SURFACE-CAPPED MOLYBDENUM SULFIDE NANOPARTICLES – A NOVEL TYPE OF LUBRICANT ADDITIVES


A.V. Topchiev Institute of Petrochemical Synthesis RAS, Leninski prosp. 29, 119991 Moscow, Russia

bakunin@ips.ac.ru

ABSTRACT

The synthesis of hydrocarbon-soluble molybdenum trisulfide nanoparticles, which are stable in hydrocarbon media, was performed by interaction of reversed microemulsions comprising molybdate anion with hydrogen sulfide in the presence of modifying compounds. The average dimension for synthesized nanoparticles was determined using SAXS and AFM techniques to be approximately 2.5 nm. The study of antifriction properties for synthesized compounds in lubricants solutions showed that nanoparticles are generally more effective in comparison to traditional molybdenum complexes.

KEYWORDS: molybdenum sulfide, nanoparticles, lubricant additives, tribology.

1. INTRODUCTION

Lubricant-soluble compounds containing molybdenum-sulfide moiety and various ligands such as dithiophosphates, dithiocarbamates are widely used as friction-modifying and antioxidant additives [1, 2]. It is supposed that antifriction properties of molybdenum and sulfur containing additives are based on MoS2 layers formed in situ on friction surfaces. However, synthesis of molybdenum containing additives is often rather complex and expensive [3].

Recent achievements in the field of nanochemistry provide synthetic possibility for obtaining nanosize particles of inorganic compounds having predetermined structure and dimensions [4]. Some attempts were made to obtain molybdenum disulfide nanoparticles via microemulsion mediated synthetic procedures [5-7] and other methods [8]. Similar procedures are developed for tungsten disulfide nanoparticles [9, 10]. Nanosize particles of inorganic compounds may be dispersed in lubricants to form relatively stable mixtures, but the better way to obtain tribologically active lubricant additives is to prepare the so-called surface-capped particles with their surface protected by compounds that strongly interact and/or react with the inorganic material [11]. Such approach is used at present for preparation of overbased detergent additives that represent in fact nanosized particles of alkaline earth metal oxide/carbonate coated with an appropriate surfactant layer [12].

Direct synthesis of MoS2 nanoparticles seems to be rather complex since it includes a step of reducing the Mo(VI) species to Mo(IV) [5, 6]. The MoS3 nanoparticles may be interesting for use as precursors of MoS2 because molybdenum trisulfide readily decomposes to disulfide at increased temperatures (e.g. in friction contact zone) [13]:

\[
\text{MoS}_3 \xrightarrow{\Delta} \text{MoS}_2 + S
\]

Moreover, most of molybdenum-containing complex compounds used as antifriction additives comprise excess sulfur atoms coordinated to molybdenum nucleus.

2. SYNTHETIC PROCEDURE

2.1. Synthesis of MoS3 nanosize particles in microemulsions

Synthetic procedure comprised creation of a reverse micellar system by dissolving a cationic surfactant cetlytrimethylammonium bromide (CTAB) in hexane-chloroform mixture (1:1 v/v) to obtain 0.1M concentration of surfactant. Aqueous solution of ammonium or sodium molybdate was added by a syringe in an amount providing a transparent liquid. The obtained microemulsion was treated with hydrogen sulfide (H2S). The reaction of molybdate anion with hydrogen sulfide was monitored by UV-Vis spectroscopy (Fig. 1).

After 24 hours the obtained spectrum corresponded good to spectrum of tetrathiomolybdate...
anion [14, 15] thus indicating complete exchange of oxygen atoms by sulfur atoms.

\[
\begin{align*}
\text{MoO}_4^{2-} & \rightarrow \text{MoSO}_4^{2-} \rightarrow \text{MoS}_2\text{O}_2^{2-} \\
\text{MoS}_2\text{O}_2^{2-} & \rightarrow \text{MoS}_3^{2-} \rightarrow \text{MoS}_3 + H^+
\end{align*}
\]

The prepared tetrathiomolybdate solution in aqueous core of the reversed microemulsion was converted into MoS₃ by addition of gaseous HCl. This resulted in disappearance of all spectral bands thus indicating the formation of MoS₃ nanoparticles within the interior of microemulsion.

Fig. 1 UV-Vis spectra of microemulsion containing molybdate anions, reaction with hydrogen sulfide.

2.2. Surface capping of MoS₃ nanosize particles

Surface-capping agents used represent compounds that chemically interact and/or adsorb strongly on molybdenum sulfide nanoparticles and contain long hydrocarbon chains as well. Some examples of agents used are presented below:

\[
\begin{align*}
\text{R} & \equiv \text{NH}_2 \\
\text{R} & \equiv \text{SH} \\
\text{R} & \equiv \text{OH} \\
\text{R} & \equiv \text{NH}_2
\end{align*}
\]

As a rule, surface-capping agents were added after microemulsion formation and before reaction with H₂S. The amount added may be varied from 10 mol. % relative to Mo and up to 10-fold excess. The properties of final product such as its solubility in organic solvents and lubricants, stability of the obtained solutions, are strongly dependent on the nature of surface-capping agent and its amount.

2.3. Isolation of surface-capped MoS₃ nanosize particles

The microemulsion containing surface-capped molybdenum trisulfide nanoparticles was distilled under reduced pressure and excess of CTAB was isolated from nanoparticles fraction by extraction with an appropriate organic solvent. After solvent removal the surface-capped MoS₃ nanosize particles were obtained as a dark-brown solid or semi-solid substance (depending on the nature of the agent used and its amount), which is soluble in organic solvents such as chloroform, tetrahydrofurane, benzene, and in hydrocarbon lubricants as well.

3. CHARACTERISATION OF NANO-PARTICLES

Composition of the surface-capped molybdenum trisulfide nanoparticles is supported by spectral data (UV-, IR-, and NMR-spectroscopy). Size determination for the surface-capped nanosized molybdenum sulfide particles using small-angle X-ray scattering (SAXS) indicates that the particles’ radius is below 3.0 nm. Size distribution curve is presented at figure 2.

Fig. 2 SAXS data for size distribution for (MoS₃)ₙ samples obtained at different water-to-surfactant ratios (W).

Results obtained using atomic-force microscopy (AFM) technique are in a good compliance with the SAXS results.

It seems that the nanoparticles formed possess rather wide size distribution starting from very small (almost molecular) dimensions and up to the above-mentioned radius of about 3.0 nm. This unusual fact may be explained on the basis of rather complex structure of bulk MoS₃ evaluated recently [16]. It is found that MoS₃ possesses no crystal structure but represents a mixture of at least four types of
molybdenum sulfide cluster \((\text{Mo}_3\text{S}_9)\) linked statistically via S-S-bridges as presented below [16].

Most probably the synthesized nanosized particle comprise different amounts of such clusters beginning from a single molecule, but the upper number of clusters is limited by initial volume of aqueous core in starting microemulsion.

4. TRIBOLOGICAL PROPERTIES

4.1. Tribometer testing

Tribological properties of surface-capped molybdenum sulfide nanoparticles were determined using SRV tribometer measurements and by Cameron-Plint TE77 High Frequency Friction Machine Friction Coefficient testing for certain petroleum-based lubricant compositions comprising nanosized surface-capped molybdenum sulfide particles. SRV procedure comprised step-by-step load increase until achievement of scuffing load with permanent measurement of friction coefficient value. Cameron-Plint testing comprised measurement of friction coefficient at a constant load but within the temperature range of 60-160°C. Comparison with molybdenum dialkyldithiocarbamate (DTCMo) (3) during SRV testing reveals excellent antifriction properties of the prepared nanoparticles (Fig. 3).

Cameron-Plint testing results include comparison to commercially available friction-modifying additives such as molybdenum dialkyldithiocarbamate (MoDTC) and ashless friction modifier (CFM) (see Fig. 4). The obtained results indicate that surface-capped molybdenum trisulfide nanoparticles decrease friction coefficient better at high temperatures.

4.2. Tribophysical layer properties

Testing of tribophysical properties for friction layers were performed using MMT microtribometer that provides low sliding speed and high contact pressures. Friction testing was performed using probe-surface pair.

Microtribometer testing unit provides possibility of simultaneous registration of electric and friction characteristics during sliding of a spherical specimen (Ø4 mm) on a surface (rectangular sheet 10×40 mm). The unit comprises (see Figure 5): surface sheet 1, loading mechanism 3 with spherical specimen holder 2, friction force measuring unit 4, and drive unit 5.

Conductivity and friction force were measured simultaneously using IBM-type PC. This approach to friction pair investigation provides information about changes in friction surfaces both geometrical- (in local friction roads) and time-dependent (cycle-dependent) ones.
higher and more stable contact electrical resistance if formed are more wear-resisting; this follows from coefficient (below 0.15). The protective tribofilms expressed in lower and more stable friction molybdenum trisulfide nanoparticle, which is advantages of the composition containing coefficient nanoclusters, 'New reactor for production of tungsten disulfide hollow onion-like (inorganic fullerene-like) nanoparticles', Interscience Publishers, N.-Y.-London.

6. CONCLUSIONS

Surface-capped molybdenum sulfide nanosize particles represent a novel class of tribologically active additives that demonstrate excellent friction-modifying and anti-scuffing activity.

REFERENCES


Partial support of this work by ISTC under grant #1577 and CRDF under grant #RC1-545 is gratefully acknowledged.