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Low-Temperature Synthesis of Supported Hydrodesulfurization Catalysts Based on Chevrel Phases

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Abstract—A new method has been developed for the synthesis of finely dispersed, highly active, supported hydrodesulfurization catalysts based on Chevrel phases. It is hypothesized that the modification of MoS_2 with cobalt or nickel, which enhances the catalytic activity, and the same modification of Chevrel-type systems are of the same nature. The modifiers act through electron density donation into the conduction band of the active component. The increase in catalytic activity is due to the decrease of the effective charge of the molybdenum ion. The catalysts undergo partial restructuring during the reaction.

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Conventional catalysts for the removal of organosulfur impurities from petroleum are molybdenum disulfide–based, alumina-supported catalysts modified with cobalt or nickel. However, in recent years, catalysts containing polynuclear complexes of molybdenum have received greater attention. The main focus has been on bulk molybdenum sulfides, including those based on Chevrel phases ($M_xMo_6S_8$) with a large specific surface area [1, 2]. The interest in these catalysts stems from the assumption that, for more effective removal of organosulfur impurities, it is desirable to have variable-valence molybdenum ions. The Chevrel phases satisfy this requirement. Depending on the nature of the element B, the formal valence of molybdenum in these phases can vary between 2 and 2.7. This alters the collective properties of the phase so as to make it conductive. The valence of molybdenum can also be changed by a chemical reaction and by the adsorption of hydrogen when it is one of the reactants. Catalysts of this type, primarily $Ln_xMo_6S_8$, show high activity in thiophene hydrodesulfurization [3]. The problem is to prepare a supported catalyst because the specific surface area of bulk phases decreases dramatically during the reaction. At present, supported Chevrel-phase catalysts are prepared by sulfiding supported polynuclear molybdenum and cobalt (nickel) complexes [4] or by reducing the catalyst MoS_2/Al_2O_3 with hydrogen at a high temperature [5]. Using these methods, it is difficult to obtain a single-phase system in which the active component has a large specific surface area.

In this study, the active phase of hydrodesulfurization catalysts based on Chevrel phases was prepared by the method described by Solorza-Feria et al. [6]. Mo_6S_8 nanoparticles were synthesized in solution and were then deposited onto a support. The resulting catalysts were tested in thiophene hydrogenolysis and were characterized by the EXAFS method.

EXPERIMENTAL

Catalyst preparation. Molybdenum sulfide catalysts were synthesized in an inert atmosphere at 140°C from sulfur and molybdenum hexacarbonyl in *o*-xylene using the procedure reported in [6]. The TiO_2 (anatase) support (Hombifine brand, Sasol) with a specific surface area of 140 m^2/g was added to the suspension. The resulting catalyst was dried in flowing argon at 140°C. $Co–Mo_6S_8/TiO_2$ catalysts were synthesized by cobalt pivalate ($Co[(CH_3)_3CCOO]_2$) sorption onto Mo_6S_8/TiO_2 from an acetone solution followed by drying in flowing argon at 140°C for removal of the organics and by sulfiding in an H_2S flow.

Mo–Ru catalysts were prepared by a similar procedure using ruthenium dodecacarbonyl. The ratios of molybdenum to ruthenium were the same as in known stoichiometric sulfides.

Elemental analysis. The molybdenum, cobalt, and sulfur contents of the catalyst were determined by X-ray fluorescence analysis using a VRA-30 instrument with a Cr-anode X-ray tube. The amounts of the elements were determined with an error of 10%.

EXAFS spectroscopy. EXAFS spectra were recorded using a VEPP storage ring at an electron energy of 2 GeV and an electron current of 90 mA in the transmission mode near the *K*-edge of molybdenum absorption. The spectrometer had a Si(111) double-crystal split monochromator and proportional chambers as detectors. EXAFS data were processed by a standard procedure, using the VIPER program [7] to separate the oscillating component of the absorption

Table 1. Activity of molybdenum and cobalt–molybdenum catalysts based on Chevrel phases in the thiophene decomposition reaction

Designation	Formula of the catalyst	S/Mo	[Mo], wt %	[Co], wt %	$w \times 10^9$, mol/(g_{Cat}) s	$w \times 10^9$, mol/(g_{AC}*) s
GO70	$(Co\text{-}MoS_2)/Al_2O_3$	2.08	7.05	–	2900	22670
68KB	Mo_6S_8/TiO_2	1.30	6.95	–	1370	13650
71KB	Mo_6S_8/TiO_2	1.33	7.63	–	1100	9980
75KB	Mo_6S_8/TiO_2	1.33	11.9	–	3100	18000
68aKB	$(Co\text{-}Mo_6S_8)/TiO_2$	1.30	6.95	1.08	2540	22850
71aKB	$(Co\text{-}Mo_6S_8)/TiO_2$	1.30	4.79	0.59	1050	14000
71bKB	$(Co\text{-}Mo_6S_8)/TiO_2$	1.32	4.70	1.09	2210	28000
71cKB	$(Co\text{-}Mo_6S_8)/TiO_2$	1.35	5.30	1.79	3400	36000
76KB	$(Co\text{-}Mo_6S_8)/TiO_2$	1.32	5.48	4.13	5000	41600

* AC = active component.

Table 2. Activity of Chevrel-type molybdenum–ruthenium catalysts in thiophene decomposition

Designation	Formula of the catalyst	[Mo], wt %	[Ru], wt %	$w \times 10^9$, mol (g Cat)$^{-1}$ s^{-1}
72KB	$Mo_4Ru_2S_8/TiO_2$	4.33	2.3	4500
73KB	$Mo_2Ru_4S_8/TiO_2$	6.01	13.7	3340

coefficient and the FEFF-7 program [8] to calculate the modeling parameters. XANES spectra were recorded using the same procedure with 0.4-eV energy increments.

Catalytic activity. The catalytic activity of catalyst samples in thiophene hydrogenolysis was measured in a flow reactor at 400°C and a hydrogen pressure of 1 atm. The initial concentration (C_0) of thiophene (Acros Organics) was 1.2×10^{-3} mol/l. Hydrogen was purified using a molecular-sieve column cooled with liquid nitrogen. Before measurements, catalyst samples (0.25–0.50 mm size fraction) were conditioned in the reaction mixture for 3 h. The catalyst weights (20–200 mg) and feed flow rates were chosen so as to ensure the necessary conversion.

RESULTS AND DISCUSSION

Activity and elemental analysis data for the molybdenum and cobalt–molybdenum catalysts are presented in Table 1. The same data for the ruthenium–molybdenum catalysts are given in Table 2. The last column in Table 1 lists the thiophene decomposition activities of the catalysts per gram of the active component. A typical electron micrograph of Mo_6S_8 is presented in Fig. 1.

It is clear from Fig. 1 that the active phase of the catalyst appears as separate filaments, which are characteristic of the Mo_6S_8 structure and ensure a high degree of dispersion. Because the samples were X-ray amorphous, analyses for the presence of the Chevrel phase were carried out by EXAFS spectroscopy. Identification was based on the coincidence of the observed interatomic distances in the environment of molybdenum with published data [9, 10]. It was demonstrated that the synthesis indeed yields particles having the same local structure as the Chevrel phases.

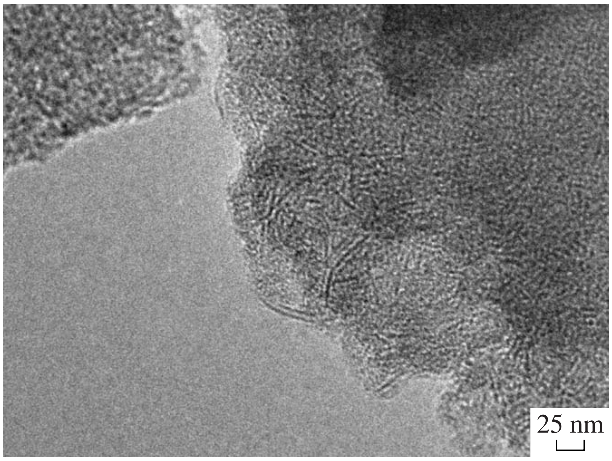

Fig. 1. Electron micrograph of Mo_6S_8/TiO_2.

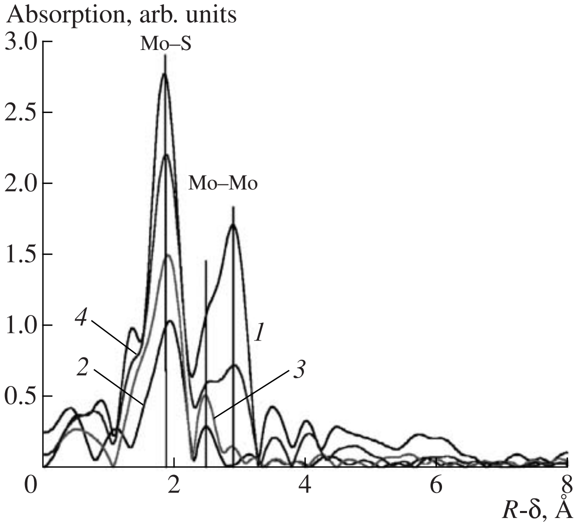

Fig. 2. Radial distribution of atoms around molybdenum in (*1*) MoS_2, (*2*) Mo_6S_8, (*3*) Mo_6S_8/TiO_2 (initial), and (*4*) Mo_6S_8/TiO_2 (after the reaction).

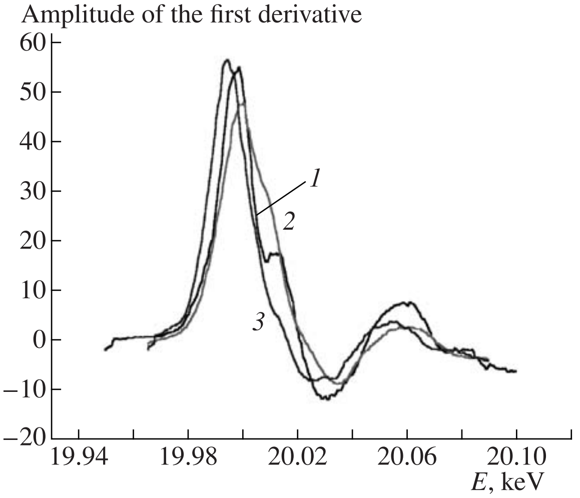

Fig. 3. First derivatives of *K*-edge absorption for molybdenum in (*1*) MoS_2, (*2*) Mo_6S_8/TiO_2 (initial), and (*3*) Mo_6S_8/TiO_2 (after the reaction).

Catalytic tests demonstrated that the cobalt-free catalysts are comparable in activity with the commercial cobalt-containing catalyst GO70. As the amount of supported molybdenum is increased, the catalytic activity grows up to the values typical of the commercial catalyst. As the amount of introduced cobalt is increased over the amount of cobalt in the bulk Chevrel phase $Co_2Mo_6S_8$, the catalytic activity continues to increase. This is evidence that the modification of the catalyst with cobalt changes its electronic structure and that the amount of cobalt bound to the ultrafine particles of the Chevrel phase exceeds the amount of cobalt in the bulk phase.

According to the literature, the modification of the Chevrel phase with cobalt takes place via the attachment of cobalt cations to the chain structure of Mo_6S_8 (which consists of molybdenum ion octahedra surrounded by sulfur) through Co–S bond formation. Here, we deal not with local interaction, but with electron density transfer between the modifying cation and the sulfide nanoparticle as a whole, which alters the collective electronic properties of the active phase.

EXAFS data for the environment of molybdenum are presented in Fig. 2 and Table 3. These data confirm the formation of the Mo_6S_8 structure. A feature differentiating the Mo_6S_8 structure from the MoS_2 structure in the EXAFS method is a shortened Mo–Mo distance. This distance is 3.14 Å in MoS_2, while the average Mo–Mo distance for the Mo_6S_8-type structures is 2.7 Å, which was actually observed in our experiments. According to the literature [9], the mean coordination numbers in Mo_6S_8 are 7 for the Mo–S distance and 4 for

Table 3. EXAFS data for the local environment of molybdenum catalysts

Sample	Mo–S		Mo–Mo		Mo–Mo		$\sigma^2 \times 10^4$, Å^{-2}	E_0, eV	*R* factor, %
	R, Å	coordination number	*R*, Å	coordination number	*R*, Å	coordination number			
MoS_2	2.39	4.50	3.15	3.78	–	–	14.5	7.08	30.2
81KB* (initial)	2.42	3.24	–	–	2.78	0.58	33.2	1.72	12.0
81KB**	2.38	3.49	3.14	2.26	2.79	0.42	49.4	–1.69	25.5
82KB* (initial)	2.43	2.27	–	–	2.75	2.27	49.4	1.21	42.7
82KB**	2.39	3.37	3.15	1.82	2.79	0.34	42.5	–1.74	23.0
68KB**	2.41	2.65	3.25	1.26	2.87	0.40	23.6	4.76	35.0

Note: E_0 is the shift of the absorption edge, σ is the Debye–Waller factor, and the *R* factor is the disagreement coefficient.
* S/Mo = 1.35 (81KB) and 1.30 (82KB); [Mo] (wt %) = 10.28 (81KB) and 9.84 (82KB).
** Catalysts examined after the reaction.

the Mo–Mo distance. Like the coordination numbers in earlier structural studies of fine-particle molybdenum disulfide [11], the coordination numbers determined here by EXAFS spectroscopy are underestimated because of structure distortions. However, the fact that the mean Mo–Mo distance in the synthesized catalyst is shorter than the same distance in MoS_2 and is close to the Mo–Mo distance determined by X-ray diffraction for the Chevrel phases confirms the formation of Mo_6S_8 rather than finer particles.

The *K*-edge XANES spectra of molybdenum confirm that the environment of molybdenum has the symmetry of an octahedron. Figure 3 plots the first derivative curves for the absorption edges of molybdenum. The peaks in these curves are broadened and are shifted to lower energies by 1.2 eV relative to the same peaks for crystalline MoS_2. The shifts were measured for the position of the main maximum in the first derivative of the XANES spectra. According to Zubavichus et al. [12], the assumption that the environment of molybdenum has an octahedral symmetry, not a prismatic symmetry like that in bulk molybdenum disulfide, is proved by the broadening of the derivative at the absorption edge of molybdenum. The shifts of the absorption edge toward lower energies are evidence that the molybdenum ion in the catalyst has a lower effective charge than the same ion in bulk MoS_2.

Another way in which the electronic structure of the active component of the catalyst can be modified is by partial replacement of molybdenum ions in the octahedron by another ion, e.g., ruthenium. Two stoichiometric mixed sulfides of molybdenum and ruthenium are known, namely, $Mo_4Ru_2S_8$ and $Mo_2Ru_4S_8$. Specific catalytic activity data for these compounds in involved in the same reaction under the same conditions are listed in Table 2. Clearly, the substitution of ruthenium for molybdenum markedly enhances the catalytic activity. This is in agreement with the fact that the lower energy shift in the *K*-edge XANES spectrum of molybdenum increases to 2.8 eV.

The structure of the catalysts after the reaction is of independent interest. It is widely held that bulk Chevrel-type catalysts have a stable structure and that the decline of catalytic activity during the reaction is due only to the decrease in their specific surface area. However, the conclusion that the structure is invariable might arise from the small specific surface area of the catalysts, while structural measurements are always taken from the bulk of a phase. For the catalysts examined in this study, it is clear from Fig. 2 that, after a 24-h-long test in the thiophene hydrodesulfurization reaction, the catalysts have another structure. A longer Mo–Mo distance is observed, but the coordination number for the Mo–Mo distance around 2.8 Å is changed only slightly (Table 3). Note that, according to X-ray diffraction data [13], the environment of molybdenum in nearly all Chevrel phases is heavily distorted and is characterized by a set of up to three similar distances for both the Mo–S and Mo–Mo bonds. Because of fundamental limitations of the EXAFS method, it is impossible to simulate the complete set of distances without a loss in the reliability of the results. Therefore, the values determined by the coordination number method are somewhat conventional and, in this case, depend strongly on the symmetry of the compound. It is likely that the appearance of Mo–Mo distances similar to the same distances in molybdenum disulfide and the conservation of the coordination number typical of the Chevrel phases for the short Mo–Mo distance are due to the partial elimination of sulfur from the structure and to cluster restructuring and do not mean that part of the molybdenum passes into the disulfide phase. A similar set of distances is observed for the compound Mo_7S_8 [14].

CONCLUSIONS

A new method has been developed for the synthesis of finely dispersed, highly active, supported hydrodesulfurization catalysts based on Chevrel phases.

It is likely that the modification of MoS_2 with cobalt or nickel, which enhances the catalytic activity, and the same modification of Chevrel-type systems are of the same nature. This means that the essential factor here is the change in the collective properties of the entire particle due to the interaction between the cation and the conduction band of the nanoparticle (electron donation), not the local interaction between the modifier cation and the nearest molybdenum cation. A decrease in the effective charge of the molybdenum ion enhances the activity of the catalyst. The catalysts undergo partial restructuring during the reaction.

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REFERENCES

1. Thompson, R.K., Hilsenbeck, Sh.J., Paskach, T.J., McCarley, R.E., and Schrader, G.L., *J. Mol. Catal. A: Chem.*, 2000, vol. 161, p. 75.
2. Ooi, S., Zhang, H.B., and Hinode, H., *React. Kinet. Catal. Lett.*, 2004, vol. 82, no. 1, p. 89.
3. Hilsenbeck, Sh.J., McCarley, R.E., Goldman, A.I., and Schrader, G.L., *Chem. Mater.*, 1998, vol. 10, p. 125.
4. Paskach, T.J., Hilsenbeck, Sh.J., Thompson, R.K., McCarley, R.E., and Schrader, G.L., *J. Alloys Compd.*, 2000, vol. 311, p. 169.

5. Harel-Michaud, V., Pesnel-Leroux, G., Burel, L., Chevrel, R., Geantet, G., Cattenot, M., and Vrinat, M., *J. Alloys Compd.*, 2001, vols. 317–318, p. 195.
6. Solorza-Feria, O., Ellmer, K., Giersig, M., and Alonso-Vante, N., *Electrochim. Acta*, 1994, vol. 39, p. 1647.
7. Klementiev, K.V., *VIPER for Windows*, Freeware, www.desy.de/~klmn/viper.html; Klementev, K.V., *J. Phys. D: Appl. Phys.*, 2001, vol. 34, p. 209.
8. Rehr, J.J. and Ankudinov, A.L., *Radiat. Phys. Chem.*, 2004, vol. 70, p. 453.
9. Chevrel, R., Sergent, M., and Prigent, J., *J. Solid State Chem.*, 1974, vol. 102, p. 54.
10. Hilsenbeck, Sh.J., McCarley, R.E., and Goldman, A.I., *Chem. Mater.*, 1995, vol. 7, p. 499.
11. Kochubey, D.I. and Babenko, V.P., *React. Kinet. Catal. Lett.*, 2002, vol. 77, no. 2, p. 237.
12. Zubavichus, Y.V., Golub, A.S., Lenenko, N.D., Slovokhotov, Y.L., Novikov, Y.N., and Danot, M., *Mater. Res. Bull.*, 1999, vol. 34, nos. 10–11, p. 1601.
13. Potel, M., Gougeon, P., Chevrel, R., and Sergent, M., *Rev. Chim. Miner.*, 1984, vol. 21, p. 509.
14. Belin, S., Chevrel, R., and Sergent, M., *Mater. Res. Bull.*, 1998, vol. 33, p. 43.