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O.P. PARENAGO*, G.N. KUZMINA*
V.D. TEREKHIN*, K.YU. BASHARINA*

Antifriction and antiwear properties of molybdenum sulfides nanosized particles synthesized using nitrogen containing ionic liquids

Key words

Molybdenum compounds, thermolysis, molybdenum sulfides, nanoparticles, solubility, lubricants, antifrictional and antiwear properties.

Summary

We have developed the synthesis pathways of molybdenum trisulfide nanoparticles that are soluble in hydrocarbon media and demonstrate their activity as antifrictional and antiwear additives to lubricants. Bis(tetraalkylammonium)tetrathiomolybdates as precursors of molybdenum trisulfide nanoparticles are synthesised by the interaction of ammonium thiomolybdate with tetraalkylammonium halides, including alkyl groups of the various types. The properties of synthesised molybdenum compounds were determined by UV- and IR-spectroscopy and by thermogravimetric analysis. The molybdenum trisulfide nanoparticles were formed by thermolysis of these compounds, and their sizes and size distribution were determined by small angle X-ray spectroscopy. The antifrictional and antiwear activity of molybdenum compounds and MoS_3 nanoparticles were evaluated using various types of tribometers.

* A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky prospect, 29, Moscow, Russia, parenago@ips.ac.ru

1. Introduction

Sulfur containing molybdenum compounds are well known as the most active friction modifiers. Molybdenum disulfide is applied for many years as an additive to lubricants. Natural MoS_2 (α-MoS_2) has hexagonal structure (a trigonal prism) of the layered type and is similar to graphite in form. The layers of such a compound have the low shear resistance. They promote "smoothing" of the micro-surface, thus reducing the specific pressure and friction coefficient [1].

This compound, however, is not soluble in most solvents, including lubricants. This is why its application is limited to the grease additives [2], and sulfur containing molybdenum compounds are usually applied for the fabrication of synthetic lubricants [3]. The molybdenum dialkyldithiophosphates (MoDTP) and dialkyldithiocarbamates (MoDTC) are most widely used in practice [4,5]. These molybdenum compounds reveal fine antifrictional and antiwear properties, but their synthesis is extremely difficult, poorly reproducible and requires the use of carefully cleaned solvents that are free of oxygen. Additionally, hazardous and toxic substances (amines, phosphorus pentasulfide and carbon disulfide) are used as initial reagents.

As it has been shown by many authors (see, for example [3-6]), the MoDTP and MoDTC decompose to molybdenum disulfide in the course of tribological contact of rubbing metal surfaces, i.e. in the conditions of increased loadings and heated molybdenum.

It is known that molybdenum is capable of forming some sulfides, including molybdenum trisulfide, MoS_3, depending on the valence condition. This compound is thermally unstable; and, while being heated, it easily forms the more stable molybdenum disulfide with the elimination of elemental sulfur [7, 8].

In this connection, it was interesting to synthesise the nanoparticles of molybdenum trisulfide, to provide their solubility and stability in a hydrocarbon media for their subsequent test as tribological active additives to lubricants. To synthesise nanoparticles, the technique of thermal decompositions of molybdenum sulfur containing compounds in a hot amphiphilic matrix was used.

2. Experimental

The synthesis of MoS_3 nanoparticles was performed in a glass reactor through the interaction of a DMFA solution of ammonium thiomolybdate with tetraalkylammonium halides at 25^{o}C for one hour [9]. An additional increase in temperature up to 150^{o}C and mixing for two hours causes the precipitation of molybdenum trisulfide. The solvent was removed in a vacuum after cooling of

the mixture, and MoS_3 particles were extracted with i-octane. The quantitative elemental analysis shows [Mo] : [S] ratio in the range of 1:2.5 - 1:3.1.

Special compound-modifiers were proposed to provide the solubility of molybdenum trisulfide nanoparticles in hydrocarbon media, in particular, in lubricants that are can coordinate with nanoparticles and keep them in the solution. The amines and ammonium derivatives, dithiophosphorus acids, derivatives of dialkyldithiocarbamic acids and, also, the alkylated succinamide have been used as such modifiers. Our solution of nanoparticles was stable at least for 1 year in the presence of the last modifier. Modifiers are typically entered into a reaction mixture through the interaction of ammonium thiomolybdate with tetraalkylammonium halides when their mass relation to the molybdenum is ~ 4.

MoS_3 nanoparticles were characterised by UV- and IR-spectroscopy and thermo-gravimetry methods. The thermolysis mechanism of bis(tetraalky-lammonium)tetrathiomolybdates was studied by IR Fourier spectroscopy in a special cell. The sizes of MoS_3 nanoparticles were determined by small angle X-ray scattering technique (SAXS). Tribological properties were studied by different types of tribometers. The metal surface subjected to the friction process was studied by atomic force microscopy (AFM).

3. Results and discussion

It has been shown that at the first stage, the following exchange reaction took place:

$$2R_4N^+X^- + (NH_4)_2MoS_4 \rightarrow [(R_4)N]_2MoS_4 + 2NH_4X, \quad (1)$$

Where X = Cl or Br.

Our studies of reaction products of the thermal decomposition of molybdenum containing compounds show that, besides molybdenum sulfides, by-products like sulfur- and nitrogen containing compounds are formed:

$$(R_4N)_2MoS_4 \rightarrow 2R_3N + R_2S + MoS_3 \quad (2)$$

$$(R_4N)_2MoS_4 \rightarrow 2R_3N + R_2S_2 + MoS_2 \quad (3)$$

The target of further examination was to study the effect of the alkyl group nature in nitrogen containing compounds on the mechanism of MoS_3 nanoparticles formation and on their properties, and in particular, on their sizes. For this purpose the following compounds have been used as initial reagents for interaction with ammonium thiomolybdate: $[(C_4H_9)_4N]Br$, $[(CH_3)_2(C_{18}H_{37})_2N]Br$, $[C_{16}H_{33}(CH_3)_3N]Br$, $[CH_3(C_8\text{-}C_{10})_3N]Cl$ and $[CH_3(C_8H_{17})_3N]Cl$. The thiomolybdate derivatives as precursors of nano-MoS_3 formation have been received, isolated, and studied. It

should be stressed that the following compounds have been synthesised and described for the first time: $[(CH_3)_3C_{16}H_{33}N]^+_2[MoS_4]^{-2}$, $[CH_3(C_8H_{17})_3N]^+_2[MoS_4]^{-2}$, $[CH_3(C_8\text{-}C_{10})_3N]^+_2[MoS_4]^{-2}$ and $[(CH_3)_2(C_{18}H_{37})_2N]^+_2[MoS_4]^{-2}$. The synthesised molybdenum complexes have been characterised by optical spectroscopic techniques. In the UV-spectral region of studied compounds, all bands are similar to the ones described in the literature for such compounds [10]. They have three pronounced maxima at 475, 324 and 245 nm, corresponding to σ (Mo-Mo) $\rightarrow\pi^*$ (Mo-S) and σ (Mo-Mo) $\rightarrow\sigma^*$ (Mo-S) electronic transitions in tetrahedral $MoS^{2}_{4}{}^{-}$ groups [11].

The results obtained from IR spectra of molybdenum compounds are given in Table 1.

Table 1. IR absorption bands of bis(tetraalkylammonium)tetrathiomolybdares

N, n/n	Mo-compound	ν(Mo=S), cm^{-1}	N(C-N), cm^{-1}	N(C-C), cm^{-1}
I	$[(C_4H_9)_4N]_2MoS_4$	467	940	1479,1377, 734
II	$[C_{16}H_{33}(CH_3)_3N]_2MoS_4$	470	930	1467, 1378, 720
III	$[CH_3(C_8H_{17})_3N]_2MoS_4$	469	942	1463, 1377, 719
IV	$[CH_3(C_8\text{-}C_{10})N]_2MoS_4$	473	942	1466, 1379, 722
V	$[(CH_3)_2(C_{18}H_{37})_2N]_2MoS_4$	466	942	1467,1375, 721

There are characteristic bonds which correspond to functional groups Mo = = S and CN in molecules besides of the bands belonging to C-C-bonds.

Thermal characteristics of synthesized bis(tetraalkylammonium)tetrathio-molybdates were studied gravimetrically. The following thermal stability series of bis(tetraalkylammonium)tetrathiomolybdates has been received from the data:

$[C_{16}H_{33}(CH_3)_3N]_2MoS_4 > [(C_4H_9)_4N]_2MoS_4 > [CH_3(C_8H_{17})_3N]_2MoS_4 >$
$[CH_3(C_8\text{-}C_{10})N]_2MoS_4 > [(CH_3)_2 (C_{18}H_{37})_2N]_2MoS_4$.

The regularities of $[(R_4)N]_2MoS_4$ thermolysis, leading to nano-MoS_3 formation was studied using the special cell and a IR-Fourier spectrometer. The dynamics of Mo-derivatives decomposition is given in Fig. 1 at different temperatures. The most intensive band (at 469 cm^{-1} has weak, but quite a pronounced "shoulder" is found at 447 cm^{-1}. These bands are related to valence vibrations of Mo=S-bond, and the most intensive one belongs to $MoS^{2}_{4}{}^{-}$ anion. The "shoulder" at 447 sm^{-1} belongs, most likely, to Mo=S-bonds as well, but in more complicated thiomolybdate clusters.

As indicated in Fig. 1, the intensity of bands related to Mo=S-bond decreases with temperature quite significantly. Further the bands at 500-530 cm^{-1} appear and start to grow in intensity with temperature 140°C. According to [12], these bands can be associated with the S-S-bond in the bridge cluster structures of thiomolybdates. The intensity of these bands decreases with temperature at 140°C. Above 180°C, the bands characterising Mo=S and S-S-bonds disappear in the spectrum of the compound. Such temperature behaviour of the S-S-bond is the indirect confirmation of the intermediate formation of MoS_3 that turns to molybdenum disulfide by further heating.

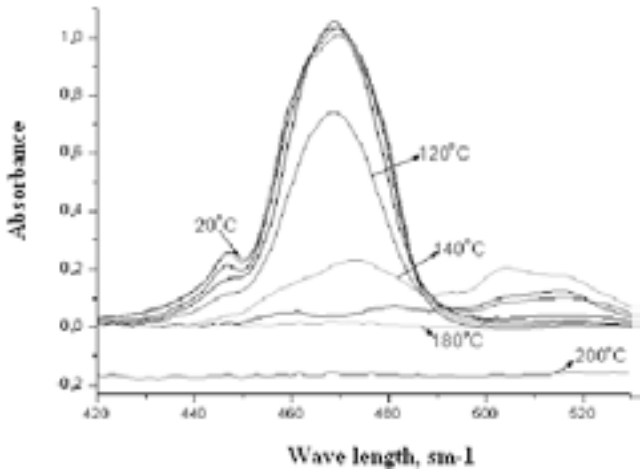

Fig. 1. IR-spectra of [(C4H9)4N]2MoS4 ih the absorbance region of Mo = S-bonds

The thermolysis of Mo-compounds results in the isolation of nano-MoS_3. The element analysis shows S:Mo ratios in the rage from 2.5:1 to 3.1:1.

To reveal the nanoparticles sizes and size distribution, the SAXS-technique was used (Fig. 2, Table 2).

Our studies show (see Fig. 2) that the particles obtained by the thermolysis of butyl derivative have a quite narrow unimodal distribution with average diameter ~ 50 nm.

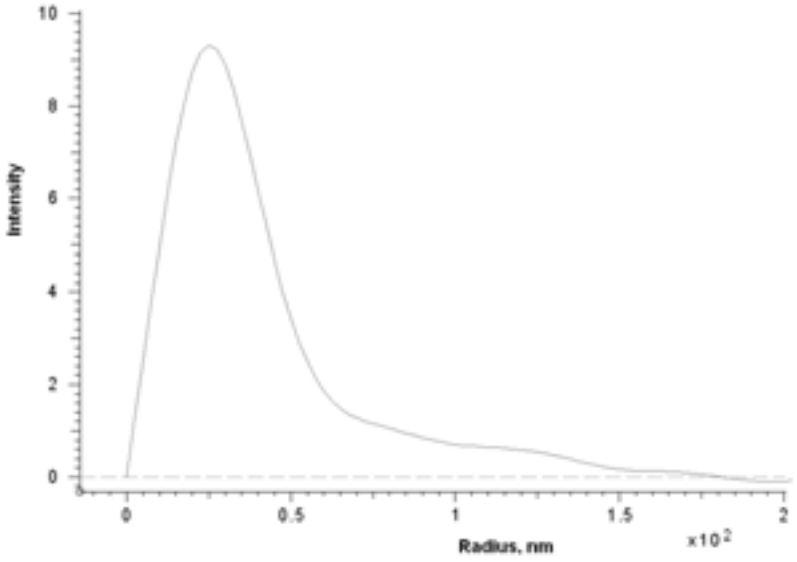

Fig. 2. Size distribution of nano-MoS_3, obtained by thermolysis of $[(C_4H_9)_4N]_2MoS_4$

Table 2. The sizes of nano-MoS_3, obtained by thermolysis of $[R_1R_2R_3R_4N]_2MoS_4$

Mo-compounds	Size distribution	Nanoparticles diameter, nm	
		1 signal	2 signal
$[(C_4H_9)_4N]_2MoS_4$ (I)	Unimodal	50	-
$[C_{16}H_{33}(CH_3)_3N]_2MoS_4$ (II)	Bimodal	17	64
$[CH_3(C_8H_{17})_3N]_2MoS_4$ (III)	Unimodal	70	-
$[CH_3(C_8\text{-}C_{10})N]_2MoS_4$ (IV)	Tetramodal	30	65
$[(CH_3)_2(C_{18}H_{37})_2N]_2MoS_4$ (V)	Bimodal	15	56

As indicated in Table 2, the unimodal distribution of sizes takes place for the molybdenum compounds (with rather short alkyl groups - I and III) with the nanoparticle diameters being quite large. The nanoparticles formed from molybdenum compounds with rather long alkyl radicals (II and V) are characterised by the bimodal distribution of the sizes (with 16 nm and 60 nm average size). For nanoparticles obtained based on Mo-compounds, which include a composition (C_8-C_{10}) of alkyl fragments, the tetramodal distribution was shown. In this case, one narrow peak corresponds to the size of 30 nm. Three groups of particles with a rather low concentration of 65, 100 and 175 nm diameter were found here (the last two groups are not presented in Tab. 2).

The antifrictional and antiwear properties have been studied for both bis(tetraalkylammonium)tetrathiomolybdates and nano-MoS_3 (obtained from these compounds). The antiwear activity of $[R_1R_2R_3R_4N]_2MoS_4$ was tested by a four-ball tribometer. In this case, solutions of Mo-compounds in dioctylphtalate were used as a model of synthetic lubricant, and the samples were loaded with 200 N for 60 min.

As indicated in Fig. 3, concerning the dependence between wear spot diameter and [Mo] concentration in solution, all the Mo-compounds reveal antiwear activity in the examined range of molybdenum concentration but do not affect the anti-scuffing property, i.e. the critical loading of seizure P_k in the presence of Mo-compounds does not change. The highest efficiency is revealed for $[(C_4H_9)_4N]_2MoS_4$. This can be caused by the highest rate of its decomposition in the course of friction and the formation of triboactive molybdenum sulfides. For the same reason, the least antiwear activity is found for the complex having two bulk octadecyl groups (compound V).

The ability of Mo-compounds to reduce the friction coefficient was examined for two [Mo] complexes at 200-500 ppm concentrations. The tests performed on tribometer (with "disk-block" friction couple) show that the compounds under study demonstrate antifrictional properties and reduced friction coefficient with respect to the pure lubricant.

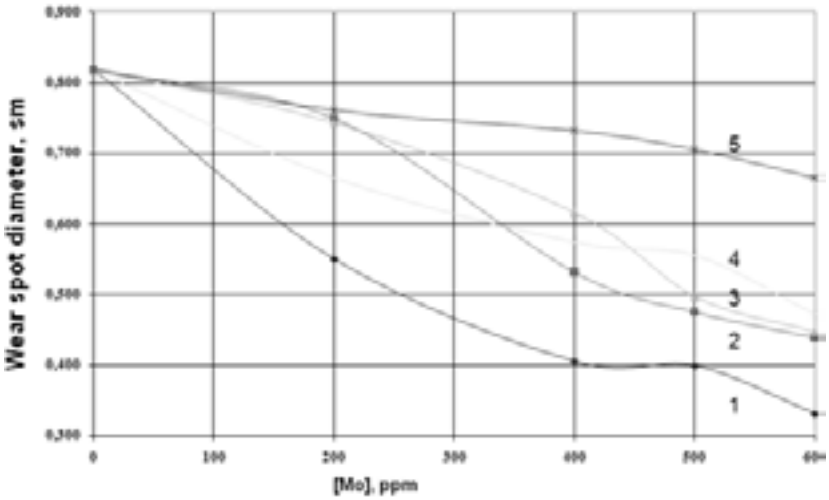

Fig. 3. Dependence between wear spot diameter and [Mo] concentration in dioctylphtalate solution; the curve number corresponds to the number of Mo-compound in the Tables 1 and 2

To determine a metal surface profile, the AFM technique was used. In the case of pure lubricant, the average arithmetic deviation of a surface profile in the area of wear (measured in a direction perpendicular to the wear direction) was 100±20 nm at 16 μm base length. When the Mo-compound with lubricant are used, the profile diagram has 5±1.5 nm deviation of a surface profile in the area of wear (at the same 16 μm base length). The AFM analysis shows that the presence of the Mo-additive results in considerable (more, than 10 times) smoothing (reduction of roughness) of the metal surface, which confirms indirectly the formation of the MoS_2 layer, making strong impact on the modification of surface profile.

The dependence between the friction coefficient and loading presented in Fig. 4 for solutions of Mo-compounds based on nano-MoS_3 in Vaseline oil clearly demonstrate their antifrictional properties. According to the data, the greatest effect is reached in the case of nano-MoS_3, obtained from the tetrabutyl derivative of molybdenum.

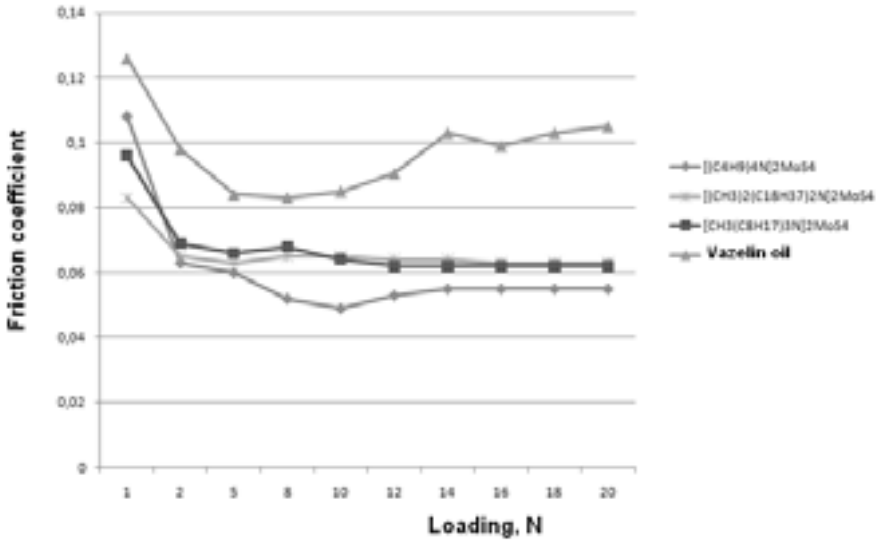

Fig. 4. The dependence between the friction coefficient and the loading value for nanoparticles, obtained from different Mo- compounds

Therefore, in this work, a new approach to nano-MoS_3 synthesis is realised, and a means of obtaining their stable dispersions in lubricants is found. The characteristics of MoS_3 nanoparticles and their activity as antifriction and antiwear additives to lubricants are determined.

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