Synthesis of Efficient Oil-Soluble ZnAl_2O_4 Nanoparticles

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Oil-soluble spinel zinc aluminate (ZnAl_2O_4) nanoparticles with narrow size distribution were synthesized *via* a hydrothermal method and modified *in situ* by oleic acid. The nanoparticles have been characterized by means of scanning electron microscopy, infrared spectrum and powder X-ray diffraction. The dispersion stability of the ZnAl_2O_4 nanoparticles in lubricant oil has been measured by ultraviolet spectrophotometer. The results show that the modified nanoparticles are nearly monodisperse with good dispersion stability in lubricant oil. Due to the excellent disperse stability, the tribology performance of these modified ZnAl_2O_4 nanoparticles was also estimated and showed that they are promising for potential application as antifriction additives in lubricant oil.

Key Words: ZnAl_2O_4 , Surface modification, Oil-soluble, Lubricant oil additives, Tribology.

INTRODUCTION

Aluminate spinels have shown tremendous applications in a wide range of areas, including as opto-mechanical, catalysts, ceramics, abrasives, antithermal coating in aero-space vehicles and electro-conductive materials¹⁻⁶. In recent years, the synthesis of ZnAl_2O_4 nanoparticles has received more and more attention owing to their high thermal stability, high mechanical resistance and low surface acidity, which are very important for antifriction uses. However, inorganic nanoparticles have a strong tendency to agglomerate and show poor dispersion stability in organic solvents and oil, which highly restricts their potential applications. Hence, synthesis of oil-soluble ZnAl_2O_4 nanoparticles with good dispersion stability in organic solvents is of great interest. More attention and control are necessary during the annealing process to avoid ZnAl_2O_4 nanoparticles agglomeration and improve dispersion capacity in organic solvents. Fortunately, this problem could be resolved by using some special preparation technique, for an example, the preparation of nanoparticles with surface-modification of organic compounds⁷⁻¹².

It is found that agglomeration of nanoparticles can be reduced by surface modification *in situ*¹³. The process of surface-modification *in situ* is a polyreaction-like where the hydrolysis product of inorganic salt is used as monomer and modifier as chain terminator^{14,15}. Accordingly, synthesis and surface-modified are processed simultaneously in only one system. This method not only improves dispersivity of nanoparticles, but also simplifies the operation^{16,17}.

In this paper, the hydrothermal synthesis and surface-modification *in situ* with oleic acid of ZnAl_2O_4 nanoparticles were processed in one step. The ZnAl_2O_4 nanoparticles were characterized and its dispersivity was also measured. Such oil-soluble ZnAl_2O_4 nanoparticles showed superior dispersion stability in lubricant oil and even appeared totally transparent in the oil. Finally, the tribological performances of such obtained ZnAl_2O_4 nanoparticles as additives in lubricant oil were investigated. It shows industrial application potentialities in improving the lubricant oil performances.

EXPERIMENTAL

Preparation of oil-soluble ZnAl_2O_4 nanoparticles: The reagents in the experiments such as $\text{Zn}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, polyethylene glycol (PEG)-6000 (dispersing agent), oleic acid, absolute ethyl alcohol, *etc.*, were analytical pure reagents.

The ZnAl_2O_4 nanoparticles were prepared by a hydrothermal method and *in situ* modified with oleic acid. Firstly, starting materials of $\text{Zn}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ (3.6 g, 0.02 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (12.3 g, 0.03 mol) were separately dissolved into 131.2 mL absolute ethyl alcohol to form two clear solutions, followed by the addition of 0.009 g polyethylene glycol-6000 (0.3 wt. %) into the above two solutions. Secondly, ammonia (4.5 mL) in 100 mL of 95 % ethyl alcohol was added drop by drop to the above $\text{Zn}(\text{OAc})_2$ solution with ultrasonicated stirring and 14 mL ammonia was added to the above $\text{Al}(\text{NO}_3)_3$ solution with strong mechanical and stirring ultrasonicated. So two gels were formed. Thirdly, the two gels were washed

with ethanol (95 %) three times and then were mixed. Finally 10 wt. % oleic acid (0.3 g) was added into the mixed gel. After stirring for 24 h, the obtained mixture composed of AlOOH and Zn(OH)_2 was put into an autoclave at temperature of 220 °C and pressure of 4 MPa. After 2 h reaction, the modified ZnAl_2O_4 nanoparticles were finally obtained.

The unmodified sample was prepared in the same way without adding any oleic acid modification.

X-ray diffraction pattern was obtained on a D₈ ADVANCE with $\text{CuK}\alpha$ radiation. Scanning electron microscopy analysis was performed with a FEI FEG Quanta 250 microscope. Infrared spectrum was obtained using a Nicolet 380sx infrared spectrophotometer. Dispersivity of ZnAl_2O_4 nanoparticles in lubricant oil was measured by using a UV-2600 spectrophotometer.

The anti-friction properties of ZnAl_2O_4 nanoparticles were evaluated by thrust-ring test on a MMW-10G vertical universal friction testing machine (made in Jinan, China). The lubricant oil is a type of mineral oil widely used in industries. Tribological tests were conducted under the pressure of 200 N with a rotating speed of 1200 rpm for 0.5 h (where the plate sample was sliding against a 45 # steel column).

A series of specimen with different concentration (0, 0.05, 0.1, 0.5, 1 wt. %) of nanoparticles were tested. Tests were conducted for each oil sample and friction coefficient was recorded throughout each test by means of a load transducer positioned to measure the lateral force on the ball specimen.

RESULTS AND DISCUSSION

Characterization of the ZnAl_2O_4 nanoparticles: Fig. 1 shows the XRD pattern of the synthesized ZnAl_2O_4 nanoparticles. The diffraction peaks are consistent with spinel zinc aluminate at $2\theta = 31.136^\circ$, 44.578° , 64.692° , 36.494° , 58.750° . This indicates that the phase of the prepared ZnAl_2O_4 nanoparticles is of high purity equiaxed crystals of spinel zinc aluminate.

Fig. 1. XRD pattern of ZnAl_2O_4 nanoparticles

The SEM images of the typical unmodified and modified ZnAl_2O_4 nanoparticles are shown in Fig. 2. The unmodified ZnAl_2O_4 nanoparticles are severely aggregated, while the

modified ones are uniform and nearly monodisperse. This indicates that the agglomeration of ZnAl_2O_4 nanoparticles has been effectively prevented by *in situ* modification. The modified particles in Fig. 2b are observed to show a fuzzy morphology, which is probably due to coating of modifier-oleic acid on the particles surface. Fig. 2c shows the particle size distribution of ZnAl_2O_4 . It is found that the particles have an average size of about 89 nm.

Fig. 2. TEM photographs of ZnAl_2O_4 particles (a) unmodified, (b) modified, (c) Size histograms of ZnAl_2O_4 nanoparticles

Fig. 3 shows the surface modification mechanism for grafting oleic acid molecules on ZnAl_2O_4 . There are a large amount of hydroxyls on the surface of ZnAl_2O_4 , making the nanoparticles highly hydrophilic. The carboxyl groups of oleic acid could react with the surface hydroxyls of ZnAl_2O_4 , thus grafting oleic acid molecules on ZnAl_2O_4 . This process will make the nanoparticles lipophilic and finally improves the dispersion stability of ZnAl_2O_4 in lubricant oil.

The surface modification of ZnAl_2O_4 has been examined by IR analysis. Fig. 4 compares the infrared spectra of the unmodified and modified ZnAl_2O_4 nanoparticles using oleic acid. The characteristic band at 856 cm^{-1} in both curves is caused by the stretching vibration of Al-O-Zn bonds of ZnAl_2O_4 nanoparticles. It is found that a wide absorption band of -OH at *ca.* 3400 cm^{-1} , which is due to the hydroxylation of ZnAl_2O_4 nanoparticles surface caused by absorbed water. The

Fig. 3. Scheme of the oleic acid grafting on the solid surface of ZnAl_2O_4 Fig. 4. FTIR spectra of unmodified and modified ZnAl_2O_4 nanoparticles

obvious adsorption bands at 1710 and 2854 cm^{-1} which appear in the modified sample can be assigned to C=O stretch vibration and the symmetric CH_2 stretch vibration from oleic acid, which indicates that oleic acid molecules have been successfully modified on the surface of ZnAl_2O_4 ^{11,12}.

Dispersive capacity in lubricant oil: The absorbance (also called optical density) A is defined as: $A_\lambda = \lg(I_0/I)$, where I is the intensity of light at a specified wavelength λ that has passed through a sample (transmitted light intensity) and I_0 is the intensity of the light before it enters the sample or incident light intensity (or power). The better nanoparticles are dispersed in solvent, the more constant the light absorbance of solution is. So the dispersivity of modified ZnAl_2O_4 nanoparticles in lubricant oil can be measured by its absorbance.

The modified ZnAl_2O_4 nanoparticles were added into lubricant oil at a concentration of 1 wt. %. Fig. 5 shows the scatter of absorbance of pure lubricant oil and oil sol changing with time. Linear fitting was used to analyze two curves. The two dotted lines (A), (B) are lines of linear regression. The linear fitting equations were calculated as eqn. 1 and 2,

$$y_A = -3\text{E-}05x + 0.3143 \quad (1)$$

$$y_B = -4\text{E-}05x + 0.0057 \quad (2)$$

Equation 1 and 2 show that two regression straight lines are almost parallel with the Time-axis. That is to say the absorbance is nearly constant and shows no obvious changes with time. So the oil with ZnAl_2O_4 nanoparticles is also called oil sol. This indicates the modified ZnAl_2O_4 nanoparticles can stably dispersed in lubricant oil.

Fig. 5. Absorbance-time scatter of (a) oil (b) oil . with 1 wt % ZnAl_2O_4 nanoparticles

Friction reduction properties: Fig. 6 shows the variation of friction coefficient with time in thrust-ring test. In the experiment, the friction coefficients were measured every second. The friction coefficients averaged from every 150 original data were plotted in Fig. 6. It shows that the friction coefficients of oil doped with ZnAl_2O_4 nanoparticles are all smaller than that of pure oil (0 wt. %). Averages of each set of friction coefficients and their reductions are shown in Table-1. It is shown that the reductions are large when the additive concentration of ZnAl_2O_4 nanoparticles is 0.05, 0.5 and 1 wt. %. The largest reduction of 18.5 is achieved at the concentration of 0.1 wt % of ZnAl_2O_4 nanoparticle added, exhibiting the best anti-friction performance. With further increase of the ZnAl_2O_4 concentration, the reduction coefficients tend to decrease.

Fig. 6. Friction coefficient curve with time tested with different concentration of ZnAl_2O_4 TABLE-1
COMPARISON OF FRICTION COEFFICIENT
REDUCTION PERCENTAGE

Additive concentration	0 wt. (%)	0.05 wt. (%)	0.1 wt. (%)	0.5 wt. (%)	1 wt. (%)
Friction coefficient	0.054	0.047	0.044	0.053	0.048
Average reduction (%)	0	11.7	18.5	8.5	9.9

Conclusion

In conclusion, oil-soluble ZnAl_2O_4 nanoparticles were successfully prepared *via* a hydrothermal method and modified

in situ by oleic acid. The synthesized spherical ZnAl_2O_4 nanoparticles have an average diameter of 89 nm and exhibit superior dispersivity and stability in lubricant oil. The tribology study on these particles as additives in lubricant oil reveals their potential application in lubrication.

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