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Synthesis of Spherical Zirconia by Precipitation Between Two Water/Oil Emulsions

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Abstract

Microparticles of ZrO_2 are produced by using precipitation method between two emulsion solutions. First, two solutions of stable reverse emulsion (water-in-oil) are prepared and mixed to form gelled precipitates, using normal heptane as the continuous oil phase and aqueous solutions of zirconium oxyacetate and aqueous ammonia as the suspending droplets. Through a series of operations, including distillation, filtration and washing, the dried precursors are obtained. After calcining the precursors at $750°C$, ZrO_2 powder with a tetragonal structure is obtained. Principle factors that influence the emulsion stability, which subsequently affects the morphology and particle size of ZrO_2 powder, are investigated, including the type and concentration of surfactant, volume ratio of water/oil, concentration of solute in water phases, and mixing intensity and time for emulsion formation. Four kinds of anionic surfactants are put to test for emulsion stability; among them Span 40 and Span 80 are considered as suitable surfactants for producing spherical microparticles of ZrO_2, which has a size range from several hundred nanometers to micrometers depending on the synthesis conditions. © 1999 Elsevier Science Limited. All rights reserved

Keywords: emulsions, powders-chemical preparation, ZrO_2, spherical particles.

1 Introduction

Zirconia possesses special properties of low thermal conductivity, high mechanical strength, and high fracture toughness. Therefore, it is useful in many applications, such as structural and high-temperature ceramics. Specifications on particle size, shape, and size distribution of powder are required for ceramic processing. Ceramic powder consisting of microparticles with spherical morphology and narrow size distribution are desirable, as they result in high packing density, low sintering temperature, and uniform microstructure. A variety of techniques, including hydrothermal treatment, hydrolysis of alkoxide solutions (sol–gel method), chemical precipitation, spray drying, spray roasting, spray hydrolysis, gas-phase reaction, and precipitation in emulsion, for controlling the properties of ceramic powder have been investigated. Although the sol–gel method,[1,2] spray hydrolysis process,[3] and emulsion technique[4,5] are successful in the preparation of spherical ceramic microparticles, the raw materials (metal alkoxides) of sol–gel and spray hydrolysis processes are too expensive to use in a large-scale production. Therefore, emulsion technique is adopted to reduce the cost of producing spherical microparticles.

Recently, a series of reports revealed the reverse emulsion technique for preparing ceramic particles with spherical morphology, such as Y_2O_3, Al_2O_3, TiO_2, and ZrO_2. Spherical Y_2O_3 particles were prepared by using either an emulsion precipitation method[6,7] or an emulsion evaporation method.[8,9] Sarikaya and Akine[10] prepared spherical hollow Al_2O_3 particles from the stable w/o-type emulsion by evaporation. TiO_2 particles, with the size distribution in the range of $0.1\sim2\,\mu m$, were prepared by using an emulsion precipitation method,[11] which was also used by Shyu and Cambria[12] to prepare $30\sim80\,\mu m$ ZrO_2 particles in solid or hollow state with spherical morphology. According to the work of Kanai *et al.*,[13] the optimum conditions for preparing $ZrO_2 \cdot Y_2O_3$ spherical particles in the sol–emulsion–gel method were determined as follows: $50\,ml$ heptane, $0.2\,g$ Span 80, $0.5\,ml$ water containing 3.75×10^{-4} mole $ZrOCl_2$. Under the optimum conditions they obtained particles with an average diameter between 0.2 and $0.3\,\mu m$. Using the sol–emulsion–gel method, weakly agglomerated ZrO_2 of spherical clusters, which

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comprised of 4~10 nm particles, were produced by Sangeeta et al.[14] Following the same technique, Gao et al.[15] prepared Y-TZP powder with an average size of 14 nm, which were weakly agglomerated into polyhedral or spherical shape. They[14,15] chose $ZrO(NO_3)_2 \cdot nH_2O$ (zirconyl nitrate) as the raw material instead of $ZrOCl_2 \cdot nH_2O$, because they thought the nitrogen-containing compounds lead to easier and cleaner burnout as compared with chloride-containing compounds. Kanai et al.,[13] Sangeeta et al.[14] and Gao et al.[15] used ammonia gas bubbling through the emulsion solution, which contained Zr^{2+} aqueous droplets, to obtain gelled precipitates and then agglomerated ZrO_2 particles were obtained.

In the process of producing ceramic powder in the reverse emulsion, a surfactant must be added into the mixture of oil and water to lower the interfacial tension between the oil/water phase. When the HLB (hydrophile–lipophile balance) value of surfactant ranges between 3 and 7, a water-in-oil emulsion is obtained.[16,17] In this work, different types of surfactant, including Span 40, Span 80, Span 85, and Arlacel 83, were used to examine the emulsion stability. Then, the two-emulsion technique, i.e. precipitation by contact between two emulsion solutions, was employed to prepare spherical zirconia microparticles. Two w/o emulsions, one of aqueous zirconium oxyacetate in heptane and the other one of aqueous ammonia in heptane, with the same w/o ratio and surfactant weight were prepared separately. The two stable solutions of w/o emulsion were mixed to form slurry containing gelled precipitates. After removal of water, the slurry went through a series of operations to recover the precipitates. Then the particle size dis-tribution and surface area were measured and the surface structure and particle morphology were examined. The principal factors, including the concentration of zirconium ion, the mixing intensity and time during emulsion formation, the volume ratio of w/o, and the concentration of surfactant that influence the stability of emulsion and the properties of the ZrO_2 particles were investigated when Span 40 or Span 80 were used as the surfactant.

2 The Two-Emulsion Technique

To produce spherical ceramic powder, ammonia gas is introduced by bubbling through the emulsion solution containing Zr^{2+} aqueous droplets as reported by Kanai et al.[13] and Sangeeta et al.[14] The ammonia gas dissolves first and then diffuses through the oil phase to reach the micelles where the hydrolysis of the metal-containing compound takes place to form the product 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. As a result, the size distribution of the produced particles might be wider. To overcome this problem, the two-emulsion technique is employed.

The basic idea of the two-emulsion technique is illustrated in Fig. 1. Two reverse-emulsion solutions, in which zirconium oxyacetate aqueous droplets or aqueous ammonia droplets is suspending in the oil phase by adding a surfactant, are prepared separately and mixed together with agitation. The contact between zirconium oxyacetate and ammonia can be achieved by the diffusion of ammonia through oil phase as route 1, or by the
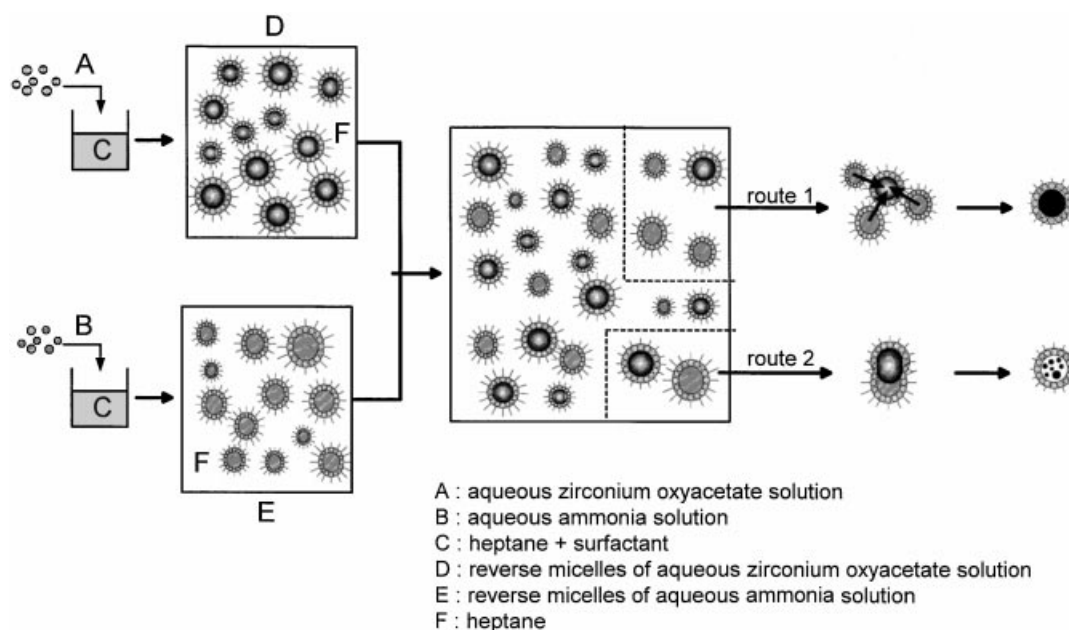

A : aqueous zirconium oxyacetate solution
B : aqueous ammonia solution
C : heptane + surfactant
D : reverse micelles of aqueous zirconium oxyacetate solution
E : reverse micelles of aqueous ammonia solution
F : heptane

Fig. 1. The possible mechanisms of particle formation in the precipitation method between two w/o emulsions.

coalescence of different types of droplets, such as route 2. The emulsion droplets serve as micro-reactors where nucleation and crystal growth occur. The ammonia concentration in the oil phase is more uniform regardless of the contact mechanism as compared with the bubbling technique. Thus, the size, size distribution, and shape of produced particles, which are related to the size of emulsion droplets, can be controlled. Because the diffusion rate of ammonia is slow for route 1, the supersaturation generated in the droplet is mild and the ZrO_2 particles may grow to almost the same size as emulsion droplets. On the other hand, the supersaturation generated in the droplets is high due to the coalescence of different types of droplets as route 2, there will be more numbers of crystal with smaller size. If there are more than three droplets involved in the coalescence process, it is possible to produce particles with the size being larger than the droplets.

3 Experimental Procedure

The flow chart for preparing zirconia powder in the reverse emulsions is shown in Fig. 2. The first step was to prepare two solutions by mixing 300 ml normal heptane (L.C. Grade; ALPS) and a certain amount of surfactant in a 500 ml beaker with a magnetic stirrer at ambient temperature. After the surfactant was completely dissolved in the oil phase, two aqueous solutions of equal volume, one containing aqueous ammonia (28%; Nacalai Tesque) and the other zirconium oxyacetate (Nacalai Tesque), were added to the beakers separately. The mixtures were then subjected to ultrasonic agitation

(Misonix, Sonicator XL2020) for several minutes and the temperature raised to 38~40°C. Once the stable emulsions were formed, the size distribution of water droplet in the emulsion solutions was determined by a sound wave analyzer (PEN KEM, DT-1200). Four anionic surfactants have been tested for the preparation of stable emulsion. Then, the two stable emulsions were mixed and stirred with a magnetic stirrer under room temperature 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 heptane. The apparatus of 'Barret Moisture Trap', which is a modified 'Dean Stark Moisture Trap',[13] is illustrated in Fig. 3. Then the precipitates of ZrO_2 precursor were filtered and washed with ethyl alcohol (99·5 vol%) or acetone and repeated with deionized water to remove the residual surfactant and ions, then dried at room temperature for 24 h. Finally, white ZrO_2 powder was obtained by calcining at 750°C for 2 h.

The sonicator used to prepare emulsion solutions contains four components: power output, 20 kHz convertor, tapped horn, and flat tip. The diameters of horn tape and flat tip were chosen by the volume to be processed and intensity required. In the experiment, two tapped horns, titanium 200 standard and 305 high intensity, were used and the differences between the two horn types are list in Table 1. The differences between the two tapped horns are the processing volume and the power range. The processing volumes are 25~500 and
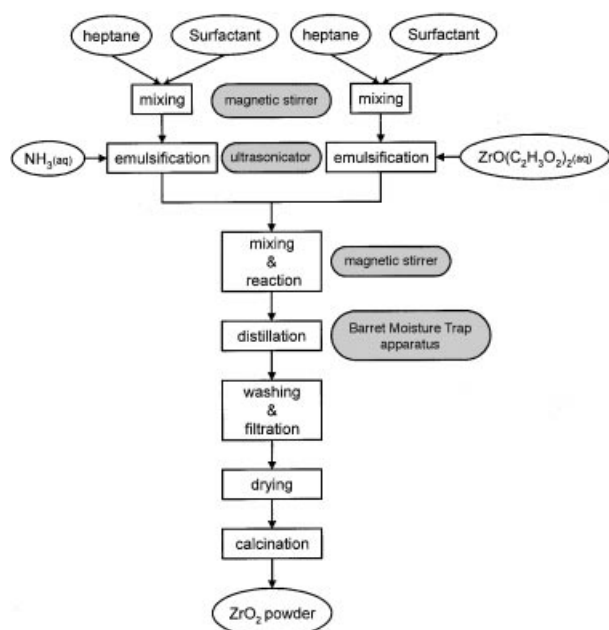

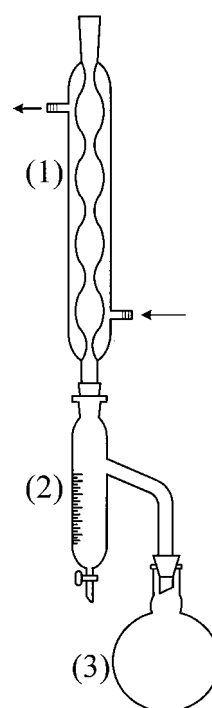**Fig. 2.** Flowchart for preparing ZrO_2 powder.

Fig. 3. Distillation apparatus: (1) condenser (2) barret moisture trap; (3) round-bottom flask.

Table 1. Specifications of the two horn types, standard and high intensity

	Standard horn	High intensity horn
Part no.	200	305
Processing volume (ml)	10∼250	25∼500
Tip diameter (mm)	12·7	19·1
Amplitude (μm)	120	120
Power (W)	0∼165	0∼220

10∼250 ml for the high intensity and low intensity horn, respectively, and the power ranges are 0∼220 and 0∼165 W for the high intensity and low intensity horn, respectively.

Characteristics of the precursor 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 2010), and the surface structure and particle morphology examined by a scanning electron microscope (Hitachi, S-800).

4 Results and Discussion

4.1 Characteristics of emulsion
There are many factors, including type and concentration of surfactant, concentration of aqueous phase, volume ratio of water to oil phase, and mixing intensity and time of emulsion formation, that affect the characteristics of emulsion, which would subsequently influence the properties of ZrO_2 powder. Among the factors investigated in this study the most important one is the type of surfactant. The characteristics of emulsion under consideration are the stability and droplets size distribution.
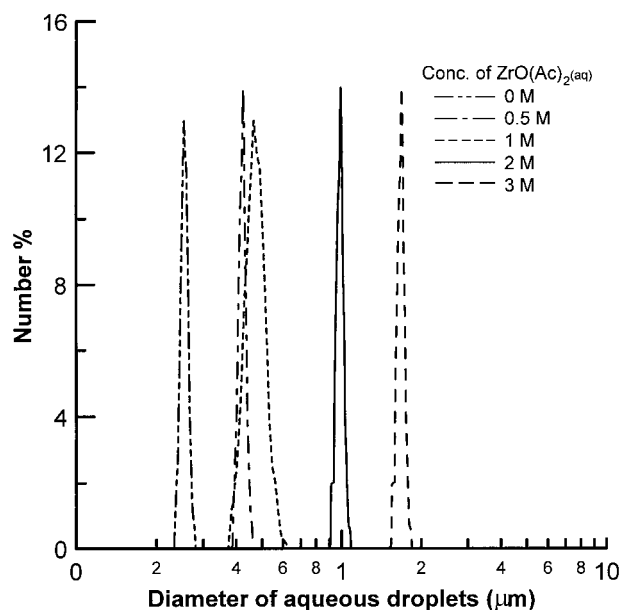
4.1.1 Emulsion stability
Four anionic surfactants purchased from Sigma Company, Span 85 (Sorbitan Trioleate, HLB = 1·8), Arlacel 83 (Sorbitan Sesquioleate, HLB = 3·7), Span 80 (Sorbitan Monooleate, HLB = 4·3), and Span 40 (Sorbitan Monopalmitate, HLB = 6·7), were put to test for the emulsion stability, which are listed in Table 2 depending on the surfactant type, Zr^{2+} concentration, and volume ratio of w/o. Other variables, such as ammonia concentration and surfactant weight, are kept constant because they are less significant in a certain range. It should be noted that the mixing time is 3 min using the standard tapped horn; any mixing time below 2 min does not produce emulsion solutions. If Span 85 is used as the surfactant, the emulsions are unstable for all cases. Using Arlacel 83, the emulsions are unstable at high ratio of w/o (5/100 and 2/100) or at high concentration of $ZrO(Ac)_2$ (3 M), and stable over 12 h at low w/o ratio (1/100) and low $ZrO(Ac)_2$ concentration (1 and 2 M). Span 80 is a more suitable surfactant than Span 85 and Arlacel 83, since the emulsions are stable over 12 h at w/o ratio of 1/100 regardless of $ZrO(Ac)_2$ concentration (from 0·5 to 3 M). However, when the volume ratio of w/o becomes higher (2/100 and 5/100), the

Table 2. Stability of the emulsions using various types of surfactant[a]

Surfactant	Concentration of $ZrO(Ac)_{2(aq)}$	Volume ratio of w/o	Stability of emulsion
Span 85 (HLB = 1·8)	1 M	5/100	Unstable, phases separated quickly
	1 M	2/100	Unstable, phases separated quickly
	1 M	1/100	Unstable, phases separated in 3∼4 min
	2 M	1/100	Unstable, phases separated in 3∼4 min
	3 M	1/100	Unstable, phases separated in 3∼4 min
Arlacel 83 (HLB = 3·7)	1 M	5/100	Unstable, phases separated in 15 min
	1 M	2/100	Unstable, phases separated in 15 min
	1 M	1/100	Stable over 12 h
	2 M	1/100	Stable over 12 h
	3 M	1/100	Unstable, phases separated in 30 min
Span80 (HLB = 4·3)	1 M	5/100	Unstable, phases separated in 15 min
	1 M	2/100	Unstable, phases separated in 15 min
	0·5 M	1/100	Stable over 12 h
	1 M	1/100	Stable over 12 h
	2 M	1/100	Stable over 12 h
	3 M	1/100	Stable over 12 h
Span 40 (HLB = 6·7)	1 M	5/100	Unstable, phases separated in 10 min
	1 M	2/100	Stable over 12 h
	0·5 M	1/100	Stable over 12 h
	1 M	1/100	Stable over 12 h
	2 M	1/100	Stable over 12 h
	3 M	1/100	Stable over 12 h

[a]Operation conditions chosen: 300 ml heptane, surfactant/oil ratio 0·4 (1·2 g surfactant/300 ml heptane), concentration of aqueous NH_3 solution 14 M, ultrasonic mixing intensity 165 W using standard tapped horn, and mixing time 3 min.

emulsions are unstable at Zr^{2+} concentration of 1 M. The most stable emulsions are prepared by using Span 40. Besides the w/o ratio of 1/100, the emulsion also stable at w/o ratio of 2/100 and $ZrO(Ac)_2$ concentration of 1 M. The HLB values of Span 40 and Span 80 are within the range of the optimum HLB value, 3~7, for stable reverse emulsions.[16,17]

4.1.2 Droplet size distribution of stable emulsion

The size of water-phase droplets in emulsion is one of the important characteristics of emulsion because it would influence the size of the produced particles. To study the effect of Zr^{2+} concentration on the droplet size, the mixing time was set at 3 min using the standard horn of 165 W and the reverse emulsions so obtained are stable for more than 12 h. The size distributions of the water-phase droplets at various Zr^{2+} concentration are shown in

Fig. 4. The effect of Zr^{2+} concentration on the size distribution of aqueous droplets using Span 80 as surfactant and w/o volume ratio of 1/100. The other operating conditions are the same as those in Table 2.
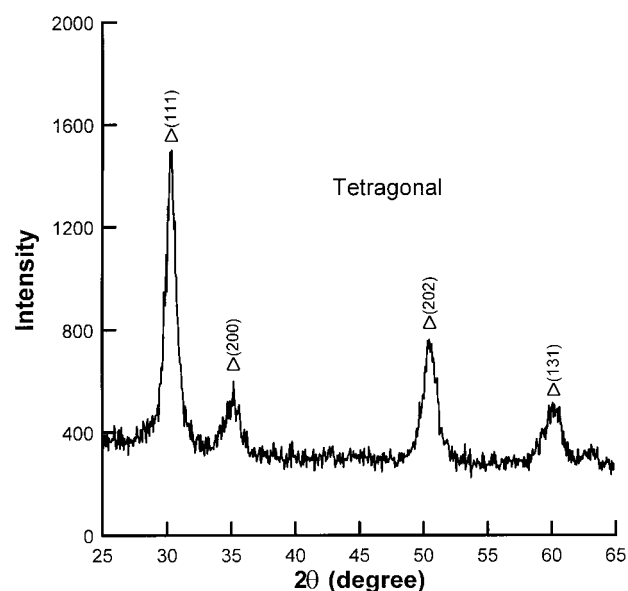
Fig. 6. X-ray diffraction pattern of ZrO₂ ultra particles calcined at 750°C for 2 h. The operating conditions are the same as those in Fig. 5. (Ref: JCPDS card ♯ 17-923).
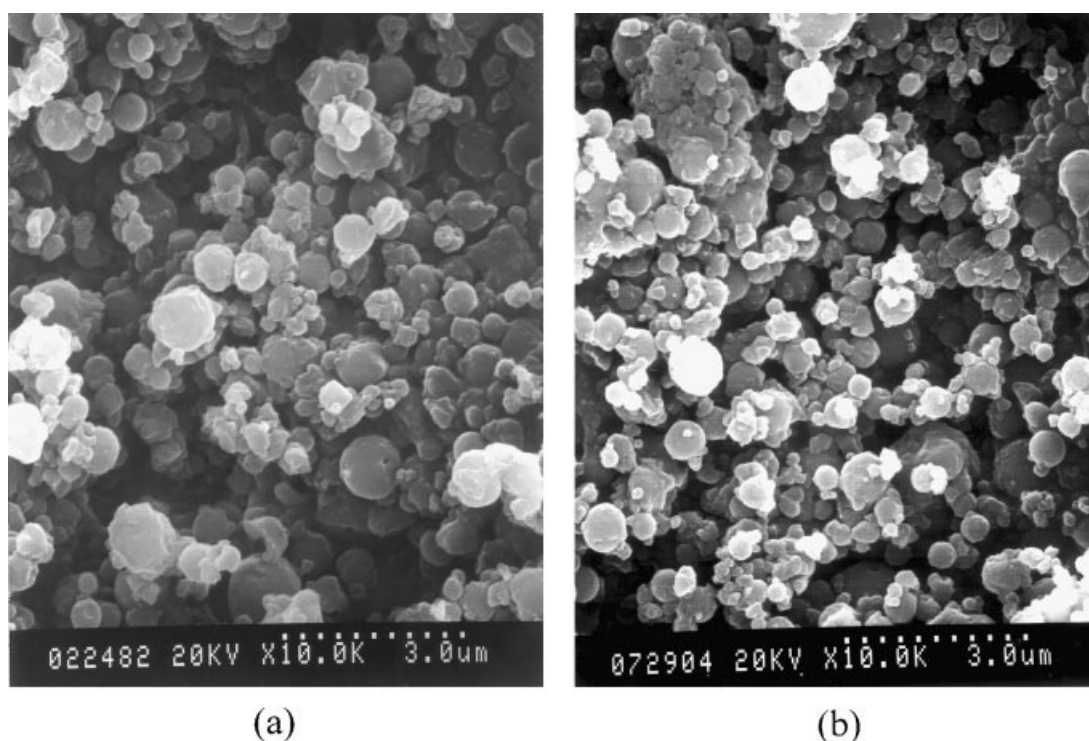
Fig. 5. Scanning electron micrographs of (a) precursors and (b) ZrO₂ powder for the Zr^{2+} concentration of 0·75 M. The other operation conditions are the same as those in Fig. 4.

Fig. 4. It appears that the size of the water-phase droplets is quite uniform for all Zr^{2+} concentrations from 0 to 3 M. The size distribution curve of droplets shifts to smaller size when the Zr^{2+} concentration decreases. Submicron droplets can be obtained when Zr^{2+} concentrations are less than 2 M. According to these results, submicron ZrO_2 particles might be obtained since the submicron droplets serve as microreactors for producing particles in this two-emulsion technique.

4.2 Effects of operating variables when using Span 80 as surfactant

Because there are many factors that influence the characteristics of the ZrO_2 product crystals, we first chose the following reference conditions to perform the experiment, which are based on the optimum conditions of the work by Kannai *et al.*[13]: 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), $ZrO(C_2H_3O_2)_2$
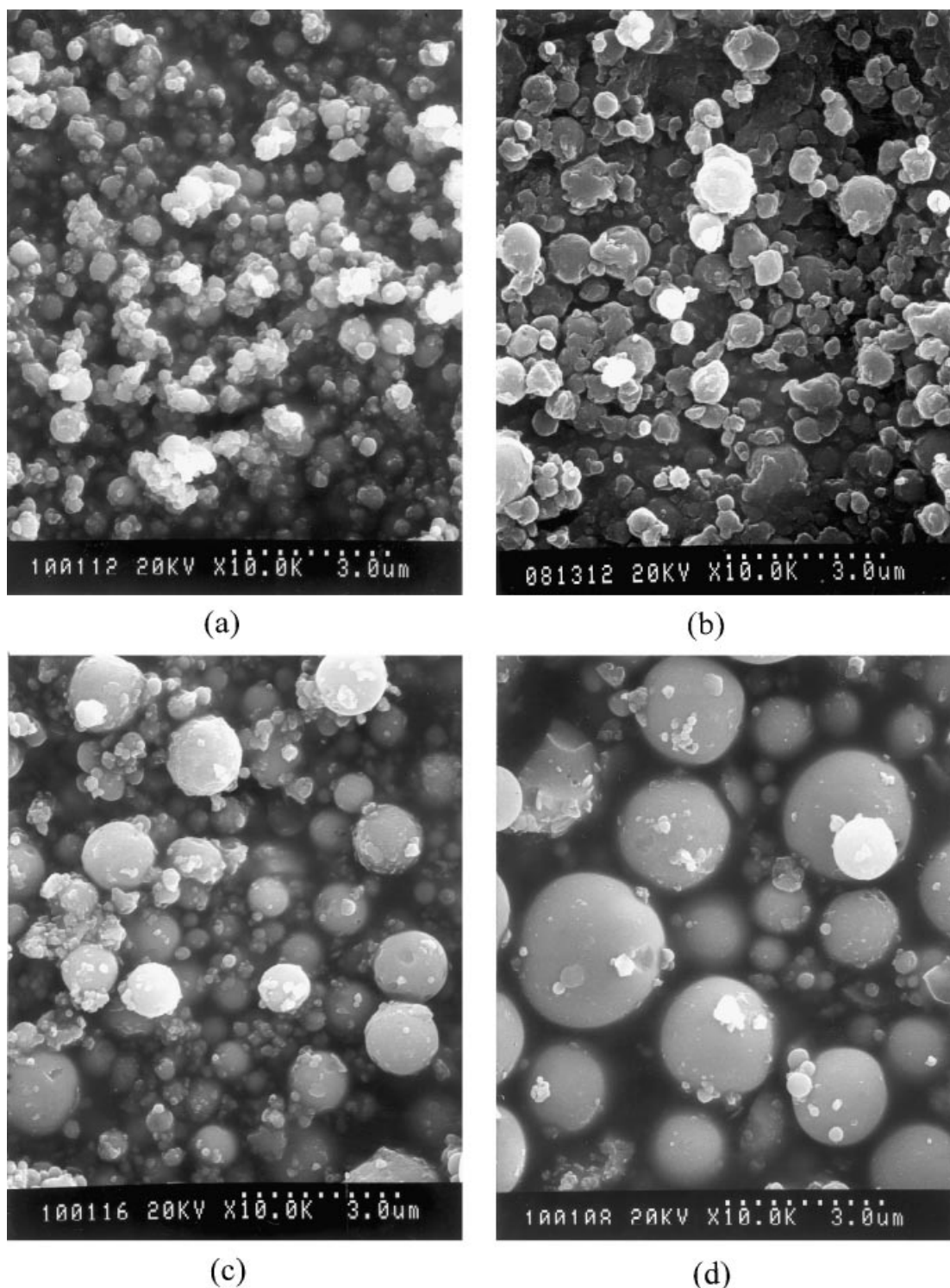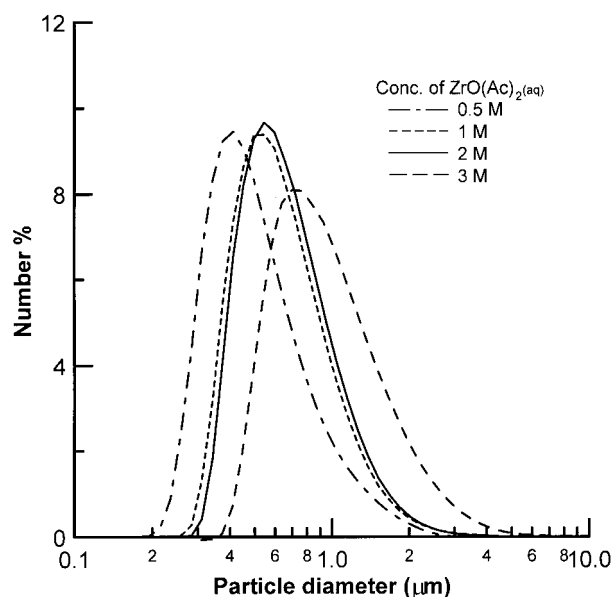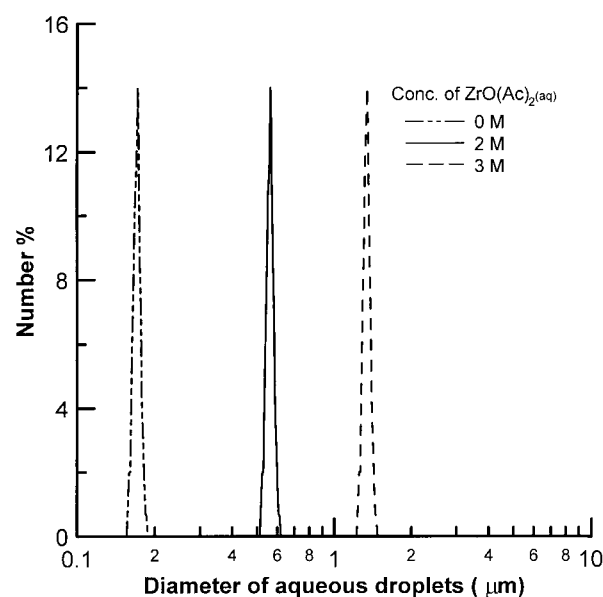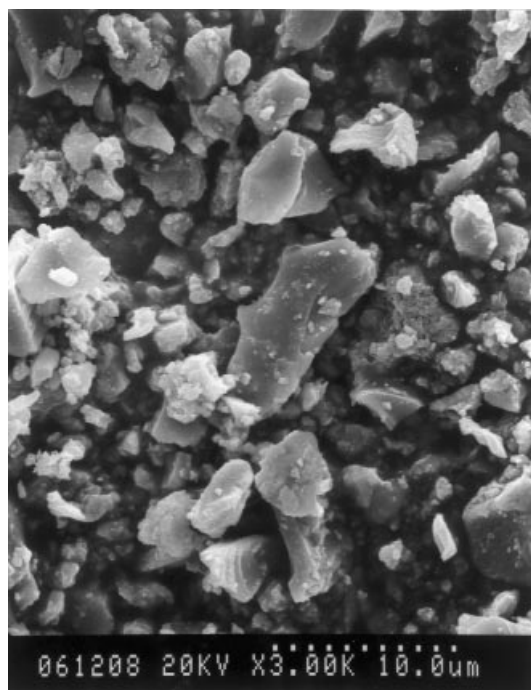

Fig. 7. Scanning electron micrographs of ZrO_2 powder for various concentration of aqueous $ZrO(C_2H_3O_2)_2$ (a) 0·5 M, (b) 1 M, (c) 2 M, (d) 3 M. The other operating conditions are the same as those in Fig. 4.

Fig. 8. Effect of $ZrO(C_2H_3O_2)_2$ concentration on the particle size distribution of the ZrO_2. The operation conditions are the same as those in Fig. 4.
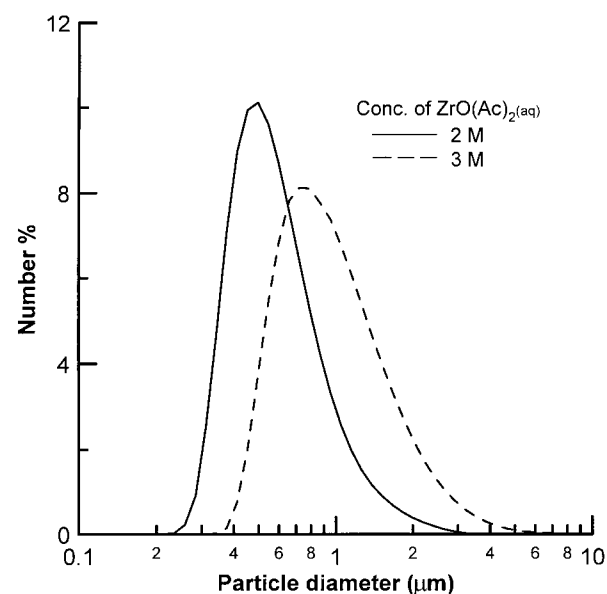

Fig. 10. The effect of Zr^{2+} concentration on the size distribution of aqueous droplets using high intensity tapped horn of 220 W. The other conditions are the same as those in Fig. 4.

Fig. 9. Scanning electron micrograph of ZrO_2 powder for the w/o volume ratio 5/100. The other conditions are the same as those in Fig. 4.


Fig. 11. Effect of $ZrO(C_2H_3O_2)_2$ concentration on the particle size distribution of the ZrO_2. The operation conditions are the same as those in Fig. 10.

concentration = 0·75 M, and ammonia concentration = 14 M. Then the effects of each factor were investigated while keeping others constant. The resultant emulsion solutions prepared by using the above-mentioned conditions were stable for over 12 h when the agitation time was 3 min using the standard horn at 165 W. The produced precursors and calcined ZrO_2 particles are shown in Figs 5(a) and (b) respectively. It appears that the calcined zirconia 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,[12] is reduced to ZrO_2 in the calcination stage. The zirconia particles are spherulite with a size distribution between 0·1 and 1·0 μm. Comparing the SEM photographs of precursors and ZrO_2 powder, it is found that a small portion of the product is agglomerated during the calcination stage. The X-ray diffraction pattern of ZrO_2 microparticles is shown in Fig. 6. When compared with the JCPDS card (17-923), the tetragonal ZrO_2 is identified.

4.2.1 Effect of Zr^{2+} concentration
When the concentration of aqueous zirconium oxyacetate solution varies from 0·5 to 3 M, differences in the particle size and the degree of agglomeration have been observed. As shown in
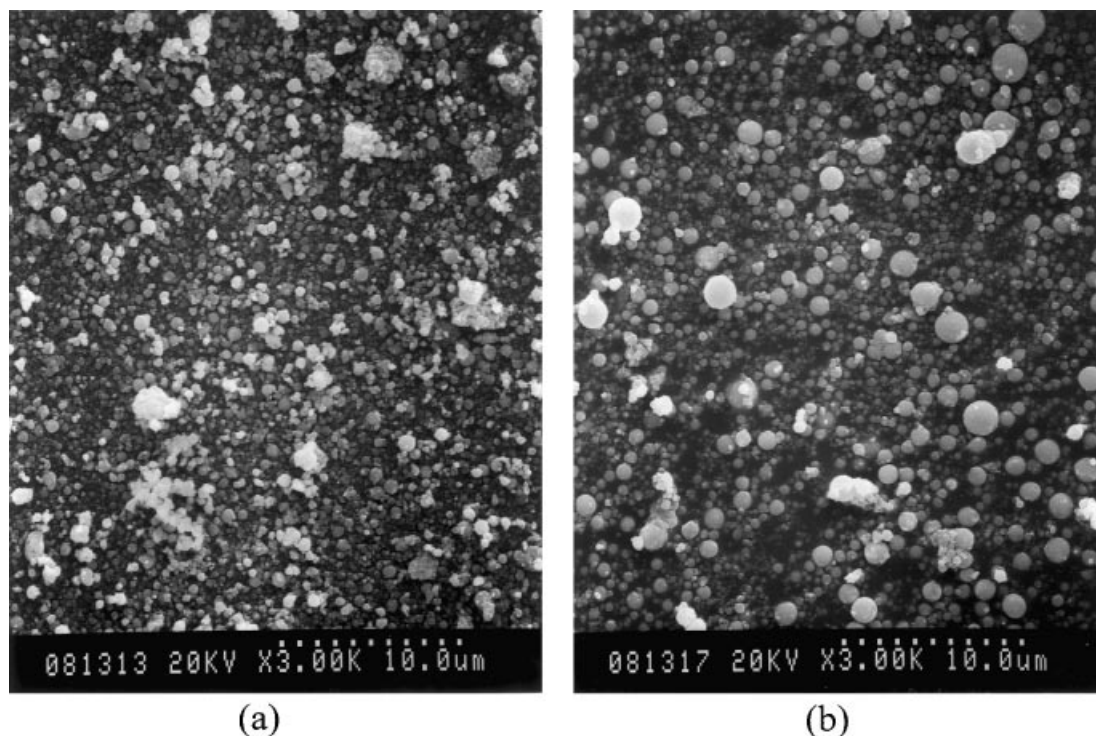
Fig. 12. Scanning electron micrographs of ZrO_2 powder for various concentration of aqueous $ZrO(C_2H_3O_2)_2$ (a) 2 M, (b) 3 M. The operating conditions are the same as those in Fig. 11.

Fig. 7, the particle size is larger, the particle size distribution is wider, and the degree of agglomeration is less when the concentration of zirconium oxyacetate becomes higher, but there is almost no difference in particle size when the Zr^{2+} concentration is between 0·5 and 1 M [compare Figs 5(b) with 7(a) and (b)]. The scanning electron micrographs of ZrO_2 powder show that the particles surface are smooth and the morphology of ZrO_2 powder is spherical for all Zr^{2+} concentrations. Besides, the specific surface area of ZrO_2 powder decreases from 12·7 to 5·2 $m^2\ g^{-1}$ when the concentrations of $ZrO(C_2H_3O_2)_2$ increases from 0·5 to 3 M. These results reveal that the ZrO_2 particles are dense and solid spheres. Figure 8 shows the particle size distribution of ZrO_2 powder obtained at various Zr^{2+} concentrations. Comparing Figs 8 with 4, we observed that the sizes of ZrO_2 particles are larger than the size of water-phase droplets and the size distribution of ZrO_2 powder is wider than the size distribution of water-phase droplets in the same experimental run. It is possible that some of the ZrO_2 particles are formed due to the coalescence of reverse micelles as illustrated in Fig. 1, and there are more than two droplets involved in the coalescence.

4.2.2 Effect of ammonia concentration
When the ammonia concentration of water-phase ranges from 4 to 14 M, the reverse emulsions are stable and the ZrO_2 powder are produced with spherical morphology at all ammonia concentrations. It

has a minor effect on the particle size and shape of the product. When the ammonia concentration is 14 M, the particle size is slightly smaller when compared with the ammonia concentration of 4 M.

4.2.3 Effect of w/o volume ratio
The w/o volume ratio affects the emulsion stability. Various ratios were tested in this experiment. When the volume ratio is 2/100 or 5/100, the emulsion is very unstable and the produced ZrO_2 particles appear irregular as shown in Fig. 9 for w/o volume ratio = 5/100. This is an expected result because at high w/o ratio the chemical reaction takes place in the bulk instead of the droplets at low w/o ratio, which gives spherical and small particles with a narrow size distribution.

4.2.4 Effect of surfactant weight
The amount of surfactant Span 80 added to the system has a significant effect on the characteristics of emulsion and thus on the characterization of particles. Varying the weight of Span 80 from 0·8 to 1·6 g, the emulsion solutions are stable for 12 h. The precursors and ZrO_2 particles with spherical morphology and few agglomerates are obtained, when the weight of Span 80 added is between 1·0 and 1·2 g. Experimental results reported by Akinc and Richardson[8] show that higher concentrations of surfactant produces smaller droplet size and thus smaller particles. However, when the amount of Span 80 added is more than 1·5 g, the produced ZrO_2 particles appear more agglomerates, presuming

that the large amount of surfactant is difficult to remove during washing.

4.2.5 *Effect of mixing intensity and time during the emulsion formation*

In the previous experiments, the emulsion solutions were prepared using the standard horn at 165 W. It is interesting to see the effect of the mixing intensity on the characteristics of emulsion and particles. Using the high intensity horn at 220 W, the

emulsions are unstable at low concentration between 0·5 and 1·5 M when the mixing time and the volume ratio of w/o are kept at 3 min and 1/100, respectively. If the concentration of zirconium oxyacetate is between 2 and 3 M, the reverse emulsion solutions become stable. The size distribution of the water-phase droplets and ZrO$_2$ powder are shown in Figs 10 and 11, respectively, for the concentration of Zr^{2+} solution being 2 and 3 M. The results are similar to that obtained by using the
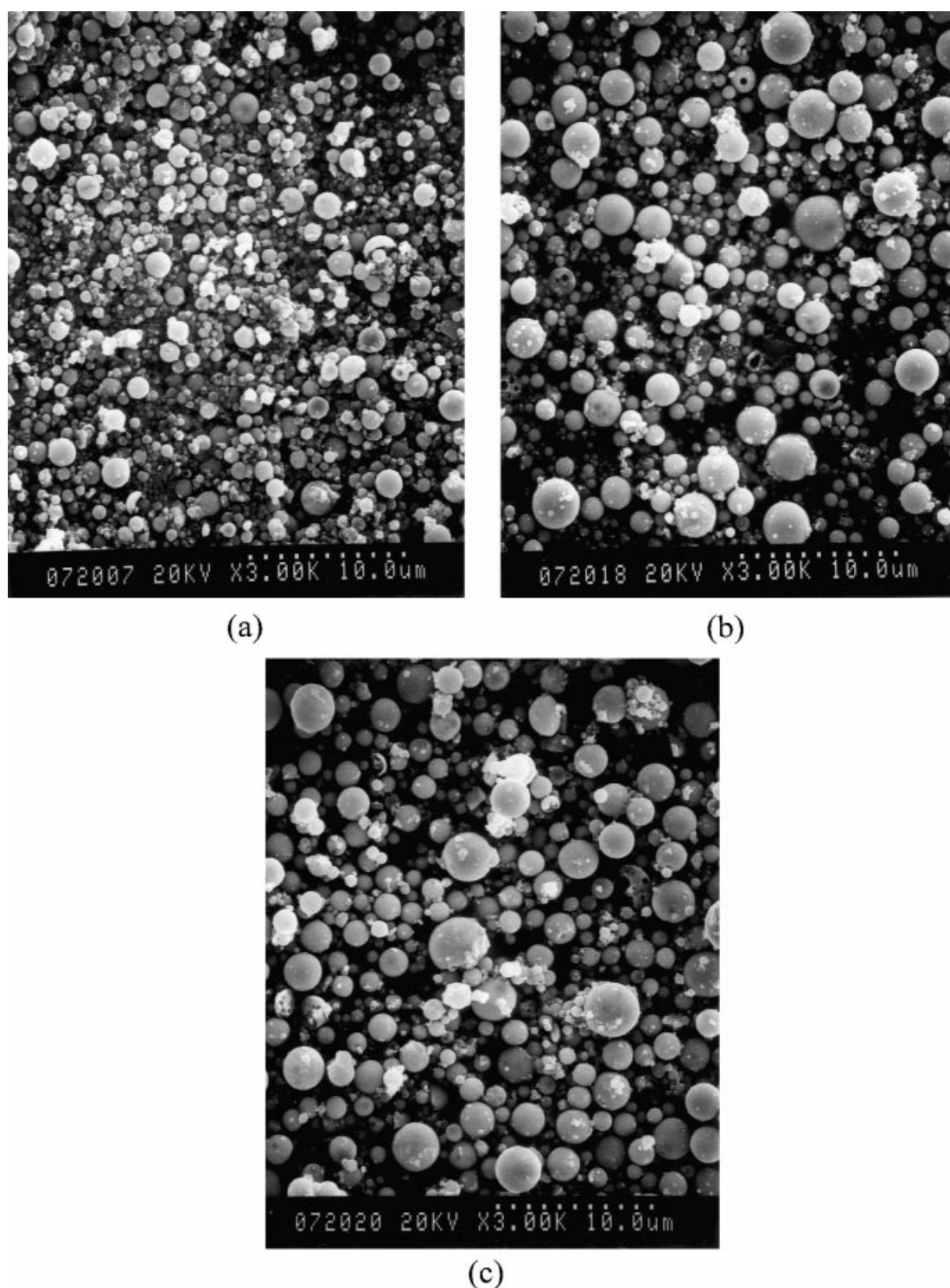
Fig. 13. Scanning electron micrographs of ZrO$_2$ powder for the w/o volume ratio 1/100 by using Span 40 as the surfactant showing the effect of ZrO(C$_2$H$_3$O$_2$)$_2$ concentration (a) 1 M, (b) 2 M, (c) 3 M. The other operation conditions are the same as those in Table 2.

standard horn of low intensity; the size distribution of water-phase droplets is narrow and shifts to larger size at high Zr^{2+} concentration (see Fig. 4) and the size distribution of ZrO_2 particles is wider than that of water-phase droplets (see Fig. 8). However, the average sizes of the water-phase droplets and ZrO_2 particles obtained by using the high intensity are smaller than that obtained by using the low intensity horn (comparing Figs 4 with 10 and 8 with 11). Figure 12 shows the SEM micrographs of the produced ZrO_2 microparticles, which are spherical in shape and larger at higher Zr^{2+} concentration. The results on morphology are similar to that by using the low intensity horn.

The mixing time during emulsion formation also affects the characteristics of emulsion is. Using the power of standard tapped horn with 165 W, the mixing time is varied from 3 min to 30 min when the concentration of Zr^{2+} solution is kept 1 M. If the mixing time during emulsion formation is more than 3 min, the emulsion solutions are unstable and the produced ZrO_2 particles appear irregular. When the mixing time during emulsion formation is 3 min, the spherical ZrO_2 microparticles are produced.

4.3 Comparison of experimental results of different surfactants

Span 40 produces more stable emulsions than Span 80 as far as the volume ratio of w/o is concerned (see Table 2). Therefore, experiments are performed to compare the results of the two surfactants, especially on the effect of Zr^{2+} concentration. While keeping the weight of Span 40 (1·2 g) and volume ration of w/o (1/100) constant, differences in the particles size and degree of agglomeration have been observed at various Zr^{2+} concentration. As shown in Fig. 13, the particle size is larger, the particle size distribution is wider, and the degree of agglomeration is less when the concentration of zirconium oxyacetate becomes higher. Similar results have been obtained for Span 80 as the surfactant. Figure 14 shows the size distribution of ZrO_2 product obtained at various Zr^{2+} concentrations using Span 40 as the surfactant. The particle size is from a few-hundred nanometers to micrometers. The average particles size of ZrO_2 for Span 40 is slightly larger than that for Span 80.

5 Conclusions

The ZrO_2 microparticles with spherical morphology are successfully prepared by the precipitation process which is caused by the contact between two emulsion solutions. In the method, two solutions of w/o emulsion, using aqueous ammonia and zirconium oxyacetate as the water phases and heptane as the oil phase, are prepared and mixed to form ZrO_2 particles. Factors that affect the size and shape of the product are investigated. The influence of surfactant type (HLB value) on the emulsion stability is drastic. The stability of emulsion significantly affects the morphology of the obtained ZrO_2 powder. When the concentration of zirconium oxyacetate ranges from 0·5 to 3 M using Span 40 or Span 80 as the surfactant, the emulsions are stable and spherical ZrO_2 microparticles are produced. When the Zr^{2+} concentration becomes higher, the particle size is larger, the particle size distribution is wider, and the degree of agglomeration is less regardless the surfactant type. A comparison of the experimental results of Span 40 and Span 80 indicates that the particle size distribution curves shift to larger sizes for all Zr^{2+} concentrations when Span 40 used as the surfactant. The size of the produced particles are from several hundred nanometers to micrometers depending on the surfactant type, mixing intensity and time, and compositions of emulsion.
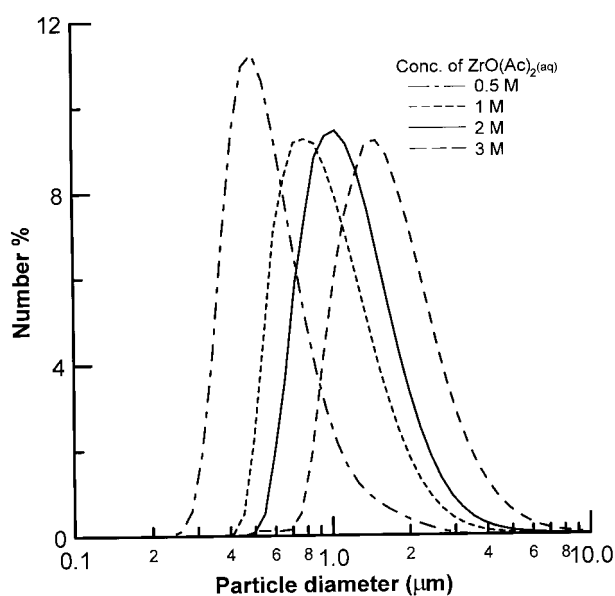
Fig. 14. Effect of $ZrO(C_2H_3O_2)_2$ concentration on the particle size distribution the ZrO_2 when the w/o volume ratio is kept 1/100 using Span 40 as the surfactant. The other operation conditions are the same as those in Table 2.

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