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Preparation of spherical hydrous-zirconia nanoparticles by low temperature hydrolysis in a reverse microemulsion

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Abstract

The zirconia nanoparticles are prepared via thermal hydrolysis of zirconyl nitrate solution below 95 °C in a stable microemulsion. Hydrolysis of zirconia salt solution was confined in the droplets of the water/CTAB/hexanol reverse microemulsion where the aqueous phase of zirconyl nitrate solution was aged at various temperatures to produce hydrous-zirconia particles. Particles size, shape, and size distribution of hydrous-zirconia varied greatly with temperature and composition of reverse microemulsion. The resulting particles are retrieved and then characterized by a transmission electron microscope for particle size, a TGA/DTA thermal analyser for reaction evolution of powder. The X-ray diffractomerter is applied for the determination of crystal phase and crystallite size of resulting particles before and after calcination. © 2004 Elsevier B.V. All rights reserved.

1. Introduction

Zirconium oxide is a widely used material especially for advanced structural, high-temperature ceramics due to its strong toughness, outstanding mechanical and low thermal conductivity at high temperature. Ceramic powder with nanosized particles, spherical shape, and uniform size distribution has a significant effect on the properties of ceramics products [1]. Controlling the particle size and shape of the precursor particles is particularly important to produce high-quality ceramics [2,3].

The production of monodisperse zirconia particles by non-hydrolytic sol–gel route has been reported [4]. This method is successful in the preparation of spherical and uniform particles, but the raw materials of alkoxide are too expensive to use in a large-scale production. Thermal hydrolysis of zirconium slat solution that takes place in a bulk solution is another way to produce colloidal particles. For example, Bleier and Cannon [5] reported that the thermal hydrolysis of zirconyl nitrate solution at 98 °C for 70 h produces 80 nm zirconia particles. Matsui and Ohgai [6]

also reported that hydrous-zirconia particles are synthesized from boiling a $ZrOCl_2$ aqueous solution for 70–220 h. The mechanism of particle formation consists of three stages, (1) generation of tetramer, $[Zr_4(OH)_8(OH_2)_{16}]^{8+}$, (2) aggregation of tetramers to form nuclei and subsequently primary crystallites, and (3) secondary aggregation of primary crystallite to produce secondary particles [6,7]. The thermal hydrolysis process is a convenient route to produce nanosized zirconia particles; however, this process needs a high temperature and a long reaction time. For practical purpose, a synthesis technique of zirconia nanoparticles should be developed to lower the reaction temperature and shorten the reaction time.

Reverse microemulsion solution is a transparent, isotropic and thermodynamically stable system with nanoszied droplets dispersed in a continuous oil phase [8]. The water droplets that are enveloped in surfactant can be treated as nanosized reactors for the formation of nanoparticles. Recently, zirconia nanoparticles were successful produced from hydrolysis of zirconium tetra-*n*-butoxide (ZTB) in a reverse microemulsion [9]. However, the hydrolysis of zirconia salt solution instead of alkoxide in reverse microemulsion has not been reported.

This study investigates the synthesis of zirconia nanoparticles by hydrolyzing a zirconium salt solution in the water/

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CTAB/hexanol reverse microemulsion. The effects of composition of reverse microemulsion and reaction time on zirconia particles are investigated. The resultant particles are characterized by electron microscopy (TEM and SEM), FT–IR, and XRD.

2. Experimental procedure

A reverse microemulsion system of water/CTAB/hexanol was selected for this study due to its wide water loading. Chemicals used in this experiment are zirconyl nitrate, surfactant cetylmethylammonia bromide (CTAB) purchased from Aldrich (USA), and hexanol from TEDIA (Japan) as oil phase. All the raw materials were used as received. The flow chart for preparing zirconia powder in the reverse microemulsion is shown in Fig. 1. The first step is to prepared a reverse microemulsion by mixing hexanol, surfactant, and a certain amount of aqueous $ZrO(NO_3)_2$ solution in a 500 ml beaker with a magnetic stirrer at ambient temperature. A few minutes after mixing, the mixture solution became transparent. Then the $ZrO(NO_3)_2$ reverse microemulsion was sealed in a jacketed reactor and heated to a selected temperature, then aged for 72 h to produce hydrous-zirconia particles. As the transparent reverse microemulsion was aged, we observed that the transparent solution gradually became translucent and finally transformed into milky white solution in a few hours after aging. After heat-treatment, the hydrous-zirconia particles were separated by centrifugation, followed by repeated washing with water and ethanol to remove the impurities and residual surfactants, and finally
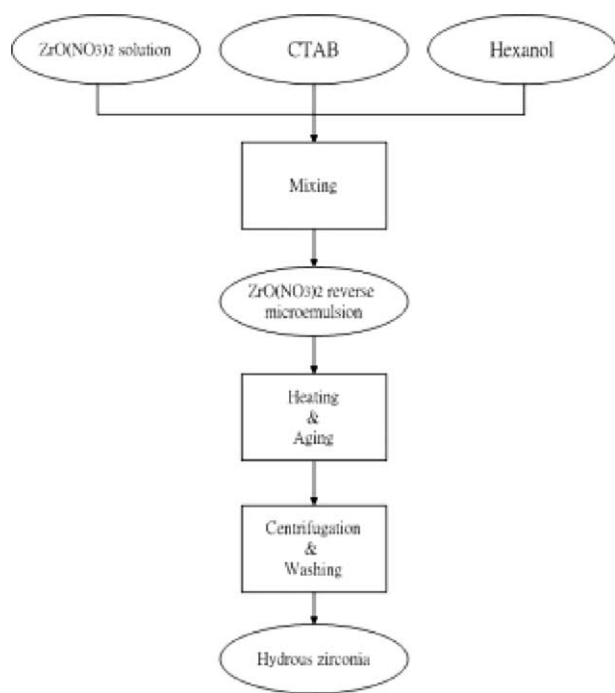
by centrifugation again to obtain hydrous zirconia particles. The particle size and morphology of resultant zirconia particles were examined by a transmission electron microscope (TEM, Hitachi-7100) and scanning electron microscope (SEM, Hitachi, S-800). The crystal structure of the product powder before and after calcination was determined by an X-ray diffractometer (Mac Science, MXP-3 TXT-7266). The average zirconia crystallite size was calculated from the Debye–Scherrer equation based on the (1 1 1) face for t-ZrO_2. The weight loss and reaction evolution of powder were determined with a thermal analyzer (TGD-7000RH, Ulvac/Riko). The TGA/DTA samples were heated from room temperature to 750 °C at a heating rate of 10 °C/min in a static air atmosphere.

3. Results and discussion

3.1. Stability of reverse microemulsion

Fig. 2 shows the stable region of water/CTAB/hexanol reverse microemulsion for pure water [10]. The water loading of this reverse micoremulsion up to 50 wt.% is quite high as compared with other systems, for example the water/span 80/IPA/cyclohexane reverse microemulsion system contains less than 5 wt.% of water [11]. The selected compositions (A, B, C, D, and E), as shown in Fig. 2, are also stable by replacing pure water with 0.2 M $ZrO(NO_3)_2$ solution. To study the feasibility of using the reverse microemulsion technique for higher temperatures, the first step is to examine the stable temperature range of water/CTAB/reverse microemulsion.

The reverse microemulsions (A, B, C, D, and E) were sealed in 50 ml Pyrex tubes and heated at 2 °C/min from 25 to 100 °C and then hold at 100 °C for 24 h. We observed that all of the reverse microemulsions were still trans-

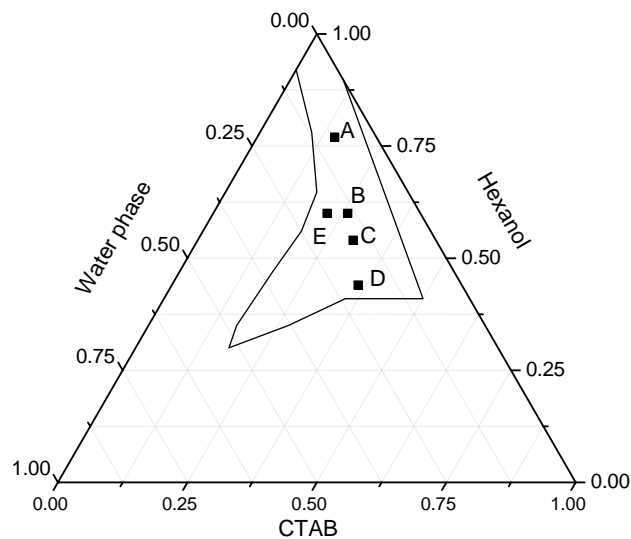Fig. 1. The flow chart for preparing zirconia particles by hydrolysis in reverse microemulsion.

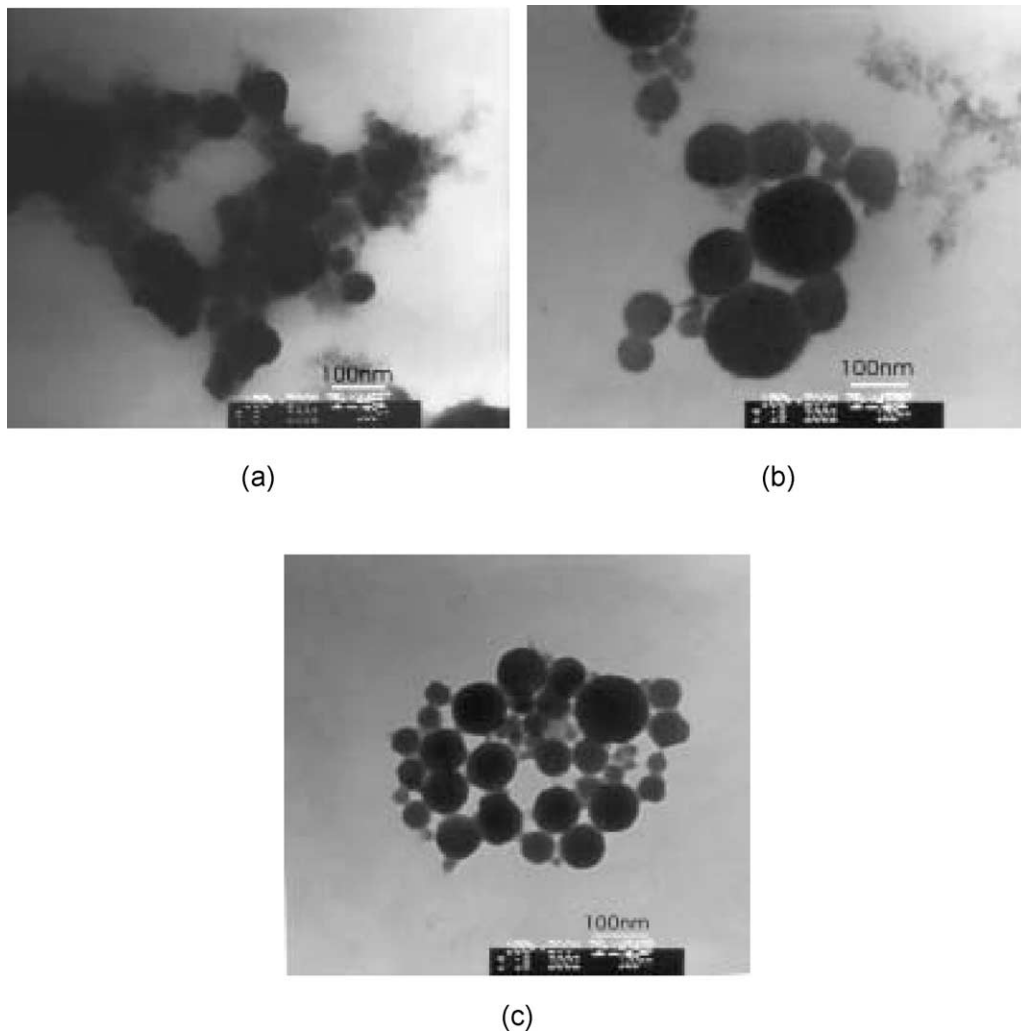Fig. 2. Stable region and the selected compositions of reverse microemulsion for this study.

Fig. 3. TEM micrographs of hydrous-zirconia particles prepared from aging the reverse microemulsion (microemulsion A) of 0.2 M ZrO(NO$_3$)$_2$ solution at (a) 95 °C, (b) 80 °C, and (c) 60 °C for 72 h, respectively.

parent after the heat-treatment. This means that this water/CTAB/hexanol reverse microemulsion with high water loading has a great thermal stability in the temperature range between 25 and 100 °C and is suitable for this experiment.

3.2. Formation of zirconia nanoparticles

To investigate the formation of nanoparticles by hydrolyzing Zr^{4+} ions in reverse microemulsion, the reaction temperatures for this study was selected at 60, 80, and 95 °C. When the microemulsion A (77 wt.% hexanol, 15 wt.% CTAB, 8 wt.% 0.2 M ZrO(NO$_3$)$_2$), was aged at 95 °C, the transparent solutions turned into milky white solutions in less than 1 h, and then fluffy precipitations formed. In contrary, when the reaction temperatures were 60 and 80 °C, the transparent microemulsion gradually became translucent light yellow solution and finally turned into milky white solution in about 1 h. After 72 h heat-treatment, the precipitates were

Table 1
The effect of operation variables on the properties of hydrous-zirconia particles

Specimen	Compositions (wt.%)			Water-to-CTAB ratio	Water-to-hexanol ratio	Particle size range (nm)	Morphology
	Hexanol	CTAB	Water				
A	77	15	8	0.53	0.10	20–250	Spherical
B	60	26	14	0.53	0.23	20–80	Spherical
C	54	30	16	0.53	0.29	20–60	Spherical
D	44	36	20	0.55	0.45	10–80	Spherical
E	60	22	18	0.82	0.3	20–150	Spherical, but with agglomeration

All samples are prepared at 60 °C by aging reverse microemulsions for 72 h.

washed and re-dispersed repeatedly with ethanol and finally subjected to TEM observation. As seen from Fig. 3(a), morphology of hydrous-zirconia particles synthesized at 95 °C is not regular in shape due to agglomeration of primary crystallite. In contrary, the resulting particles of 60 and 80 °C are spherical, but both have a wide particle size distribution,

as shown in Fig. 3(b) and (c). Based on the TEM observation, the reaction temperature of hydrolysis reaction in reverse microemulsion is an important factor that influences particle shape and size of resulting particles. When the aging temperature is 95 °C, zirconyl nitrate react vigorously in reverse microemulsion and the particle quality is difficult
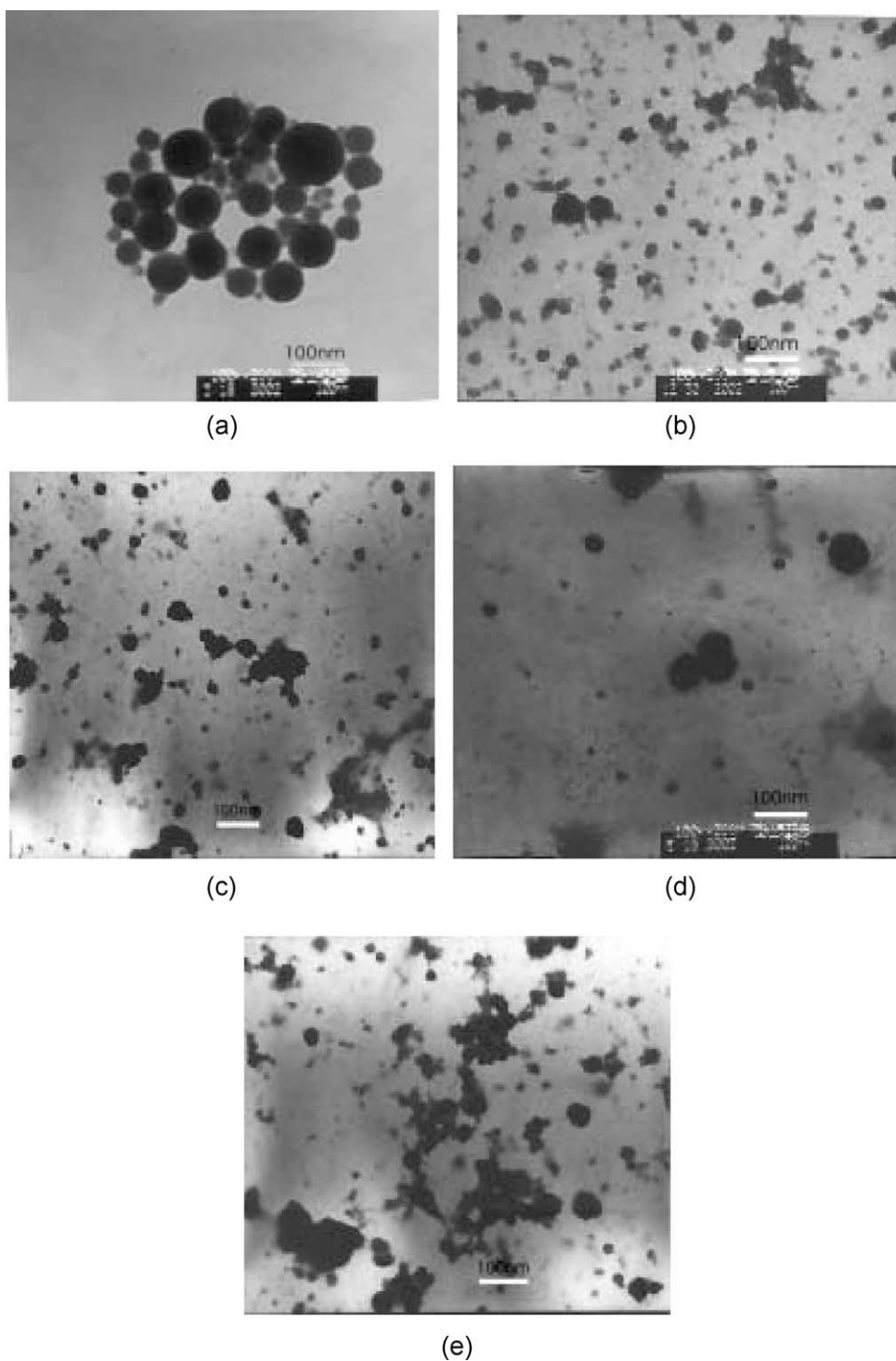

Fig. 4. TEM micrographs of hydrous-zirconia prepared from various compositions of reverse microemulsion at reaction time of 60 °C for 72 h. (a) Microemulsion A, (b) microemulsion B, (c) microemulsion C, (d) microemulsion D, and (e) microemulsion E.

to control. Therefore, lower aging temperatures, such as 60 and 80 °C, are used in our subsequent experiments.

To clarify the influence of the water-to-CTAB and water-to-hexanol weight ratio on the formation of hydrous-zirconia particles, reverse microemulsion of 0.2 M zirconyl nitrate solution with various water-to-surfactant and water-to-oil ratios were used to produce hydrous-zirconia particles. The compositions of reverse microemulsions and particle size ranges of resulting hydrous-zirconia particles are listed in Table 1.

The size distribution is rather wide for each case, and the size decreases with increasing of water-to-hexanol ratio from 0.1 to 0.45. The primary particles are spherical as shown in Fig. 4. The particles synthesized from water-to-hexanol ratio of 0.1 are nearly perfect sphere, but the size distribution is wide from 20 to 250 nm. The rather uniform hydrous-zirconia particles are observed from water-to-oil ratio of 0.23 (Fig. 4(b)). Moreover, the hydrous-zirconia obtained from aging reverse microemulsion with a water-to-hexanol ratio of 0.45 (Fig. 4(d)) contains a lot of small particles about 10 nm with some larger particles existing. The effect of water-to-CTAB ratio is also investigated. The particles produced from microemulsion of higher water-to-CTAB ratio tend to agglomerate as observed from Fig. 4(e) with a ratio of 0.82, compared to 0.53 of other runs. According to the results of this experiment, we conclude that lower water-to-hexanol and low water-to-CTAB ratio is suitable to produce spherical hydrous-zirconia particles. A scheme of formation mechanism for hydrous-zirconia particles in reverse microemulsion, as shown in Fig. 5, is helpful to explain the results of present experiment. Heating the reverse microemulsion with zirconyl nitrate causes the formation of primary hydrous-zirconia particles in droplets as the first stage. Then, larger hydrous-zirconia particles are formed by agglomeration among primary particles caused by collision of droplets, and the higher the concentration of droplets, the more the possibility to form agglomeration of particles. Besides, the Ostwald ripening seems not to be excluded, which changes the particles size distribution with more large particles.

Generally speaking, formation of zirconia particles by hydrolyzing of zirconium salt solution usually takes place at the boiling temperature of zirconium salt solution or higher temperature, and mostly cubic colloidal zirconia particles are produced [2,5,6]. In this study, hydrous-zirconia particles in spherical morphology instead of cubic particles were successfully formed by aging microemulsion of zirconyl nitrate solution at 60 °C.

3.3. Characteristics of resulting particles

The TGA and DTA curves of hydrous-zirconia particles of sample A from hydrolysis in reverse microemulsion are shown in Fig. 6. The DTA curve, curve (a), presents three major peaks; the first one is an endotherm and the oth-
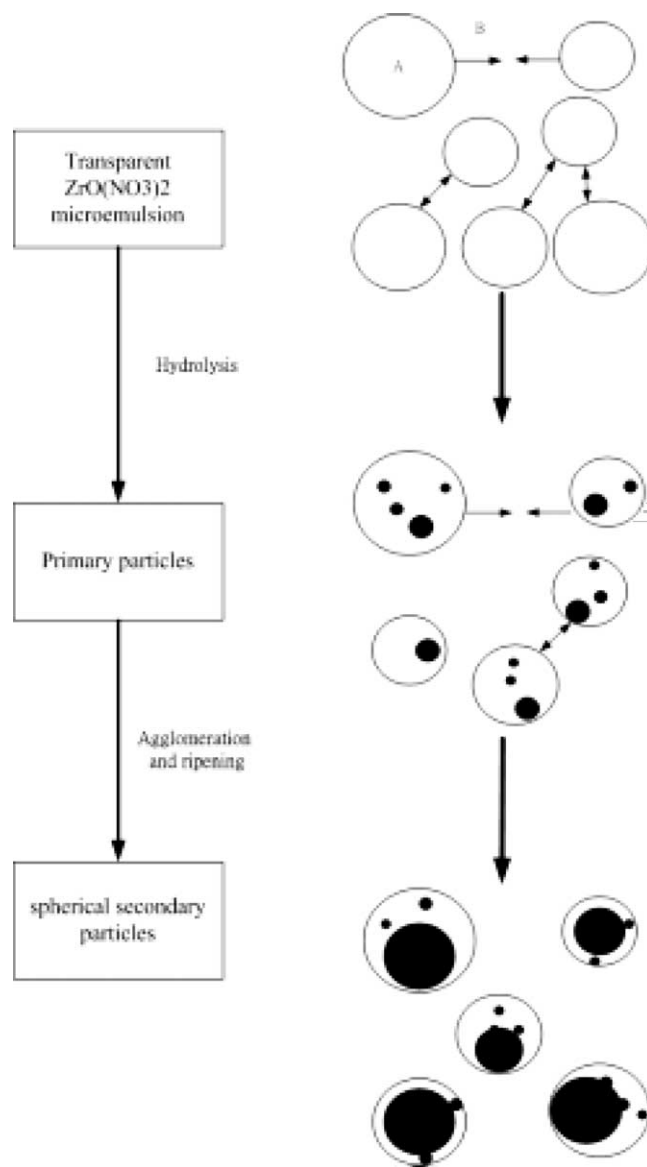

Fig. 5. The scheme of formation mechanism for hydrous-zirconia particles in reverse microemulsion, where (A) is the aqueous phase of ZrO(NO₃)₂, and (B) is the oil phase of hexanol.
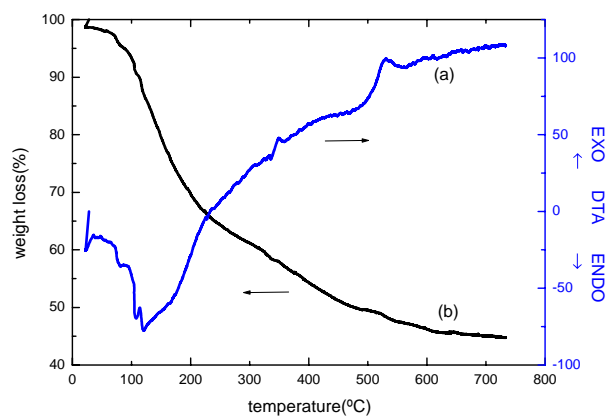

Fig. 6. DTA/TGA curves of ZrO₂ precursor in a static air atmosphere. Heating rate is 10 °C/min. (a) DTA curve and (b) TGA curve.
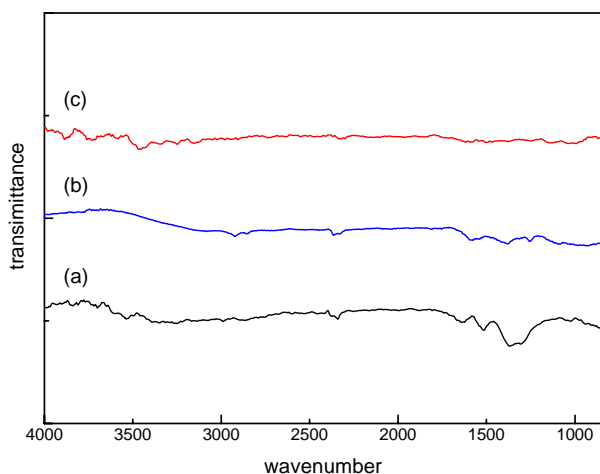
Fig. 7. The FT–IR spectrum for the zirconia particles: (a) $ZrO(NO_3)_2$ raw material, (b) zirconia powder synthesized before, and (c) after calcination at 600 °C for 1 h.

Fig. 8. The XRD patterns of the hydrous-zirconia particles synthesized at (a) 60 °C, (b) 80 °C, and (c) 95 °C for 72 h.

ers are exotherms. The broad endothermic peak appears at about 120 °C which corresponds to the elimination of residual water and solvent. On the other hand, two exothermic peaks appeared at 350 and 530 °C. The former is attributed to the oxidation of organics residues and the decomposition of nitrate group. The latter peak at 530 °C named "glow exotherm" [12] is attributed to the crystallization of zirconia from the initially amorphous and hydrous form. Besides, the TGA curve, curve (b) in Fig. 6, is leveled off at about 600 °C, meaning that the residual surfactants and impurities have been burned out completely.

The structure and chemical compositions of resulting zirconia particles were examined by using FT–IR spectrometry and X-ray diffraction analysis. The FT–IR spectra of selected samples from our experiments are presented in Fig. 7. The raw material of $ZrO(NO_3)_2$, i.e., curve (a), shows bands in the range 1300–1700 cm^{-1} and 3000–3500 cm^{-1}, which can be assigned to hydroxyl groups of molecular water ($\delta_{OH} = 1630\,cm^{-1}$), OH stretching vibrations and inorganic nitrate salts (1340–1410 cm^{-1}) [13]. In addition, all of the samples have the band at around 2340 cm^{-1} that can be attributed to the absorption of CO_2. The methyl groups of CTAB contributing two bands in the FT–IR spectrum [14], one is the band of stretching (2800–3200 cm^{-1}) and the other one is the band of bending (1300–1500 cm^{-1}), was used to detect the residual surfactant. Because the zirconia nanoparticles are formed in the droplet of the reverse microemulsion, the surfactants will then physically adsorbed on a specific face of the nanoparticles to inhibit the growth rate of the face and thus to alter the particle shape. In the FT–IR spectrum of resulting particles, curve (b), it shows that the band of inorganic nitrate salt (1340–1410 cm^{-1}) disappeared, but still has hydroxyl group (1630 cm^{-1}) and small amount of residual CTAB (2800 cm^{-1}). Curve (c) shows the FT–IR spectrum of zirconia particles that was calcined at 600 °C for 1 h. The hydroxyl group and CTAB both are removed by calcination, except the absorption of CO_2.
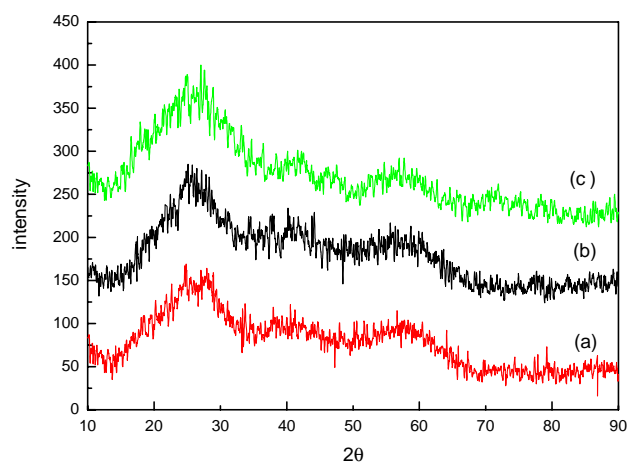
Fig. 8 presents the XRD patterns of hydrous-zirconia particles from hydrolysis in microemulsion at 60, 80, and 95 °C for 72 h. The XRD curves have no distinct diffraction peaks, even the reaction temperature was elevated to 95 °C. The XRD pattern, as shown in Fig. 9, of resulting particles after calcination at 600 °C indicates that the structure of zirconia is tetragonal and the crystallite size is 16 nm as determined by Debye–Scherrer method. The SEM and TEM micrographs shown in Fig. 10(a) and (b), respectively, indicate that the ZrO_2 nanoparticles after calcination were small, spherical crystallites, and that they agglomerated to some extent. In general, heating zirconyl nitrate or zirconyl chloride aqueous solution at boiling point usually produces crystalline particles. However, the present experiment produces amorphous hydrous-zirconia instead of monoclinic zirconia. It is attributed to the lower reaction temperature, less than 95 °C, used in this study. The TGA/DTA analysis also confirmed this observation, because the curve of DTA (Fig. 6) showed a glow exothermic peak at 530 °C, the glow exother-
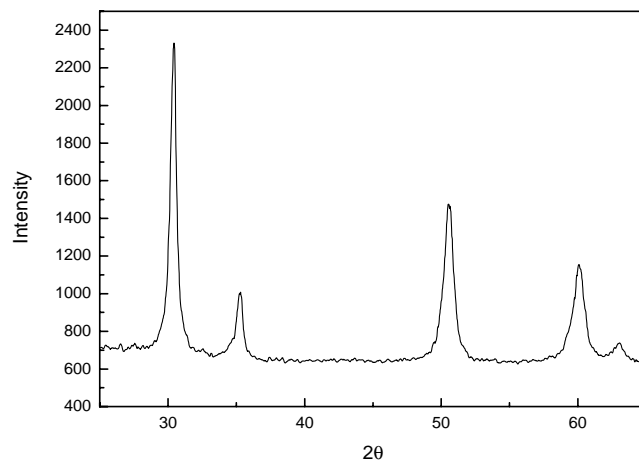

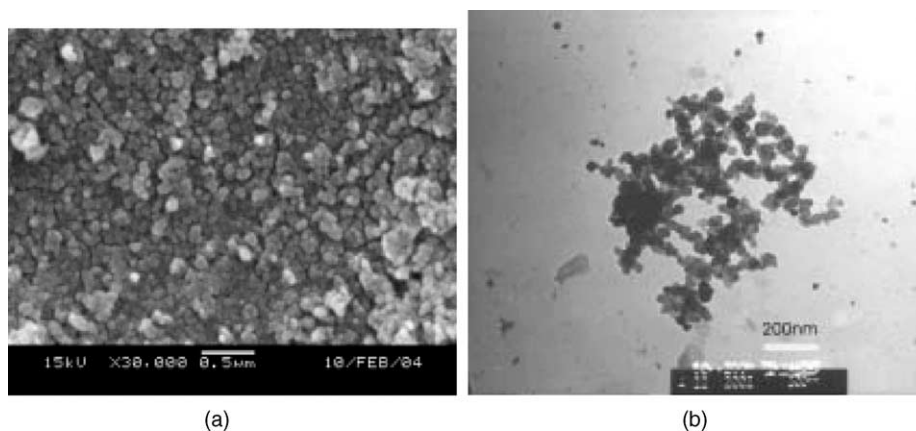Fig. 9. The XRD patterns of the hydrous-zirconia particles after calcination at 600 °C for 1 h.

(a)   (b)

Fig. 10. The (a) SEM and (b) TEM micrographs of ZrO$_2$ nanoparticles after calcination at 600 °C for 1 h. Preparation conditions: heating the microemulsion B at 60 °C for 72 h.

mic peak disappears when crystalline zirconia particles undergo heat-treatment [15].

4. Conclusion

The spherical zirconia nanoparticles instead of cube-shaped zirconia were successfully synthesized through thermal hydrolysis of zirconyl salts solution in a reverse microemulsion. The hydrous-zirconia particles synthesized at 60 °C, which is lower than the temperatures reported by other hydrolysis processes, are amorphous, and they transfer to tetragonal phase after calcination at 600 °C. In addition, the particles size and shape is greatly influenced by the reaction temperature and compositions of the reverse microemulsion. The wide size distribution of the resulting particles is attributed to collision of droplets and Ostwald ripening during the process of hydrolysis in reverse microemulsion. The compositions of reverse microemulsion for preparing spherical hyrous-zirconia particles are located in the area of lower water-to-hexanol and water-to-surfactant ratio on the phase diagram.

Acknowledgements

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