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Synthesis of Spherical Zirconia by Reverse Emulsion Precipitation
-Effects of Surfactant Type-

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Abstract-Spherical ZrO_2 microparticles were prepared in a three-phase reactor by mixing two water-in-oil emulsions with normal heptane as oil phase and aqueous solutions of zirconium oxyacetate and ammonia as water phases, respectively. The principal factors that influenced the stability of emulsion were investigated, including the surfactant type, the volume of w/o, and the concentration of zirconium ion. In this work, four anion surfactants were tested, including Span 85, Arlacel 83, Span 80 and Span 40. The most stable reverse emulsions were obtained with the surfactant Span 40. When w/o volume ratio was kept 1/100 using Span 40 or Span 80 as a surfactant, the ZrO_2 microparticles with spherical morphology were successfully prepared in the reverse emulsions at various Zr^{4+} concentrations (from 0.5 M to 3 M). The particle sizes of ZrO_2 are smaller for Span 40 as compared with Span 80 on the same Zr^{4+} concentrations. The crystalline phase of the ZrO_2 powders after calcination at 750 °C for 2 h was tetragonal.

Key words: Zirconia, Reverse Emulsion, Precipitation, Surfactant Type, Spherical Microparticles

INTRODUCTION

Specifications on particle size, shape, and size distribution of powders are required for ceramic processing. Ceramic powder consisting of microparticles with spherical morphology and narrow distribution is desirable, as it results in low sintering temperature, high packing density, and uniform microstructure. 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. The main target of this research is to prepare ZrO_2 microparticles with spherical morphology. Although the sol-gel method is successful in the preparation of spherical ZrO_2 powders, the raw materials, metal alkoxides, of sol-gel process are too expensive to use in a large-scale production. Therefore, emulsion technique was adopted to reduce the cost of producing spherical ZrO_2 fine-particles [Gao et al., 1996; Kanai et al., 1987; Ramamurthi et al., 1990; Shyu et al., 1990]. In our laboratory, the two-emulsion method, Span 80 as the surfactant, has been applied to prepare spherical zirconia particles with a size range between 0.1 μm and 1 μm when the concentration of zirconium ion was low [Lee et al., 1997]. The effects of operating variables, such as volume ratio of w/o, concentration of Span 80, and concentration of water phase, on particle morphology and size have been studied.

In the experiment 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 [Lissant, 1974; Prince, 1977]. In this work, different types of surfactant, including Span 40, Span 80, Span 85, and Arlacel 83, were used to test the emulsion stability. Then, the two-emulsion technique was employed to prepare spherical zirconia microparticles. The principal factors that influence the stability of emulsion and the properties of the ZrO_2 particles were investigated while Span 40 was used as the surfactant, including the concentration of zirconium ion, the volume ratio of w/o, and the concentration of surfactant.

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EXPERIMENTAL

The flow chart of preparing zirconia powder in the reverse emulsions is shown in Fig. 1, and the experimental conditions

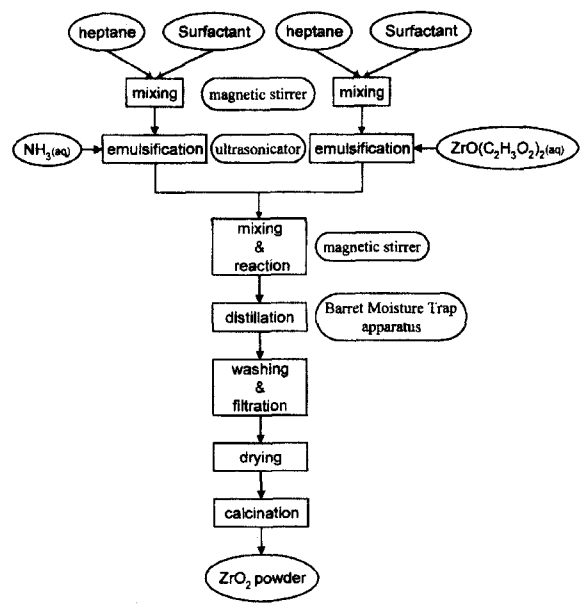

Fig. 1. Flowchart for preparing ZrO_2 powders.

Table 1. The summary of experimental conditions

Volume of oil phase	300 ml normal heptane
Volume of water phase	3-6 ml $ZrO(Ac)_{2(aq)}$
Concentration of $ZrO(Ac)_{2(aq)}$	0.5-3 M
Ultrasonic agitation time	3 min
Magnetic stirring	room temperature for 30 min
Distillation	118-130 °C for 3 h
Drying	room temperature for 24 h
Calcination	750 °C for 2 h

are summarized in Table 1. The first step was to prepare two solutions by mixing 300 ml normal heptane (L. C. Grade) with a certain amount of surfactant in a 500 ml beaker with a magnetic stirrer at ambient temperature until the surfactant was completely dissolved in the oil phase. Two aqueous solutions of equal volume, one containing aqueous ammonia and the other zirconium oxyacetate, were added to the beakers separately. The mixtures were then subject to ultrasonic agitation for 3 min and the temperature raised to 38-40 °C. Then, the two obtained solutions of 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 under temperature of 118-130 °C for about 3 h by using a "Barret Moisture Traps apparatus" to remove the unreacted water and most of the heptane. Then the precipitates of ZrO_2 precursor were filtered and washed with ethyl alcohol (99.5 vol%) (or acetone) and deionized water to remove the residual surfactant and ions, then dried at room temperature for 24 h. Finally, ZrO_2 powders were obtained by calcining at 750 °C for 2 h.

Characteristics of the precursors and calcined powders were analyzed: the crystalline phase identified by x-ray diffractometry (Mac Science MXP-3 TXT-7266), the particle size distribution measured by a static light scattering analyzer (Coulter, LS 230), the surface structure and particle morphology examined by a scanning electron microscope (Hitachi, S-800).

RESULTS AND DISCUSSION

Factors that affect the stability of emulsion and the properties of the ZrO_2 particles were investigated, including type and concentration of surfactant, concentration of aqueous phase, and volume ratio of water to oil phase. In the experiment, the following operation conditions were fixed: 300 ml heptane, surfactant/oil ratio=0.4 (1.2 g surfactant/300 ml heptane), concentration of aqueous NH_3 solution=14 M, and ultrasonic agitation time for 3 min.

1. Type of Surfactants

Four anionic surfactants, Span 85 (Sorbitan Trioleate, HLB = 1.8; Sigma), Arlacel 83 (Sorbitan Sesquioleate, HLB=3.7; Sigma), Span 80 (Sorbitan Monooleate, HLB=4.3; Sigma), and Span 40 (Sorbitan Monopalmitate, HLB=6.7; Sigma), were tested for the emulsion stability. The characteristics of the emulsions are listed in Table 2, depending on the surfactant type (HLB value), Zr^{4+} solution concentration, and volume ratios of w/o phase. If Span 85 with 1.8 HLB value was used as a surfactant, the emulsion was unstable for all cases. Using Arlacel 83 of 3.7 HLB value, the emulsions were unstable at high ratio of w/o (5/100 and 2/100) or at high concentration of ZrO $(Ac)_2$ (3 M), and

Table 2. Characteristics of the emulsions using various types of surfactant. 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, and ultrasonic agitation time: 3 min

Surfactant	Concentration of $ZrO(Ac)_{2(aq)}$	Volume ratio of w/o	Characteristics of emulsion
Span 85 (HLB=1.8)	1 M	5/100	Unstable, phase separated quickly
	1 M	2/100	Unstable, phase separated quickly
	1 M	1/100	Unstable, phase separated in 3-4 min
	2 M	1/100	Unstable, phase separated in 3-4 min
	3 M	1/100	Unstable, phase separated in 3-4 min
Arlacel 83 (HLB=3.7)	1 M	5/100	Unstable, phase separated in 15 min
	1 M	2/100	Unstable, phase separated in 15 min
	1 M	1/100	Stable for over 12 h
	2 M	1/100	Stable for over 12 h
	3 M	1/100	Unstable, phase separated in 30 min
Span80 (HLB=4.3)	1 M	5/100	Unstable, phase separated in 15 min
	1 M	2/100	Unstable, phase separated in 15 min
	0.5 M	1/100	Stable for over 12 h
	1 M	1/100	Stable for over 12 h
	2 M	1/100	Stable for over12 h
	3 M	1/100	Stable for over 12 h
Span 40 (HLB=6.7)	1 M	5/100	Unstable, phase separated in 10 min
	1 M	2/100	Stable for over 12 h
	0.5 M	1/100	Stable for over 12 h
	1 M	1/100	Stable for over 12 h
	2 M	1/100	Stable for over 12 h
	3 M	1/100	Stable for over 12 h

Fig. 2. Scanning electron micrograph of ZrO_2 particles for the w/o volume ratio 5/100 when Zr^{4+} concentration is kept 1 M. The other operation conditions are the same as in Table 2.

stable for at least 12 h at low w/o ratio (1/100) and low $ZrO(Ac)_2$ concentration (1 M and 2 M). Span 80 with 4.3 HLB value is a more suitable surfactant than Span 85 and Arlacel 83, since the emulsions are stable for at least 12 h at w/o ratio of 1/100 regardless of $ZrO(Ac)_2$ concentration (from 0.5 M to 3 M). The most stable emulsions were prepared using Span 40 with HLB=6.7. These results confirm that lower HLB values of surfactant, which range between 3 and 7, give stable emulsions of w/o type.

2. Volume Ratio of Water to Oil Phase

The w/o volume ratio affects the emulsion stability. Various ratios were tested in this experiment. When the volume ratio is higher (2/100 or 5/100), the emulsion is very unstable and the produced ZrO_2 particles appear irregular as shown in Fig. 2 for w/o volume ratio=5/100. Besides the w/o ratio of 1/100, the emulsion is also stable at w/o ratio of 2/100 and $ZrO(Ac)_2$ concentration of 1 M. Some droplets in the suspension coalesce to form a single droplet of larger size due to the unstable emulsion, and it is shown that the stability of disperse system depends on the extent of the aggregating of water phase. Therefore, at high w/o ratio the emulsion is more unstable than low w/o ratio. 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.

3. Concentration of Aqueous Phase

In studying the effect of zirconium oxyacetate concentration on ZrO_2 particle size, Span 40 was used as the surfactant since it gave the most stable emulsions. While keeping the surfactant weight (1.2 g) and w/o volume ratio (1/100) constant but varying the solute concentration from 0.5 M to 3 M, a difference in the particle size with spherical morphology and degree of agglomeration has been observed. As shown in Fig. 3, as the par-

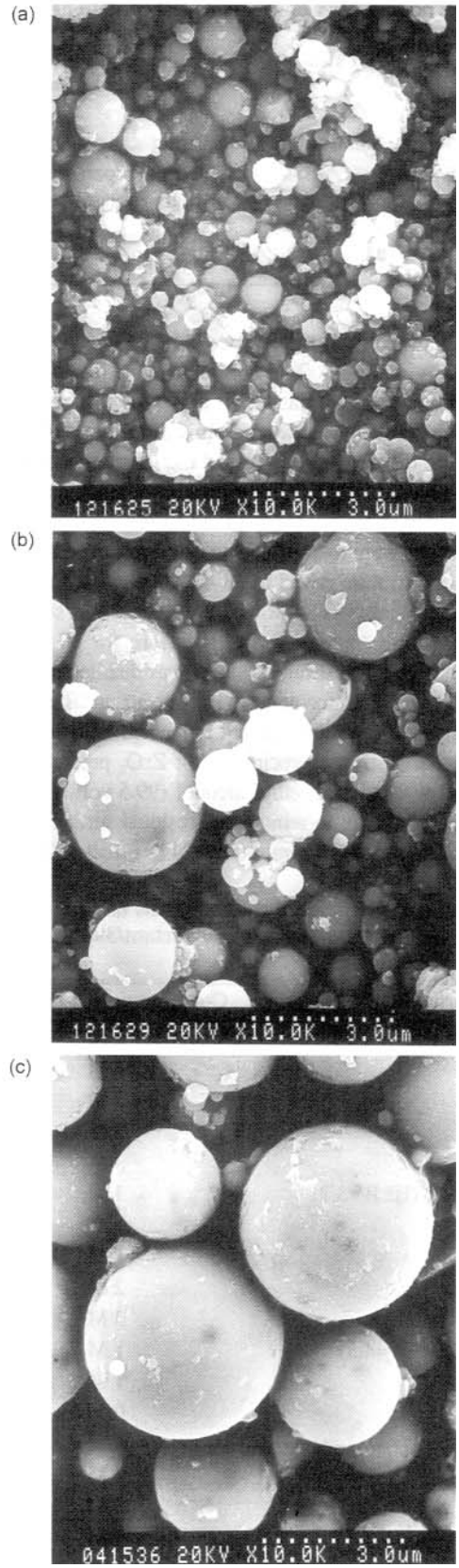

Fig. 3. Scanning electron micrographs of ZrO_2 powders for the w/o volume ratio 1/100 showing the effect of $ZrO(C_2H_3O_2)_2$ concentration using Span 40 (a) 1 M (b) 2 M and (c) 3 M. The other operation conditions are the same as in Table 2.

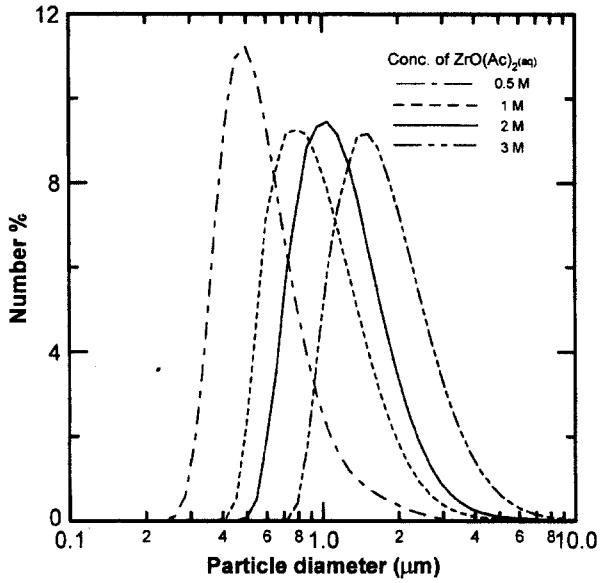

Fig. 4. Effect of $ZrO(C_2H_3O_2)_2$ concentration on the particle size distribution the ZrO_2 when the w/o volume ratio was kept 1/100 using Span 40 as a surfactant. The other operation conditions are the same as in Table 2.

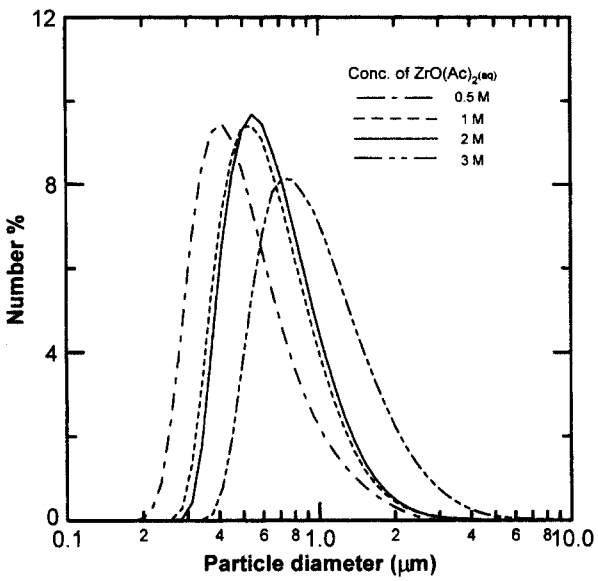

Fig. 5. Effect of $ZrO(C_2H_3O_2)_2$ concentration on the particle size distribution of the ZrO_2 when the w/o volume ratio is kept 1/100 using Span 80 as a surfactant. The other operation conditions are the same as in Table 2.

ticle 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 reported for Arlacel 83 or Span 80 used as the surfactant [Richardson et al., 1987; Lee et al., 1997]. It is possible that the size of emulsion droplets becomes smaller when Zr^{4+} concentration decreases. According to previous research by Akinc [1987], the size of ZrO_2 particles becomes bigger as the droplet size of emulsion increases. Figs. 4 and 5 show the particle size distribution of ZrO_2 product obtained at various Zr^{4+} concentrations using Span 40 and 80, respectively. The particle size was from

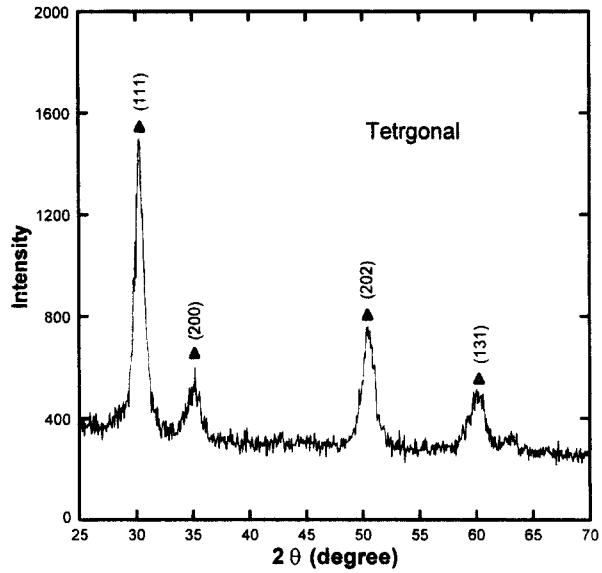

Fig. 6. X-ray diffraction pattern of ZrO_2 fine particles calcined at 750 °C for 2 h. The operating conditions are the same as Table 2 (Ref: JCPDS card # 17-923).

a few-hundred nanometers to micrometers. However, the distribution curves shift to larger sizes for the case of Span 40. Fig. 6 shows X-ray diffraction pattern of ZrO_2 fine-particles calcined at 750 °C for 2 h. When compared with the JCPDS card, the tetragonal phase of ZrO_2 was identified.

CONCLUSIONS

The ZrO_2 microparticles with spherical morphology were successfully prepared by the two-emulsion method. The influence of surfactant type (HLB value) on the emulsion stability was drastic. The stability of emulsion was found to significantly affect the morphology of the ZrO_2 powders. When the concentrations of zirconium oxyacetate ranged from 0.5 M to 3 M using Span 40 or Span 80 as the surfactant, the emulsions were stable and spherical ZrO_2 microparticles were produced. When Zr^{4+} concentration became higher, the particle size was larger, the particle size distribution was wider, and the degree of agglomeration was less. Comparison of two surfactants (Span 40 and Span 80) indicates that the particle size distribution curves shift to larger sizes at various Zr^{4+} concentrations using Span 40 as a surfactant. The particles produced were from several-hundred nonameters to micrometers depending on the surfactant type and the Zr^{4+} concentration.

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