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A Novel Heat-resisting Surfactant for the Modification of Alumina Nanoparticles

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Abstract: An easy preparation of controlled alumina nanoparticles by the solution precipitate method has been carried out using dendrimer as surfactant. The effects of the amount and size of surfactant on morphological control of powder have also been discussed.

Keywords: Alumina, nanoparticles, dendrimer, surfactant.

Metal oxides nanoparticles are of considerable interest because of their special chemical and physical properties that are determined by both size and shape [1,2]. Conventional precipitate method in solution is a simple approach for synthesizing metal oxides fine powder with the advantage of eliminating the need for milling to break up agglomerates and reducing the cost of fabrication. However, for containing many hydroxyl groups, upon postfiring step of the initial particles, condensation among surface hydroxyl groups occurs concurrently over a fairly wide temperature range [3]. Meanwhile, large amounts of water among particles will pull the particles together because of intense interfacial tension. Strong attraction usually leads to the formations of highly disordered larger aggregates rather than monodispersed particles. Accordingly, isolation of the hydrous particles or replacement of the particle surface water and hydroxyl groups with another functional group that do not condense as water and hydroxyl groups do and could eventually be removed from the production may effectively limit the aggregation of initial particles and restrict advancing of particles at elevated temperatures. Research has shown that the addition of surfactant influents the size, shape and stability of particles, Our group's study has found that for the use of different amounts of organic acid, spherical and fibrous nanoparticles were synthesized[4]. We discovered that a novel heat-resisting surfactant—poly (amideamine) dendrimer can be used to synthesize monodispersed alumina nanoparticles with controlled sizes and shapes. Dendrimer possessing spherical structure and active surfaces of carboxylic groups could interact strongly with oppositely charged ions and colloidal particles [5,6]. The number of surface functional groups and the volume of dendrimer increase with its increasing generations, which can be accurate controlled.

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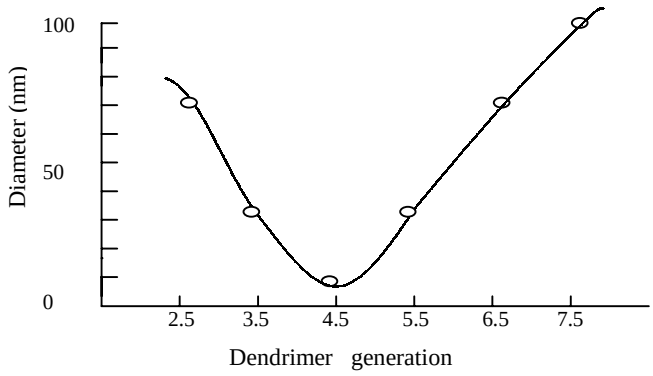
In this paper, a series of half-generation dendrimers from 2.5 to 7.5 were synthesized by means of procedure described in previous papers [7,8]. Aluminum nitrate (AR) was used as reactant of precipitation. The surfactant was dissolved to 0.1-10 wt % in the salt solution, then precipitant was added directly into the mixture. After stirring for 1 hour, the mixture was centrifuged and the cream was aged at room temperature for 1 hour in air then dried at 100°C and calcined in air in a furnace. The particle size and shape of alumina were determined by using a transmission electron microscope (TEM). The particle distribution of alumina was measured by using a particle size distribution analyzer. The thermal stability of powder and dendrimer was measured by using a thermogravimetric analyzer (TG/DTA). The crystallographic texture was determined by X-ray diffraction analysis. All experiments were preformed at room temperature.

The influence of surfactant generation and additional amount on the synthesis process is currently under investigation. **Figure 1** shows the effect of the dendrimer generations on particle size.

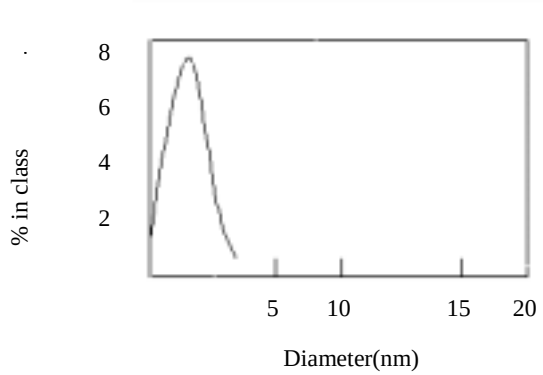
Figure 1 Variation of particle size with dendrimer generation



As can be observed, particle size decreased as the dendrimer generation increased up to 4.5, and then increased with the further increase of generation. This result suggests that the dendrimer generation is an important operation here. For the earlier generation the size of the dendrimer is too small for effective cooperative adsorption of alumina particles. With an increase of generation, dendrimers possess more carboxylic groups on their surface, so the interactions between dendrimers and alumina particles strengthen. The further increase of dendrimers generation leads to crowded surface groups, which changes the adsorption form and reduces the adsorption activity.

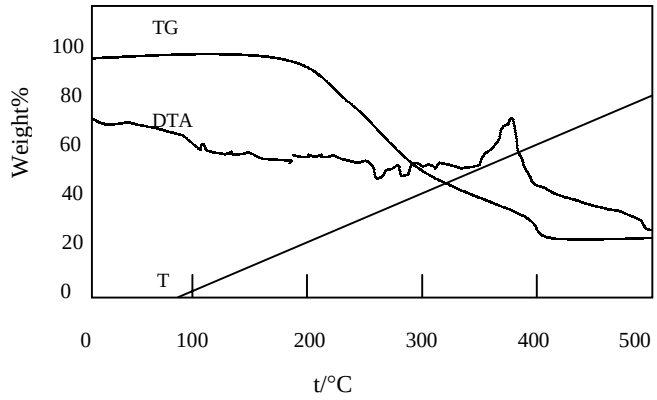
The additional amount of surfactant has effect on the formation and size distribution of particles. When the additional amount is less than 1 mg/g, dendrimer almost has no effect on particle surface modification; with the increase of the amount of dendrimer, the effect becomes obvious; and then further increase of amount of dendrimer renders the effect going from strength to weakness. In particular, the particles of alumina by addition of 1 mg/g dendrimer G (4.5) showed the smallest size (< 5 nm) and best-distribution (98 % be in the range between 2.0 to 3.5 nm)(showed by **Figure 2**). The configuration of adducts was further confirmed by X-ray crystal structure.

Figure 2 Size distribution and TEM photograph image of alumina particles



At crystallite growth stage, surfactant molecules adsorb on the nanocrystal surface, replace water and hydroxyl groups on particles surface. While aggregation and growth of crystal particles are suppressed by the presence of surfactant at the crystallite surface. Comparing to average surfactant, dendrimer has advantages of higher decomposition temperature, regular three dimensional structure and multi-functional groups. Thermal analysis (**Figure 3**) indicates that dendrimer decomposed gradually with the rise in temperature. There were about 90 % by weight left at 200°C and 20 % left at 500°C, while conventional one almost completely decomposed at 300°C. It demonstrates that dendrimer can not only render the nanocrystals in aqueous solution stable but also inhibit the particles growth and aggregation over a fairly wide temperature range. Furthermore, their spherical structure refrain themselves from self-twinning.

Figure 3 TG/DTA curve of dendrimer



Summarizing, we have demonstrated that, controlled alumina nanoparticles can be fabricated by the spontaneous solution precipitating. By adding various amount and generation three-dimension heat-resisting surfactant, controlled shape nanoparticles with size range from several nanometers to hundreds of nanometers were obtained. These particles were controlled either in size or in regular shape. This process offers a simple,

clean and economic method for making metal oxide nanometer powder directly from simple inorganic salt aqueous solution requiring no pretreatment or special handing of materials. The method has many applications in producing nanometer powders of many different materials and possibly may be applied by chemical preparation industries.

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References

1. C. M. Cieber, *Solid. State. Commun.*, **1998**, *107*, 607.
2. R. E. Smalley, B. I. Yakobson, *Solid. State. Commun*., **1998**, *107*, 597.
3. N.L. Wu, L.F. Wu, I.A. Rusakoca, A. Hamed, A. P. Litvinchuk, *J. Am. Ceram. Soc*., **1999**, *82*, 67.
4. G. L. Ning, Y. Lin, Y. Cong, B. L. Liu, *Chin. J. Sci. Instrum*., **1995**, *16*, 314.
5. M. S. Diallo, L. Balogh, A. Shafagati, J. H. Johnson, W. A. Goddard, D. A. Tomalia, *Environ. Sci. Techn*., **1999**, *33*, 820.
6. M. Goino, K. Esurni, *J. Colloid. Interface. Sci*., **1998**, *203*, 214.
7. D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, *Polym. J*., **1985**, *17*, 117.
8. D. A. Tomalia, H. Baker, J.Dewald, *Macromolecules*, **1986**, *19*, 2466.

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