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Control of zirconia particle size by using two-emulsion precipitation technique

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Abstract

Zirconia powder is synthesized in two types of reverse emulsions, i.e., macroemulsion and microemulsion. In either of the systems, two solutions of reverse emulsion, one containing Zr^{4+} aqueous droplets and the other aqueous ammonia droplets, with the same water/oil (w/o) ratio are prepared separately and mixed together to form a slurry of ZrO_2 precursors. Then the precursors are recovered and calcined to form tetragonal ZrO_2. Factors that affect the emulsion stability and particle size are investigated, including type of oil, w/o ratio, type and concentration of surfactant, concentration of aqueous solutions, and mixing intensity. The difference in particle size and thus calcination temperature is significant between the zirconia crystals produced from the two different types of emulsions. Thus, coupling the macroemulsion and microemulsion precipitation processes, the mean size of spherical ZrO_2 particles ranging from tens of nanometers to a few micrometers can be controlled. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Zirconia; Two-emulsion precipitation; Microparticles; Nanoparticles; Emulsion droplet size; Calcination temperature

1. Introduction

Zirconia powder is useful in many advanced structural, high-temperature and electrical ceramic applications, because it possesses special properties, such as low thermal conductivity, high mechanical strength, high fracture toughness, and relatively high thermal expansion coefficient. The effects of powder characteristics on the processing and the properties of the final ceramic products have long been recognized. Ceramic powder consisting of microparticles (one tenth to several micrometers) with spherical morphology and narrow size distribution is required to give low sintering temperature, high packing density, and uniform microstructure. Nanoparticles (less than 0.1 micrometers) can further enhance sinterability at lower temperatures with smaller residual pores and grain sizes.

There is a variety of techniques available for producing ceramic particles, including conventional aqueous precipitation, hydrothermal processing, hydrolysis of alkoxide solution (sol–gel method), gas-phase reaction and precipitation in reverse emulsion (Reed, 1989). The preparation of nanoparticles is much more difficult than that of microparticles. Although the sol–gel method is successful in the preparation of spherical ceramic nanoparticles, the raw materials of metal alkoxide of the process are too expensive to use in a large-scale production. Among the various techniques, precipitation of precursor particles from solution is still the most acceptable technique because of its simplicity, safety, and low cost. However, the conventional aqueous precipitation method often produces irregular-shape particles with a wide size distribution. These problems can be overcome by the reverse-emulsion precipitation technique, which thus becomes a fast-growing field (Fendler, 1987).

The first step of preforming emulsion precipitation is to find a formula for stable reverse emulsion, in which a surfactant or a mixture of surfactants must be present besides the water and oil. As far as the droplet size of emulsion is concerned, two different types of emulsions can be prepared, i.e., macroemulsion and microemulsion. Microemulsion consists of droplets at least an order of magnitude smaller than those in macroemulsion. Usually, the microemulsion is clear with the droplet size ranging from several to hundred nanometers, yet the macroemulsion is milky because of larger droplets up to micrometers (Hiemenz, 1986). Note that, as far as the size is concerned, nanoparticles

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correspond to microemulsion and microparticles to macroemulsion.

Recently, a number of systems have been demonstrated for the preparation of ceramic particles using the reverse macroemulsion technique, such as Y_2O_3, Al_2O_3, TiO_2 and ZrO_2. Zirconium-containing compounds, which are produced by the sol–emulsion–gel method, are surveyed here. A standard experimental procedure is by bubbling ammonia gas through the emulsion solution, which contains Zr^{4+} aqueous droplets, to obtain gelled precipitates and then to obtain agglomerated ZrO_2 particles ranging from submicrons to micrometers after calcination. Kanai, Rhine, and Bowen (1987) prepared a zirconium ytterbium oxide powder ($2ZrO_2 \cdot Yb_2O_3$) with an average diameter between 0.2 and 0.3 μm under the optimum conditions, which were reported as: 50 ml heptane (oil phase), 0.2 g Span80 (surfactant), 0.5 ml water containing 3.75×10^{-4} mol $ZrOCl_2$ (aqueous phase). Ramamurthi, Xu, and Payne (1990) produced agglomerated ZrO_2 powder of spherical clusters that comprised 4–10 nm particles. The powder shows good sinterability with density greater than 94% at 1100°C, and with a grain size of 0.25 μm. Later, zirconia and yttria-stabilized zirconia (YSZ) powder was produced by Shyu and Cambria (1990), having a particle size between 30 and 80 μm with spherical morphology suitable for plasma spray coatings. On the other hand, a nanosized powder of zirconia was successfully synthesized via a reverse microemulsion route (Wang, Ee, Ng, Chew, & Gan, 1997). Two solutions of microemulsion, containing 12 wt% of 0.75 M $ZrO(NO_3)_2$ aqueous solution and 2.0 M ammonia solution as the water phase, respectively, were prepared and mixed to obtain precursor particles, which were further calcined at a high temperature to form tetragonal ZrO_2. The precursor particles of zirconium hydroxide were spherical in morphology, free of agglomeration, and narrow in size distribution, approximately between 5 and 10 nm. However, the particle size of zirconia obtained after calcination was not mentioned. Besides, the amount of surfactant mixture used in the preparation of emulsion was too high, which was 35 wt% of the total emulsion solution.

Since the stable reverse macroemulsion and microemulsion have been successfully prepared, the production of ceramic powder with a mean particle size between nanometers and micrometers is possible using the two-emulsion precipitation technique. In a previous study in our laboratory (Lee, Tai, & Lu, 1999), microparticles of ZrO_2 were produced by using the two-macroemulsion precipitation method. Spherical microparticles of tetragonal ZrO_2 with a size ranging from a few hundred nanometers to micrometers were successfully prepared, after calcining the precipitation precursors at 750°C. Then, the efforts were continued by employing the two-microemulsion precipitation technique to prepare zirconia nanoparticles. The series of research work aims at developing a viable route to control ceramic particles which range from nanometers to micrometers, using zirconia as a model compound.

2. The two-emulsion technique

In the earlier works of reverse emulsion technique to produce ceramic powder, ammonia gas is introduced by bubbling to the emulsion solution containing Zr^{4+}, aqueous droplets (Kanai et al., 1987; Ramamurthi et al., 1990). The ammonia gas dissolves first and then diffuses through the oil phase to reach the emulsion droplets, where hydrolysis of the metal-containing compound takes place to form the precursor particles. Since the ammonia bubbles are not evenly distributed in the emulsion solution, the concentration of the absorbed ammonia is not uniform in the oil phase. Therefore, the reaction will not occur simultaneously to give uniform supersaturation and particle size. To overcome this problem the two-emulsion technique is employed (Wang et al., 1997; Lee et al., 1999).

The basic idea of the two-emulsion technique is illustrated in Fig. 1. Two reverse emulsion solutions, in which the droplets of metal-containing aqueous solution or aqueous ammonia are suspended in the oil phase to form emulsion by adding a surfactant or a mixture of surfactants, are prepared separately and mixed together with agitation. The interdroplet exchange rate of the solubilizate may be small. As a limiting case, the contact between metal-containing solution and ammonia is mainly achieved by the diffusion of ammonia through oil phase as route 1. On the other hand, the interdroplet exchange of the solubilizate may be due to coalescence of different types of droplets, such as route 2. The contact of reactants and subsequent reaction can be regarded as a number of sequential steps: (1) Diffusion and convection to bring the emulsion droplets together, (2) Surfactant layer opening and coalescence, (3) Diffusion of the solubilizate molecules in the temporary dimeric aggregate, (4) Reaction between solubilizate molecules, (5) Nucleation and crystal growth of precursor particles, and (6) Decoalescence to return as smaller droplets (Bommarius, Holzwarth, Wang, & Hatton, 1990).

The advantage of the two-emulsion technique is the achievement of a uniform concentration of ammonia in the oil phase regardless of the contact mechanism as compared with the bubbling technique. During the reaction, the droplets serve as microreactors where nucleation, crystal growth and nuclei agglomeration occur. Thus, the size, size distribution, and shape of produced particles from emulsion precipitation are related to the emulsion droplets and can be controlled better than the conventional precipitation, in which two solutions of reactant are mixed directly. Since the diffusion rate of ammonia is slow for route 1, the supersaturation

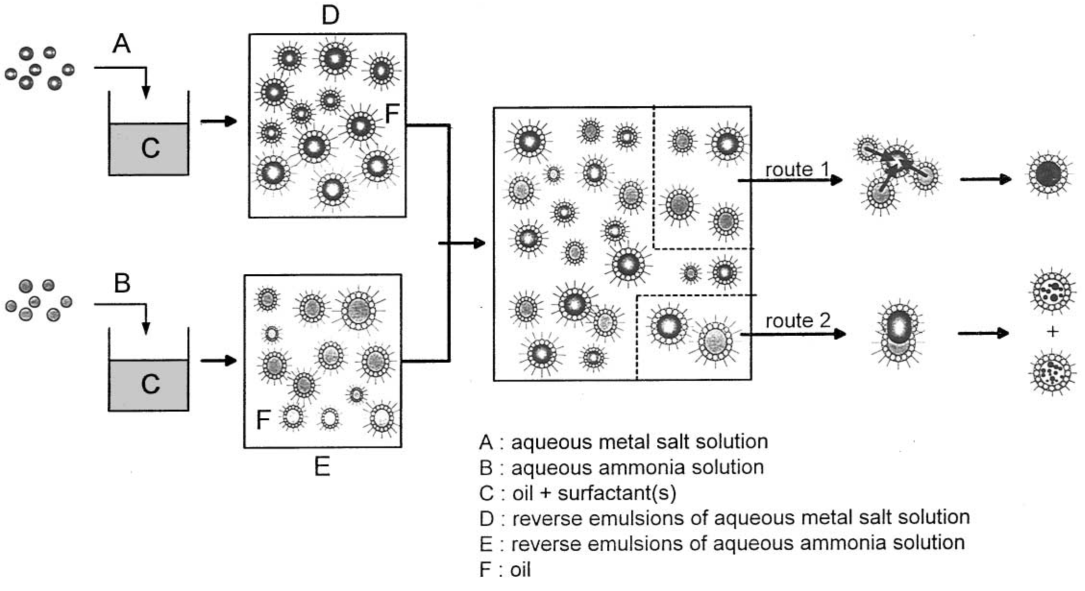

Fig. 1. The possible mechanisms of particle formation in the two-reverse-emulsion precipitation method.

generated by reaction in the droplet is mild and the precursors may have a chance to grow to large particles. On the other hand, the supersaturation is high in the droplets generated by the coalescence of different types of droplets as route 2. In this case, there will be a larger number of smaller crystals, but they tend to form agglomerates. As a result, some of the precursor particles are larger than the emulsion droplets.

3. Experimental procedure

The flow chart for preparing zirconia powder in the reverse emulsion is shown in Fig. 2. The materials and emulsification steps used in this study are somewhat different between the formation of macroemulsion and microemulsion: heptane versus cyclohexane for oil phase; Span80 versus Arlacel 83 plus isopropyl alcohol (IPA) for surfactant; ultrasonic stirring versus magnetic stirring for emulsification step. The specification of sonicator used to prepare macroemulsion has been reported elsewhere (Lee et al., 1999). Once the stable emulsion was formed, the size distribution of water droplets in the emulsion solutions was determined by a sound-wave particle size analyzer (Dispersion Technology, DT 1200), then the two stable emulsions were mixed and stirred with a magnetic stirrer for 30 min to form gelled particles. The resultant slurry was distilled at 118–130°C for about 3 h using a "Barret moisture trap apparatus" to remove the unreacted water and most of the oil. The precipitates of ZrO_2 precursor were filtered and washed with ethyl alcohol or acetone and repeated with deionized water to remove the residual surfactants and ions, then dried at room temperature for 24 h. Finally, white ZrO_2 powder was obtained by calcining the amorphous precursors to form a tetragonal structure.

Characteristics of the precursor particles and calcined zirconia powder were analyzed: the crystalline phase identified by an X-ray diffractometer (Mac Science MXP-3 TXT-7266), the particle size distribution measured by a static light scattering analyzer (Coulter, LS 230), the surface area determined by a BET analyzer (Micromeritics, ASAP 2100) and the surface structure and particle morphology examined by a scanning electron microscope (Hitachi, S-800) and a transmission electron microscope (Hitachi, H-7100).

The acoustic and electroacoustic spectrometer (DT 1200) for measuring the particle or droplet size distribution of a concentrated system uses the physical basis of acoustic attenuation. Many physical properties of the system are required in the calculation of size distribution, including viscosity of continuous phase, weight ratio of dispersed/continuous phase, as well as density, thermal expansion, heat capacity, and heat conductance of dispersed and continuous phases. Besides, the attenuation and sound speed in the continuous phase should be measured. For the macroemulsion system investigated, there is no problem to obtain the required physical properties because the continuous phase is *n*-heptane and the dispersed phase is Zr^{4+} aqueous solution. In the microemulsion solution, the cosurfactant IPA is added and distributed in the continuous phase (cyclohexane) and dispersed phase (aqueous solution). The distribution coefficient is unknown for this emulsion system: therefore, the determination of the physical properties becomes difficult. However, we assume that the added IPA goes to the oil phase and correct the attenuation and sound speed of the oil phase in the determination of droplet size.

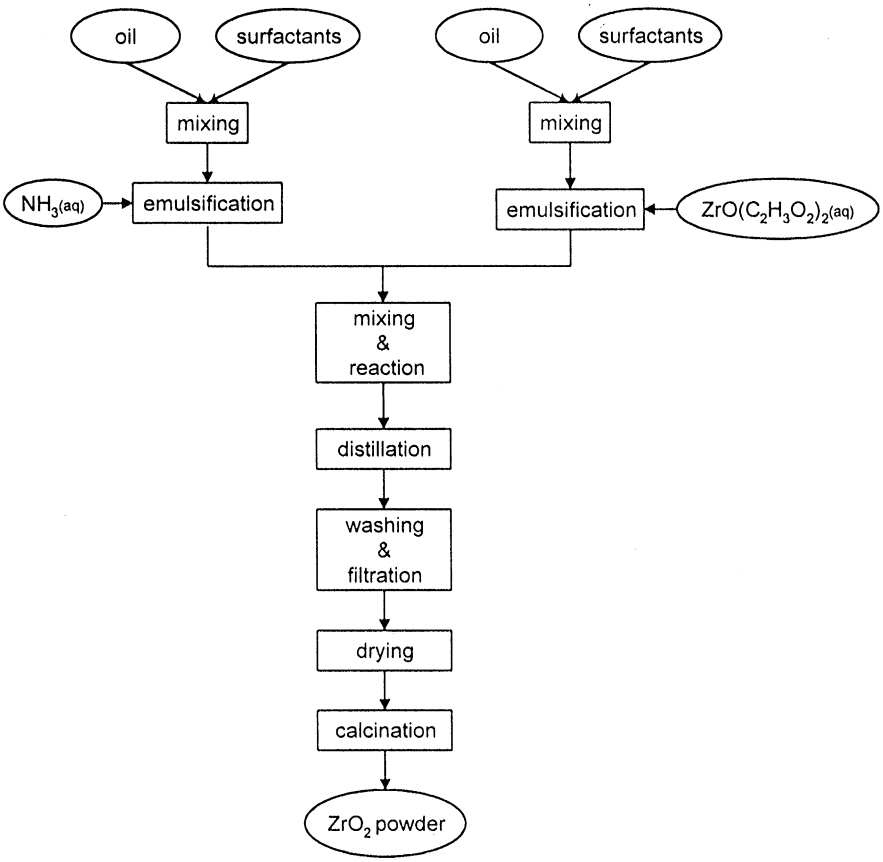

Fig. 2. Flowchart for preparing ZrO_2 powder by the two-emulsion technique.

4. Results and discussion

4.1. Characteristics of emulsion

Since the purpose of this research is to control the particle size by using the emulsion precipitation technique, the characteristics of emulsion under consideration are mainly on the stability of emulsion and droplet size distribution. There are many factors, including type and concentration of surfactant, type of oil phase, ratio of water to oil phase, and concentration of aqueous phase, that affect the characteristics of emulsion, which would subsequently influence the properties of the particles produced. From the practical point of view, the factors that influence the product yield are significant, including the concentration of aqueous phase and the ratio of w/o, which are usually not high for a stable emulsion.

4.1.1. Emulsion stability

In a previous report, Lee et al. (1999) demonstrated the effects of surfactant type, Zr^{4+} concentration, and volume ratio of w/o on the stability of macroemulsion using heptane as the oil phase. It is concluded that low Zr^{4+} concentration and low volume ratio of w/o favor the formation of macroemulsion. Stable macroemulsion is successfully prepared by using three different anionic surfactants purchased from Sigma company, Arlacel 83 (sorbitan sesquioleate, HLB = 3.7) Span 80 (sorbitan monoleate, HLB = 4.3) and Span 40 (sorbitan monopalmitate, HLB = 6.7); however, Span 40 is the most suitable one. For example, the macroemulsion is stable at Zr^{4+} concentration of 1 M and w/o volume ratio of 2/100 for Span 40, but unstable for Span 80 and Arlacel 83 at the same conditions. Besides, when the volume ratio of w/o is 1/100, the macroemulsion for Span 40 is stable as the Zr^{4+} concentration rises up to 3 M. The HLB values of the three surfactants are within the range of the optimum HLB value, 3–7, for stable reverse emulsion (Prince, 1977); however, the HLB value of Arlacel 83 is close to the lower limit and the macroemulsion formed by Arlacel 83 is less stable than that by Span 40 and Span 80. However, Binks (1998) points out that the system HLB instead of surfactant HLB should be considered because the prevailing conditions of temperature, electrolyte concentration, and oil type can all modify the geometry of the surfactant at an interface and thus affect the emulsion type and stability.

Contrary to the macroemulsion, the preparation of stable microemulsion is not successful by using heptane as oil phase or a single surfactant. Therefore, the oil phase

Table 1
Effect of cosurfactant and Zr^{4+} concentration on the stability of microemulsion. Operating conditions chosen: cyclohexane 250 g as oil phase, Arlacel 83 (HLB = 3.7) as surfactant, water/oil = 1/50, and surfactant/oil = 1/100 (by weight)

Zirconium salt		Amount of cosurfactant (IPA) (g)	Stability of microemulsion
Type	Conc. (M)		
$ZrO(NO_3)_2$	0.75	10	Unstable, phases separated in 3 min
		20	Stable over 12 h
		30	Stable over 12 h
		50	Stable over 1 day
$ZrO(Ac)_2$	0.5	50	Stable over 1 day
	1.0		Stable over 1 day
	1.5		Stable over 1 day
	2.0		Unstable, phases separated after stopping agitation

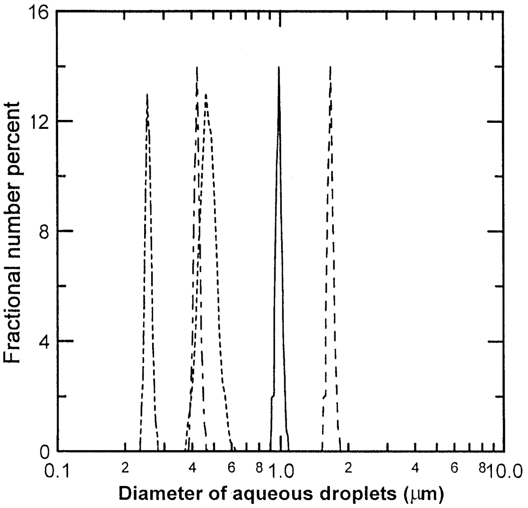

Fig. 3. Effect of Zr^{4+} concentration on the size distribution of reverse macroemulsions using Span 80 as surfactant and a w/o volume ratio of 1/100. Operation conditions chosen: 300 ml heptane, surfactant/oil ratio 0.4 g/100 ml (1.2 g surfactant/300 ml heptane), ultrasonic mixing intensity 165 W using standard horn, and mixing time 3 min. Conc. of $ZrO(Ac)_{2(aq)}$: —--— 0 M —-— 0.5 M ———— 1 M — – — – 2 M — — — 3 M.

is changed to cyclohexane and a cosurfactant is added to the system. Several alcohols have been tested as suggested by Cavalli, Marengo, Caputo, Ugazio, and Gasco (1996); however, isopropyl alcohol (IPA) is found to be suitable with the surfactant of Arlacel 83 and Span 80. The addition of cosurfactant to the formulation yields the low interfacial tension required to produce the small droplets. Alcohols with short-chain amphiphilic molecules are frequently used as a cosurfactant to reduce interfacial tension (Bourrel & Schechter, 1988). Besides surfactant and cosurfactant, there are still many factors that affect the stability of microemulsion, including water/oil ratio, surfactant/oil ratio, and concentration of aqueous phases. For example, Table 1 shows the effect of aqueous solution concentration and the amount of IPA on the microemulsion stability at room temperature which varied between 20 and 23°C. When the concentration of Zr^{4+} is at 0.75 M, the amount of IPA required for 250 g cyclohexane is more than 20 g, and the microemulsion is more stable with more IPA added up to 50 g. If the amount of IPA is fixed at 50 g, the emulsion solutions are stable for Zr^{4+} concentration up to 1.5 M and then become unstable for a further increase in the Zr^{4+} concentration.

4.1.2. Droplet size distribution of stable emulsion

The size of water-phase droplets is one of the important characteristics of emulsion because it would influence the size of the produced particles. To investigate the effects of Zr^{4+} concentration on the droplet size for the macroemulsion system, the mixing time was set at 3 min using the ultrasonic standard horn and the emulsion so obtained was stable for 12 h. The size distribution of aqueous droplets at various Zr^{4+} concentrations is shown in Fig. 3. The size of droplets turns out to be quite uniform for all Zr^{4+} concentrations ranging from 0 to 3 M. The size distribution curve of droplet shifts to smaller size when the Zr^{4+} concentration decreases. As the Zr^{4+} concentration is less than 2 M, submicron droplets will form. Therefore, it is possible to produce precursor particles with the size ranging from submicron to microns using the macroemulsion precipitation technique. On the other hand, the droplet size of ammonia droplets for the concentration kept at 14 N is quite narrow, falling between 0.1 and 0.2 μm.

For the microemulsion system, the effect of solute concentration is also investigated. The droplet size increases with the Zr^{4+} concentration varied from 0.5 to 1.5 M. The drop size distribution falls between 4 and 18 nm as shown in Fig. 4. The droplet size of 14 M aqueous ammonia falls between 10 and 100 nm with a mean size of 32 nm, which is larger than that of Zr^{4+} droplet. It appears that the droplet size distribution of microemulsion is wider than that of macroemulsion. As mentioned in the experimental section, there is some difficulty in the determination of droplet size for the microemulsion system using the acoustic spectrometer because the cosurfactant (IPA) may distribute between oil and aqueous phases; however, we assume that all IPA goes to oil phase. Therefore, the droplet size of microemulsion reported here may not be as accurate as that determined by other principles.

The characteristics of the two types of emulsions are summarized as follows: the microemulsion solution is clear with droplet size between 2 and 30 nm and the macroemulsion solution is milky with droplet size

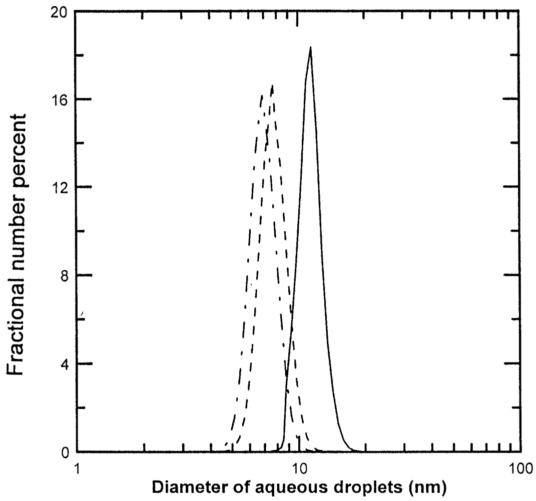

Fig. 4. Effect of Zr^{4+} concentration on the size distribution of reverse microemulsions. Oil phase: cyclohexane, surfactant: Arlacel 83; cosurfactant: isopropyl alcohol; water/surfactant/cosurfactant/oil = 2.0/1.0/20/100, based on weight. Conc. of $ZrO(Ac)_{2(aq)}$: —-— 0.5 M, ——— 1 M ————1.5 M.

between 0.1 and 10 mm; the microemulsion solution is thermodynamically stable as it is prepared by magnetic stirring and the macroemulsion solution may have a degree of kinetic stability as it is prepared by ultrasonic agitation. The different characteristics of the macroemulsion and microemulsion stated by Hiemenz (1986) are confirmed in the experiment.

4.2. Characteristics of zirconia produced from emulsion precipitation

The factors that influence the characteristics of zirconia are too many, so we first chose the following conditions as reference points, which are based on the optimum conditions used in the experiment by bubbling ammonia gas through the emulsion solution (Kanai et al., 1987): volume ratio of w/o = 1/100 (3 ml water/300 ml heptane), surfactant weight/oil volume = 0.4 (1.2 g Span 80/300 ml heptane), $ZrO(C_2H_3O_2)_2$ concentration = 0.75 M, and ammonia concentration = 14 M. The precursors produced and calcined ZrO_2 particles are spherulite. It appears that the calcined ZrO_2 particles are smaller than the precursors, presuming that the precursor, $Zr(OH)_x(CH_3COO)_{3-x}$, where x varies from 0.3 to 3.0 (Shyu & Cambria, 1990), is reduced to ZrO_2 in the calcination stage. The zirconia particle size falls between 0.1 and 1.0 μm, yet a small portion of the powder is agglomerated as shown in Fig. 5(a). Fig. 5(b) shows the ZrO_2 powder produced from an unstable microemulsion, in which the particles appear irregular. The calcined particles are identified as tetragonal ZrO_2 when the X-ray diffraction pattern is compared with JCPDS card 17–923. The characteristics of particles produced from microemulsion are similar to that from macroemulsion except for the particle size and calcination temperature to form tetragonal structure. The calcination temperature is reduced from 750°C for microparticles to 650°C for nanoparticles.

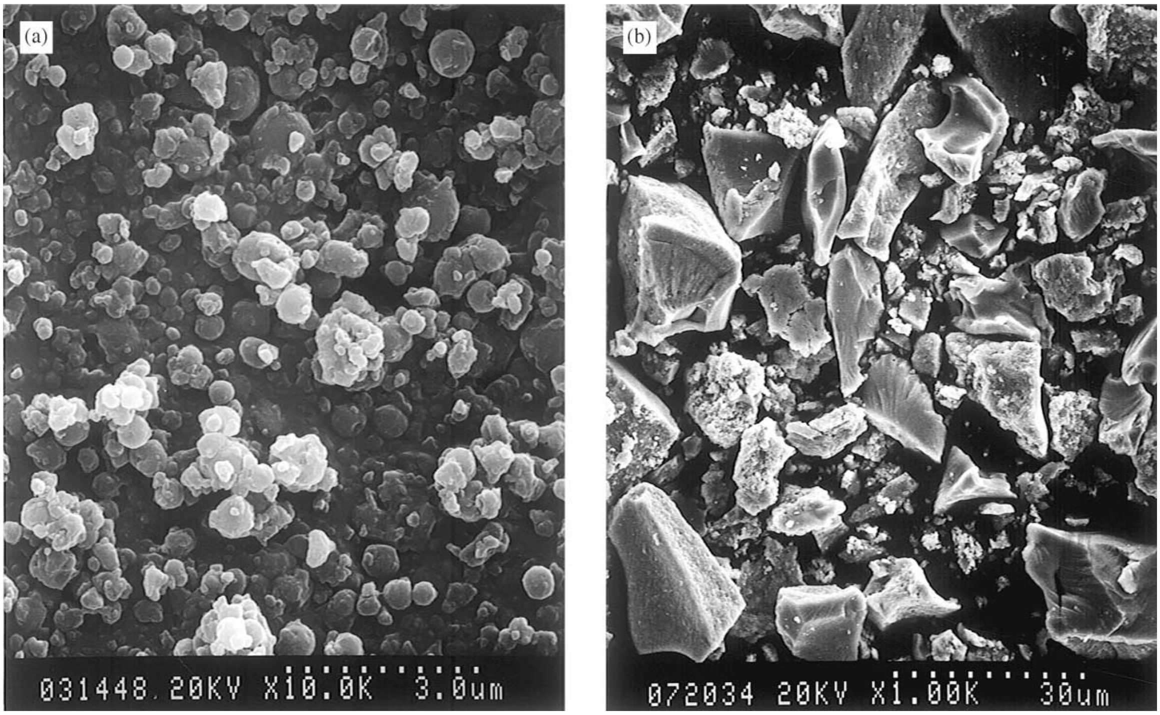

Fig. 5. Scanning electron micrographs of (a) ZrO_2 powder for the Zr^{4+} concentration of 0.75 M. (b) ZrO_2 powder from unstable macroemulsion. The other operation conditions are the same as those in Fig. 3.

4.3. *Factor affecting the particle size distribution of* ZrO_2

4.3.1. *Macroemulsion system*

Effects of several operating variables on the particle size of ZrO_2 are investigated, including Zr^{4+} concentration, ammonia concentration, w/o ratio, surfactant/water ratio, and mixing intensity. Among them, the Zr^{4+} concentration is the most significant factor. When the concentration of aqueous zirconium oxyacetate solution varies from 0.5 to 3 M, we observe the difference in particle size and degree of agglomeration. As shown in Fig. 6, the particle size is larger, the particle size distribution

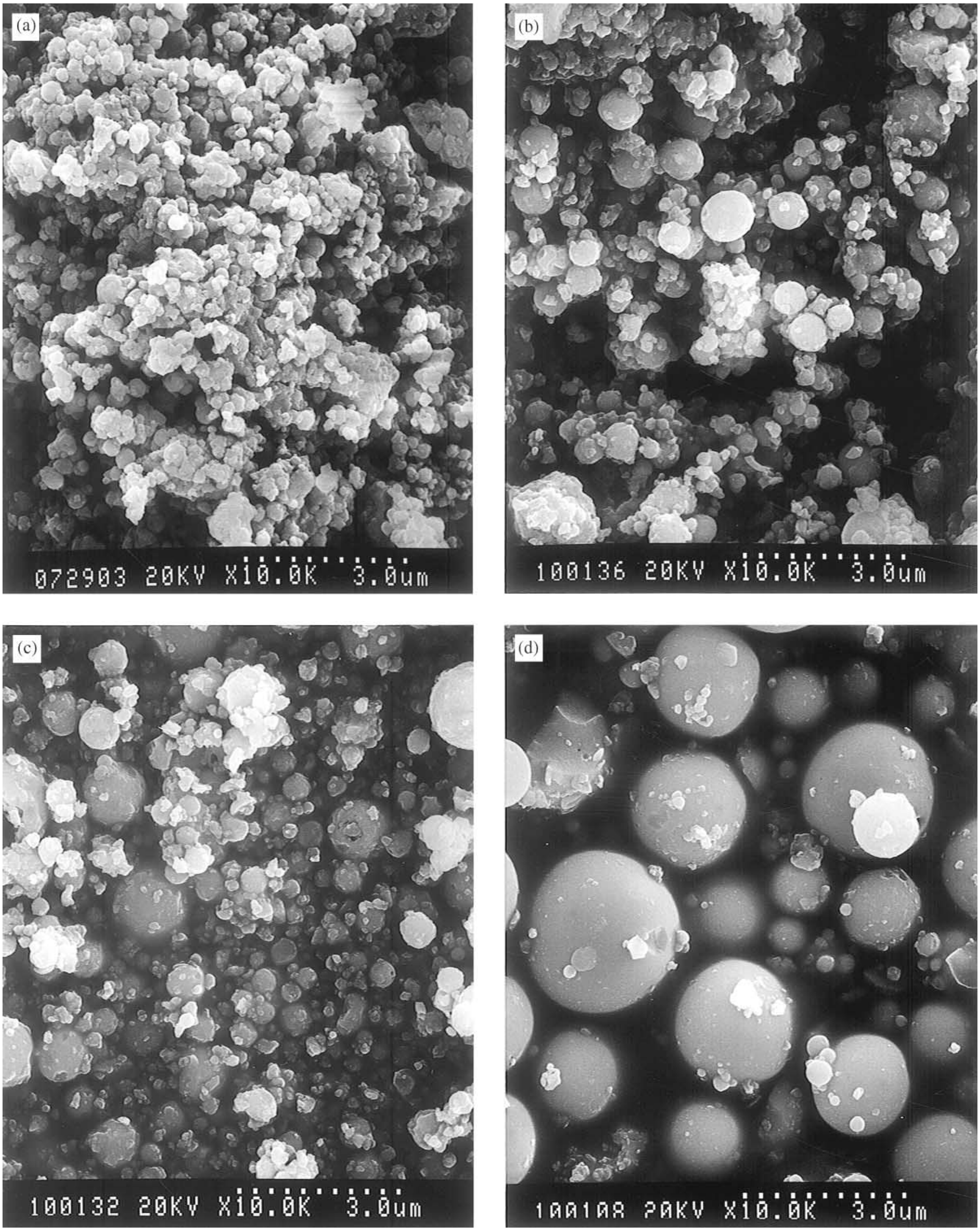

Fig. 6. Scanning electron micrographs of (a) ZrO_2 powder obtained from macroemulsions for various concentration of aqueous $ZrO(C_2H_3O_2)_2$: (a) 0.5 M (b) 1 M (c) 2 M (d) 3 M. The other operation conditions are the same as those in Fig. 3.

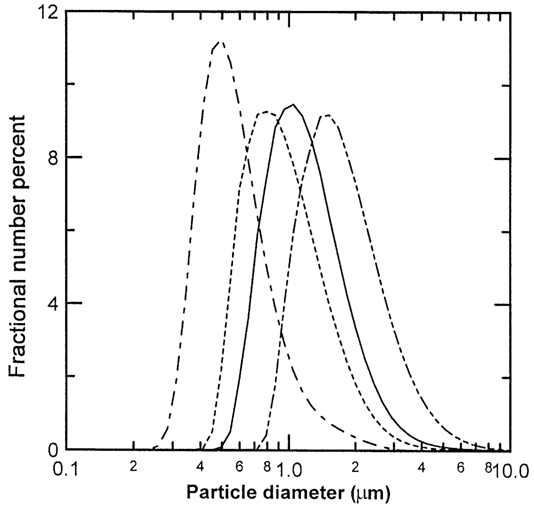

Fig. 7. Effect of $Zr(C_2H_3O_2)_2$ concentration on the particle size distribution of the ZrO_2 when the w/o volume ratio is kept as 1/100 using Span 40 as the surfactant. The other operation conditions are the same as those in Fig. 3. Conc. of $ZrO(Ac)_{2(aq)}$: —-—-— 0.5 M ———— 1 M, ——— 2 M —-—-—- 3 M.

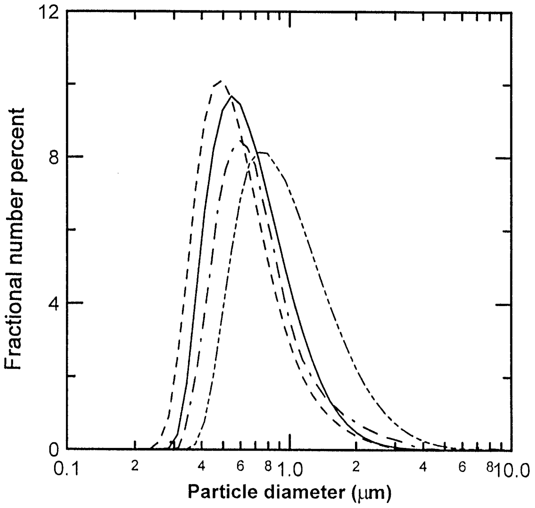

Fig. 8. Mixing effect on the particle size. high intensity : ——— 2 $MZrO(Ac)_{2(aq)}$ —-— 3 M $ZrO(Ac)_{2(aq)}$, low intensity : ———— 2 $MZrO(Ac)_{2(aq)}$ —-—-—- 3 $MZrO(Ac)_{2(aq)}$.

Table 2

Effect of solute concentration on the particle size of zirconia product. Operating conditions: water/oil (cyclohexane) = 1/50, surfactant (Arlacel)/oil = 1/100, and cosurfactant (IPA)/oil = 1/5 (by weight)

Concentration of $ZrO(Ac)_2$ solution (M)	Particle size (nm)			TEM micrographs
	TEM	BET	XRD	
0.50	5–10	28	6	Fig. 9(a)
0.75	5–20	27	5	Fig. 9(b)
1.00	10–45	35	15	Fig. 9(c)
1.50	10–50	128	27	Fig. 9(d)

is wider, and the degree of agglomeration is less when the solute concentration becomes higher, but there is no significant difference in the size of primary particles when the Zr^{4+} concentration is below 1 M (see Figs. 5(a), 6(a) and 6(b)). The particle size ranges between 0.2 and 8 μm as determined by a static light-scattering analyzer (Coulter, LS 230) when the solute concentration varies from 0.5 to 3 M. If Span 80 is replaced by Span 40, the particle size becomes larger as shown in Fig. 7, ranging from 0.3 to 10 μm. The effect of mixing intensity is shown in Fig. 8. Comparing two sets of data at different Zr^{4+} concentrations, the particle size for high ultrasonic intensity (220 W) is larger than that for low intensity (165 W). Fig. 8 also shows that the mixing effect is less than the Zr^{4+} concentration effect as far as the particle size is concerned when compared with Fig. 7.

4.3.2. Microemulsion system

The effects of the solute concentration and amount of IPA, which affect the emulsion stability, are investigated here. Table 2 shows the effects of solute concentration on the particle size, which falls between 5 and 50 nm as determined from the TEM micrographs shown in Fig. 9. The particle size is further checked by an X-ray diffractometer by using Sherrer's equation. A general trend indicates that the particle size increases with an increase in solute concentration, although the results from XRD are reversed for the concentrations of 0.5 and 0.75 M; however, the difference between them is not significant.

According to the previous work reported by Lee et al. (1999), the size of ZrO_2 microparticles and the droplet size of macroemulsion become bigger when the solute concentration increases. In this microemulsion system, the droplet size is rather independent of Zr^{4+} concentration ranging between 0.5 and 1.5 M; however the particle size of zirconia increases with an increase in Zr^{4+} concentration. Similar results have been reported for silica nanoparticles produced from reverse microemulsion (Gan, Zhang, & Chew, 1996). It is possible that in the particle formation stage nuclei agglomerate to a greater extent at higher Zr^{4+} concentration.

The effect of the amount of cosurfactant is shown in Fig. 10. An increase in the amount of cosurfactant (IPA) does not change the primary particle size when we compare Fig. 10(a) with (b), which are the TEM micrographs of zirconia particles produced from experimental runs of 20 and 50 g cosurfactant, respectively. However, the extent of agglomeration is much less when a large amount of IPA is used.

5. Conclusion

The microparticles and nanoparticles are successfully prepared by a precipitation process which is caused by

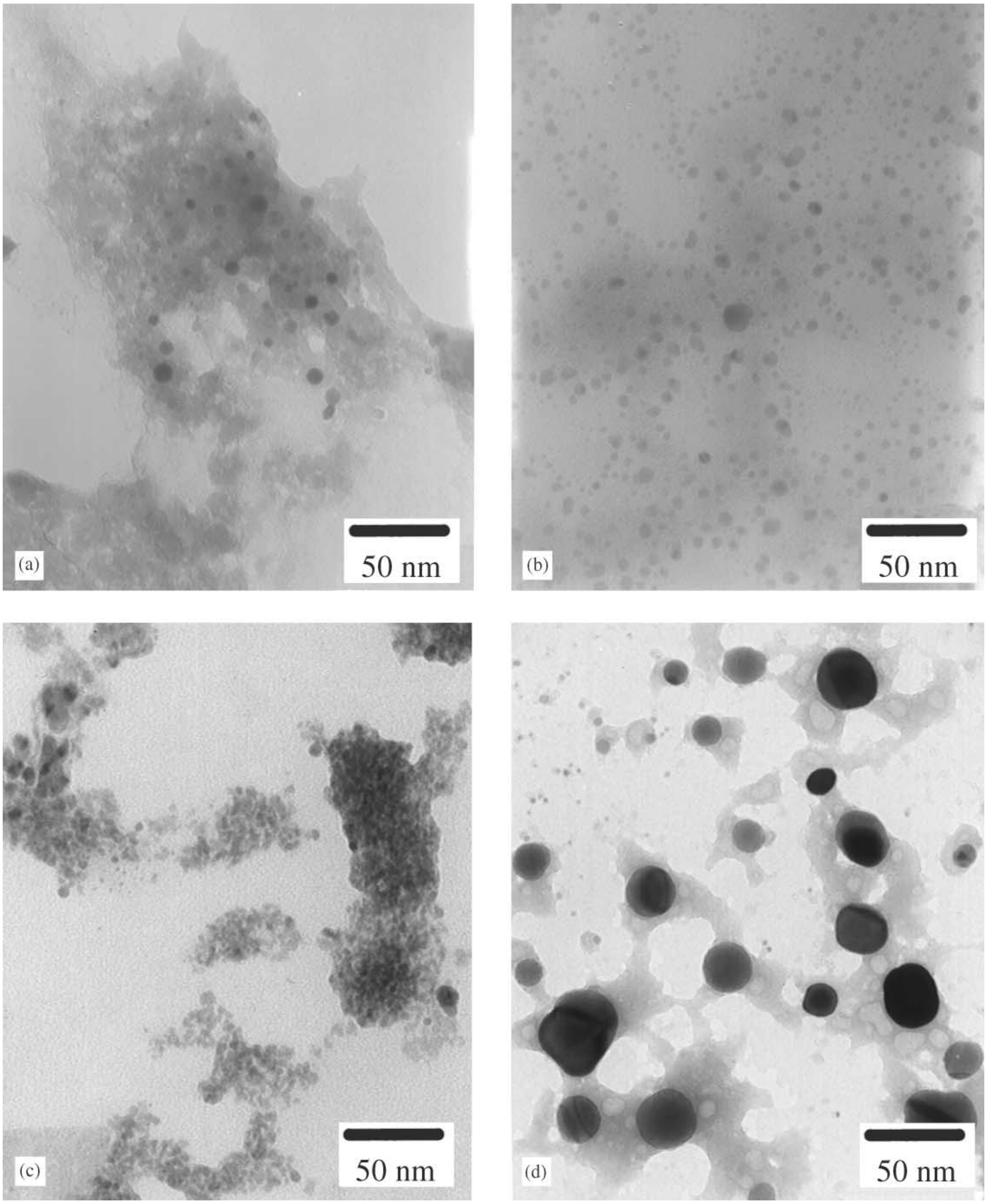

Fig. 9. TEM micrographs of ZrO_2 powder obtained from microemulsions for various concentrations of zirconium salt: (a) 0.5 M (b) 0.75 M (c) 1.0 M (d) 1.5 M.

the contact between two solutions of reverse macroemulsion and microemulsion, respectively. The materials and emulsification steps are somewhat different for the formation of macroemulsion and microemulsion and the addition of cosurfactant is essential for stable microemulsion. The characteristics of the two types of emulsion are quite different: the microemulsion solution is clear with nanosized droplets and the macroemulsion is milky with submicron to micron droplets; the microemulsion is prepared by magnetic stirring and the macroemulsion by ultrasonic agitation; the droplet size distribution of microemulsion is wider than that of macroemulsion determined by an acoustic spectrometer.

There are many factors that affect the stability of emulsion and further affect the particle morphology and size distribution of produced particles, including the type and amount of surfactant and cosurfactant, the type of concentration of zirconium salt, the type of oil phase, and

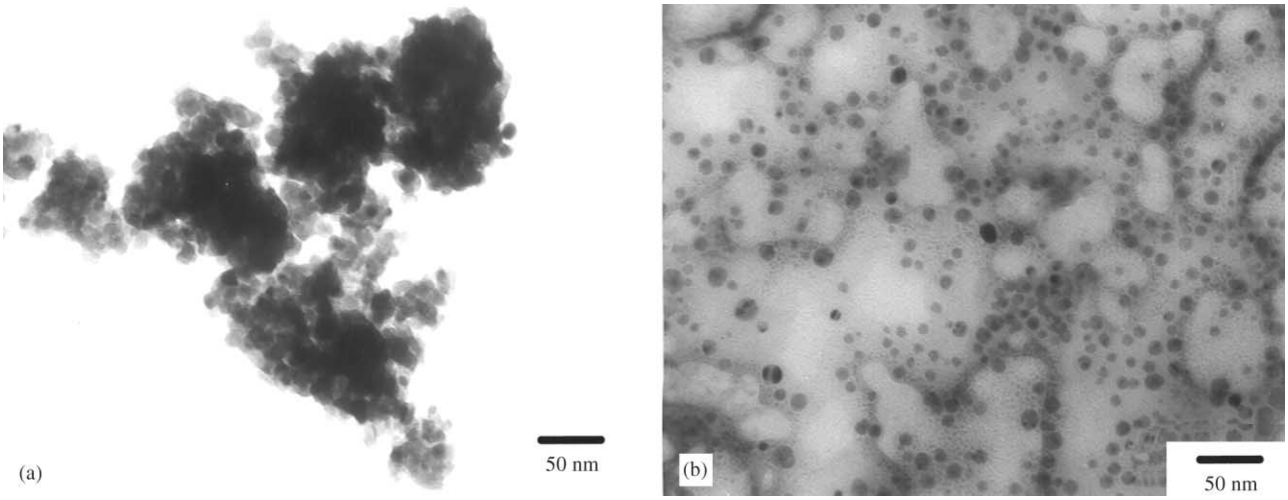

Fig. 10. TEM micrographs of ZrO_2 powder obtained from microemulsions for different amounts of cosurfactant: (a) 20 g/250 g cyclohexane (b) 50 g/250 g cyclohexane.

the water to oil ratio. From the practical point of view, the concentration of zirconium salt and the water to oil ratio are important factors.

The particle size of ZrO_2 is mainly related to the droplet size of emulsion. Thus, coupling the microemulsion and macroemulsion precipitation techniques, particle sizes ranging from tens of nanometers to a few micrometers can be controlled. The calcination temperature for tetragonal structure from amorphous precursor is reduced from 750°C for microparticles to 650°C for nanoparticles.

Acknowledgements

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