pressure of 1 atm. The initial concentration of thiophene was 1.2×10^{-3} M. Thiophene from Acros Organics was used. Impurities from hydrogen were removed on a column with molecular sieves; the column was cooled with liquid nitrogen. Before activity measurements, catalyst samples (particle size of 0.5–1.0 mm) were treated with a reaction mixture for 3 h. The rate of reaction per gram of MoS_2 at a thiophene conversion of ≈2.5% was chosen as a measure of activity. Catalyst samples (from 20 to 300 mg) and the reaction-mixture flow rate were chosen to provide the required conversion. Table 1 summarizes the results of catalytic activity measurements.

EXAFS Spectroscopy

The EXAFS spectra were measured at the EXAFS Station of the Siberian Synchrotron Radiation Center at an electron energy of 2 GeV and a current of 80 mA at the VEPP-3 electron storage ring in a transmission mode. The spectrometer had a two-crystal Si(111) channel-cut monochromator and proportional chambers as detectors. The data were treated according to a standard procedure with the use of the VIPER program [33] for separating the oscillating part of the absorption coefficient and the EXCURV 92 program [34] for simulating structural data. The spectra were simulated in a wavenumber range of 3–14 $Å^{-1}$ for data represented as $k^3\chi(k)$. Taking into account the above consideration, in the simulation, the Debye–Waller factors were fixed and taken as equal to 0.005 $Å^2$.

Electron Microscopy

The electron micrographs of samples supported on alumina were taken on a JEM 2010 transmission microscope from Jeol (Japan).

X-ray Diffraction

The samples before and after the reaction were studied by X-ray diffraction analysis on an HZG-4C diffractometer (Freiberger Praezisionmechanik, Germany) with the use of monochromated CuK_α radiation (diffracted beam flat graphite monochromator).

RESULTS AND DISCUSSION

The structure of catalysts was studied by X-ray diffraction analysis and transmission electron microscopy. According to X-ray diffraction data, the dimension of parent MoS_2 in the basal plane was no smaller than 200 Å. After supporting MoS_2 on alumina, all samples were X-ray amorphous. The catalyst prepared in accordance with the standard procedure also remained X-ray amorphous after the reaction. In all catalysts prepared by exfoliation, MoS_2 stacks underwent partial sticking because of the reaction of thiophene hydrodesulfurization; however, the number of layers was no higher than four. The dimensions of the coherent-scattering regions along the *C* axis for the catalysts were similar and equal to 25–30 Å. Other reflections, in particular, reflections that correspond to directions in the basal plane, were not observed after the reaction. It is likely that MoS_2 stacks retained strong flexures in this direction even upon sticking.

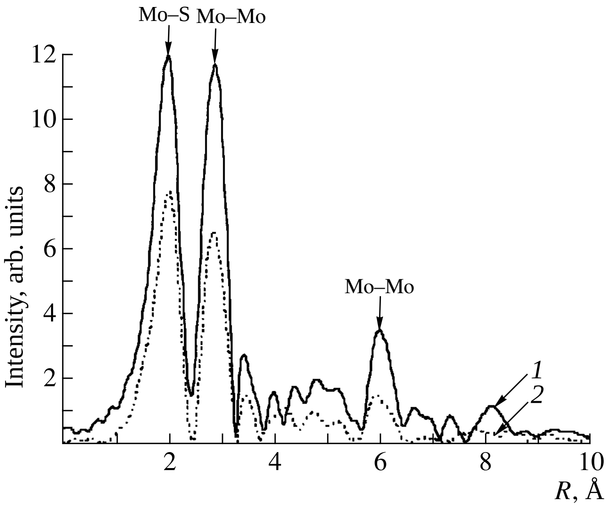

Fig. 1. Fourier transform amplitudes of the molybdenum *K*-edge EXAFS spectra of (*1*) a mechanical mixture of 5% MoS_2 in γ-Al_2O_3 and (*2*) catalyst 21KB.

Nevertheless, according to electron-microscopic data, the size remained unchanged. The average dimension of MoS_2 particles in the basal plane remained equal to 200 Å, as measured in catalyst 5KB, whereas the average particle size of MoS_2 in the reference sample was equal to 20 Å. The electron micrographs of the initial catalyst exhibited mainly single-layer particles or stacks, in which the interlayer distance is greater than that in crystallized MoS_2. All MoS_2 particles were distorted. The character of these distortions is compound bending with a great radius. The resolution of the microscope did not allow us to determine whether local deformations like charge-density wave structures occurred in the catalysts.

Figure 1 demonstrates typical radial atomic distribution (RAD) curves for the molybdenum atom. All of the RAD curves exhibited peaks corresponding to the Mo–S and Mo–Mo distances in the first and second coordination spheres of MoS_2, respectively (the Mo–S and Mo–Mo distances are 2.44 and 3.14 Å, respectively; in both cases, the coordination number is 6). In the cases of molybdenum oxidation by oxygen of the

Table 2. Effective coordination numbers (±10%) and interatomic distances (±1%) for the first and second coordination spheres Mo–S and Mo–Mo found from the Mo K-edge EXAFS spectra

Catalyst	N_{eff} (Mo–S)	R (Mo–S), Å	N_{eff} (Mo–Mo)	R (Mo–Mo), Å
Mechanical mixture of 5% MoS_2 in Al_2O_3	6.0	2.41	6.0	3.14
5KB	3.9	2.43	3.4	3.10
21KB	3.9	2.43	3.3	3.10
32KB	4.1	2.43	3.4	3.16
Standard	5.1	2.43	3.6	3.16

Table 3. Effective coordination numbers calculated from the perfect structure model of MoS_2 for the first (Mo–S, average interatomic distance 2.44 Å) and second (Mo–Mo, average interatomic distance 3.14 Å) coordination spheres with the use of a model of two distances related to a coordination sphere. Δ is the difference of interatomic distances for each spheres

ΔR_{S}, Å	ΔR_{Mo}, Å	$N(\text{S})_{\text{eff}}$	$N(\text{Mo})_{\text{eff}}$
0	0	6.0	6.0
0.05	0.02	5.4	5.8
0.07	0.05	4.8	5.1
0.09	0.07	4.1	4.3
0.09	0.09	4.3	3.0
0.09	0.11	4.3	2.3

air or the support, the RAD curves should exhibit peaks to the left of the peak that corresponds to the Mo–S distance. The absence of such a peak indicates that MoS_2 underwent no oxidation in the course of preparation and storage. The structures of all samples also exhibited a distance of 6.3 Å, which is equal to the distance from the central atom of molybdenum to the next molybdenum atom in MoS_2. The atoms of Mo in the first and second coordination spheres of a molybdenum sublattice lie along a straight line with respect to the central atom of Mo. In this case, because of the multiple scattering of photoelectrons in EXAFS spectroscopy, the intensity of the peak that corresponds to the second coordination sphere in the RAD curve can increase by a factor of 4 or higher. The intensity of this peak is very sensitive to structural distortions. The intensity of this peak dramatically decreases if atoms do not lie along a straight line, for example, because of a stack distortion. The tested catalysts exhibited such a decrease in the peak intensity that corresponds to a Mo–Mo distance of 6.33 Å. Because of this, the simulation of this peak was not performed. However, the presence of this peak suggests that molybdenum was retained as MoS_2 in the catalysts. A decrease in the peak intensity confirms the electron-microscopic data on strongly bent MoS_2 stacks.

Table 2 summarizes the interatomic distances and effective coordination numbers calculated based on the ideal structure model. The 2H modification typical of MoS_2 exhibits a layered structure of S–Mo–S stacks. The sulfur environment of molybdenum exhibits prismatic symmetry (the Mo–S distance is 2.44 Å, and the coordination number is 6). Six molybdenum atoms occur in the next coordination sphere (3.14 Å). Table 2 indicates that, as distinct from bulk MoS_2, the catalysts exhibited underestimated coordination numbers for both Mo–S and Mo–Mo distances, although the coordination numbers would be equal to 6 because the catalysts are not oxidized and the stacks are great. It is likely that the calculated coordination numbers were underestimated because the model used for calculations was inconsistent with the real catalyst structure. This effect cannot be explained by the occurrence of anionic vacancies because this requires the removal of one-third of the sulfur atoms; this removal results in the final fracture of the structure. Strong structural distortions in MoS_2 result in the splitting of the first coordination sphere (which is described by one interatomic distance in the ideal structure model) of catalysts into several close distances, which appear as one peak in EXAFS spectroscopy because of insufficient spatial resolution. Not all distances can be determined by this technique, and the simulation of a set of close distances using a single distance allowed us to determine only an effective coordination number. The same effect was also observed for Mo–Mo distances. In this case, the greater the scatter of distances within a coordination sphere, the lower the effective coordination number calculated using the model with a single interatomic distance. Table 3 illustrates to what extent model calculations underestimated effective coordination numbers, as compared to real values, depending on the difference between distances within one coordination sphere, based on the assumption that there are only two such distances. We estimated that, in the catalysts tested, differences between interatomic distances within one coordination sphere can be as high as 0.1 Å. The degree of structural distortions in the active component of the catalysts was evaluated by the difference between coordination numbers calculated using the ideal structure model of MoS_2 and coordination numbers in real samples.

Other quantitative information on the structural distortions of MoS_2 can be obtained from the molybdenum *K*-edge XANES spectra. Figure 2 demonstrates the first-order derivatives of the molybdenum *K*-edge absorption spectra of catalyst 21KB, which exhibited the greatest differences from the standard MoS_2. The XANES curve for crystalline MoS_2 exhibits a shoulder to the right of the main peak; in the catalyst, this shoulder is shifted to the left. Yang and coauthors [35, 36] studied aqueous suspensions of single-layer MoS_2, which were prepared by exfoliation using EXAFS and

XANES techniques. Based on data obtained by X-ray diffraction analysis [37] and Raman spectroscopy [38], this shift of the shoulder to the left was ascribed to the transition of 2H-MoS_2 to 1T-MoS_2, that is, to a change in the symmetry of the environment from trigonal prismatic to octahedral. It is likely that a simple distortion in the symmetry of molybdenum environment also results in such a shift of the shoulder to the left. Presently, there is no data on a correlation between the shift and the degree of transition between the prismatic and octahedral environments of molybdenum. However, this transition was maximal in sample 21KB, which exhibited a maximum specific activity.

Thus, the strongly underestimated coordination numbers and special features of the EXAFS spectra allowed us to state that, in the test samples, MoS_2 exhibited a distorted structure, most likely, of the type of charge-density waves, and sample 21KB was the most distorted.

The studies were performed *ex situ*. Under reaction conditions, the adsorption of reactants may induce additional structural distortions. It is believed that, under reaction conditions, the coverage of the basal plane, which is highly developed in catalysts prepared by exfoliation, with adsorbed hydrogen and thiophene molecules is considerable. It is known from published data that electron donation to the conduction band of MoS_2 occurs in this adsorption; it can change the electronic state and the local structure of MoS_2 and govern the catalytic activity of the catalyst.

The MoS_2/Al_2O_3 samples prepared by different procedures with different MoS_2 particle diameters and different degrees of structural distortions would be expected to exhibit different catalytic activities. For example, in accordance with universally accepted notions of the localization of thiophene activation centers on the edge planes of molybdenum disulfide, the catalytic activity per gram of MoS_2 would be expected to decrease with MoS_2 particle diameter, because the ratio of the number of molybdenum atoms on the edge plane to the total number of Mo atoms decreases in this case.

At the same time, data in Table 1 indicate that the catalytic activity of the three samples prepared by exfoliation was close to, or even higher than, the activity of the standard sample. The activity of sample 21KB was almost three times higher than the activity of the standard catalyst. In this case, the MoS_2 particle diameter in sample 21KB was greater than the diameter of these particles in the standard catalyst by a factor of ~10.

This is inconsistent with the commonly accepted statement that thiophene is activated on only the edge planes of MoS_2. It is believed that thiophene activation can also take place on the defect-free basal plane MoS_2 because of macroscopic structural distortions.

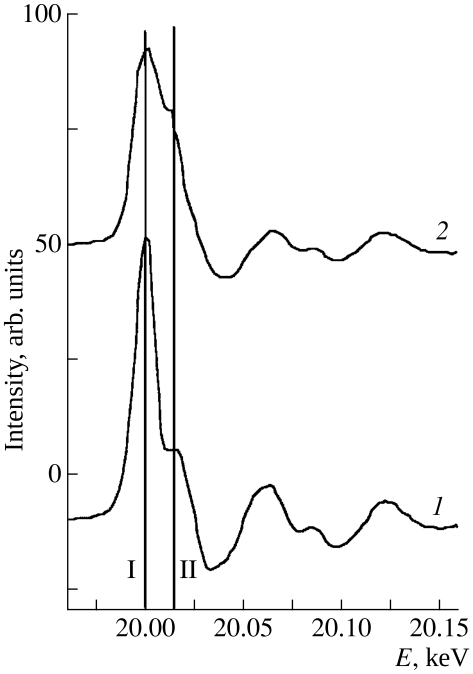

Fig. 2. First-order derivatives of the molybdenum *K*-edge XANES spectra of (*1*) the mechanical mixture and (*2*) catalyst 21KB: (*I*) positions of inflection points in the spectra and (*II*) positions of shoulders in the spectra.

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