Asian Journal of Chemistry; Vol. 23, No. 2 (2011), 705-708

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Study of Surface Modification of ZrO_2/SiO_2 Nanocomposites with Aluminum Zirconium Coupling Agent

WEI LI, SHAOHUA ZHENG, SHIYU MA, HAIYANG DING, DA JIAO and BINGQIANG CAO*

School of Materials Science and Engineering, University of Jinan, Jinan 250022, P.R. China

*Corresponding author: E-mail: mse_zhengsh@ujn.edu.cn; mse_caobq@ujn.edu.cn

(*Received*: 22 March 2010; *Accepted*: 27 September 2010) AJC-9143

In this studies, the ZrO_2/SiO_2 composite nanoparticles are prepared by *situ*-modified method and the ZrO_2/SiO_2 composite nanoparticles are modified by aluminum zirconium coupling agent. By using the particle size analysis, it is confirmed that the mean particle size of modified ZrO_2/SiO_2 composite nanoparticles is 55 nm and its distribution is uniform. The dispersion of modified ZrO_2/SiO_2 composite nanoparticles is analyzed by the absolute value of ZrO_2/SiO_2 nanoparticles Zeta potential. Through transmission electron micrograph (TEM) observation, it is found that aluminum zirconium coupling agent improve the dispersibility of ZrO_2/SiO_2 composite nanoparticles. The hydroxyl groups on the surface of ZrO_2/SiO_2 composite nanoparticles can interact with hydroxyl groups of aluminum zirconium coupling agent and an organic coating layer is formed. The formed covalent bands are testified by Fourier transform infrared spectra (FT-IR). The dispersion stabilization of modified ZrO_2/SiO_2 composite nanoparticles in lubricating oil is significantly improved due to the introduction of grafted polymers on the surface of nanoparticles.

Key Words: Additive, Surface modification: ZrO_2/SiO_2 composite nanoparticles, Lubricants.

INTRODUCTION

In recent years, much attention has been paid to nanoparticles, which possess novel optical, electronic and chemical properties absent in bulk materials[1]. Nanoparticles as lubricating oil additives are one of the most important researches. It is reported that when some nanoparticles were added into the lubricating oil, their lubrication properties can be effectively improved[2-6], which is better than the traditional solid lubricant additives and becomes a promising new lubricating material. Ming *et al.*[7] reported that using $CaCO_3$ nanoparticles as PAO base oil additives can dramatically improve the load-carrying capacity, as well as the anti-wear and friction-reduction properties of PAO base oil. In addition, higher applied load, moderate frequency, longer duration time and lower temperatures were beneficial to the deposition of $CaCO_3$ nanoparticles accumulating on rubbing surfaces. It is also found that there are different interactions when two or more nanoparticles lubricant additives are added, such as adduct effect, synergy and antagonism effects[8]. Although these effects have obvious influence on the performance of lubricating oil when nanoparticles are used as additives. But nanoparticles have a strong tendency to agglomerate due to its high surface energy and have weak combination with the polymer matrix because of badly consistent interface[9-12]. So the surface modification of nano-particles is a difficult task. The crux lies in the fact how to well disperse inorganic nanoparticles in lubricating oil and how to improve their interfacial interaction. This has been the critical procedure to prepare high-performance nanocom-posites.

In previous work, a series of molecular coupling agent, such as tercopolymer BA-MAA-AN[13], tercopolymer BA-MMAVTES[14], tercopolymer was synthesized to modify nanoparticles, which was applied to prepare nanoparticles/rubber composites. Due to the strong interface action, these nanocomposites exhibit unique hybrid properties including good heat-resistance, good wear-resistance and good dynamic mechanical properties[1].

Now, there are several methods to modify the surface of nanoparticles in literatures. Swihart and coworkers[15,16] grafted octadecyltri methoxy silane, octadecene or undecylenic acid on to the surface of silicon nanoparticles. TEM, FT-IR (Fourier transform infrared spectra), photoluminescence measurements were used to describe the results. Kang and coworkers[17], used covalent graft polymerization and block copolymerization to modify the chlorinated SiO_2 (SiO_2-Cl) by atom transfer radical polymerization (ATRP).

In this paper, ZrO_2/SiO_2 composite nanoparticles were prepared with *situ*-modified method and surface was modified by aluminum zirconium coupling agent. Such modified ZrO_2/SiO_2 nanoparticles showed good dispersion stability in lubricating oil. The dispersion of modified ZrO_2/SiO_2 nanoparticles as well as the mechanism of stable colloidal dispersion was discussed in lubricating oil, whose polar is quite low. The using efficiency of aluminum zirconium coupling agent as a modifier was also studied.

EXPERIMENTAL

Superficial modification of ZrO_2/SiO_2 composite nanoparticles: Zirconium acetate oxygen was added to 100 mL alcohol (95 %) and heated stirring to form a sol. The pH value was set at 9-10 by ammonia solution. After three times washing with alcohol (95 %), ZrO_2 precursor was prepared; 0.025 mol TEOS was added to 100 mL alcohol (95 %), then the ZrO_2 precursor was added. Next 0.026 g ammonium hydrogen fluoride was added and heated stirring to form a sol. The pH value was set at 9-10 by ammonia solution. After three times washing with alcohol (95 %), ZrO_2/SiO_2 precursor was prepared. The ZrO_2/SiO_2 precursor was dissolved with 150 mL alcohol (95 %). The aluminum zirconium coupling agent was added and the concentration was 0.6 wt %. The molecular structure of aluminum zirconium coupling agent was shown in Fig. 1. The solution was mixed 1.5 h before put into the autoclave. The reaction conditions were set as follows: temperature 220 ºC, pressure 3.6 Mpa, time 2 h. The powder was put out until the reactor cooled to room temperature. Then the modified ZrO_2/SiO_2 composite nanoparticles were made.

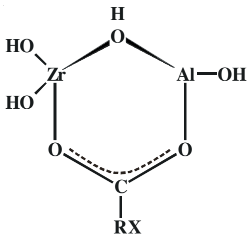


Fig. 1. Molecular structure of aluminum zirconium coupling agent

ZrO_2/SiO_2 composite nanoparticles were analyzed by Laser Particle Size analyzer and Zeta-potential analyzer. By observing transmission electron micrograph (TEM), it was found that the dispensability of ZrO_2/SiO_2 composite nanoparticles was improved. The formed covalent bands were testified by Fourier transform infrared spectra (FT-IR). By these instrumental analysis, the nanoparticles particle size, morphology and modification effect were observed. Finally, the modified effort of ZrO_2/SiO_2 composite nanoparticles was obtained.

RESULTS AND DISCUSSION

Particle size analysis: Fig. 2 is the image of particle size distribution of ZrO_2/SiO_2 nanoparticles. The particle size of modified ZrO_2/SiO_2 nanoparticles is uniform. Most particle size is between 45-60 nm and the mean particle size is 55 nm. It can be seen that 99.9 % nanoparticles is below 100 nm by cumulative curve.

Decentralized stability analysis: The reunions between nanoparticles are characterized by Zeta potential absolute value. The value is greater and the reunion is slighter. The absolute value of ZrO_2/SiO_2 Zeta potential is shown in Fig. 3.

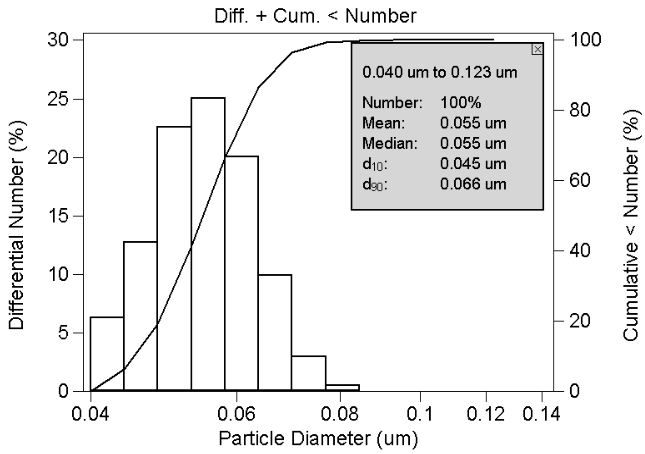


Fig. 2. Image of particle size distribution of ZrO_2/SiO_2 nanoparticles

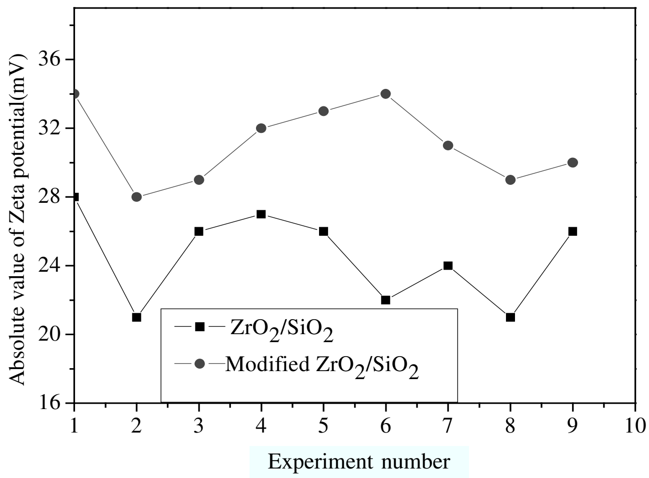
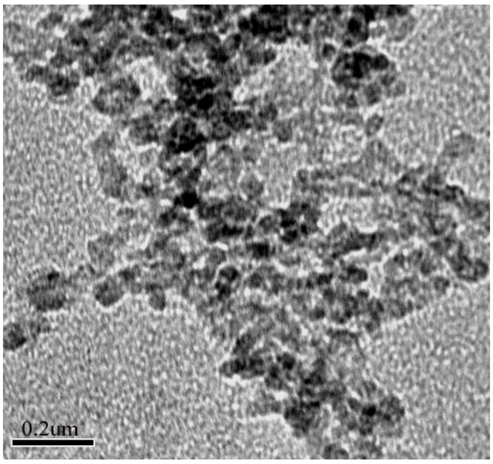


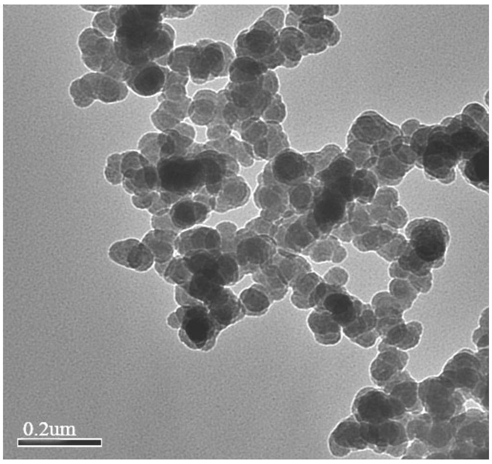
Fig. 3. Absolute value of ZrO_2/SiO_2 nanoparticles Zeta potential

As shown in Fig. 3, Zeta potential absolute value of modified ZrO_2/SiO_2 nanoparticles is greater than native ZrO_2/SiO_2 nanoparticles. This indicate that static repellency of modified ZrO_2/SiO_2 nanoparticles becomes bigger than native ZrO_2/SiO_2 nanoparticles. The modified ZrO_2/SiO_2 is well dispersed in lubricating oil.

Fig. 4 displays the TEM images of native ZrO_2/SiO_2 composite nanoparticles and modified ZrO_2/SiO_2 composite nanoparticles. The obvious agglomeration can be seen in the images of native ZrO_2/SiO_2 composite nanoparticles (Fig. 4a) and the homogeneous dispersion can be seen in the images of modified ZrO_2/SiO_2 composite nanoparticles (Fig. 4b). This is because that aluminum zirconium coupling agent layers is coated on the surface of ZrO_2/SiO_2 composite nanoparticles and the agglomeration has been reduced. This suggests that physical bonding or chemical bonding occurs between the polarity bond of aluminum zirconium coupling agent and hydroxide group, unsaturated bond or suspension bond. The macromolecular chains grafted on the surface of ZrO_2/SiO_2 composite nanoparticles bring mutual exclusion and steric hindrance effect, thus the surface free energy has been reduced correspondingly and the agglomeration controlled. All the results above further illustrate that aluminum zirconium coupling agent has played an important role in the dispersion of ZrO_2/SiO_2 composite nanoparticles.



(a) Unmodified ZrO_2/SiO_2 nanoparticles



(b) Modified ZrO_2/SiO_2 nanoparticles

Fig. 4. TEM images of ZrO_2/SiO_2 composite nanoparticles

FT-IR analysis: Fig. 5 compare the infrared spectra of ZrO_2/SiO_2 composite nanoparticles before and after modification. Two new peaks are observed at 2376 and 2174 cm^{-1}, which can be attributed to TBDMS and alkynes absorption peak, respectively. The appearance of these two peaks indicates that the surface of modified ZrO_2/SiO_2 composite nanoparticles is changed. Nanoparticles surface changed from inorganic phase to organic phase. This is due to that aluminum zirconium

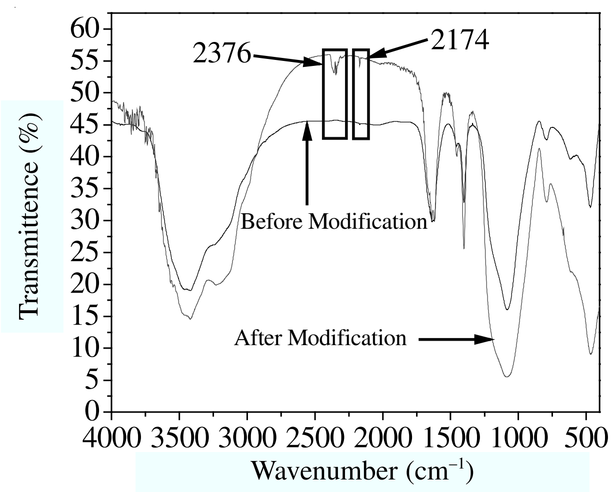


Fig. 5. Infrared spectrum of ZrO_2/SiO_2 composite nanoparticles

coupling agents bond with the ZrO_2/SiO_2 composite nanoparticles surface hydroxyl. The surface of ZrO_2/SiO_2 composite nanoparticles is successfully modified. The role mechanism is shown in Fig. 6. The surface of ZrO_2/SiO_2 composite nanoparticles is successfully modified.

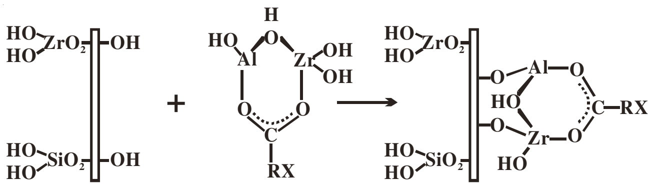


Fig. 6. Role mechanism of aluminum zirconium coupling agent

Oil-soluble analysis: The ZrO_2/SiO_2 nanoparticles are added into lubricating oil and then the absorbency of nano-oil with time is observed by ultraviolet spectrophotometer, as shown in Fig. 7. The absorbency is greater and the dispersion of nano-oil is well. After 56 h, the absorbency of nano-oil with modified ZrO_2/SiO_2 nanoparticles is stable. But the absorbency of nano-oil with native modified ZrO_2/SiO_2 nanoparticles is still becoming little. This indicates that modified ZrO_2/SiO_2 nanoparticles can steadily exist in lubricating oil.

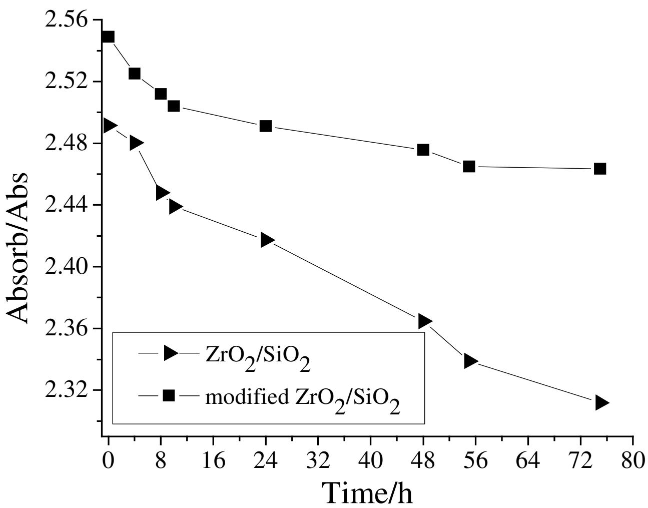


Fig. 7 Absorbency curve of nano-oil with time

The nano-oil is put aside at room temperature for 56 h and then the image of oil-soluble about nano-oil with nanoparticles is shown in Fig. 8. As can be seen from Fig. 8a, native ZrO_2/SiO_2 nanoparticles are insoluble in oil. However, the modified ZrO_2/SiO_2 nanoparticles are soluble in oil (Fig. 8b). this is due to reason that the surface of nanoparticles changed from inorganic phase to organic phase.

The hydroxyl groups (-OH) from ZrO_2/SiO_2 nanoparticles can interacted with hydroxyl groups from aluminum zirconium coupling agent to form complex on the surface of ZrO_2/SiO_2 nanoparticles. Consequently, no matter what reaction occurred, the graft copolymers are initially grafted or anchored on the surface of the particles at one or several spots. The other terminal of aluminum zirconium coupling agent is organic polymer chain, which fulfills steric hindrance between inorganic nanoparticles. All above factors give rise to the homogeneous dispersion of ZrO_2/SiO_2 nanoparticles in lubricating oil and maintain a stable colloidal dispersion for a long time. This is visualized in Fig. 8. They are the photographs of dispersion stabilized of ZrO_2/SiO_2 nanoparticles in dimethyl benzene with time.

(a) Unmodified ZrO_2/SiO_2 nanoparticles (b) Modified ZrO_2/SiO_2 nanoparticles

Fig. 8. Photographs of oil-soluble about nano-oil with nanoparticles

Conclusion

ZrO_2/SiO_2 composite nanoparticles are modified by aluminum zirconium coupling agent. Study results show that aluminum zirconium coupling agent has been anchored on the surface of ZrO_2/SiO_2 composite nanoparticles, the modified ZrO_2/SiO_2 composite nanoparticles present a more stable colloidal dispersion in lubricating oil than that of untreated ZrO_2/SiO_2 composite nanoparticles.

ACKNOWLEDGEMENTS

The authors acknowledged the financial support from National Science Foundation of China (51002065). One of the authors, Bingqiang Cao is an Oversea Taishan Scholar and thanks the start-up support from University of Jinan for a new faculty.

REFERENCES

1. Y.L. Tai, J.S. Qian, Y.C. Zhang and J.D. Huang, *Chem. Eng. J.*, **141**, 354 (2008).
2. V.E. Red'kin, *Chem. Tech. Fuels Oil*, **40**, 164 (2004).
3. Z. Hu and J.X. Dong, *Wear*, **216**, 87 (1998).
4. J.X. Dong, Z.S. Hu and G.X. Chen, *Tribol. Int.*, **31**, 219 (1998).
5. Q.B. Guo, M.Z. Rong, G.L. Jia, K.T. Lau and M.Q. Zhang, *Wear*, **266**, 658 (2009).
6. Ah-Young Jee and M. Lee, *Curr. Appl. Phys.*, **9**, e144 (2009).
7. M. Zhang, X.B. Wang, X.S. Fu and Y.Q. Xia, *Tribol. Int.*, **42**, 1029 (2009).
8. G. Sui, W.H. Zhong, X. Ren, X.Q. Wang and X.P. Yang, *Mater. Chem. Phys.*, **115**, 404 (2009).
9. M.L. Zhang, G.L. Ding, X.Y. Jing and X.Q. Hou, *Appl. Surf. Tech.*, **31**, 64 (2004).
10. Q.-L. Zhang, L.-C. Du and Y.-X. Weng, *Phys. Chem.*, **B108**, 15077 (2004).
11. A.D. Pomogailo, *Polym. S. Seri.*, **C48**, 85 (2006).
12. F. Nsib, N. Ayed and Y. Chevalier, *Prog. Org. Coat*, **55**,. 303 (2006).
13. R. Xia, Y.H. Zhang, Q.R. Zhu, J.S. Qian, Q.N. Dong and F.S. Li, *J. Appl. Polym. Sci.*, **107**, 562 (2008).
14. R. Xia, M.H. Li, Y.C. Zhang, Q.R. Zhu and J.S. Qian, *J. Appl. Polym. Sci.*, **107**, 1100 (2008).
15. X.G. Li, Y.Q. He and M.T. Swihart, *Langmuir*, **20**, 4720 (2004).
16. H.S. Fengjun, M.T. Swihart and E. Ruckenstein, *Langmuir*, **21**, 6054 (2005).
17. F.J. Xu, Q.J. Cai, E.T. Kang and K.G. Neoh, *Macromolecules*, **38**, 1051 (2005).