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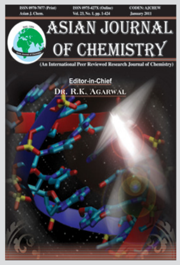

Preparation and Surface-Modification of Alumina/Silica Composite Nanoparticles

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In this work, alumina/silica (Al_2O_3/SiO_2) composite nanoparticles were prepared using aluminum isopropoxide and tetraethyl orthosilicate as raw materials. We prepared Al_2O_3 and SiO_2 precursors with sol-gel method and Al_2O_3/SiO_2 composite nanoparticles by hydrothermal method, respectively. We *in situ* modified Al_2O_3/SiO_2 composite nanoparticles and optimized the modifier and modification route. The characterizations of the Al_2O_3/SiO_2 composite nanoparticles were performed with transmission electron microscopy, X-ray diffraction, infrared spectroscopy and Zeta potential analysis. Under the optimized modification conditions, the modified Al_2O_3/SiO_2 composite nanoparticles had good dispersion and suspension. The surface of the Al_2O_3/SiO_2 composite nanoparticles was changed from hydrophile into lipophilicity.

Key Words: Hydrothermal method, Alumina/Silica, Composite nanoparticles, Surface modified.

INTRODUCTION

Further investigation of nanotribology shows that the nanoparticles has novel property antiwear, antifriction and high load in the field of lubrication and tribology. It can be used as new lubricant antiwear agent[1,2]. They reveal specific property due to their strong correlation in quantum mechanics[3]. They can also adsorb on the mating surfaces then form nanoparticles or film on the friction surface. In the course of friction the nanoparticles function as "molecule bearing" so as to protect the rub friction, they have excellent lubrication and antifriction performance. So, adding nano-lubricating materials to lubricating oil, which can notably improve the lubricity and load-carrying capacity of the lubricating oil. This has injected new vitality into the development of lubricating oil[4,5].

Silica nanoparticles have a strong activity because of high specific surface area and small particle size. However, it easily agglomerate in organic mediums due to their small size and high surface area. Surface-modification is an effective route to acquire monodisperse nanoparticles. It can obviously improve the lubricant performance, such as antiwear, antifriction and extreme pressure. After modification, the surface of silica nanoparticles change from hydrophile to lipophilicity due to the reduction of alcohol. So, the silica nanoparticles have a steady dispersion system in lubricating oil.

Alumina nanoparticles also have many excellent properties, such as high strength, high hardness, antiwear and corrosion resistant[6]. Alumina nanoparticles have better antifriction and antiwear property. However, the small particle size leads to high surface area and high surface energy[7]. So they shows poor dispersion capacity in non-polar media and they easily agglomerate in polar media, to play a direct impact on their performance. The effect is not ideal even after modification.

In this study, we mixed Al_2O_3 nanoparticles and SiO_2 nanoparticles in order to make two kinds of nanoparticles complement each other. The surface of Al_2O_3/SiO_2 composite nanoparticles had a change from hydrophile to lipophilicity by modified. We researched the dispersion and suspension of Al_2O_3/SiO_2 composite nanoparticles in lubricating oil. This paper used aluminum isopropoxide and tetraethyl orthosilicate (TEOS) as main raw material, prepared precursors by sol-gel method and finally Al_2O_3/SiO_2 composite nanoparticles was synthesized by hydrothermal method. In the course of hydrothermal preparation, we modified the surface of Al_2O_3/SiO_2 composite nanoparticles by *in situ* modification and analyzed and characterized the Al_2O_3/SiO_2 composite nanoparticles.

EXPERIMENTAL

All chemical reagents with high purity were used as received. The Al_2O_3/SiO_2 composite nanoparticles were prepared with hydrothermal method (GSH-025-type autoclave, Weihai Huixin Chemical Machinery). The whole experimental procedures as following: 8.14 g aluminum isopropoxide was weighed in flask that has three orifice and 100 mL distilled water and 1 mL 69 % concentrated nitric acid were added. Then the flask was kept in temperature control electric heating instrument. The solution was heated and changed from clouding to clarity. Left the solution for cooling and then added 0.5 g NaOH in order to form AlOOH gel. 13.42 mL tetraethyl orthosilicate was measured in one beaker and 100 mL 95 % concentrated ethanol and 0.0624 g ammonium bifluoride were added. The solution was stired under constant temperature still the $Si(OH)_4$ gel came out. The AlOOH gel and $Si(OH)_4$ gel were mixed and stired for 0.5 h. Then we used distilled water washed the mixed gel four times and 95 % concentrated ethanol washed two times. 0.5 wt % silane coupling agent was added in it, then it was stired for 3 h. After 24 h, the synthesized solution was put into autoclave and setted the temperature was 493 K. The sample was heated for 1 h, then insulated for 2 h. We acquired organic modified Al_2O_3/SiO_2 composite nanoparticles that had favourable dispersion. Then according to 1 wt % addition we put Al_2O_3/SiO_2 composite nanoparticles into ChangCheng lubricating oil, it was ultrasonic dispersion for 0.5 h to produce a stable dispersion system. It was kept for 24 h. The dispersion of Al_2O_3/SiO_2 composite nanoparticles that in the lubricating oil was observed. The test applied orthogonal table L9 (34) of 4 factor 3 level to perform orthogonal test. The table of factor level as Table-1.

The size and morphology of Al_2O_3/SiO_2 composite nanoparticles were examined with transmission electron microscope (JEM-2010). The crystalline of Al_2O_3/SiO_2 composite nanoparticles was tested with X-ray diffraction spectroscopy (D8, Bruker). Infrared spectroscopy (Nicolet 380) was used to determine the effect of surface modification. Zeta Pals potentiometer was applied to determine the value of Zeta potential.

RESULTS AND DISCUSSION

TEM analysis: In Fig. 1(a) the TEM images of Al_2O_3/SiO_2 composite reveals that before modification the particles were needle and all the diameters of particles were less than 50 nm. The mass among particles were severe. However, from Fig. 1(b), it is observed that after modification, the particles were elliptical. The diameters of particles are smaller than 50 nm and the agglomeration among particles was decreased. It suggested that the modified agent covered the surface of Al_2O_3/SiO_2 composite nanoparticles and played a role of isolation. Better dispersion was made by the modified agent.

X-ray diffraction analysis: The sample had five obvious diffraction peaks, the first was the steamed bread peak of SiO_2. The following four peaks were due to Al_2O_3. As a result of the small diameter of nanoparticles, the growth of particles were restricted, so the Al_2O_3/SiO_2 composite nanoparticles were amorphous (Fig. 2).

Infrared spectroscopy analysis: Fig. 3 compares the infrared spectra of Al_2O_3/SiO_2 composite nanoparticles before and after modification with silane coupling agents. It is shown

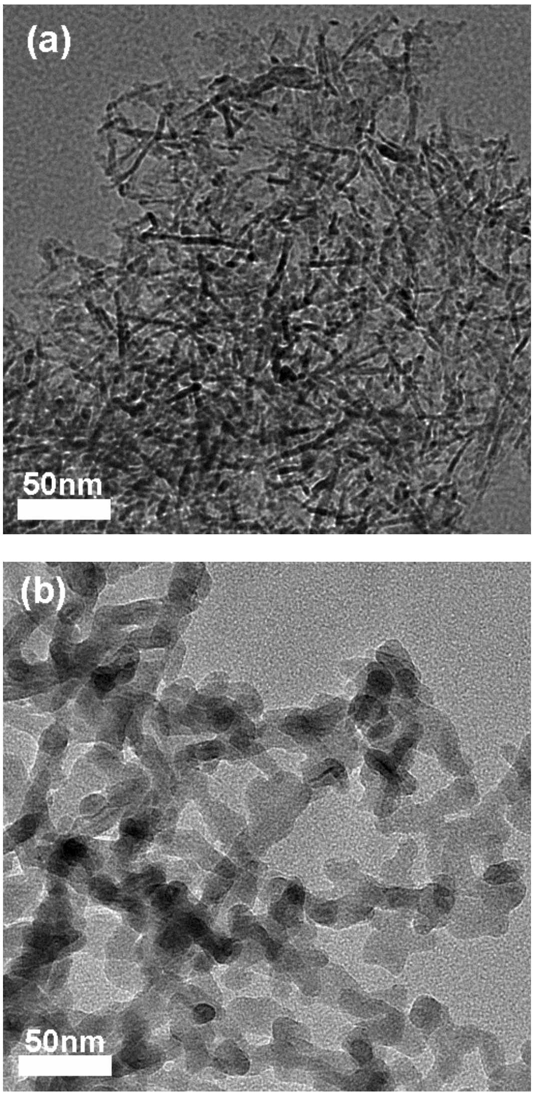

Fig. 1. TEM images of Al_2O_3/SiO_2 composite nanoparticles (a) before and (b) after modification

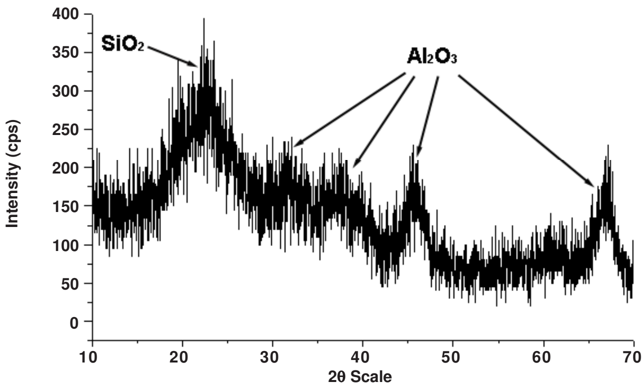

Fig. 2. XRD pattern of Al_2O_3/SiO_2 composite nanoparticles after modification

TABLE-1
FACTOR LEVEL OF ORTHOGONAL TEST

Level	Factor			
	Al_2O_3/SiO_2 proportion	Kind of modified agent	Dosage of modified agent (wt%)	Temperature of preparation (K)
1	1:1	Silane coupling agent	1.0	493
2	1:3	Titanate coupling agent	0.5	473
3	3:1	Aluminum zirconium coupling agent	0.3	453

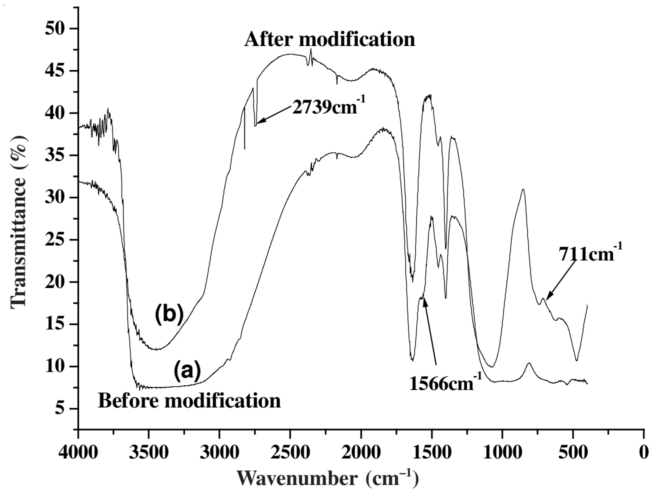

Fig. 3. Infrared spectroscopy curve of Al_2O_3/SiO_2 composite nanoparticles

that after modification the methyl absorb apex that the same as the methyl absorb apex of silane coupling agent was appeared in 2739 cm^{-1}. In 1566 cm^{-1} the bridge hydroxide absorb apex was almost disappeared and the flex oscillate absorb apex of COO-Al came out in 711 cm^{-1}. This fully illustrated that silane coupling agent successfully modified the surface of Al_2O_3/SiO_2 composite nanoparticles, achieved the change of the surface of Al_2O_3/SiO_2 composite nanoparticles from hydrophile to lipophilicity, there were chemical bonds between surface of Al_2O_3/SiO_2 composite nanoparticles and silane coupling agent.

Zeta potential analysis: Zeta potential is an important indicator which characterizes if the particles are electrification. The bigger the absolute value of Zeta potential is, the better dispersion has the matter in solution, as the system of solution more steady, also the extent of agglomerate is much lower[8]. Table-2 shows Zeta potential test parameter of before and after modification Al_2O_3/SiO_2 composite nanoparticles. From the data of Table-2 it is observed, the average value of Zeta potential augmented from 30.73 mV before modification to 35.10 mV after modification, which suggested that after modification the surface of Al_2O_3/SiO_2 composite nanoparticles,

TABLE-2
ZETA POTENTIAL TEST PARAMETER
BEFORE AND AFTER MODIFICATION

State of Al_2O_3/SiO_2 composite nanoparticles	Average value of Zeta potential (mV)
Before modified	30.73
After modified	35.10

polarity took place change, bring static ostracize force, the dispersion and agglomerate phenomena of Al_2O_3/SiO_2 composite nanoparticles was improved.

Conclusion

Using hydrothermal method, the preparation and surface-modification of Al_2O_3/SiO_2 composite nanoparticles were successfully achieved. We obtained the optimal scheme was as following: the best mol ratio of Al_2O_3 to SiO_2 is 1:3, modified agent is silane coupling agent, dosage is 0.5 wt % and temperature of preparation is 220 ºC. All the diameters of Al_2O_3/SiO_2 composite nanoparticles are smaller than 50 nm. The Al_2O_3/SiO_2 composite nanoparticles have better dispersion stability in lubricating oil after modification. The nanoparticles were added to the lubricating oil and can significantly improve the performance of lubricating oil. It can also reduce the wear between mechanical components. The service life of mechanical components was extended. Most of all, a lot of energy can be conserved. The development of nanoparticles antiwear and antifriction addtivities show more important applications.

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