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Preparation of spherical ultrafine zirconia powder in microemulsion system and its dispersibility

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Abstract

The water droplets in the microemulsion system of cyclohexane/water/Triton X-100/hexyl alcohol can act as the nanoreactors which solubilize zirconium oxychloride and ammonia separately. The precipitation reactions will take place in the confined spaces determined by the droplets size. The minute original reactors help us obtain ultrafine spherical zirconia powder with uniform diameter distribution and weak aggregate. The content of soluble ions, especially high valence contra-ions is lower in the powder than that in other commercial powders. Comprehensively, analyzing zeta potential and rheological characteristics of the zirconia aqueous suspension, we conclude that the powder has perfect dispersibility.

Keywords: D. Zirconia; Microemulsion; Spherical powder; Dispersibility

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1. Introduction

Nowadays, the field of communication is undergoing a worldwide revolution. Optical fiber has been utilized in communication and its supply is increasing in the new century. The consumption of optical fiber connectors as the photopassive device will increase in an annual rate of growth 23% in the near 5 years [1]. In optical fiber connector, two ferrules contact each other precisely to continuously transmit optical signal in the optical fiber. The ferrule is the most important part of the optical fiber connector. Its highly precision demand makes it the key technology during connector manufacture. About 95% of the ferrules are made of zirconia ceramics. As we know, high quality of ceramics are based on the excellent performance of powder. So in order to meet the rapid increasing market of optical fiber connector, it is necessary to pursue an advanced method to produce zirconia powder with excellent properties and high production outcome.

At present, ultrafine zirconia powder prepared via the method of chemical co-precipitation or hydro-thermal cannot match the request for producing the precise ferrules for optical fiber connector. The powder is usually random shaped and has severe conglobation as well as low sintering activity.

Microemulsion method was invented as an effective process of preparing nanoparticles in the 1980s [2]. Microdroplets, in which reactants are solved, act as nanoreactors. Spherical powder with uniform dimensional distribution and good dispersibility can be obtained by such method via adjusting the size of reactors and other reaction conditions. So the microemulsion method has been utilized to prepare nano powders, such as Cu, PZT, Bi, and $BaTiO_3$ [3–7]. Lee and co-workers [8,9] took heptane and cyclohexane as oil phase and Span 80 + Arlacel 83 + isopropanol as surfactants to solubilize reactants in the volume ratio of water and oil: 1/100 to 5/100. Zirconia powder acquired had good spherical shape. However, its diameter is up to 2–8 μm. Qiu et al. [11] took xylol/Tween 80/zirconium (yttrium) nitrate aqueous solution to form the microemulsion system. Spindle or approximate spherical powder is obtained through the reaction, which took place while ammonia gas was introduced into the system. The powder still had some shortcomings, such as severe conglobation and high second diameter of 0.3–1.0 μm. Yang and Li [10] employed water/cyclohexane microemulsion system and prepared pure zirconia powder

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with the diameter lower than 10 nm and the specific area up to 197 m^2/g. The powder could be utilized as adsorbent or the carrier of catalyst. Further, cyclohexane/Triton X-100/pentanol/water was taken by Tang et al. [12] as the microemulsion. Ultrafine spindle zirconia powder of monoclinic with the diameter of 4–20 nm was prepared while a relative low reactant concentration was employed.

In this work, a water/oil microemulsion consisted of cyclohexane/water/Triton X-100/hexyl alcohol is invented to prepare ultrafine spherical zirconia powder via the reaction which takes place between the precipitant and zirconium salt solved in the nanoreactors. Furthermore, the powder's properties and its dispersed behavior are investigated deeply.

2. Experimental procedures

2.1. Mechanism of the reaction in the microemulsion system

The principle of the nanoreactor in the microemulsion is shown in Fig. 1. The authors employ cyclohexane as the oil phase, Triton X-100 as the surfactant, and hexyl alcohol as the assistant surfactant. The above-mentioned three matters are sufficiently admixed with water in a certain ratio until a transparent emulsion C is formed. Some C is used to solubilize A ($ZrOCl_2$ + 3%mol $Y(NO_3)_3$) and other C solubilizes B (ammonia). The two resultant mixtures are dispersed respectively into an oil phase F. Thus, two stable water/oil microemulsions D and E are obtained. Microdroplets in D and E are spherical shape with minute diameters: 10–100 nm and their sizes can be adjusted artificially. If D and E are mixed effectively, the water phase solubilized in the droplets is a good medium for the certain reaction when the microdroplets collide each other. Thus, the different reactants in different water nuclei exchange each other and the reaction takes place. Since the reactants are limited in the dispersed nanoscale water nuclei, it is a precondition to accomplish the potential reaction that the reactants exchange via colliding between two water nuclei [8,9]. Instant dimer G can be formed while the droplets collide each other. The instant dimmer provides water channel for the two droplets to exchange reactants at this moment. The formation of instant dimer changes the shape of surfactant membrane, so it has high energy and will separate in a very short time. Just during the uninterrupted combination and separation, the reaction takes place and then molecules engender. Several molecules aggregate as a nucleus, which accelerates the reaction as a catalyst. More and more resultant molecules adhere on the nucleus to form a particle at last. Such process is named as autocatalysis. Since the nucleus grows only in the microwater droplets of microemulsion and the droplets have a certain shape and size, the shape and size of resultant particles are determined by the water droplets. All of the resultant deposition is almost consisted of single particle spherical zirconium hydroxide. After washing, filtering, calcinations, and so on, ultrafine spherical zirconia powder with excellent dispersibility is obtained.

2.2. Determination of oil/water/surfactant (including assistant surfactant) ternary phase diagram

When the oil phase, water phase, and surfactant are mixed together in an appropriate ratio, a stable microemulsion in thermodynamics will form spontaneously without any impressed energy. In order to acquire the solubilization capability of such system on the water phase, the oil/water/surfactant phase graph is studied. In this experiment, the content of oil phase (cyclohexane) is certain, the content of surfactant (Triton X-100 + hexyl alcohol) changes gradually. The water phase ($ZrOCl_2$) + 3 mol% $Y(NO_3)_3$ and 25 wt.% ammonia is titrated into the system via micropipette. As a result, the ternary phase graph is acquired as shown in Fig. 2. It can be seen that microemulsion can be obtained in the enclosed area. The symbol asterisk (∗) refers to the adopted data in the experiment.

2.3. Powder preparation

In the room temperature, $ZrOCl_2{\cdot}8H_2O$ and $Y(NO_3)_3{\cdot}6H_2O$ are confected into a 1.0 mol/l precursor solution

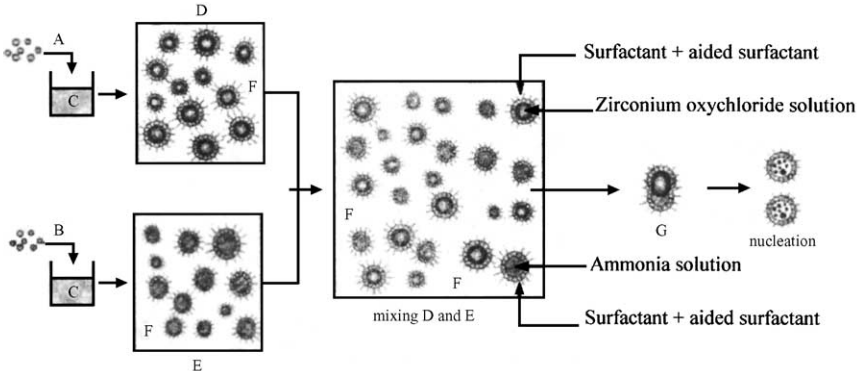

Fig. 1. The mechanism of the reaction in the microemulsion system. A, zirconium oxychloride; B, ammonia water; C, cyclohexane + surfactant + aided surfactant; D, reverse micelles aqueous ammonia solution; F, cyclohexane; G, instant dimer.

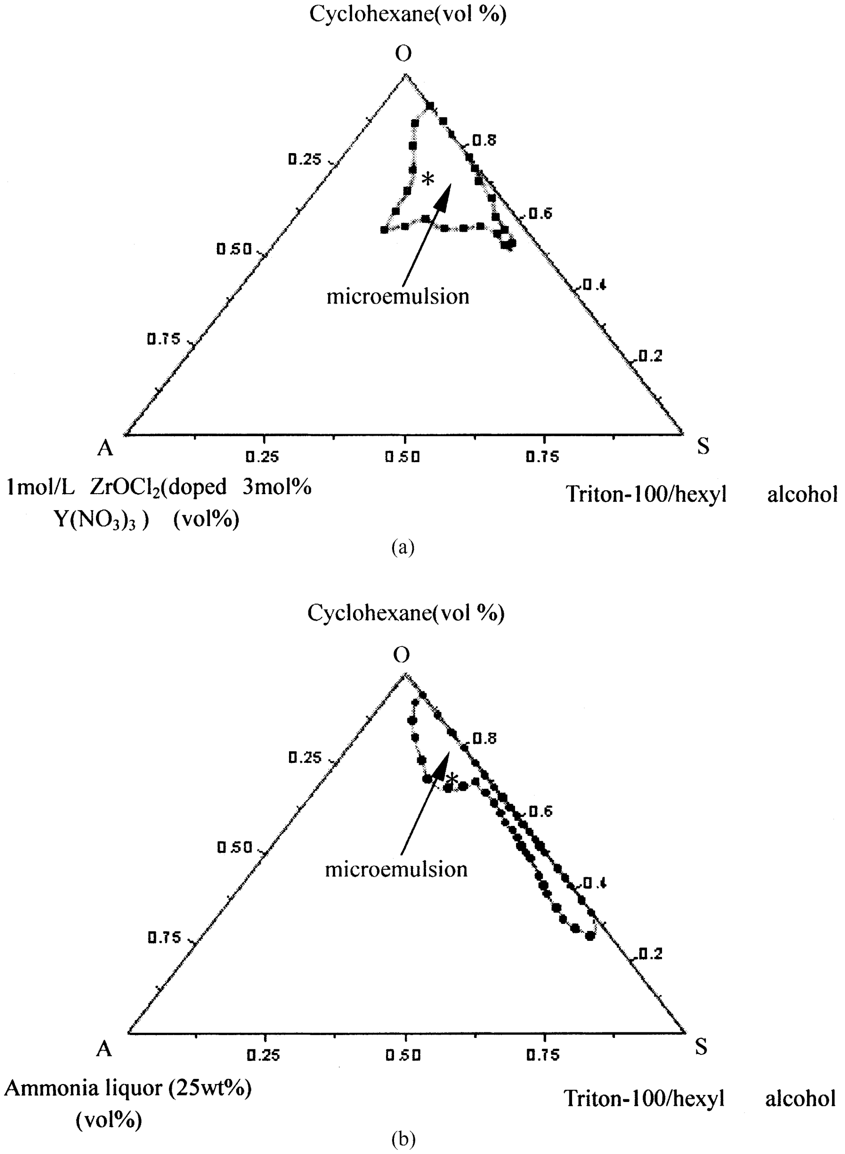

Fig. 2. Ternary phase diagrams established at room temperature for the systems consisting of oil phase (cyclohexane), as well as surfactants (Triton X-100 + hexyl alcohol) and various aqueous solution: (a) oil/surfactant/zirconium oxychloride solution (1 mol/l); (b) oil/surfactant/aqueous ammonia solution (25 wt.%).

according to the ratio of 3 mol% yttria. Then, some other minute assistants are added into the solution. Since the resultant system is a uniform water solution, $ZrOCl_2·8H_2O$ and $Y(NO_3)_3·6H_2O$ can be mixed uniformly in a molecular scale.

The oil phase solution is prepared with cyclohexane as the oil phase, Triton X-100 as the surfactant, and hexyl alcohol as the assistant surfactant in the sequential volume ratio 77/13/10. The zirconium (yttrium) salt solution and ammonia are added into the oil phase solution, respectively. Two colorless transparent microemulsions C and D are obtained after a slight shake. Each 50 ml of C and D is stirred together via a magnetic stirrer for 5 min. Then, the mixture is heated to 70–80 °C and the gel of $Zr(OH)_4$ is acquired after reflux process. The gel is washed with 99.5 vol.% alcohol repeatedly until no Cl^- can be detected out with $AgNO_3$ solution. Next, a filtering process on the gel is taken in the vacuum. After that, the gel is dried in an oven under 100 °C for 12 h. The dried gel is calcinated separately under 400, 450, 500, 550, 600, 650, 700, 800 °C for 1 h. As the result, different ultrafine zirconia powders are obtained finally.

2.4. Powder specification

Powder granularity analysis is taken with BI-XDC Granularity Analyzer of Brookhaven Cooperation, USA; powder phase composition is detected by D/max-RB high power polycrystal X-ray Diffractometer of Japan; powder's pattern and surface state are observed by JEM-200CX TEM of JEOL Corporation, Japan; powder specific area is measured by Nova 4000 Seris Specific Area Analyzer of Quantachrome Instruments Corporation; powder's zeta potential in aqueous suspension is measured by ZetaPlus-Meter of Brookhaven Cooperation; electric conductivity of free ion is measured by digital conductivity gauge (model DDS-11A_T, Shanghai Rex Instruments Factory, China); the infinitesimal organic remainings on powder surface is detected by Raman Spectrometer Model RM2000 of RENISHAW Cooperation, UK; Modular Compact Rheometer (Model MCR300, Germany) is adopted to analyze rheological properties of the zirconia aqueous suspensions.

3. Experimental results and analysis

3.1. Powder size distribution and pattern feature

The size distribution of the powder calcined under 800 °C is shown in Fig. 3. It can be seen that the zirconia powder prepared by the method of microemulsion is very fine up to nanoscale. And its size distribution graph has only a single peak. It is just because the reaction proceeds in the microdroplets and the $Zr(OH)_4$ gel obtained is almost entirely consisted of single particles, which has a minute diameter determined by the growth of the nucleus. However, it is necessary to say that because water is adopted as the dispersed medium during the light diffraction measuring and nanoscale powder will conglobate in water. Therefore, the granular diameter as the measured result of the experiment is greater than its actual value in fact.

The pattern feature and size of the powder observed by TEM are shown in Fig. 4. The granular diameter is small and uniform almost without any conglobation. The granular size is about 30–40 nm. From its X-ray diffraction spectra (Fig. 5), the diffraction peaks of (1 0 1), (1 1 2), and (2 0 2) crystal planes are taken out to be analyzed with the following Scherrer formula: $D_{hkl} = 0.89\lambda/\beta_{hkl}\cos\theta$. Thus, the granular size is calculated by the above formula and the acquired average value is 31 nm. On the other hand, by BET method, the specific area of the powder is obtained as 33.13 m^2/g. According to this datum, the granular size of the powder is calculated as 28 nm by formula $d = 6/A_s\rho$. It can be seen that the three resultant granular sizes gotten from TEM, XRD, and BET are concordant almost entirely.

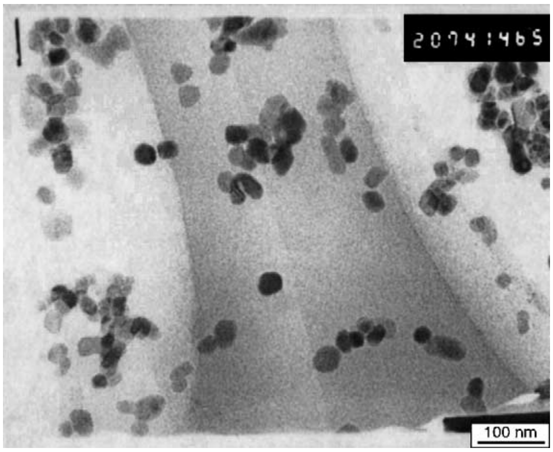

Fig. 4. TEM micrograph of the zirconia powder calcined at 800 °C (100,000×).

3.2. Charged behavior of the zirconia powder in aqueous suspensions

The stability of the zirconia aqueous suspensions is closely related to the charged behavior of the zirconia powder in water. The powder with high surface zeta potential is comparatively easy to stably disperse and suspend because of its high surface charge density and the followed strong repulsive force between particles. Fig. 6 is the zeta potential curves of the zirconia powders calcined at 600 and 800 °C, respectively. It can be seen that the isoelectric point of the powders is about at pH 6. When pH is 2–3.3, the positive zeta potential is largest. While pH 9–11 corresponds to the

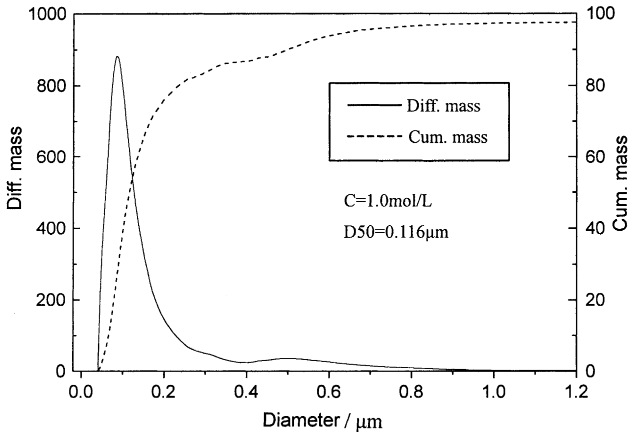

Fig. 3. The result of diameter measurements. *C*, concentration of aqueous zirconium oxychloride solution; calcination temperature: 800 °C.

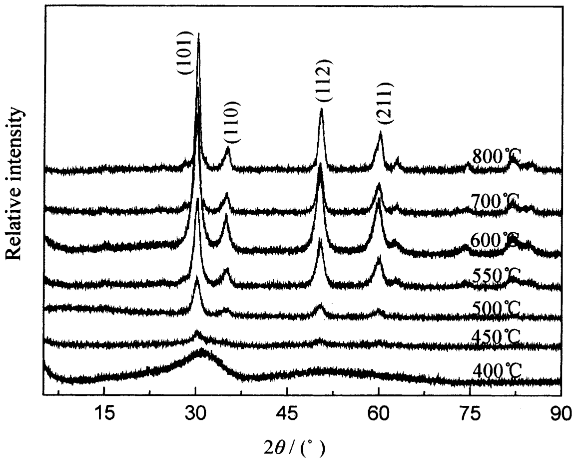

Fig. 5. X-ray patterns of the powders under different calcination temperatures.

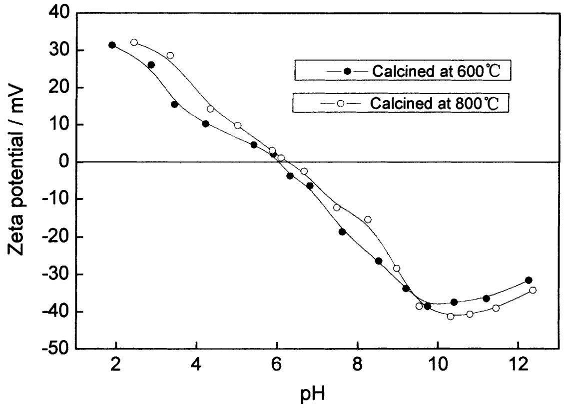

Fig. 6. Zeta potential curves of the zirconia powders calcined at different temperatures.

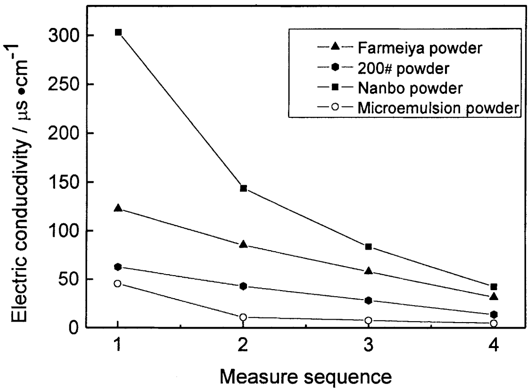

Fig. 8. Electric conductivities of centrifuged clear liquid from several zirconia powder thin suspensions.

largest negative zeta potential. The above result is roughly in accordance with that of the reference [13]. From the graph, we should notice another phenomenon that in both acidic and basic condition the absolute value of zeta potential of the powder calcined at 800 °C is larger than that of power calcined at 600 °C, but the isoelectric point of these two kinds of powers is nearly the same. The explanation for this phenomenon is that the organic substances, such as cyclohexane and Triton X-100, used in powder preparation still remained in paucity in the powders calcined at 600 °C. The nanoparticles were coated with these infinitesimal remainings, which reduce the charging capacity of the particle surface. Absorbing contra-ions in the suspensions, the charged particle surface generates double layer, which gives rise to the zeta potential. The weak charging capacity owing to organic coating results in the attenuated double layer and then the reduced zeta potential. For the sample calcined at 800 °C, the organic substances on the particle surface have been nearly burnt out (showed in Fig. 7). The huge naked surface area of the ultrafine powder makes it easy to adsorb ions and other impurities in the suspension. Therefore, the charging capacity of the particle has been improved, leading to the increasing of the zeta potential. Because cyclohexane is non-polar compound and Triton X-100 is non-ionic surfactant, their infinitesimal remainings cause no shift of the isoelectric point of the powder in aqueous suspension.

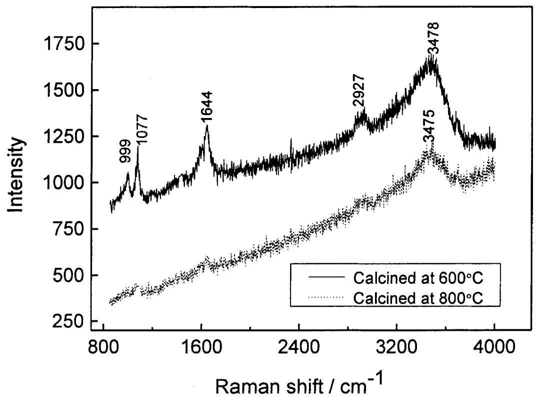

Fig. 7. Raman spectra of the zirconia powders calcined at different temperatures. Note: Raman peaks of monoclinic, tetragonal, and cubic zirconia are between 100 and 700 cm^{-1}.

3.3. *The soluble ions in the zirconia powders*

The soluble ions in aqueous suspensions is one of the important factors that affect the dispersibility of the powder. The concentration of soluble ions can be characterized by ion-specific conductivity. But in order to avoid the particle's effect on the electric conductivity in the electrical field, we measured the conductivity of the supernatant layer of the suspension after it had been centrifuged. Because only the free ions in the pregnant liquor can be separated from the ultrafine particles through centrifugation while the ions absorbed on close bed of the particle surface cannot dissolve into the pregnant liquor, the acquired conductivity can be considered as that of the free ions in powders alone. In the experiment, dilute suspensions have been prepared according to the ratio of 1 g zirconia powder to 50 ml de-ionized water and then stirred for 20 min. Then, we measure the electric conductivity of the supernatant layer subjected to centrifugation for 30 min at 4000 rpm. After the first measuring, we pour out the supernatant layer, add de-ionized water the same volume as last time, stir for 20 min, centrifuge for 30 min at 4000 rpm, and then measure the conductivity of the supernatant layer. The rest may be deduced by analogy till to the fourth time. The result is shown in Fig. 8.

It can be seen from the result that the powder prepared by microemulsion has the lower ion-specific conductivity than the other commercial zirconia powder has. This proves that the quantity of the free ions in emulsion powder is smaller than that in others. According to the noted DLVO Theory [14–16], a certain concentration of electrolyte will elevate the zeta potential and be in favor of dispersibility. Whereas if the electrolyte concentration is over dense and especially if the electrolyte contains more contra-ions (namely, the ions with charge opposite to that absorbed on the particles' surface), the contra-ions in diffusion layer will be squeezed to close bed, leading to thinner diffusion layer and reduced zeta potential. This can be explained by the formula of double layer effective thickness [17]:

$$\frac{1}{\kappa} = \left[\frac{\varepsilon_r \varepsilon_0 RT}{4\pi F^2 \sum_i C_i Z_i^2}\right]^{1/2}$$

In the formula, $1/\kappa$ is the effective thickness of double layer; ε_r is the dielectric constant of the suspension; ε_0 is the dielectric constant in vacuum; Z_i is the ion valency; C_i is the ion concentration; and F is the Faraday constant. The formula tells us that the effective thickness of double layer is related to the ion concentration and ion valency. The higher the ion concentration, the thinner the double layer. The higher the valency in suspension, the thinner the double layer.

According to Schulze–Hardy rule [18], the effect of ion valency on dispersibility can be visually described as following: critical ion concentration of coagulation caused by univalent, bivalent and tervalent contra-ion will decrease at the ratio of $1{:}(1/2)^6{:}(1/3)^6$, thus it can be seen that the reduction of content of the soluble contra-ions, especially the high valency contra-ions is beneficial to improve the dispersibility of the powder. For testifying the above viewpoint, content of the various ions in the powders has been analyzed in detail through the method of ion chromatograph. From the result, Table 1, we can know that the powder prepared by microemulsion has lower content of the soluble contra-ions and especially the high valency contra-ions (Ca^{2+}, Mg^{2+}) than that other commercial zirconia powders have. Therefore, we can conclude that the powder prepared by microemulsion has excellent dispersity.

3.4. Rheological properties of the zirconia aqueous suspensions

Fig. 9 gives the rheological curves of the zirconia suspensions in which the powder is prepared by microemulsion method. In the graph, logarithm coordinates is applied for the purpose of enlarging the differences between various curves. From the graph, we can find out the rheological properties of the zirconia suspensions. The characteristics of the suspension shows shear thinning when the volume fraction is less than 30%, whereas when the volume fraction exceeds 30% the suspension would also exhibit shear thinning at lower shear rate. But if the shear rate continues to be increase, the curves indicate shear thickening characteristics.

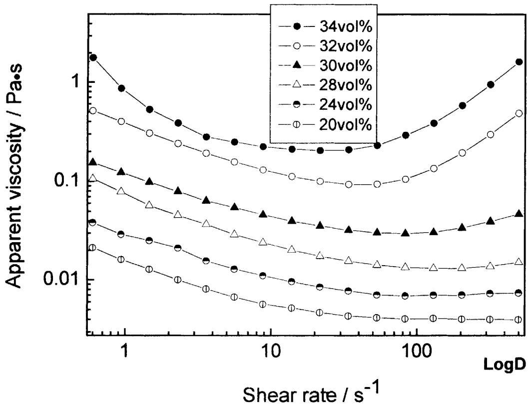

Fig. 9. The apparent viscosity of the different zirconia powders (log scale).

Furthermore, the critical shear rate from shear thinning to shear thickening is lessening with the increasing of the volume fraction. This can be explained by formation of particle clusters and its decomposition in the suspension. Because the relative viscosity represents the amount of free solvent that depends on the quantity of particle clusters, shear thinning and shear thickening actually reflects the change of particle clusters in the suspension.

In thermodynamics, the formation of particle clusters is related to potential energy determined by the distance between particles. In kinetics, the formation of particle clusters is related to the frequency of particles collision and the probability of forming clusters owing to collision. The amount of particle clusters depends on the following two factors [19]: the hetero-coagulation induced by Brownian movement and the orthokinetic coagulation induced by velocity gradient. In the static suspension there is the balance of particle clusters' formation and decomposition. At lower shear rate, particles collision induced by Brownian movement dominates the homeostasis process. Though the shear operation has increased the collision frequency induced by velocity gradient, the collision frequency induced by Brownian movement has decreased at the same time. In this state, the formation of particle clusters has been disturbed, reducing its amount of formation to less than that of decomposition. So the amount of particle clusters at stable shear state is less than that in the static suspension. Then, the solvent content encapsulated in the particle clusters reduces therefore the content of free solvent raises in the suspension. The raising of free solvent is reflected

Table 1
Content of soluble ions in several zirconia powders (μg/g)

Sample	Ion									
	K^+	Na^+	NH_4^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}
Microemulsion	24.4	22.6	65.4	<1	<1	63.4	76.9	1.5	<0.1	<0.1
200# powder	29.2	87.7	67.7	89.4	15.1	223.6	429.3	<0.1	21.2	35.2
Nano powder	73.0	173.6	178.4	136.7	13.8	140.7	2813.8	<0.1	<0.1	15.6
Farmeiya powder	69.9	218.7	152.4	95.6	8.4	143.1	1416.2	<0.1	<0.1	<0.1

through the decrease of relative viscosity (shear thinning) in macroscopy.

With the increasing of shear rate, the relative viscosity goes on decreasing. The orthokinetic coagulation induced by shear operation will continuously enhance accompanying the hetero-coagulation continuously weaken. But when the viscosity goes up to a certain value, the enhancing and weakening would reach a balance. The amount of particle clusters in the suspension is nearly a constant. The macrophenomenon at this time is that relative viscosity does not change with shear rate any more.

If shear rate keeps on increasing, the viscosity gradient will be very large in the suspension, resulting in the increasing of the collision frequency of the particles. Under the huge viscosity gradient, the formation rate of kinetics particle clusters is larger than the decomposition rate of thermodynamics particle clusters. So the total amount of particle clusters increases, and then the relative viscosity becomes larger, shear thickening appears simultaneously. For dense suspension the particles have relative higher collision frequency because of the small distance between particles, though the mentioned condition is probably at lower shear rate. The above collision frequency has gradually matched that of the thin suspension disturbed at high shear rate. As a result, the critical shear rate from shear thinning to shear thickening is relative lower for the dense suspension.

4. Conclusion

The water droplets in the microemulsion system of cyclohexane/water/Triton X-100/hexyl alcohol can act as the nanoreactors that solubilize zirconium oxychloride and ammonia, respectively. When the above-mentioned two different kinds of the reactors collide, a certain reaction will occur and ultrafine spherical zirconia powder with uniform diameter distribution can be obtained in a nanoscale and its diameter is about 30–40 nm. 100% tetragonal crystalline grain of the powder can be obtained when the calcined temperature reaches 500 °C. For the powder experienced 800 °C calcining, the organic substances on the particles has been nearly burnt out, so it has higher zeta potential than that calcined at temperature 600 °C. The powder prepared by microemulsion method has lower content of the soluble contra-ions and especially of the high valency contra-ions (Ca^{2+}, Mg^{2+}) than other commercial zirconia powders have. This is in favor of improving its dispersibility in aqueous suspension. The characteristics of the zirconia aqueous suspension shows shear thinning when the volume fraction is less than 30%. When the volume fraction exceeds 30%, it also exhibits shear thinning at lower shear rate, but if the shear rate continues to increase it will exhibits shear thickening characteristics. Furthermore, with the increasing of the volume fraction, the critical shear rate from shear thinning to shear thickening is lessening.

Acknowledgements

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