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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 materials[1-6]. 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 compounds[7-12].

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 $Zn(OAc)_2·6H_2O$, $Al(NO_3)_3·9H_2O$, 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 $Zn(OAc)_2·6H_2O$ (3.6 g, 0.02 mol) and $Al(NO_3)_3·9H_2O$ (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 $Zn(OAc)_2$ solution with ultrasonicated stirring and 14 mL ammonia was added to the above $Al(NO_3)_3$ 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 ºC 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 D_8 ADVANCE with CuK_α 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 2θ = 31.136º, 44.578º, 64.692º, 36.494º, 58.750º. This indicates that the phase of the prepared $ZnAl_2O_4$ nanoparticles is of high purity equiaxed crystals of spinel zinc aluminate.

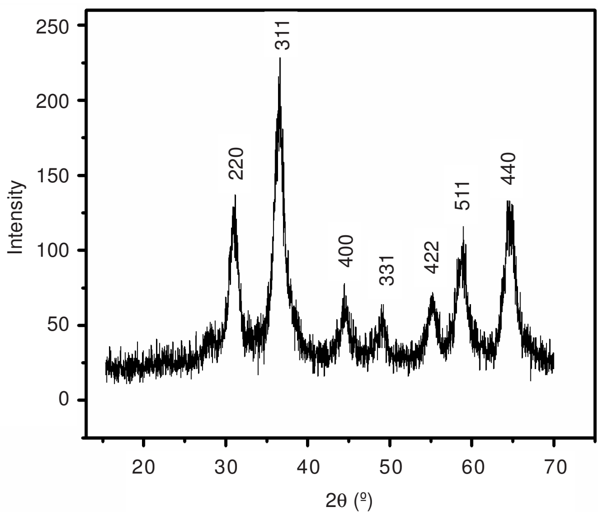

Fig. 1. XRD pattern of $ZnAl_2O_4$ nanoparticles

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.

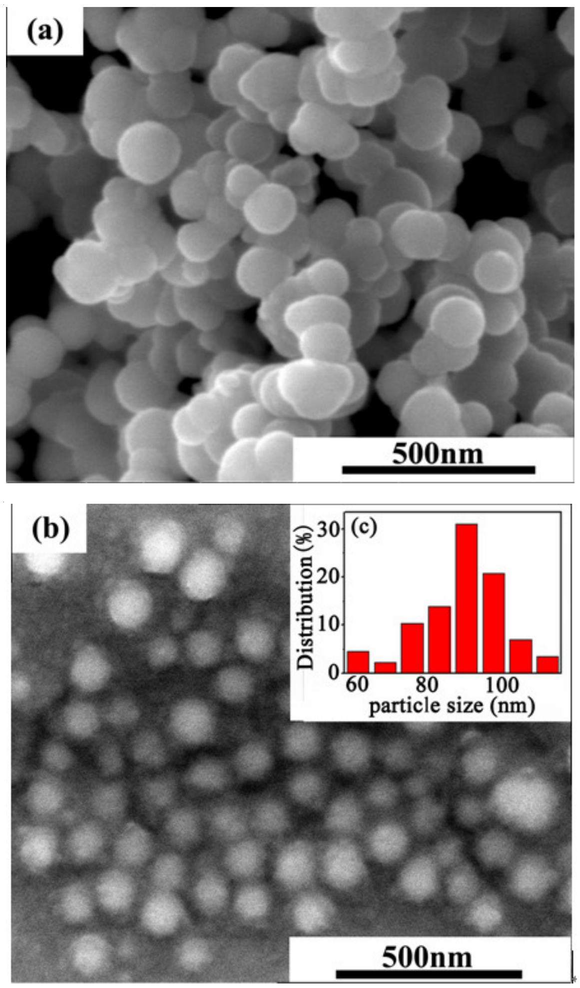

Fig. 2. TEM photographs of $ZnAl_2O_4$ particles (a) unmodified, (b) modified, (c) Size histogranms of $ZnAl_2O_4$ nanoparticles

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

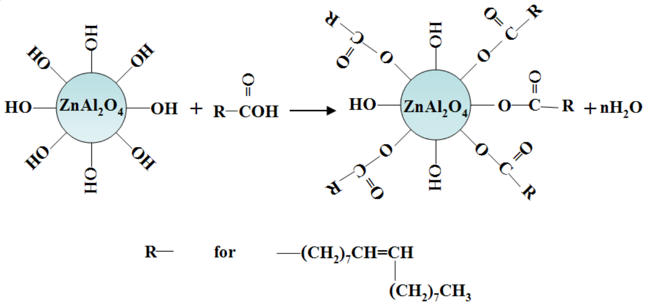

Fig. 3. Scheme of the oleic acid grafting on the solid surface of $ZnAl_2O_4$

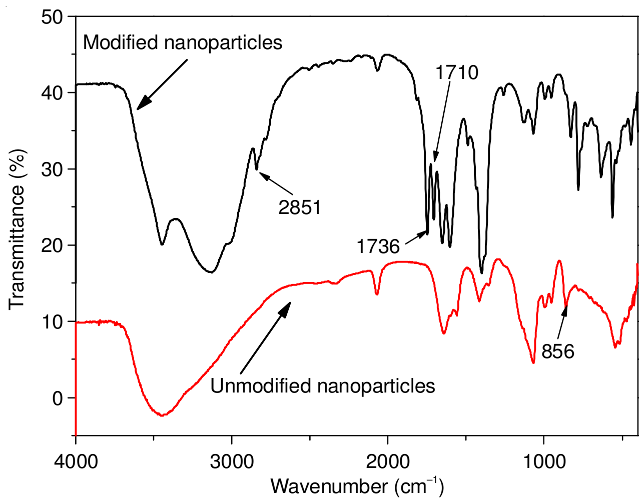

Fig. 4. FTIR spectra of unmodified and modified $ZnAl_2O_4$ nanoparticles

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,

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

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

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.

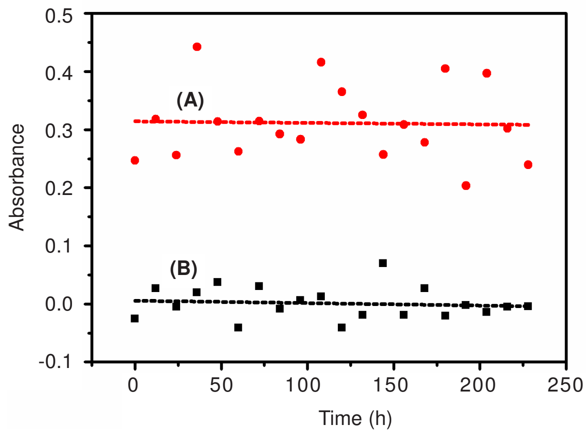

Fig. 5. Absorbance-time scatter of (a) oil (b) oil . with 1 wt % $ZnAl_2O_4$ nanoparticles

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.

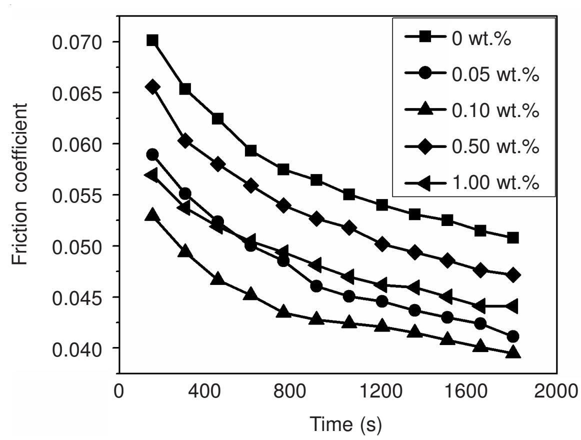

Fig. 6. Friction coefficient curve with time tested with different concentration of $ZnAl_2O_4$

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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