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Non-Hydrolytic Synthesis and Tribological Properties of Al_2O_3 Sol

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Oil-soluble Al_2O_3 sol was obtained *via* nonhydrolytic method. The aluminium trichloride was used as the precursors. Oleic acid and acetone was used as oxygen donor. The dispersion medium was lubricating oil. Al_2O_3 sol was characterized through X-ray diffraction analysis, UV-VIS spectrophotometer and scanning electron microscopy. Tribological properties of Al_2O_3 sol was studied through the four-ball friction test and thrust ring friction test. The results showed that the as-obtained Al_2O_3 nanoparticles in Al_2O_3 sol were dispersed very well with the size of about 80 nm and 20 # mechanical oil has a best lubricating effect with 14.74 % decreasing amplitude of friction coefficient and 9.86 % decreasing amplitude of wear scar diameter when Al_2O_3 sol was doped with 9 wt %.

Key Words: Nonhydrolytic, Al_2O_3 Nanoparticles, Antiwear, Additive.

INTRODUCTION

Within the broad family of functional materials, nanoparticles are particularly attractive with respect to applications in catalysis, sensing, energy storage and conversion, optics and electronics[1,2]. In recent years, attempts were made to use nanoparticles as lubricant additives to improve their lubrication properties[3]. The increase of lubrication properties mainly depends on interfacial conditions such as normal load, geometry, relative surface motion, sliding speed, surface roughness, vibration and lubrication[4-7]. In a case where the dispersion stability of nanoparticles in lubrication is bad, sedimentation and clogging may occur. As concentration increases, the lubrication properties improve, but high a concentration causes a decrease of lubrication due to agglomeration and precipitation[8,9]. Now that preparation of nanoparticles with good dispersion stability in lubricating oil is of prime importance.

Sol-gel process is a favourable method for its low-temperature synthesis of nanoparticles. Aqueous sol-gel chemistry is rather complex, mainly due to the high reactivity of the metal oxide precursors and the double role of water as ligand and solvent. In many cases, the three reaction types (hydrolysis, condensation and aggregation) occur almost simultaneously and are difficult to control individually, so slight changes in experimental conditions result in altered particle morphologies, a serious issue regarding the reproducibility of a synthesis protocol. Furthermore, the quality of final product extremely depends on the amount of the water and pH[9-12]. All of these largely limit the widespread applications of sol-gel method. Thus, in order to synthesize nanoparticles simply and unrestrictedly, it is necessary to improve the aqueous sol-gel method. The present paper describes an innovative and simple sol-gel process for the preparation of nanoparticles at relatively low temperature without any water and out of the limit of pH, that is, the nonhydrolytic sol-gel method.

Nonhydrolytic sol-gel[13-16] method is a condensation reaction by different ways of heating reactants, leading to a formation of sol or gel, without the hydrolytic of metal alkoxides. The nonhydrolytic sol-gel method has emerged as an alternative route for the preparation of nanopartaicles under milder conditions than those employed in traditional methods.

In this paper, the Al_2O_3 sol was obtained *via* non-hydrolytic method. The aluminium trichloride was used as the precursors. Oleic acid and acetone was used as oxygen donor. The dispersion medium was lubricating oil.

EXPERIMENTAL

Sample preparation: The oil-soluble Al_2O_3 sol was prepared *via* nonhydrolytic method as follows, (1) A moderate amount of $AlCl_3$ was slowly placed in a 200 mL beaker, in which a moderate amount of lubricant base oil, oleic acid and acetone were added. (2) The beaker were sealed with plastic wrap and operated under magnetic stirring at room temperature for 12 h. (3) The stirred materials were transfered into a high pressure autoclave, heating and stirring at 135 ºC for 5 h, then cooling to room temperature. The oil-soluble Al_2O_3 sol was obtained and it had good organic compatibility and suspensibility.

As comparison, the unstable Al_2O_3 sol was prepared *via* aqueous method in the presence of water. Similarly, A moderate amount of deionized water was added in step (1), leading to a hydrolysis reaction of aluminium ion.

Sample characterization: The compositions of sample were characterized through German Bruker D8 X-ray diffractometer. The shape and size of the sample were observed by America FEI QUANTAFEG250 field emission electron microscope. The dispersion stability of Al_2O_3 sol in 20 # machanical oil was studied by UV-VIS spectrophotometer.

Studies of tribological properties: The resulting Al_2O_3 gel was added into 20 # mechanical oil. And the mass concentration was 0 wt %, 3 wt %, 9 wt %, 15 wt %. The oil was ultrasound dispersing in ultrasonic clearing machine for 0.5 h, respectively. Then, the lubricating oil containing Al_2O_3 nanoparticles with different mass concentration were obtained. Set for 48 h, the four-ball friction test and thrust ring friction test were respectively processed by a friction-abrasion testing machine (MMU-10G, Jinan).

RESULTS AND DISCUSSION

X-ray diffraction analysis: The XRD patterns of Al_2O_3 sol after heat-treatment at 800 ºC for 2 h was shown in Fig. 1. According to the main peaks appeared at 2θ = 14.274º, 27.946º, 38.271º, 49.353º, 64.677º. Thus it is suggested that the aluminum oxide crystals can be obtained from Al_2O_3 sol after heat-treatment at 800 ºC for 2 h.

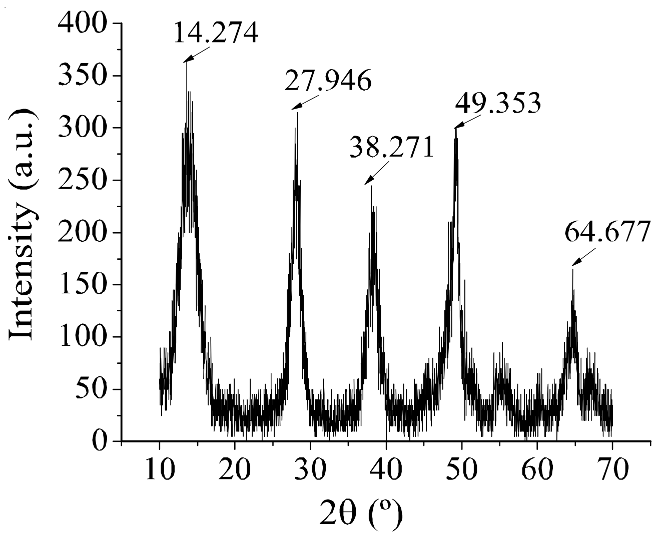

Fig. 1. XRD patterns of Al_2O_3 sol after heat treatment at 800 ºC for 2 h

SEM analysis: SEM images of Al_2O_3 nanoparticles obtained *via* aqueous sol-gel method and nonhydrolytic method were shown in Fig. 2. The obvious agglomeration can be seen in the images of Al_2O_3 nanoparticles obtained in the presence of water (Fig.2a). Al_2O_3 nanoparticles obtained *via* nonhydrolytic method without any water (Fig. 2b) was found to be dispersed very well with the size of about 80 nm and less agglomeration.

In presence of water, the precursor consists of fine particles that have been joined together by hydroxyls to form a network structure similar to a gel. The oxygen bridge bonds retained after the dehydration of the connecting hydroxyls adsorbed on the particle surfaces lead to the hard agglomeration of particles[17,18].

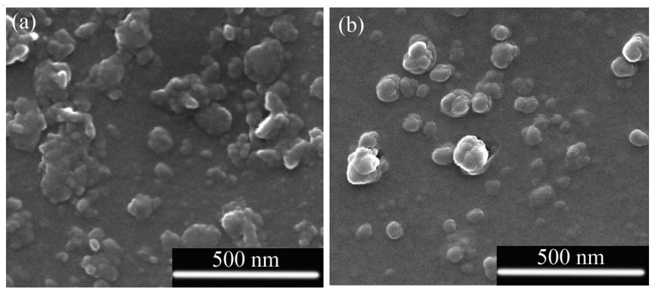

Fig. 2. SEM image of Al_2O_3 nanoparticles; (a) obtained in the presence of water; (b) obtained without any water

In absence of water, nanoparticles were dispersed very well as shown in Fig. 2b. That was because that the hard agglomeration formed by the oxygen bridge bonds disappeared and the macromolecular chains grafted on the surface of nanoparticles bring mutual exclusion and steric hindrance effect, thus the surface free energy has been reduced correspondingly and the agglomeration is controlled.

Dispersion stability analysis: The as-obtained Al_2O_3 sol was added into 20 # mechanical oil at a concentration of 30 wt %. Fig. 3 shows the curves of absorbance changes with time. In order to find out the trend of the three curves, the linear regression analysis was used to process the data. The linear regression equations were calculated as eqns. 1-3:

$$y_{a'} = 0.00004x + 2.1542,\ R_a^2 = 0.0019 \quad (1)$$

$$y_{b'} = 0.0001x + 2.3707,\ R_b^2 = 0.006 \quad (2)$$

$$y_{c'} = -0.0001x + 2.3707,\ R_c^2 = 0.0121 \quad (3)$$

From eqns. 1-3, it is known that the absorbance of the three samples scarcely changed with time, which indicated that not only the as-obtained Al_2O_3 sol was very stable, but also was the 20 # mechanical oil doped with Al_2O_3 sol at the mass concentration of 30 wt %.

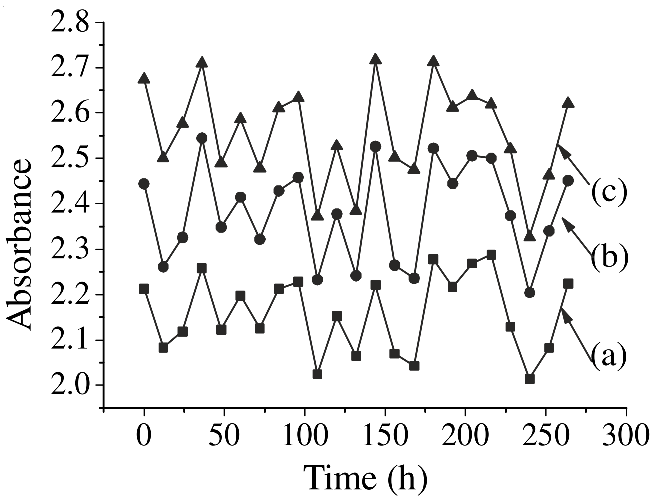

Fig. 3. Absorbance-time line chart of (a) oil; (b) oil+ 30 wt % Al_2O_3 sol; (c) Al_2O_3 sol

Friction-wear test results and analysis

Thrust ring friction coefficient analysis: The variation of friction coefficient with time under different additive concentration of Al_2O_3 sol is shown in Fig. 4. The friction coefficient obviously decreases with increasing concentration of Al_2O_3 sol up to 9 wt % and then presents an increasing trend with increasing concentration to 15 wt %. The data show that the friction coefficient of the samples studied has a lowest value and decreasing amplitude of 14.74 % when 9 wt % of Al_2O_3 sol is present.

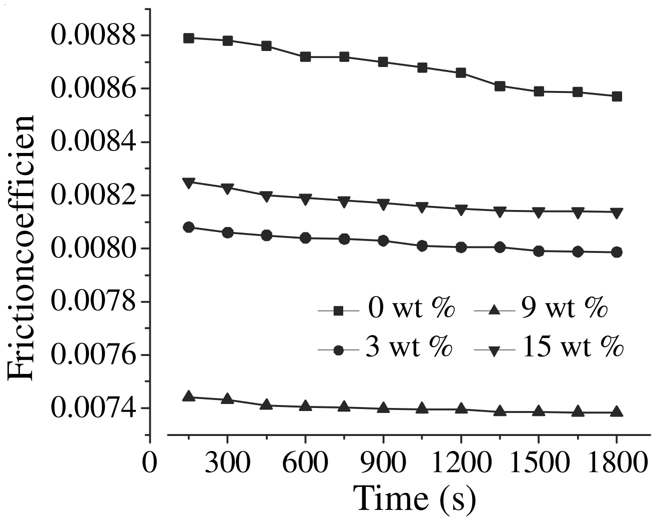

Fig. 4. Curves of friction coefficient changes with time

Wear scar of four ball analysis: The variation of wear scar diameter with additive concentration is shown in Table-1. The mechanical oil with higher concentration (below 9 wt %) of Al_2O_3 sol exhibited a lower wear scar diameter in comparison with the unfilled mechanical oil. Then it increases with further increasing concentration of Al_2O_3 sol. The data show that the wear scar diameter has a lowest value when 9 wt % of Al_2O_3 sol is present.

TABLE-1
VARIATION OF WEAR SCAR DIAMETER (WSD) WITH ADDITIVE CONCENTRATION

Number	0 wt % (µm)	3 wt % (µm)	9 wt % (µm)	15 wt % (µm)
1 #	351.55	335.12	312.12	340.21
2 #	342.47	324.83	305.94	333.66
3 #	301.69	286.92	279.51	295.78
Average WSD	331.90	315.62	299.19	323.22
Decreasing amplitude of WSD	0	4.91	9.86	2.62

Fig. 5 shows the images of No. 2 wear scar rubbed under pure oil (a) and oil doping with 9 wt % Al_2O_3 sol (b), respectively. Compared with that of Fig. 5a, the wear scar in Fig. 5b presents that the horizontal diameter has a 10.67 % decline, the furrows becomes shallower which seems to be filled with something. These showed that the mechanical oil by adding a certain amount of Al_2O_3 sol could play well antiwear effects in the friction pairs.

Conclusion

(1) Al_2O_3 sol in an oil phase system with good organic compa-tibility and dispersion stability was immediately obtained *via* a non-hydrolytic method, using the aluminum trichloride as the precursors, oleic acid and acetone as oxygen donor, lubricating basic oil as dispersion medium.

(2) As concentration increases, the lubrication properties improve, but high a concentration causes a decrease of lubrication. With 9 wt % Al_2O_3 sol filled mechanical oil, the lubricating effects reach a best value which the friction has a 14.74 % decline and the wear scar diameter has a 10.67 % decline.

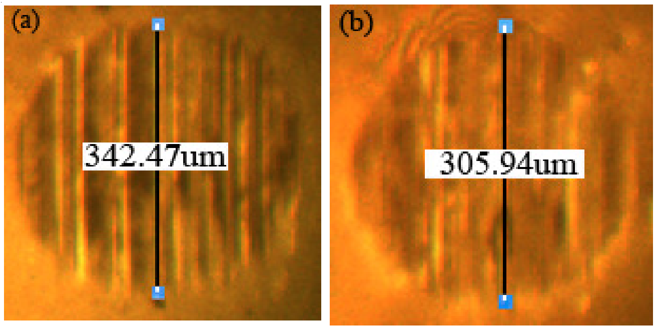

Fig. 5. Images of wear scar of NO.2 ball rubbed under different oil; (a) Pure 20 # mechanical oil; (b) oil doped with 9 wt % Al_2O_3 sol

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REFERENCES

1. Y.L. Tai, J.S. Qian, Y.C. Zhang and J.D. Huang, *Chem. Eng. J.*, **141**, 354 (2008).
2. W. Ye, T. Cheng, Q. Ye, X. Guo, Z. Zhang and H. Dang, *Mater. Sci. Engg.*, **A359**, 82 (2003).
3. H. Zhang, L. Tang, Z. Zhang, L. Gu, Y. Xu and C. Eger, *Tribol. Int.*, **43**, 83 (2010).
4. M. Zhang, X. Wang, X. Fu and Y. Xia, *Tribol. Int.*, **42**, 1029 (2009).
5. W. Huang, Y. Fu, J. Wang, Z. Li and M. Liu, *Tribol. Int.*, **38**, 775 (2005).
6. K. Lee, Y. Hwang, S. Cheong, L. Kwon, S. Kim and J. Lee, *Curr. Appl. Phys.*, **9**, e128 (2009).
7. A.-Y. Jee and M. Lee, *Curr. Appl. Phys.*, **9**, e144 (2009).
8. Q.B. Guo, M.Z. Rong, G.L. Ji, K,T. Lau and M.Q. Zhang, *Wear*, **266**, 658 (2009).
9. C. Mao, X. Dong, T. Zeng, H. Chen and F. Cao, *Ceramics Int.*, **34**, 45 (2008).
10. M. Niederberger, *Acc. Chem. Res.*, **40**, 793 (2007).
11. A. Cestari, L.C. Bandeira, P.S. Calefi, E.J. Nassar and K.J. Ciuffi, *J. Alloys Comp.*, **472**, 299 (2009).
12. L. Bourget, R.J.P. Corriu, D. Leclercq, P.H. Mutin and A. Vioux, *J. Non-Cryst. Solids*, **242**, 81 (1998).
13. J. Zhu, J. Yang, Z.-F. Bian, J. Ren, Y.-M. Liu, Y. Cao, H.-X. Li, H.-Y. He and K.-N. Fan, *Appl. Catal. B: Environ.*, **76**, 82 (2007).
14. G. Guo, J.K. Whitesell and M.A. Fox, *J. Phys. Chem. B*, **109**, 18781 (2005).
15. M. Niederberger, *Acc. Chem. Res.*, **40**, 793 (2007).
16. M. Niederberger, G. Garnweitner, N. Pinna and G. Neri, *Prog. Sol. State Chem.*, **33**, 59 (2005).
17. J. Huang, Sol-Gel Principle and Technology, Beijing: Chemical Industry Press, Vol. 9, pp. 160-161 (2005).
18. J. Wang, S. Zheng and R. Zeng, *J. Am. Ceram. Soc.*, **92**, 1217 (2009).