The Preparation of Nanostructured ZrO_2 Microspheres

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Spherical reunion powders composed of tetragonal and cubic phase ZrO_2 have been prepared for the first time via a coupling route of w/o (water in oil) emulsion with dimethyl oxalate homogenous precipitation. The as-prepared ZrO_2 microspheres and the precursor powders were analyzed and characterized by TG-DTA, XRD, and SEM. The formation mechanism of these powders is discussed in detail. Experimental results indicate that the coupling route may accomplish the one-step synthesis of ZrO_2 microspheres possessing well-rounded spherical shape and narrow size distribution, which consists of closely attached nanoparticles, the microspheres are approximately 5–10 µm in size.

Ceramic powders which consist of nanoparticles with spherical morphology and narrow size distribution possess low sintering temperature, high packing density, and uniform microstructure.[1–4] In general, attempts have been made to eliminate the reunion between nanoparticles during the preparation of nanopowders. In this project, however, the reunion between nanoparticles will be used in completing the granulation of powders so as to prepare a kind of microspheres which are composed of nanometer powders. The nanometer powders can further enhance sintering ability at lower temperatures,[5–8] and the as-prepared ceramics possess smaller residual pores and grain sizes if an appropriate technological process is carried out.[9] During the research process, spherical reunion nanopowders will be prepared by using cheap chemical reagents via the coupling route of w/o emulsion with dimethyl oxalate homogenous precipitation. Due to the special structure of emulsion, metal salt was dissolved in the water droplets wrapped up in surfactant enveloped by oil phase. Therefore, spherical particles will be produced in the water droplets through chemical reaction.[10–13] At the same time, the uniform-sized primary nanoparticles would have been prepared in the water droplets through homogenous precipitation, which is another method for the preparation of nanoparticles. The precipitate can be uniformly generated on-site by the precursors via homogenous precipitation because this route not only reduces the concentration gradient of reactants but also controls the size distribution of nanoparticles effectively.[14] For this reason, there are lots of reports on preparation of nanoparticles via homogenous precipitation so far.[15–19] Therefore, the microspheres reunited with numerous uniform-sized primary nanoparticles will be prepared via the coupling route of w/o emulsion with homogenous precipitation. Owing to surface tension of water and capillary action of emulsion water droplets during the drying process of agglomerate nanopowders, strong adhesion can be formed between primary nanoparticles.

All the reagents used in experiments are of analytical grade. At room temperature, $Zr(NO_3)_4 \cdot 2H_2O$, $Y(NO_3)_3 \cdot 6H_2O$, and dimethyl oxalate were confected into precursor solution in which the ratio of yttria was 3 mol %, and certain solution was taken to a burette. At the same time, Span-80 was put in a beaker, and xylene was added into the beaker to form oil phase by the stirring of a magnetic stirrer. The solution from the burette was then added into the beaker to form w/o emulsion which was then heated to about 90 °C. The magnetic stirrer was kept running during the process of adding and heating. Then the beaker was put aside for 1 h to form precipitate. After being washed and filtered, the precipitate was dried at 90 °C under vacuum for 2 h. Finally, the dried precipitate was calcinated at 600 °C for 3 h.

The morphology and the size of the resulting particles were measured by scanning electron microscopy (SEM). Dried powders were thermally decomposed by carrying out thermogravimetry and differential thermal analysis (TG/DTA) heating at a rate of 10 °C min^{-1} up to the temperature of 1000 °C. The crystalline phases of calcined powders were recorded by X-ray diffractometry (XRD).

Figure 1 shows the TG/DTA curves of ZrO_2 precursor powders heated in air up to 1000 °C. It can be seen from the DTA curve that an endothermic peak appears at about 99.78 °C, and the weight loss of TG curves corresponding to DTA curve is very small, about 2% of the total weight loss. As the emulsion system is a kind of w/o emulsion, a small amount of free water is adsorbed on the surface of oil phase. Therefore, this peak can be attributed to the removal of free water (or excess water). An obvious exothermic peak appears at about 359 °C. It can be seen from the TG curve that the weight loss is very obvious at this stage, about 75% of the total weight loss. As the majority of the experimental samples is organic substance, this peak can be attributed to the release of heat from the organic combustion. Furthermore, a sharp exothermic peak appears at about 512.98 °C. It can be seen from the TG curve that the weight loss is about 25% of the total weight loss, which is related to the decomposition and crystallization of amorphous ZrO_2 precursor powders.[20] The TG curve becomes smooth at 600 °C, which
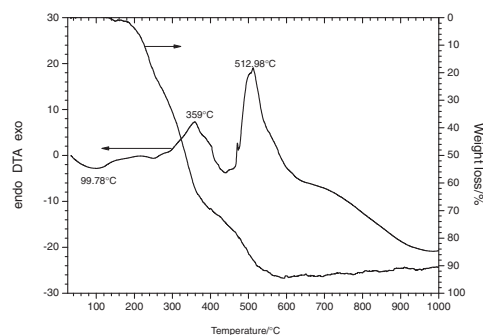

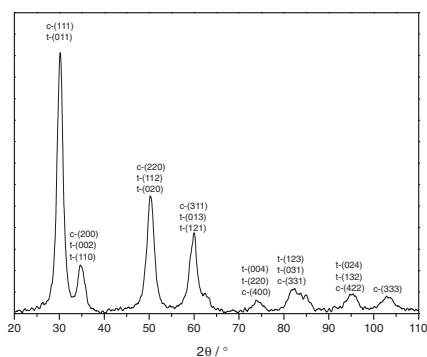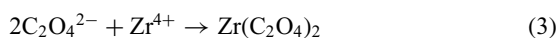
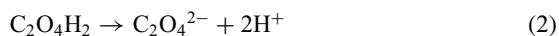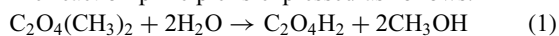**Figure 1.** Typical DTA/TG curves of precursor powders.

Figure 2. X-ray diffraction spectrum of powders at 600 °C calcination temperature.
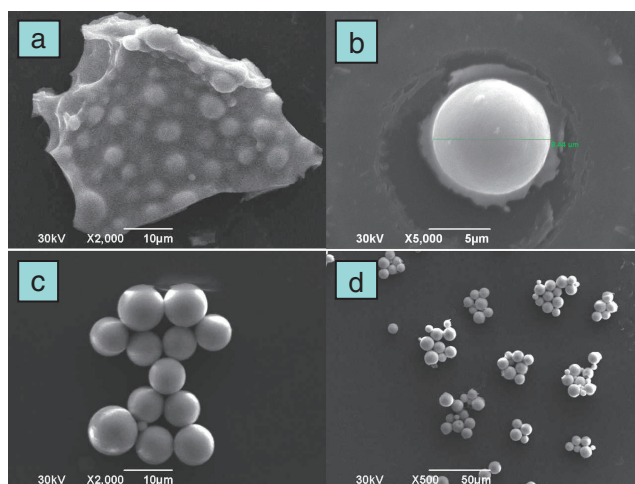

Figure 3. SEM of nanometer reunion powder microspheres. (a) The dried precursor powders, (b) the single sphere of calcined powders, (c) and (d) multispheres of calcined powders.

indicates the weight loss has finished. Moreover, there is no obvious endothermic or exothermic peak between 600 to 1000 °C on the corresponding DTA curve, which suggests that ZrO_2 (Y_2O_3) does not have crystal transformation in this stage. In other words, the crystal transformation of ZrO_2 (Y_2O_3) has finished before 600 °C, and its crystalline phase is tetragonal and cubic phase, which is proven by the XRD diffraction spectrum of ZrO_2 (Y_2O_3) at 600 °C calcination temperature as shown in Figure 2.

Figure 3 shows the SEM pictures of ZrO_2 microspheres. It can be seen from Figure 3a that the spherical structure of powders has already existed in the dried precursor powders. In addition, the shape of calcined powders (shown in Figure 3b) is a well-rounded sphere, and the size of particle is about 10 μm. Moreover, it can be observed from Figures 3c and 3d that the each sphericity of particles is complete, and the grain-size distribution is approximately 5–10 μm. This indicates that the coupling route can control the shape and the size distribution of particles.

During synthesis of $Zr(C_2O_4)_2$ via homogenous precipitation, it is required to dissolve dimethyl oxalate and $Zr(NO_3)_4$ in water to get mixed solution. Because the inducing time of hydrolysis of dimethyl oxalate would be greatly reduced with the increase of the solution temperature, and $C_2O_4^{2-}$ would be produced homogenously in solution via ionizing dimethyl oxalate. The reaction principle is expressed as follows:

$$C_2O_4(CH_3)_2 + 2H_2O \rightarrow C_2O_4H_2 + 2CH_3OH \quad (1)$$

$$C_2O_4H_2 \rightarrow C_2O_4^{2-} + 2H^+ \quad (2)$$

$$2C_2O_4^{2-} + Zr^{4+} \rightarrow Zr(C_2O_4)_2 \quad (3)$$

The $Zr(C_2O_4)_2$ particles would precipitate homogenously and simultaneously in the solution. Therefore, it is possible to control the size distribution of the $Zr(C_2O_4)_2$ particles. As it is difficult to control the growth and the aggregation of particles in homogenous precipitation; therefore, it is hard to control the shape of particles by this method.

In this work, the uniform w/o emulsions were prepared first by adding the appropriate amount of span-80 and xylol into the mixed solution of dimethyl oxalate and zirconium nitrate. The water droplets of emulsion would be employed as the micro-reactors, within which the homogenous precipitation of dimethyl oxalate with zirconium nitrate takes place. The water droplets of emulsion would enlarge through the growth and aggregation of primary particles when the stable nuclei of $Zr(C_2O_4)_2$ were

formed. As the size of aggregate particles reached the interface of water droplets, the surfactants would cover the particle surface and hinder its further growth, this helped to reduce the size of aggregate particles. On the other hand, the $Zr(C_2O_4)_2$ primary particles have narrow size distribution because the water droplets contain identical reactant concentration inside and locate in a similar surrounding, which leads to the same reaction. It can be observed that this coupling route not only eliminates the gradient of precipitation concentration but also confines the space of the precipitating reaction. This is neither similar to the ordinary microemulsion route from which the mixing process of microemulsion with another reactant was usually needed nor similar to the conventional homogenous precipitation route from which the precipitates were deposited in the whole aqueous solution. It is possible to synthesize particles with spherical shape and narrow size distribution by this coupling route. In addition, it should be pointed out that temperature gradient in the reaction solution would affect the synchronism of hydrolysis reaction and precipitate reaction in water droplets. As a result, the size distribution of the particle would increase.

Figure 4 is the preparation process diagram of the reunion powder microspheres. With the increase of temperature, the water droplets of w/o emulsion will homogenously precipitate to produce primary nanopowders. Owing to the special structure of emulsion, metal salts are dissolved in the water droplets wrapped up in surfactant enveloped by oil phase. Therefore, spherical particles will be produced in the water droplets through chemical reaction. At the same time, uniform-size primary nanopowders will be prepared in the water droplets by using homogenous precipitation. Because of the surface tension of water and capillary action of emulsion water droplets during the drying process of agglomerate nanopowders, strong adhesion can be formed between primary nanoparticles which will lead to the formation of agglomerated body when the reunion powders are sintered.

In this work, spherical reunion powders composed of tetragonal and cubic phase ZrO_2 containing 3 mol % Y_2O_3 have been prepared via the coupling route of w/o emulsion with dimethyl oxalate homogenous precipitation, in which xylene
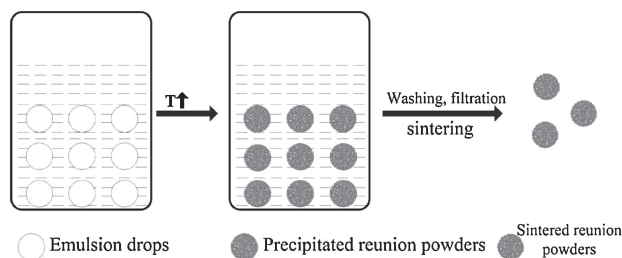
Figure 4. The preparation process of reunion powder microspheres.

was used as the oil phase, span-80 as the surfactant, and an aqueous solution containing $Zr(NO_3)_4$, $Y(NO_3)_3$, and dimethyl oxalate as the water phase. The ZrO_2 powders possess well-rounded spherical shape and narrow size distribution. The microspheres are approximately $5–10\,\mu m$ in size, which consist of closely attached nanoparticles.

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