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The synthesis of MoS_2 particles with different morphologies for tribological applications

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ABSTRACT

Three types of molybdenum disulfide (MoS_2) particles with the morphologies of flower-like, microspheres and nanosheets, were successfully fabricated by solvo/hydrothermal route. The tribological behaviors of the synthesized MoS_2 particles as lubricating additives of the liquid paraffin were investigated using a ball-on-disk tribotester. The results showed that all the synthetic MoS_2 particles could improve the lubricating property of the liquid paraffin. In the case of heavy load, nanosheets MoS_2 presented more excellent friction and wear reduction behaviors as compared with the other two types of MoS_2 particles. The reason of the optimal lubricating performance of nanosheets MoS_2 was discussed based on their exfoliation into ultrathin nanosheets and nano fragments during the friction tests.

1. Introduction

Due to the excellent electrical conductivity, perfect chemical stability and high mechanical strength, transition metal dichalcogenides MS_2 (M = Mo, Ti, W, and V) have been the focus of extensive studies over the past decades [1]. As a typical metal disulfide, molybdenum disulfide (MoS_2) has attracted more and more interests for its potential applications in the fields of solid lubricants [2], catalysis [3], electrocatalysis [4], high-density batteries [5] and solar energy cells [6]. In recent years, MoS_2 particles have gained more attentions as lubricating additives due to their excellent friction-reducing, antiwear performances [7] and extreme pressure capacity [8]. Numerous applications of MoS_2 particles as lubricating additives can be found in the gearbox oil [9], engine oil [10,11] and metal working fluid [12,13].

The influence of the morphology of MoS_2 particles on the tribological properties of the oils has been widely investigated by many authors. For example, Hu et al. [14] found that nanoballs MoS_2 was more efficient in improving the tribological behavior of the liquid paraffin comparing with nanoslices MoS_2. They attributed such phenomenon to the chemical stability of the layerclosed spherical structure of nanoballs MoS_2. In another case, Pranhakar et al. [15] pointed out that nanosheets MoS_2 performed better than nanoballs MoS_2 in improving the lubrication effect of the polyalphaolefin oil. They ascribed this to the reason that nanosheets MoS_2 could slip at asperities and be deformed into individual nanosheets at interfaces. However, in the work of Kogovesk et al. [16], the size and morphology of MoS_2 particles had little or no influence on the tribological performance of the polyalphaolefin oil. In addition, it has been reported that the friction-reducing and antiwear properties of MoS_2 particles are closely related to the contact pressure [17]. Till now, there is no an identical view on the question that how do the morphology of MoS_2 particles and the contact pressure influence the tribological properties of the oils. Especially, in some cases, contradictory conclusions were proposed by different literature [14,15]. More work is needed to investigate the influence of the morphology of MoS_2 particles on the ability to improve the lubricating property of the oils with respect to the contact pressure.

A variety of synthetic techniques, such as the solvo/hydrothermal method [18], chemical solution route [19], high temperature sulfurization [20], chemical vapor deposition [21], microwave method [22] and even laser ablation [23], have been developed to prepare MoS_2 particles. While most of these methods involve either a high temperature procedure or a complicated manipulation, which may result in the increased cost and further limit their application potential. The solvo/hydrothermal method, which possesses the advantages of low temperature, simple fabrication process, and high purity of products, is considered as the most promising technique to fabricate MoS_2 particles. In addition, it is easy to obtain MoS_2 particles with various morphologies by the solvo/hydrothermal method, such as mico/nanoflowers [24,25], nanosheets [26], micro/nanospheres [27,28], and nanowires [29].

In this work, the solvo/hydrothermal method was employed to synthesize three types of MoS_2 particles. Meanwhile, the tribological

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performances of the oils dispersed with these synthesized MoS_2 particles were evaluated by a tribotester. The objective of this paper is to investigate the influence of the morphology of MoS_2 particles on the ability to improve the tribological properties of the oils. In addition, the lubricating mechanisms of the synthesized MoS_2 particles in the oils under different contact pressures were discussed.

2. Experimental details

2.1. Materials and synthesis method

The chemicals used to synthesize MoS_2 particles in this work, including sodium molybdate dihydrate ($Na_2MoO_4{\cdot}2H_2O$), thiourea ($(NH_2)_2CS$), hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$), oleylamine ($C_{18}H_{37}N$), ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$), glycol ($(CH_2OH)_2$), and polyethylene glycol with average molecular weight of 400 (PEG-400), were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All chemicals were used as received without further treatment.

Three types of MoS_2 particles, including the morphologies of flower-like (FLs), microspheres (MSs), and nanosheets (NSs), were synthesized by the solvo/hydrothermal method. Table 1 lists the reaction precursors and solvents used to fabricate the MoS_2 particles. The typical synthetic procedure is as follows: the precursors were firstly dissolved into the solvent with the aid of magnetic stirring for 30 min. Then, the reaction solution was transferred into a 50 mL polyphenylene-lined steel autoclave and was kept in an electric oven at 200 °C for 18 h. After cooling to room temperature naturally, the black precipitate of MoS_2 particles was collected by filtration, washed with distilled water and ethanol for three times, dried at 40 °C for 6 h under vacuum.

2.2. Materials characterization and tribological tests

The crystal structures and phases of the samples were identified using an X-ray diffractometer (XRD, Thermo Fisher ESCALAB 250Xi) with Cu Kα radiation (λ = 1.54056 Å), and a Raman spectrometer (Horiba JobinYvon HR800, 514.5 nm). The sizes and morphologies of the synthesized MoS_2 particles were observed using a scanning electron microscope (SEM, LYRA3TESCAN) equipped with energy dispersive X-ray spectroscopy (EDS), and a transmission electron microscope (TEM, JEM-2010). The chemical compositions of the samples were determined by an X-ray photoelectron spectrometer (XPS, PHI Quantera).

The MoS_2 particles were dispersed into the liquid paraffin (LP) by sonicating for 30 min. Then, the lubricating performances of these oils were examined on a ball-on-disk tribotester (Optimal SRV 4) at 25 °C. An AISI-52100 steel ball with diameter of 10 mm was chosen as the upper specimen. The hardness of the ball is 61–63 HRC and its surface roughness is 25 nm. The lower counterpart was an AISI-52100 steel disk with diameter of 24 mm, height of 7.88 mm, and surface roughness of 50 nm. During the friction tests, the upper ball slid reciprocally against the stationary disk with stroke of 2 mm and frequency of 50 Hz, which gave a mean speed of 200 mm/s. Each friction test was performed for 1 h and was repeated at least three times. After friction tests, the specimens were cleaned with acetone and then the wear tracks on the specimens were examined by SEM and a white-light interference profilometer (Phase Shift MicroXAM-3D). The XPS and auger electron spectrometer (AES, PHI 700) were also used to investigate the tribo-reaction film inside the wear tracks. Meanwhile, a transversal cut of the wear track for TEM observation was made by the technique of focused ion beam (FIB).

Table 1
The reaction precursors and solvents used for synthesizing MoS_2 particles with different morphologies.

Morphology	Reaction precursor	Reaction solvent
Flower-like MoS_2 (FLs)	0.6 g $Na_2MoO_4{\cdot}2H_2O$ 0.75 g $(NH_2)_2CS$ 0.725 g $NH_2OH{\cdot}HCl$	30 mL distilled water
Microspheres MoS_2 (MSs)	0.60 g $Na_2MoO_4{\cdot}2H_2O$ 0.75 g $(NH_2)_2CS$ 0.725 g $NH_2OH{\cdot}HCl$	10 mL $C_{18}H_{37}N$ 15 mL $(CH_2OH)_2$ 5 mL PEG-400
Nanosheets MoS_2 (NSs)	0.618 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ 1.14 g $(NH_2)_2CS$	8.75 mL distilled water 8.75 mL PEG-400

3. Results and discussion

3.1. Characterizations of MoS_2 particles

The XRD patterns of the natural MoS_2 powders (Beijing Deke Daoking Technology Co., Ltd, lateral size of 1.5 μm) and the synthesized MoS_2 particles are shown in Fig. 1. It can be seen that there are nine diffraction peaks at 2θ = 14.42°, 29.04°, 32.72°, 33.54°, 35.92°, 35.60°, 44.18°, 49.84° and 58.36° found in the spectrum of the natural MoS_2. These peaks correspond to the (002), (004), (100), (101), (102), (103), (006), (105) and (110) planes of the hexagonal MoS_2, respectively (JCPDS No. 37-1492). As for the flower-like MoS_2 (FLs), the diffraction peaks at 2θ = 14.32°, 32.52°, 42.54° and 58.76° are observed, which are assigned to the (002), (100), (103) and (110) planes of the hexagonal MoS_2 (JCPDS No.37-1492), respectively. With regard to the microspheres MoS_2 (MSs), there is only one broad peak corresponding to the (100) plane of the hexagonal MoS_2 (JCPDS No.37-1492) observed. As to the nanosheets MoS_2 (NSs), the diffraction peaks at 2θ = 32.34°, 32.56°, 42.52° and 57.22° can be attributed to the (100), (102), (103), (110) planes of the hexagonal MoS_2 (JCPDS No.37-1492). It should be noted that there are two new peaks at 2θ = 8.6° and 17.6° (not found in the natural MoS_2, FLs and MSs) observed in the NSs, which is considered to be the result that (002) and (004) planes of MoS_2 shift to lower diffraction angles. According to a previous report [27], the expanded interlayer distance between MoS_2 layers could result in this phenomenon. By using the Bragg equation, the interlayer distances for the (002) plane in the natural MoS_2, FLs and NSs are calculated to be 0.614, 0.625 and 1.008 nm, respectively. It can be seen that the NSs present a larger (002) interlayer spacing comparing with the natural MoS_2. Meanwhile, the domain size of the MoS_2 particles can be extracted from the Scherrer equation: $D = K\gamma/\beta\cos\theta$, where D, K, γ, β and θ are the mean size of the ordered (crystalline) domains, the Scherrer constant (K = 0.89), the X-ray wavelength (0.154056 nm), the line broadening at half the maximum intensity (FWHM) and the Bragg angle, respectively. According to this equation, the crystallite sizes (D) along (002) are calculated to be 49, 10, and 9 nm for the natural MoS_2, FLs and NSs, respectively. This result suggests that synthesized MoS_2 particles tend to stack together in a limited way. It is also noticed that the diffraction peaks of the synthesized MoS_2 is much weaker as compared with the natural MoS_2, illustrating a lower crystallinity for the synthesized MoS_2. After annealed at the

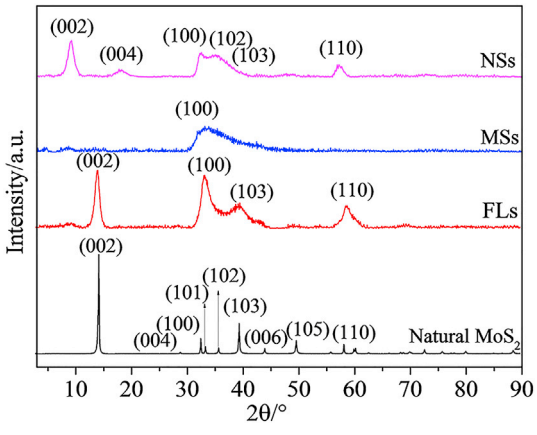

Fig. 1. XRD patterns of the natural MoS_2 powders and the fabricated FLs, MSs, NSs.