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# Study on a new, environmentally benign method and its feasibility of preparing nanometer zirconia powder

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#### Abstract

In this paper, a new method to prepare nanometer zirconia is described, and the mechanism is discussed briefly. It is proposed that the coordinated water of zirconium oxychloride acts as a microzone actuating medium in the preparation of zirconia powder. The method was realized by agitating a solid mixture of sodium hydroxide and zirconium oxychloride, whose intermediate and final products were studied by X-ray fluorescence analysis (XRF), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and transmission electron microscopy (TEM). It was found that the nuclei of zirconia were formed under the superalkaline condition and polycrystallized at 400°C. The experiments showed that the powder obtained was tetragonal/cubic zirconia, with narrow particle size distribution (average size about 7 nm), and contained and less than a trace (<10 ppm) of chlorion. The by-product of the new process can be recycled as chemical raw material after simple treatment. Compared with traditional methods, the new method is environmently benign, with low energy consumption, convenient manipulation, easy source recycling, and low pollution. © 2000 Elsevier Science Ltd. All rights reserved.

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# 1. Introduction

Zirconia is an important ceramic material with wide applications in various fields such as engineering ceramics, piezoelectrics, and solid electrolytes [1,2]. Although there are many

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methods to prepare nanometer zirconia, some of them [3,4] require costly prerequisites, and some of them [5,6] require complex processes that result in heavy pollution and energy consumption. An environmently benign method to prepare the powder is needed.

Nanometer zirconia powder is traditionally prepared by calcinating zirconium hydroxide made by a chemical precipitation method [5,7], which requires a large amount of distilled water as actuating medium. When synthesizing zirconium hydroxide, the solution must be stirred violently to disperse the floccule. Further, some kinds of organic solvents [8] with little surface tension have been used to eliminate water to decrease the aggregation. Both factors result in wasting source and energy. A sol-gel method [6] has been developed in which an organic compound is employed to separate zirconium hydroxide molecules by a steric stabilization mechanism. Although this method can work well to some degree, the sol has to absorb the humid air or water to hydrolyze into gel, which results in pollution from high contents of organic compositions.

It is well known that particles attract each other more easily through a liquid medium than through a solid-state medium. Given that an organic compound can be employed as a steric stabilizer, could the separator be in solid state? Further, would it be possible to utilize the coordinated water of the zirconium oxychloride as a microzone-actuating medium so that the reaction stays in quasi solid state because of the small quantity of water from the coordinated water of zirconium oxychloride. If so, after the intermediate compound is synthesized, it could be separated in the microzone and then the nanometer powder could be prepared. If the solid mixture were stirred, would the heat released between the particles transform intermediate zirconium hydroxide into zirconia? To answer these questions, a series of experiments was carried out.

### 2. Experimental

Analytically pure sodium hydroxide and zirconium oxychloride were employed as raw materials. An appropriate amount of sodium hydroxide was put into an agitator, then zirconium oxychloride was added step by step while agitating the mixture to ensure an identical superalkaline condition. When the reaction finished, the mixture was washed with distilled water. After quickly precipitating, the product was filtered and washed several times and dried in an oven to obtain soft white powder. The chlorion content of the powder calcinated at various temperatures was determined by X-ray fluorescence analysis (XRF-1700 model) and the phase was determined by X-ray diffraction (XRD, Rigaku D/max model) using Cu K $\alpha$  radiation. The particle size and morphology were observed by transmission electron microscopy (TEM, JEOL 200CX model). The binding energy of zirconium was analyzed by X-ray photoelectron spectroscopy (XPS, ESCA/PHI-500X model). In addition, zirconium hydroxide as reference material was prepared with ammonia as precipitant and pH = 10 by the chemical precipitation method. To examine the difference of structure between the two precipitates, a dissolve test using hydrochloric acid was carried out. The by-product of the new process was treated with hydrochloric acid to neutralize the filtered solution, and then was detected by X-ray diffraction of the same model.

## 3. Results and discussion

#### 3.1. Content of chlorion in the sample

No chlorion was detected by XRF in the powder prepared with a 1:2 ratio of zirconium oxychloride to sodium hydroxide; however, the content of chlorion in the powder may have been beyond the limit of the apparatus (10 ppm). A trace of chlorion was detected in the zirconium hydroxide prepared by the chemical precipitation method after it was washed, following the same procedure as that of the new method. These results suggest that a difference may exist between the structures of the precipitates.

#### 3.2. Dissolve test using hydrochloric acid

To confirm whether a difference between the structures exists, the zirconium hydroxide prepared by the chemical precipitation method and the precipitate obtained by the new method were each dissolved in hydrochloric acid (1 M/liter). The zirconium hydroxide disappeared quickly, and the solution quickly returned to a transparent status. However, the precipitate remained suspended in the hydrochloric acid even after the addition of a stronger acid, nitric acid. After the powder was filtered, washed, and dried, the mass was reduced less than 5%. These results show that a difference in structures exists. Because the precipitate obtained by the new method did not dissolve in the hydrochloric acid, and, according to XRF, contained less than a trace (<10 ppm) of chlorion, it is evident that it is zirconia.

### 3.3. The phase and particle size of the sample

X-ray diffraction patterns of the powder with increasing temperature are shown in Fig. 1. Although at room temperature the powder was mostly amorphous, a widened peak can be seen in the pattern. After the powder was calcinated at 200°C, the pattern shows a narrower peak. With a further increase in temperature, the characterized peaks emerge. After 500°C, the existing diffraction peaks become narrower and higher, which correspond to the standard value of tetragonal/cubic zirconia. No trace of monoclinic zirconia was found and no other peaks were detected by XRD.

From the X-ray line broadening measurement, the particle size is calculated to be about 7 nm. This result is in accordance with the TEM observation, shown in Fig. 2. It is clear that the powder is nanometer, with a narrow particle size distribution.

#### 3.4. The binding energy of zirconium

The as-obtained powders at room temperature and after being calcinated at 200 and 500°C were analyzed by XPS to determine the chemical status of zirconium. The results are shown in Fig. 3. The binding energies of zirconium at room temperature, 200°C, and 500°C were determined to be 181.8, 181.6, and 182 eV, respectively, which are all similar to the standard value of zirconia (182.2 eV). XRD showed the main phase of the powder calcinated at 500°C to be tetragonal/cubic zirconia; thus, it was chosen as reference material. The patterns in Fig.



Fig. 1. XRD patterns of the powders after being calcinated at different temperatures.

3 are similar to each other, implying that the nuclei of the zirconia are synthesized during agitation of the mixture and only grow during the process of calcination. In other words, the chemical status of zirconium remains the same with the growth of the zirconia particles.

## 3.5. The explanation for the reaction

When two particles with little mass and small size conflict during mechanical agitation, the contact area is rather small, and the collision force is also small. However, because of the small contact area, the stress over the region of contact point is high. Further, the contact time



Fig. 2. The morphology of particles after being calcinated at 500°C.



Fig. 3. XPS spectra of zirconium ion after being calcinated at different temperatures.

is very short, allowing only little time for the particle to release heat and stress. Hence, the particle goes from the stress-free status to the highly stressed status within a very short duration, leading to very high stress gradients. Further, most of the collision energy is dissipated over the small contact area; thus, the energy density is rather high. All factors contribute to increased temperature over localized spots and cause thermally induced mobility. In addition, the coordinated water can dissolve sodium hydroxide at the molecular level and thus facilitate the reaction in the microzone-actuating medium. Because the apparent status is solid, not liquid, atom mobility is so small that, if a compound is formed, it remains fine.

#### 3.6. The recycle of by-product

To neutralize the filtered solution, hydrochloric acid was used to form sodium chloride, which can be detected by X-ray diffraction. The by-product of the new method can be recycled as chemical raw material after simple treatment. The new method has such advantages as low source consumption and low pollution. In contrast, with traditional methods, it is difficult to refine and recycle the by-products, because the contents are low and the compositions are complex.

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