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Influence of synthesis conditions on the preparation of zirconia powder by the glycothermal method

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Abstract

Nanocrystalline zirconia powders have been prepared by the reaction of zirconium *n*-propoxide in 1,4-butanediol and 1,5-pentanediol at 300 °C for 2 h. The influences of concentration of zirconium *n*-propoxide in the solution and drying condition on primary and secondary particle size, and pore system of the powders were investigated. When 1,4-butanediol was used, increasing the concentration of zirconium *n*-propoxide increased the primary and secondary particle size and BET surface area while the physical properties of zirconia prepared in 1,5-pentanediol were not affected by such factors. To investigate the effect of drying method, glycol was removed from the autoclave at reaction temperature instead of by the conventional process in which the product is washed in methanol and air-dried. This change improved the pore system of powders prepared in 1,5-pentanediol, probably through the reduction of coagulation among the ultrafine particles during the drying process.

Keywords: D. Zirconia (ZrO_2); Glycothermal method; Nanocrystal

1. Introduction

Zirconia is an important material because of its use in different areas of chemistry such as in ceramics and catalysis. Its catalytic properties are especially promising because zirconia has both acidic and basic properties as well as a high thermal stability. For a number of reactions, zirconia is used as a catalyst support because higher activity and selectivity can be obtained.

Diverse physical and chemical synthesis routes have been reported in the literatures for the preparation of ultrafine zirconia particles. Practical preparation methods are still under development in order to obtain zirconia with controlled particle size and textural properties. A common preparation route consists of the calcination of the hydrous zirconia obtained from hydrolysis of zirconium salts in various media. It was found that the properties of zirconia obtained by hydrolysis depend on several chemical parameters. Chuah et al. [1–3] reported that the time and temperature of digestion and the pH of digestion medium are important factors that determine the surface area of zirconia. The influence of digestion is explained in terms of the enhanced agglomeration of primary particles during digestion and the strengthening of the network structure. This led to higher thermal stability. Lin and Duh [4] studied the influence of the concentration of the stock solution on specific surface area and crystallite size in the system CeO_2–Y_2O_3–ZrO_2 [4]. The crystal phase and specific surface area are also influenced by the drying conditions of the hydrous zirconia. Murase et al. [5] reported that hydrous zirconia synthesized from the hydrolysis of zirconium salt solution forms secondary particles by aggregation of primary particles with diameter less than 10 nm. Matsui et al. [6] found that primary particle size of the hydrous zirconia decreased as the $ZrOCl_2$ concentration increased and was independent of the reaction temperature. However, the secondary particle size of hydrous zirconia first increased monotonically, and then decreased with increasing $ZrOCl_2$ concentration. A hydrothermal method is also widely used to produce fine zirconia powders. Processing variables such as pH, concentration, temperature and time have important influences on the crystal structure of ZrO_2 [7–9].

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Inoue et al. [10] studied the thermal decomposition of zirconium alkoxides in organic solvents. Ultrafine zirconia can be obtained directly from such a reaction at 300 °C. However, characterization of the powder as a function of the synthesis parameters has not been reported. The present work investigates the effect of solvent and the zirconium concentration on the particle size and surface area of zirconia. Also, we examine the influence of drying conditions on the specific surface area and pore structure of the resulting zirconia.

2. Experimental

A selected amount of zirconium tetra *n*-propoxide (7–25 g) was added to 100 ml of a glycol (1,4-butanediol or 1,5-pentanediol) and this mixture was placed in a 300 ml-autoclave. After the atmosphere inside the autoclave was replaced with nitrogen, the mixture was heated to 300 °C at a heating rate of 2.5 °C/min and was kept at that temperature for 2 h. After cooling to room temperature, the resulting powders were collected after repeated washing with methanol by centrifugation. They were then air-dried. To investigate the effect of drying conditions, after a glycothermal reaction time of 2 h the valve of the autoclave was slightly open to release organic vapor from the autoclave by flashing while keeping the temperature at 300 °C. The valve was held opened until pressure inside the autoclave decreased to atmospheric level. With this method, dry powders were obtained directly after cooling without washing with methanol. The calcination of products was carried out in a box furnace for 1 h.

Powder X-ray diffraction (XRD) patterns were collected on a SIEMENS XRD D5000 instrument using CuK_α radiation and a carbon-monochromator. Crystallite size was calculated by the Scherrer equation from the half-height width of the {111} diffraction peak of the tetragonal phase. Scanning electron microscopy was performed on a JSM-5410LV unit. The surface area of the samples was measured using N_2 adsorption by the Brunauer–Emmett–Teller (BET) method. A micromeritics ASAP2000 system was employed. Pore size distribution of the samples was calculated on the basis of the N_2 desorption isotherm by using the methods proposed by Barrett, Joyner and Halenda (BJH).

3. Results and discussion

3.1. Effect of zirconium n-propoxide (ZNP) concentration in the mother liquor on zirconia powder

To examine the effect of ZNP concentration, the amount of glycol used in the reaction was fixed and the amount of ZNP was varied from 7 to 25 g. ZrO_2 powders obtained from both glycols are white powders. Figs. 1 and 2 show the XRD patterns for powders prepared from both glycols using different ZNP concentrations. The XRD patterns indicate tetragonal crystalline zirconia for all as-synthesized products. No other crystal structures were observed. The dependence of crystallite size on ZNP concentration is given in Fig. 3. The crystallite size of zirconia prepared in 1,4-BG was slightly increased by increasing the ZNP concentration whereas the crystallite size was independent of ZNP concentration using 1,5-PeG. Since the dependence of crystallite size in the two glycols on ZNP concentration is completely different, the crystallization pathway of zirconia

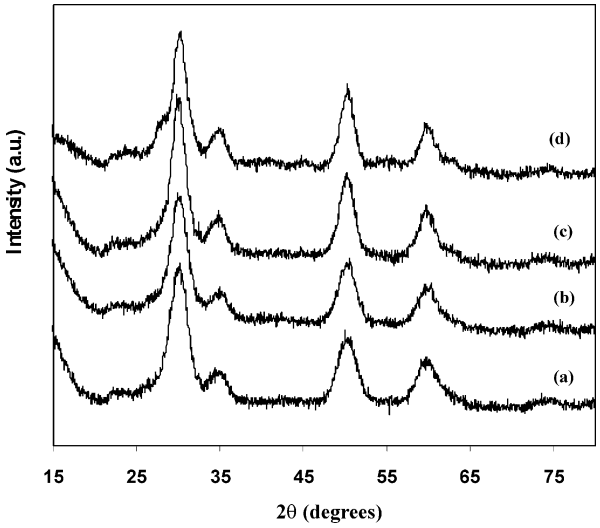

Fig. 1. XRD patterns of the powders obtained by the reaction of zirconium tetra *n*-propoxide (ZNP) in 1,4-butanediol at 300 °C for 2 h by using ZNP concentration of (a) 0.21 mol/dm^3 (b) 0.3 mol/ dm^3 (c) 0.4 mol/dm^3 and (d) 0.62 mol/dm^3.

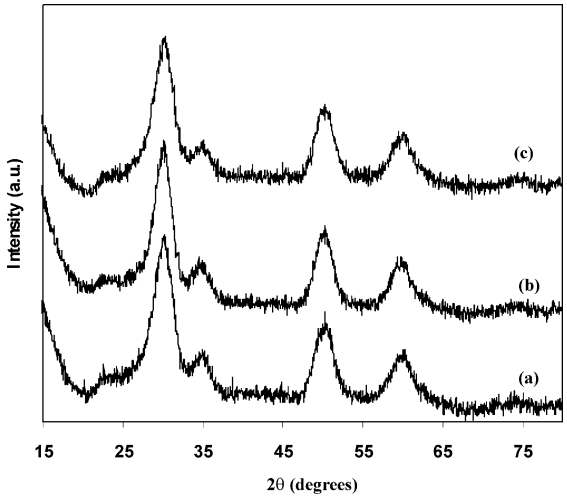

Fig. 2. XRD patterns of the powders obtained by the reaction of zirconium tetra *n*-propoxide (ZNP) in 1,5-pentanediol at 300 °C for 2 h by using ZNP concentration of (a) 0.21 mol/dm^3 (b) 0.4 mol/dm^3 and (c) 0.62 mol/dm^3.

in the two solvents is probably different. To examine crystallization pathway in both solvents, the mixture was cooled down once the temperature reached 250 °C. It was found that the use of 1,5-PeG gave a homogenous solution (i.e., glycoxide) with no solid suspension. Normally, a glycoxide is formed in the glycothermal synthesis at low temperature, for example the reaction of titanium tetra-isopropoxide in 1,4-butanediol at 200 °C [12]. Thus, solids crystallize from the glycoxide. We believe that crystallization and crystal growth of zirconia in 1,5-PeG proceeds by precipitation from the glycoxide. Thus, our explanation of the independence of zirconia crystal size on ZNP concentration is that nucleation in 1,5-PeG is rapid leading to an excess of nuclei and thereby reducing the glycoxide concentration that is required for crystal growth. Increasing ZNP concentration, only increases the numbers of nuclei present.

On the other hand, the synthesis in 1,4-BG by cooling after the temperature reached 250 °C yielded a solid precipitate that we have not been able to identify. The XRD pattern of this phase is shown in Fig. 4. The diffraction peaks in the XRD pattern occurred at low angles (7° and 8° 2θ). A scanning electron micrograph of this unidentified phase is shown in Fig. 5. Large particles in the figure are aggromerates of small spherical particles with rough surfaces. In 1,4-BG, particle nucleation and growth mechanisms are not clear. However, the zirconia particle seems to crystallize from a solid-state transformation of this unidentified phase. We plan to investigate this unidentified phase in further work.

Typical SEM images for the products prepared in 1,4-BG using different ZNP concentrations are shown in Fig. 6. The powders have a spherical shape and a dense mass and seem to be formed by aggregations of primary particles. The SEM photograph shows these secondary particles as separate microspheres. Interestingly, the lower the initial ZNP concentration, the smaller the size of the secondary particle. This result is consistent with the work of Hu et al. [11]. They synthesized zirconia by precipitation of $ZrOCl_2$ in mixed alcohol–water solutions and found that submicrometer-size spheres were obtained from 0.2 M $ZrOCl_2$ whereas nanometer-size spheres were produced when 0.05 M $ZrOCl_2$ was used. They reported that the particle growth took place by aggregation of microspheres and further agglomeration of small aggregates. In the present work, we can see boundaries of small microspheres that agglomerated to form larger secondary particles. These boundaries are indicated by arrows in Fig. 6. Increasing ZNP concentration increases mean micro-

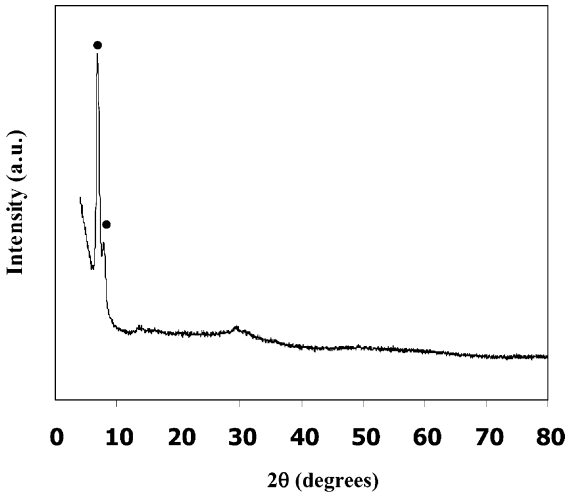

Fig. 4. XRD pattern of the powders obtained by the reaction of zirconium tetra *n*-propoxide in 1,4-butanediol (ZNP concentration of 0.4 mol/dm^3) and cooling autoclave once the temperature reached 250 °C.

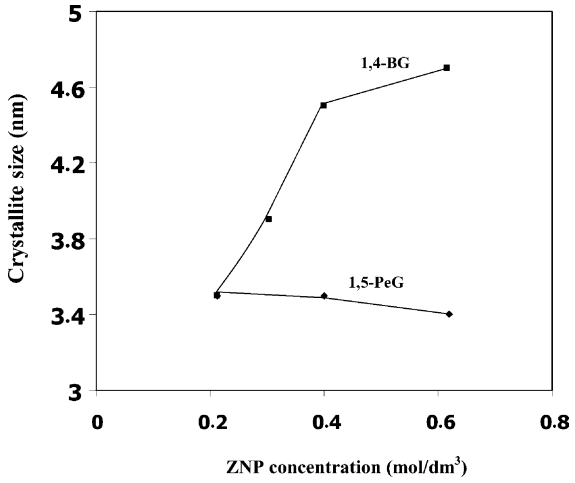

Fig. 3. Dependence of the crystallite size of zirconia particles prepared in 1,4-butanediol and 1,5-pentanediol on the zirconium tetra *n*-propoxide concentration.

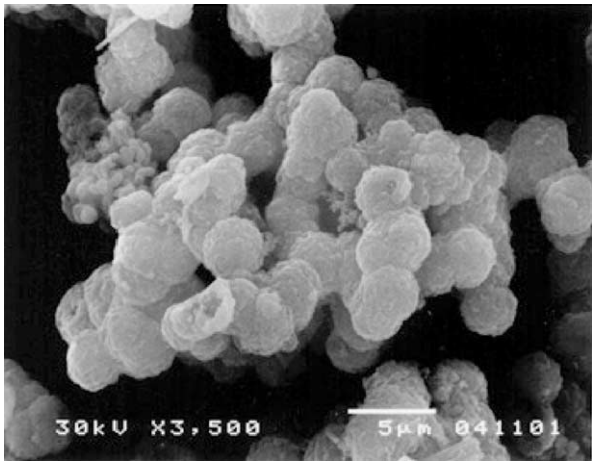

Fig. 5. Scanning electron micrograph of powders obtained by the reaction of zirconium tetra *n*-propoxide in 1,4-butanediol (ZNP concentration of 0.4 mol/dm^3) and cooling autoclave once the temperature reached 250 °C.

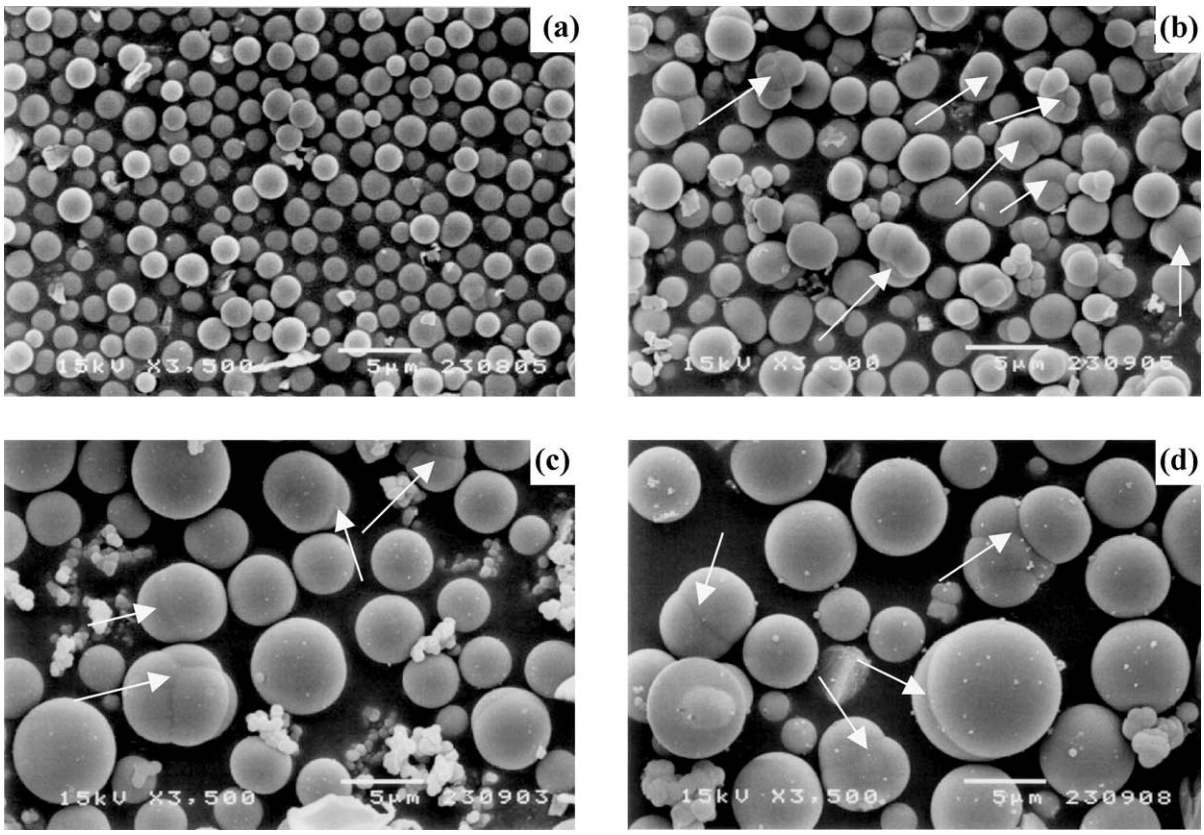

Fig. 6. Scanning electron micrographs of the powders prepared by the reaction of zirconium tetra *n*-propoxide in 1,4-butanediol at 300 °C for 2 h by using ZNP concentration of (a) 0.21 mol/dm^3 (b) 0.3 mol/dm^3 (c) 0.4 mol/dm^3 and (d) 0.62 mol/dm^3.

sphere diameter while reducing sharply the number of small microspheres. Thus, concentration appears to play a role in particle agglomeration. It is also possible that some of the larger zirconia microspheres crystallized directly from particles of the unidentified phase. Fig. 6(c) shows that the microspheres have about the same dimension as the particles in Fig. 5 that make up the irregular, loosely structural aggregate. From this observation, production of zirconia microspheres with various sizes becomes possible when 1,4-BG is used for synthesis.

In contrast, secondary particles of zirconia prepared in 1,5-pentanediol seem to have a single size distribution and perhaps a single mean size, which is independent of ZNP concentration, as may be seen in Fig. 7.

The isotherms of products obtained in 1,4-BG with various amounts of ZNP in solution are shown in Fig. 8, after calcination at 600 °C for 1 h. With increasing ZNP concentration, the shape of isotherms gradually changed from one resembling type I to type IV with the appearance of a hysteresis loop. The corresponding pore size distributions are shown in Fig. 9. With a high concentration of ZNP in the mother liquor, mesopore peaks can be seen [curves (c) and (d)]. However, these disappear for the zirconia produced with relatively low ZNP concentrations (0.21 and 0.3 mol/dm^3) due to the existence of a micropore system [curves (a) and (b) in Fig. 9]. Since the as-synthesized crystallite size is relatively small when the concentration of ZNP is low, we believe that the degree of aggregation among primary particles must be high, perhaps due to their relatively high surface free energy. Therefore, we attribute the preeminence of micropores in the powders prepared with a relatively low ZNP concentration to aggregation of nanoparticles. The modal pore diameter was observed to be approximately 8 nm, when the ZNP concentration exceeds 0.4 mol/dm^3. The specific surface area and pore volume of the as-synthesized products and calcined samples, prepared for different ZNP concentrations, are given in Table 1. As expected, the BET surface area and pore volume increased slightly with increasing ZNP concentration. According to the above results, it is clear that secondary particle size, BET surface area and pore system of zirconia prepared in 1,4-BG depends on the ZNP concentration. Therefore, it is possible to control the properties of zirconia particles by adjusting the amount of ZNP in starting solution.

The results of BET analysis of products prepared in 1,5-pentanediol are given in Table 2. The specific surface area of zirconia is only slightly affected by ZNP concentration. The surface area after calcination and pore volume are presumably similar for all powders prepared, as the ZNP concentration varied from 0.2 to 0.61 mol/dm^3.

3.2. Effects of drying condition on zirconia powder

To examine the effect of drying conditions on zirconia powder, instead of washing the product with methanol and then drying at room temperature, the glycol was removed from the autoclave by flashing at reaction temperature after 2 h reaction time. Thus dry powder was obtained directly. The morphologies of the powders obtained by the reaction of ZNP 15 g in 1,4-BG and 1,5-PeG with the drying in the autoclave after flashing off glycol are shown in Fig. 10(c) and (d), respectively.

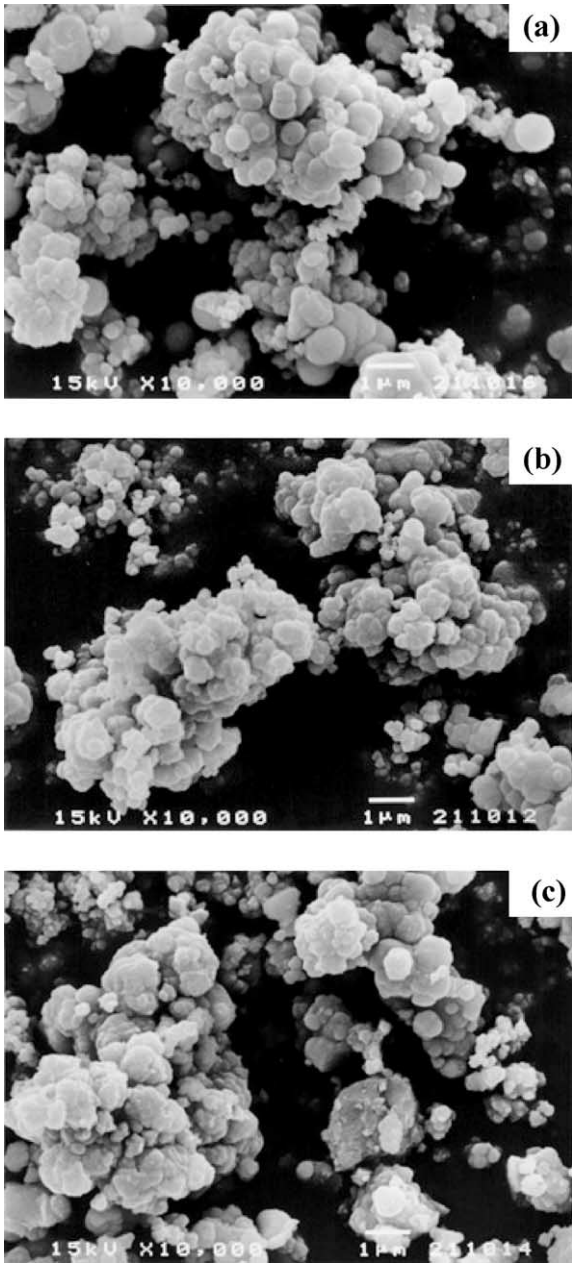

Fig. 7. Scanning electron micrographs of the powders prepared by the reaction of zirconium tetra *n*-propoxide in 1,5-pentanediol at 300 °C for 2 h by using ZNP concentration of (a) 0.21 mol/dm^3 (b) 0.4 mol/dm^3 and (c) 0.62 mol/dm^3.

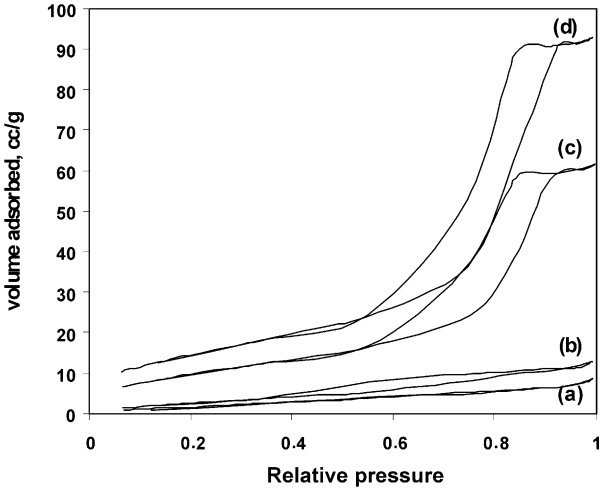

Fig. 8. Typical adsorption/desorption isotherms of the zirconia prepared in 1,4-butanediol by using ZNP concentration of (a) 0.21 mol/dm^3 (b) 0.3 mol/dm^3 (c) 0.4 mol/dm^3 and (d) 0.62 mol/dm^3. All samples were calcined in air at 600 °C for 1 h.

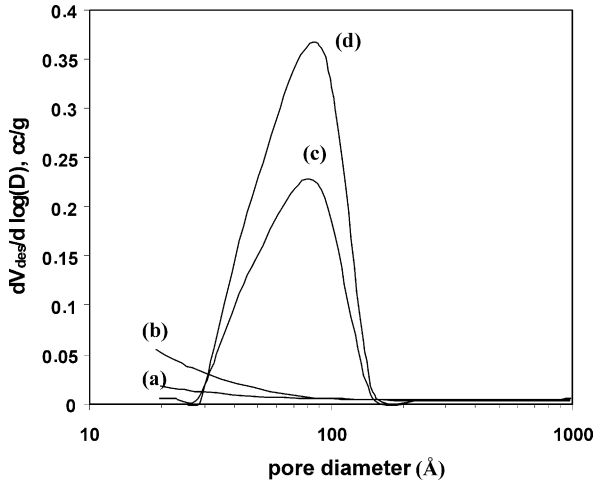

Fig. 9. Pore size distributions of the zirconia prepared in 1,4-butanediol by using ZNP concentration of (a) 0.21 mol/dm^3 (b) 0.3 mol/dm^3 (c) 0.4 mol/dm^3 and (d) 0.62 mol/dm^3. All samples were calcined in air at 600 °C for 1 h.

Table 1
Effects of ZNP concentration on the BET surface area and pore volume for zirconia synthesized in 1,4-butanediol at 300 °C for 2 h

ZNP concentration (mol/dm^3)	BET surface area (m^2/g)		Pore volume[c] (cc/g)	
	As-syn[a]	600 °C[b]	As-syn[a]	600 °C[b]
0.21	147	8.5	0.05	0.01
0.3	196	11	0.10	0.02
0.4	225	37	0.19	0.10
0.62	205	54	0.22	0.14

[a] The as-synthesized powders obtained by the glycothermal method.

[b] Powders were obtained by glycothermal method and then were calcined at 600 °C for 1 h.

[c] The average pore volume.

Table 2
Effects of ZNP concentration on the BET surface area and pore volume for zirconia synthesized in 1,5-pentanediol at 300 °C for 2 h

ZNP concentration (mol/dm^3)	BET surface area (m^2/g)		Pore volume[c] (cc/g)	
	As-syn[a]	600 °C[b]	As-syn[a]	600 °C[b]
0.21	144	10.1	0.09	0.02
0.4	165	10.2	0.08	0.02
0.62	91	7.1	0.06	0.01

[a] The as-synthesized powders obtained by the glycothermal method.
[b] Powders were obtained by glycothermal method and then were calcined at 600 °C for 1 h.
[c] The average pore volume.

For comparison, the SEM images of products dried in air after washing with methanol are given in Fig. 10(a) and (b). When powders prepared in 1,5-PeG were dried in the autoclave, the as-prepared zirconia powder consists of fine particles and seems highly porous. However, morphology of powder obtained in 1,4-BG is not affected by the drying condition as seen in Fig. 10(a) and (c). These results suggest that for the case of zirconia prepared in 1,5-PeG, aggregation of primary particles occurred during the drying stage driven by the surface tension of the liquid between the particles. The degree of aggregation decreased when the powder was dried by removal of the glycol at reaction temperature. On the other hand, aggregation of particles prepared in 1,4-BG probably took place during the reaction resulting in the formation of dense aggregates, which were difficult to break down in the drying stage. Typical adsorption/desorption isotherms of zirconia powders obtained in 1,5-PeG with different drying conditions are depicted in Fig. 11 and show that the type of isotherm and hysteresis loop changed dramatically with the drying condition. When the powder was dried by removal of glycol at reaction temperature instead of washing in methanol and air-drying, the isotherm of the powder changed from type I to type IV (classification of Brunauer, Deming, Deming and Teller (BDDT)) [13] with the emergence of a hysteresis loop. The overlap of adsorption and desorption curves [Fig. 11(a)] in the isotherm for the product washed in methanol and air-dried indicates the existence of many very narrow micropores in the powder because the formation of a hysteresis loop is due to capillary condensation in mesopores. As seen in Fig. 11(d), the type IV isotherm with a type-H1 hysteresis loop (IUPAC nomenclature) [13] is appropriate to powders with both mesopores and macropores but with

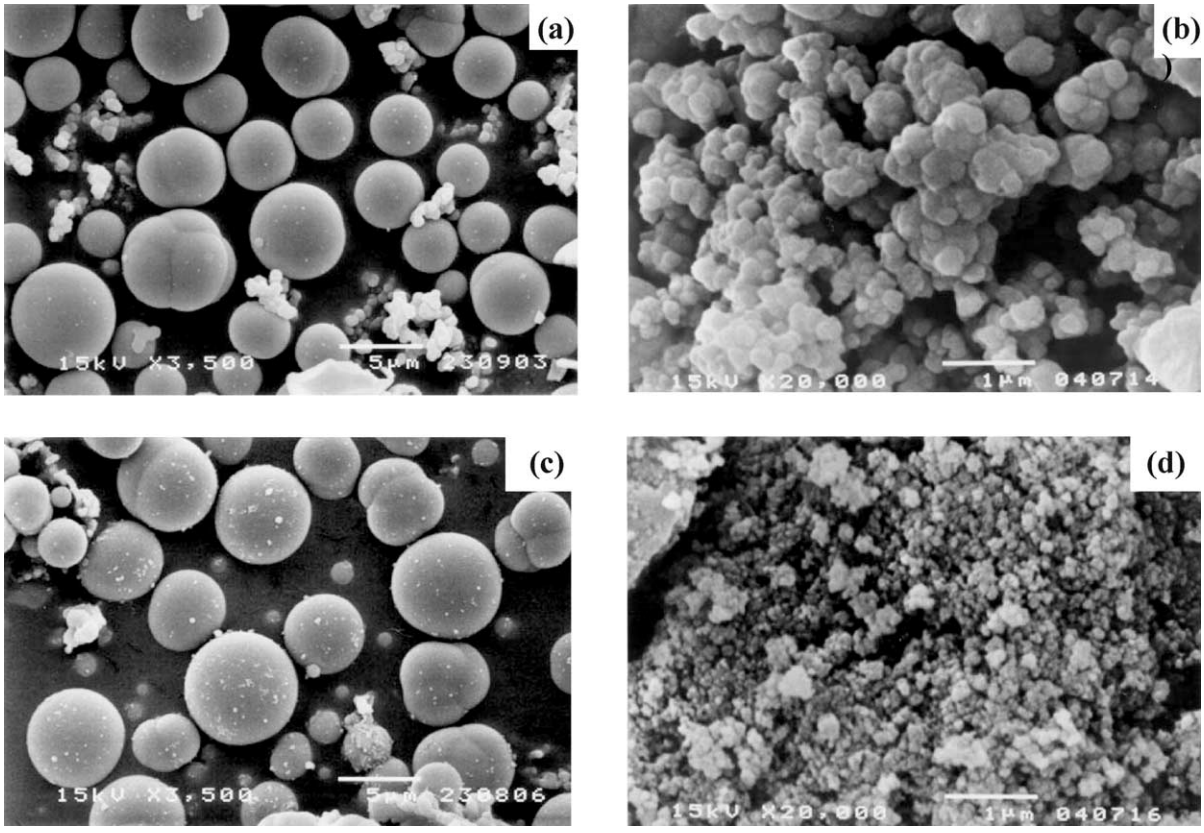

Fig. 10. Scanning electron micrographs of zirconia prepared in 1,4-butanediol (left) and 1,5-pentanediol (right). Top: the product were washed with methanol and air-dried. Bottom: the product were dried by removal of glycol at the reaction temperature.

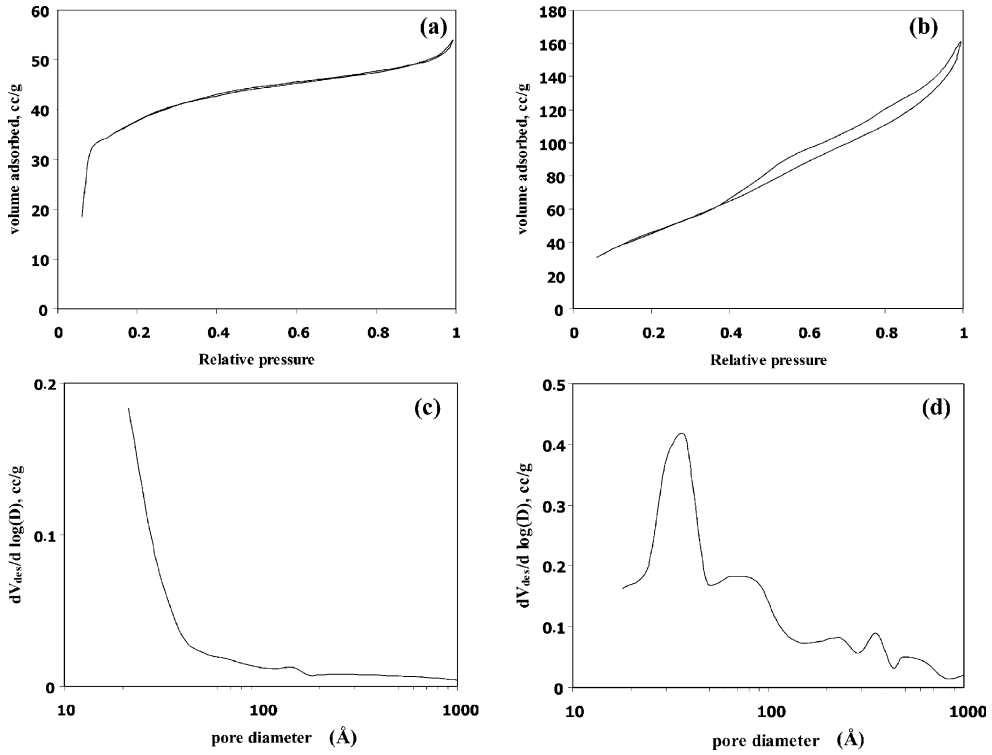

Fig. 11. Typical adsorption/desorption isotherms and pore size distributions of as-synthesized zirconia prepared in 1,5-pentanediol. Left: the product was washed by methanol and air-dried. Right: glycol was removed at the reaction temperature.

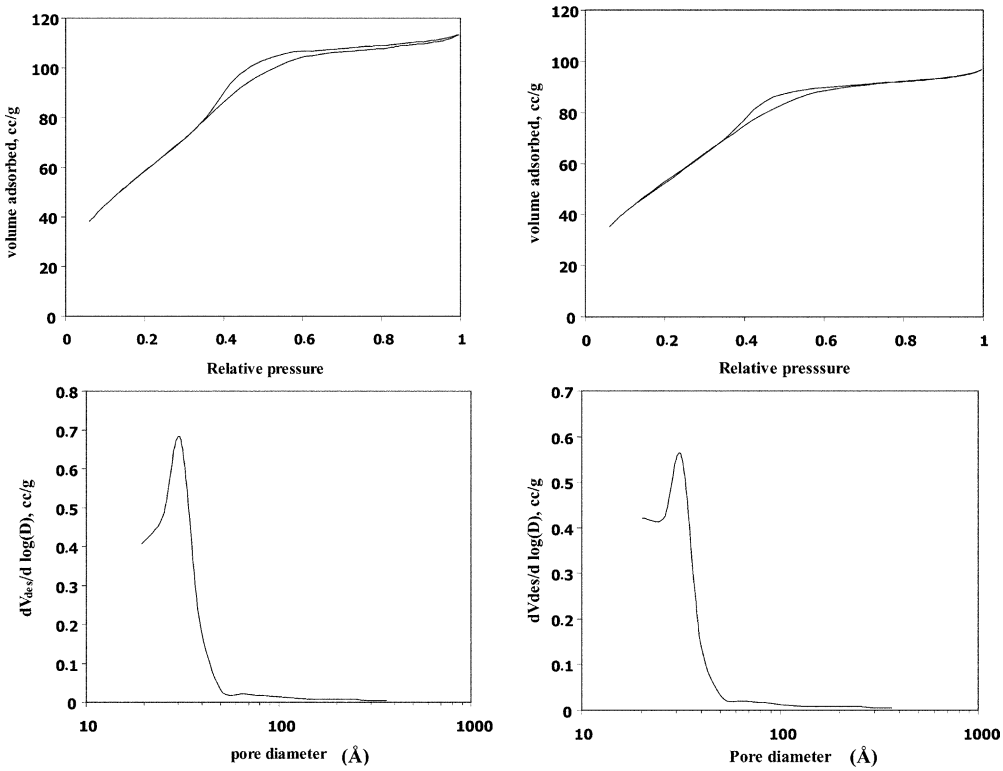

Fig. 12. Typical adsorption/desorption isotherms and pore size distributions of as-synthesized zirconia prepared in 1,4-butanediol. Left: the product was washed by methanol and air-dried. Right: glycol was removed at the reaction temperature.

a negligible contribution of microporosity. This change corresponds to an increase of modal pore diameter to around 3 nm for the powder dried by removal of glycol at reaction temperature (see Fig. 11). These results suggest that the pore system of zirconia prepared in 1,5-PeG is improved when glycol evaporates and is removed at reaction temperature because aggregation during drying is prevented. Thus the original pore structure of the powders is preserved. These results are similar to the previous work [14] reporting that drying by removal of solvent under supercritical conditions suppresses the formation of liquid–gas interfaces inside pores and thus reduces the stress on pore structure. The isotherm of zirconia powder prepared in 1,4-BG was of type I, characteristic of a microporous texture and a relatively small surface area (Fig. 12). Drying by removal of solvent at reaction temperature did not alter the isotherm and pore size distributions. These results correspond well with our discussions of SEM images above that suggest that aggregations in this powder occurred probably during reaction rather than during drying. Apparently, the pore structure of powders prepared in 1,4-BG cannot be altered by different drying conditions.

4. Conclusions

Synthesis conditions, i.e., concentration of zirconium *n*-propoxide and drying method, affect the primary and secondary particle size and BET surface area of zirconia powders. Use of 1,4-butanediol as the reaction medium gave microsphere zirconia particles formed by aggregation of small primary particles. The secondary particle size and BET surface area increased with increasing the ZNP concentration. Glycol removal at reaction temperature did not change the pore system of the powder because the aggregation of primary particles probably occurred during the reaction process. Physical properties of zirconia obtained in 1,5-pentanediol were not affected by ZNP concentration, whereas the pore system of the powders prepared in 1,5-pentanediol was improved when the powder was dried in an autoclave by flashing. Improvement results from the reduction of aggregation among the ultrafine particles during drying.

Acknowledgements

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