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Preparation of spherical zirconium salt particles by homogeneous precipitation

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Spherical basic zirconium sulphate particles were prepared by homogeneous precipitation in mixed solutions of zirconium sulphate and urea. Values of $[SO_4^{2-}]/[Zr^{4+}]$ and $[urea]/[Zr^{4+}]$ in starting mixed solutions and cooling rate may affect the formation of spherical particles. Complexes such as $[Zr(OH)_n]^{4-n}$ could prevent the formation and thus lead to gel precipitation. In addition, spherical particles could only be obtained in the presence of SO_4^{2-}; for NO^{3-} and Cl^-, only gel precipitation occurred.

1. Introduction

Particles of so-called "ideal ceramic powders" should be regularly shaped, of uniform size and therefore capable of being closely packed [1]. Uniformly sized spherical particles can be closely packed with a packing density of 74.05%. Barringer *et al.* [2] obtained uniformly sized zirconia particles by controlled alkoxide hydrolysis and, therefore, very close packing of the particles [3, 4]. However, the alkoxide hydrolysis process is tedious with low yield and high cost. Matijevic *et al.* [5, 6] prepared some regularly shaped oxide, hydroxide and salt particles by hydrolysing inorganic salt solutions at boiling temperatures; however, this process is also time-consuming and low yielding. Spherical particles of some hydroxides can also be obtained by homogeneous precipitation using urea, as the urea can slowly give out OH^- in solution on decomposition during heating, so the pH value may be increased very slowly and homogeneously over the whole solution [7, 8]. Spherical or even uniformly sized aluminium hydroxide was obtained by this method [8–10], which is simple, time saving and controllable. However, reports had not been found of preparing spherical particles of zirconium hydroxide or zirconium salts using this method. This paper presents the results of preparing spherical zirconium sulphate particles using homogeneous precipitation.

2. Materials and methods

The starting materials were zirconium oxychloride (chemical grade), urea (analytical grade) and ammonia (chemical grade). Zirconium sulphate (or nitrate) solution was obtained by dissolving newly precipitated zirconium hydroxide in H_2SO_4 or HNO_3 solutions. Zirconium hydroxide precipitate was prepared by adding zirconium oxychloride to ammonia solution followed by filtration and repeated washing to remove Cl^-. In a series of prepared zirconium sulphate solutions, the molecular ratios of $[SO_4^{2-}]/[Zr^{4+}]$ were 1.28, 3.00, 4.56, and 6.00 and 9.00, respectively, and for zirconium sulphate–urea mixed solutions the molecular ratios of $[urea]/[Zr^{4+}]$ were 29.2, 36.6, 43.6, 67.5 and 125, respectively, while the Zr^{4+} concentration was maintained at $0.0543 \text{ mol l}^{-1}$.

Mixed zirconium salt–urea solutions were heated in a water bath with a blender to keep the temperature homogeneous. Precipitation could be clearly observed as the bath was made of glass. Temperature control accuracy was ± 1 °C. To prevent contamination, the solution was put in a volumetric flask with a spigot which allowed gas to bubble out when the internal pressure was higher than atmospheric pressure, but prevented dust from dropping in.

At a certain holding time after the start of precipitation, the precipitated solution was cooled in air or water (room temperature was around 20 °C). The precipitates were then taken from the solutions and washed with distilled water with the help of centrifugal sedimentation. The morphology of the precipitates was observed by scanning electron microscopy (SEM, JCXA-733) and the crystallite phases by X-ray diffraction (XRD, RAX-10). Crystallite size was determined by X-ray diffraction-line broadening (XRD-LB) [11].

3. Results

3.1. Conditions for the formation of homogeneous precipitates

3.1.1. Effect of anions

Particulate precipitation could only be obtained in sulphate solution of zirconium, not in nitrate and oxychloride solutions.

3.1.2. Effect of $[SO_4^{2-}]/[Zr^{4+}]$ and $[urea]/[Zr^{4+}]$

At a certain concentration of Zr^{4+} in solution, the value of $[SO_4^{2-}]/[Zr^{4+}]$ and $[urea]/[Zr^{4+}]$ influenced the formation of particulate precipitation. Fig. 1 shows such an effect (at 85 °C). In region I, the particulate precipitation could be obtained within 30 min, and the pH value when precipitation occurred was less

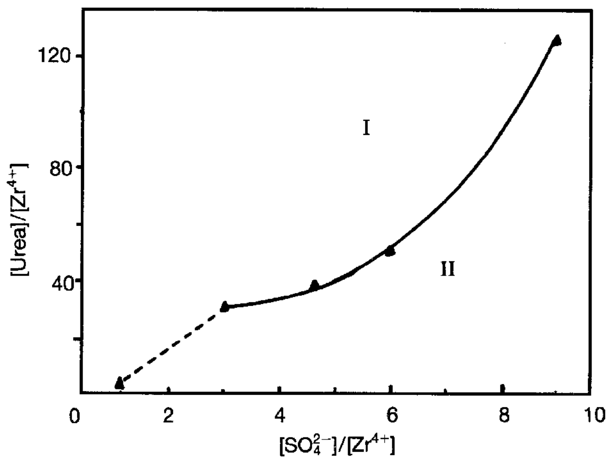


Figure 1 Formation conditions of particulate precipitation, which could form in region I, but not region II.

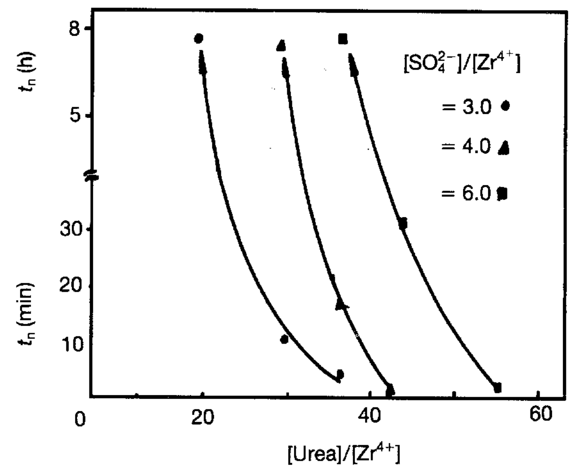


Figure 2 Time needed (t_n) for the occurrence of particulate precipitation as a function of [urea]/[Zr^{4+}].

than 1.14; in region II, only gel precipitates could be obtained when heated for more than 5 h (no precipitates formed within 5 h, and the pH value reached 7–8 when precipitation occurred).

Fig. 2 shows the effect of [urea]/[Zr^{4+}] on the time (t_n) needed for precipitation to occur at different [SO$_4^{2-}$]/[Zr^{4+}] (85 °C). At a certain [SO$_4^{2-}$]/[Zr^{4+}], when [urea]/[Zr^{4+}] was greater than a certain value, particle precipitates could be obtained within a short time (< 30 min); as [urea]/[Zr^{4+}] decreased, the time needed for precipitation increased quickly; when the [urea]/[Zr^{4+}] was less than a certain value, no particulate precipitation could be obtained. As mentioned above, in such a solution only gel precipitation occurred after heating for more than 5 h (as indicated by arrows in the figure).

3.1.3. Effect of other factors

Compared to the above two factors, others were less effective in influencing precipitation. However, if the concentrations of Zr^{4+} were too low, the precipitated particles may be too fine to be taken out with centrifugal sedimentation (4000 rev min^{-1}). In addition, heating temperature may affect the time needed for precipitation to occur: at lower temperatures more time was needed.

3.1.4. Formation of particulate precipitation during cooling

For solutions in which particulate precipitation did not occur after 30 min heating, it could still be obtained during cooling before gel precipitation. Particulate precipitation occurred when the temperature was below about 35 °C.

3.1.5. pH value for the formation of particulate precipitation

The pH value of the sulphate solution of zirconium was around 0.2, and rose to about 1.14 when urea solution was added. Particulate precipitation could be obtained in 14 min in a solution of [SO$_4^{2-}$]/[Zr^{4+}] = 4.56, and [urea]/[Zr^{4+}] = 36.6 at 85 °C. After holding for 15 min at 85 °C from the start of precipitation the solution was cooled and the pH value slightly increased with increasing time, as shown in Table I (H–P). The pH value was also measured for a solution ([urea]/[Zr^{4+}] < 30) in which particle precipitation did not occur after holding for less than 5 h, as shown in Table I (C–P).

TABLE I Change of pH value with cooling time (min)

Time (min)	0	8	18	38	80	290	Overnight
T (°C)	85	67	55	35[a]	26	21.5	18
H–P				1.00	1.15	1.22	1.30
C–P				1.09	1.18	1.32	1.34

H–P: precipitation occurred during heating at 85 °C.
C–P: Precipitation occurred during cooling to 35 °C.
[a] At this temperature pH began to be measured.

In addition, unlike particulate precipitation, once gel precipitation occurred in solution, the pH value swiftly rose to above 7.

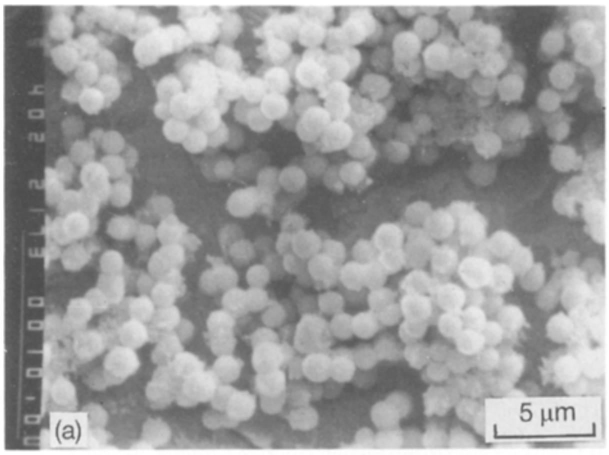
3.2. Particle morphology of precipitates

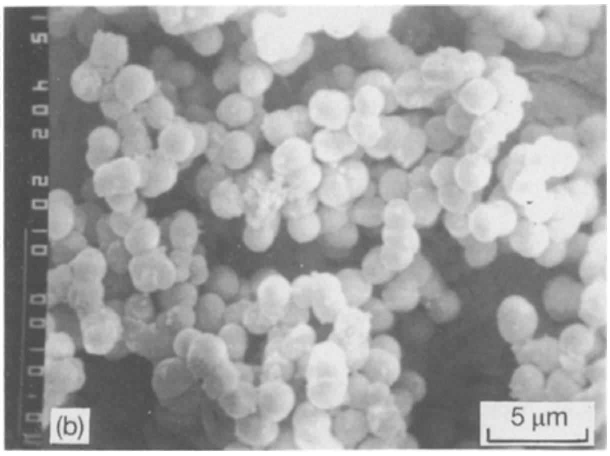
3.2.1. Effect of holding time

Particulate precipitation could be obtained in 14 min in a solution of [SO$_4^{2-}$]/[Zr^{4+}] = 4.56, and [urea]/[Zr^{4+}] = 36.6 at 85 °C. The precipitate was held at 85 °C for different times (t_h) before cooling in air. Fig. 3 shows the particle morphology (SEM) for holding for (a) 15, (b) 60 and (c) 120 min. It can be seen that, at t_h = 15 min, the relatively large spherical particles are of uniform size (primary particles), however, in addition there were many small particles (secondary particles) adhering to the spherical particles. When the holding time was increased the small particles disappeared, while the previously uniformly sized primary particles at t_h = 15 min became non-uniformly sized.

3.2.2. Effect of cooling method

During cooling in air the precipitated particles continued to grow. Fig. 4 shows the particle morphology





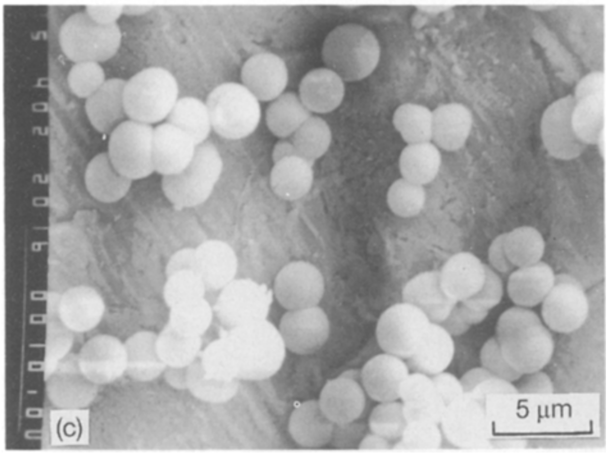


Figure 3 Morphology of particles precipitated at 85 °C for t_h = (a) 15 min, (b) 60 min, and (c) 120 min, cooled in air for 20 min.

of cooling for (a) 10, (b) 60 and (c) 120 min, for solutions of $[SO_4^{2-}]/[Zr^{4+}] = 4.56$ and $[urea]/[Zr^{4+}] = 36.6$, at 85 °C holding for 15 min from the start of precipitation. With increased cooling time, relatively large and uniformly sized primary particles became non-uniformly sized and additional very small (secondary) particles disappeared.

For solutions in which particulate precipitation did not occur after holding for less than 5 h, particulate precipitation could be obtained during cooling. Fig. 5 gives the morphology of particles yielded during cooling to 35 °C (RT = 20 °C), and after being held for 120 min from 35 to 24 °C, for solutions of $[SO_4^{2-}]/[Zr^{4+}] = 4.56$ and $[urea]/[Zr^{4+}] = 30$, and being held at 85 °C for 180 min without the occurrence of precipitation. It is clear that particles thus formed were spherical and no secondary particles formed. However, if the cooling rate was increased (e.g., secondary cooling in water at 20 °C), only very fine particles (even finer than secondary particles) were produced, some of which cannot be sedimented from the solution with centrifugal sedimentation).

3.2.3. Effect of holding temperature

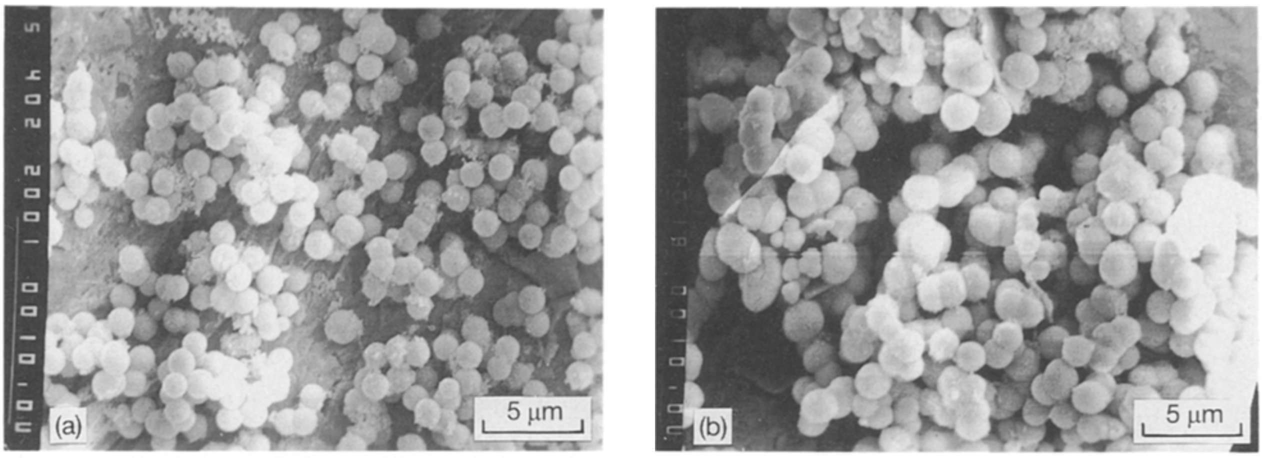
Different times (t_n) were needed for the occurrence of particulate precipitation at different heating temperatures, and heating temperature would also affect the size of precipitated particles. Fig. 6 shows the morphology of particles precipitated from the solution of $[SO_4^{2-}]/[Zr^{4+}] = 4.56$ and $[urea]/[Zr^{4+}] = 36.6$, holding at 75 °C for 15 min from the start of precipitation; the cooling times were (a) 20 min, (b) 200 min and (c) 24 h, respectively. Similar to those at 85 °C, with increased cooling time the previously uniformly sized spherical particles became non-uniformly sized and the small secondary particles disappeared.

3.3. Chemical and thermal analysis of precipitates

Table II gives the chemical and thermal analysis of the particle precipitates. In addition to ZrO_2 and H_2O there was some SO_4^{2-} (CO_3^{2-} was negligible). The presence of SO_4^{2-} altered the pH value at which precipitation began. The pH value for the occurrence of the particle precipitates was less than 1.1; however, that for $ZrO(OH)_2$ precipitation is 1.91 at $[Zr^{4+}] = 0.0534\ \mathrm{mol\,l^{-1}}$.

Fig. 7 shows the DTA-TG (differential thermal analysis–thermal gravity) spectra of (a) particulate and (b) gel precipitates. It can be seen that there were two weight loss steps (correspondingly two endothermal peaks) during heating for particulate precipitation: one at the lower temperature (~ 200 °C) corresponds to the evaporation and decomposition of water and/or OH^- groups, and the other at the higher temperature (740–750 °C) is for the decomposition of SO_4^{2-} (the weight loss at 746 °C was approximately equal to the amount of SO_3 given by chemical analysis). For gel precipitation, weight loss was basically completed before 300 °C with only one endothermal peak (the exothermal peak at 438 °C corresponds to the phase transformation of zirconia from the monoclinic to the tetragonal phase). Besides, the total weight loss of gel precipitate was less than 25%, while that of particulate precipitation reached 45%. So the gel precipitate was zirconium hydroxide without SO_4^{2-} involved in the precipitate. In addition, homogeneous precipitation of zirconium nitrate and oxychloride with urea also yielded hydroxide gel.

SO_4^{2-} was involved in particulate precipitation, and from the data given in Table II and Fig. 7a, the particle precipitate was inferred to be a basic



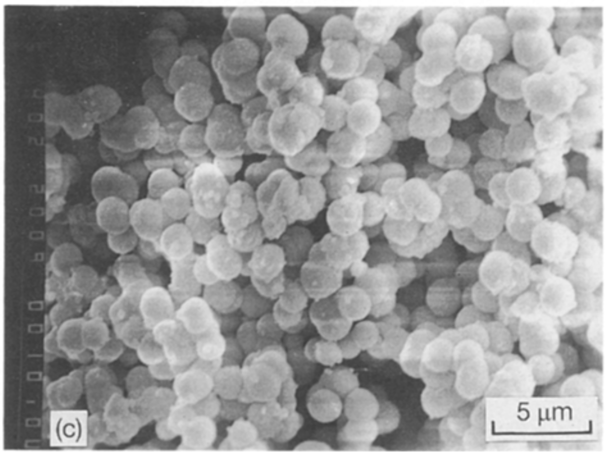


Figure 4 Morphology of particles precipitated at 85 °C for $t_h = 15$ min, cooled in air for (a) 10 min, (b) 60 min and (c) 120 min.

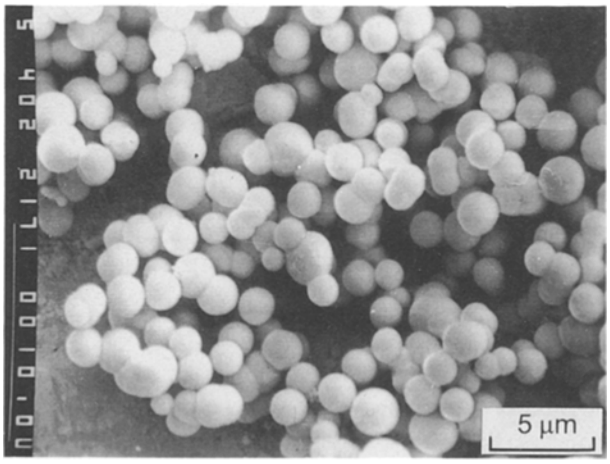


Figure 5 Morphology of particles formed during cooling to about 35 °C in air.

zirconium sulphate as follows

$$Zr_2(SO_4)(OH)_6 \cdot 6H_2O \qquad (1)$$

or

$$Zr_2O_2(OH)_2(SO_4) \cdot 6H_2O. \qquad (2)$$

The sulphur and ZrO_2 contents in the above formulae are 7.16% and 55.0%, respectively, in agreement with the data of thermal gravity analysis, but a little different from that given by chemical analysis, as lengthy drying occurred before chemical analysis was performed, leading to the evaporation of some water.

4. Discussion

4.1. Concentration conditions for particulate precipitation

From formula (1), at the precipitation equilibrium

$$[Zr^{4+}][OH^-]^3[SO_4^{2-}]^{1/2} = K_a \qquad (3)$$

At a certain temperature, K_a (equilibrium constant) is a constant. As $[Zr^{4+}]$ was fixed in this study, $[OH^-]$ and $[SO_4^{2-}]$ were the factors affecting precipitation. As $[\text{urea}]/[Zr^{4+}]$ is increased, formula (3) can be satisfied more easily since urea gives OH^- on heating. In addition, as SO_4^{2-} was introduced as H_2SO_4, for $[H^+] = 2[SO_4^{2-}]$, and $[OH^-] = 10^{-14}[H^+]^{-1}$ (25 °C, 1 atm), so before the decomposition of urea

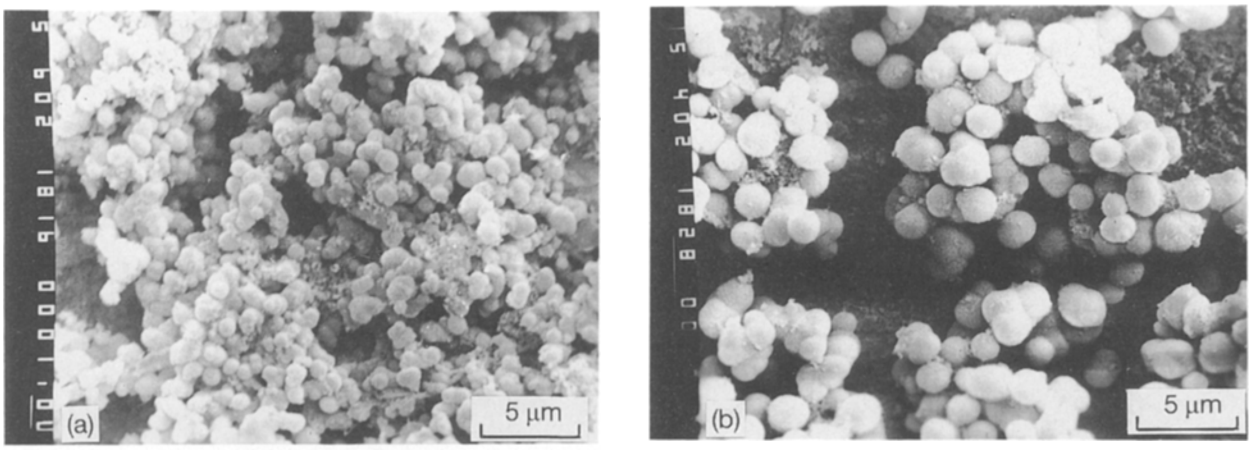
$$[Zr^{4+}][OH^-]^3[SO_4^{2-}]^{1/2} = \times 1.25 \times 10^{-41}[Zr^{4+}][SO_4^{2-}]^{-5/2} \qquad (4)$$

So, as $[SO_4^{2-}]/[Zr^{4+}]$ increases, precipitation is less likely to take place. For higher $[SO_4^{2-}]/[Zr^{4+}]$, particulate precipitation could be obtained at much higher $[\text{urea}]/[Zr^{4+}]$.

As $[Zr^{4+}] = 0.0534$ mol l^{-1} $[SO_4^{2-}] = 0.0534 \times 4.56 = 0.245$ mol l^{-1} and the pH value at the beginning of precipitation is 1.14, so K_a is calculated to be $10^{-40.2}$ (85 °C).

During cooling, K_a decreased with the decrease in temperature, so if particulate precipitation did not occur during holding, it could still occur during cooling. When cooling slowly, the degree of oversaturation of the mixed solution was low with less nucleate formed, so particles could grow larger; conversely, if the cooling rate was too high (e.g., in water-cooling), the degree of oversaturation was high with a high concentration of nucleate formed (through lowering the concentration of $[Zr^{4+}]$), so particles would not grow fully.

This reasoning can be used to explain the formation of fine secondary particles adhered to uniformly sized primary particles. As shown in Figs 3a and 4a, if the holding time (t_h) and cooling time were too short, and the solution temperature and $[Zr^{4+}]$ and $[SO_4^{2-}]$ was relatively high, the temperature drop might be large



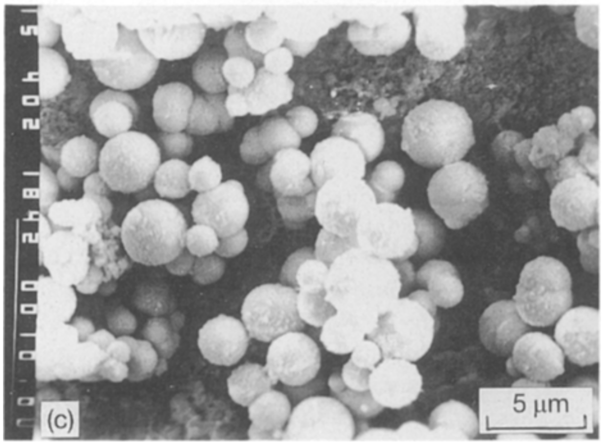


Figure 6 Morphology of particles precipitated at 75 °C for 15 min and cooled for (a) 20 min, (b) 200 min, and (c) 24 h.

TABLE II Results of chemical analysis (CA) and thermal gravity analysis (TG) of particulate precipitates

Component		ZrO_2	S	C	H_2O	Σ
Content	CA		7.85	0.54		
(wt %)	TG	55.0	7.76		23.5	98.5

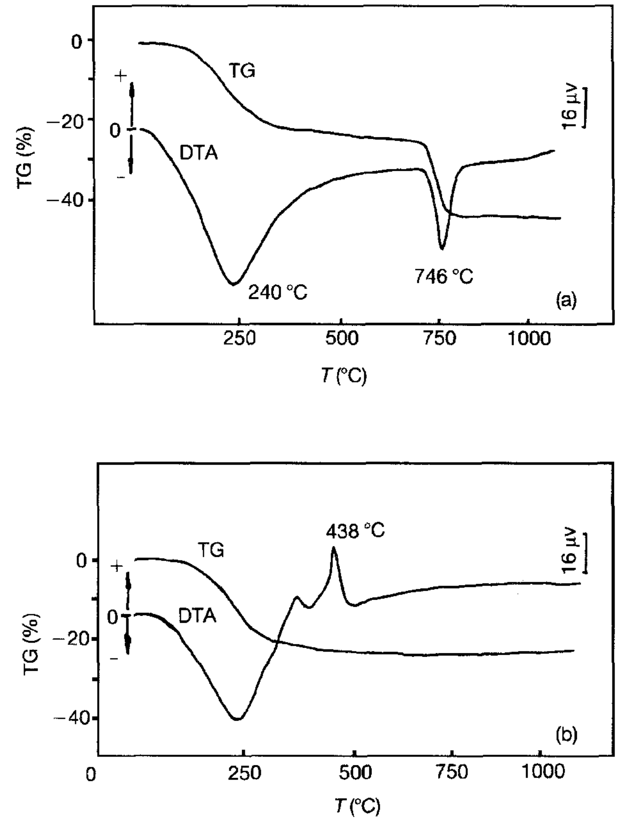


Figure 7 Thermal decomposition behaviour (DTA-TG) of (a) particulate precipitate and (b) gel precipitate.

during centrifugal sedimentation, and the system would easily reach the nucelation limit again, resulting in secondary particle formation in addition to the previously formed uniformly sized primary particles which resulted from the first nucleation during holding [10]. If the holding time was increased substantially, or the precipitate was cooled in air for long enough, the uniformly sized spherical particles could grow larger by consuming Zr^{4+} and other ions; during centrifugal sedimentation the nucleation limit might not be reached so no secondary particles formed, as shown in Figs 3b, c, and 4b, c.

The mechanism of formation of uniformly sized spherical particles of basic zirconium sulphate during homogeneous precipitation is that the solution only yields one burst of nuclei (the nucleation limit was reached only once), the same as that of aluminium hydroxide particles discussed in a previous paper [10].

4.2. Formation of gel precipitation

According to Equation 3, lengthy heating would result in particulate precipitation in spite of different $[SO_4^{2-}]/[Zr^{4+}]$ and $[urea]/[Zr^{4+}]$; however, as indicated above, in some conditions gel precipitate would form instead of particle precipitates. This phenomenon might result from the formation of a series of complexes $[Zr(OH)_n]^{4-n}$ ($n = 1, 2, 3$). Under certain conditions, if Equation 3 can be satisfied in a short time, particulate precipitation will occur. In contrast, under other conditions Equation 3 cannot be satisfied, while the complexes might form by consuming Zr^{4+} and OH^- in solutions, thus lowering the concentration of free Zr^{4+} and OH^- in solutions and preventing the formation of particulate precipitation. In these solutions zirconium hydroxide precipitation would form after lengthy heating when $[OH^-]$

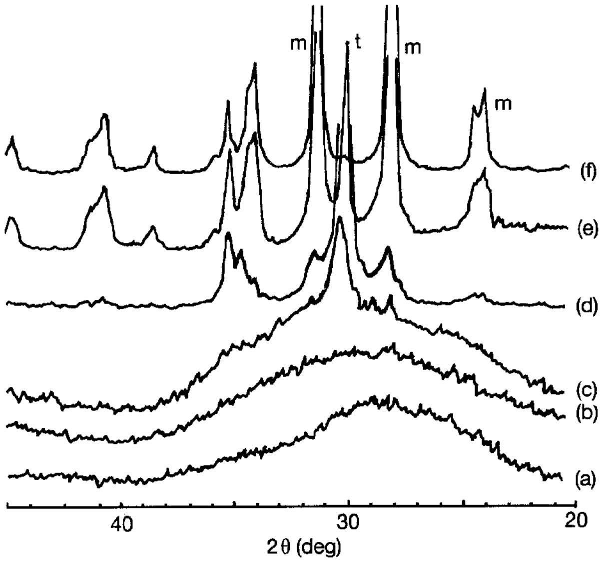


Figure 8 XRD spectra for particulate precipitate (a) and calcined powders at (b) 420, (c) 500, (d) 600, (e) 700 and (f) 800 °C.

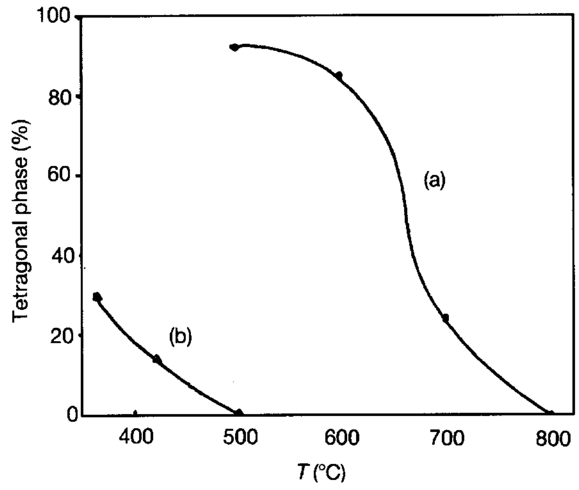


Figure 9 Content of tetragonal zirconia in calcined powders of (a) particulate and (b) gel precipitates as a function of calcining temperature.

reaches the nucleation limit of zirconium hydroxides. On gel precipitation, the pH value swiftly increased to above 7, much higher than that (1.91 for $[Zr^{4+}] = 0.0534 \text{ mol l}^{-1}$) for the occurrence of hydroxide precipitation.

The effect of anions on spherical particulate precipitation is similar to that on aluminium hydroxide particles, which has been discussed elsewhere [10].

4.3. Phase transformation behaviour during decomposition

Tetragonal zirconia particles can exist at room temperature as a metastable phase because of its lower surface tension than the monoclinic [12]; on heating the tetragonal crystallites grow larger and the tetragonal phase will transform to the monoclinic. Fig. 8 shows XRD spectra for powders after calcining particulate precipitates at various temperatures for 25 min. At $\leqslant 500$ °C the powder was amorphous as decomposition of SO_4^{2-} had not taken place. With the decomposition of SO_4^{2-} at elevated temperatures, tetragonal (or, possibly, cubic) zirconia began to form and at about 800 °C transformed to the monoclinic phase. Unlike the particulate precipitates, the gel precipitates crystallize out at lower temperatures (< 400 °C) and the monoclinic phase occurs even on crystallization, as shown in Fig. 9. Fig. 10 shows the temperature-dependence of crystallite size of the two kinds of precipitates. It can be seen that the critical size [13] of the phase transformation from tetragonal to monoclinic was 35 nm and less than 20 nm for particulate and gel precipitates, respectively. Lower phase transformation temperatures and critical size of gel precipitates may result from the effect of water vapour during decomposition of zirconium hydroxide, which is believed to lower the surface tension difference between the tetragonal and monoclinic phases [13] and therefore promote the phase transformation.

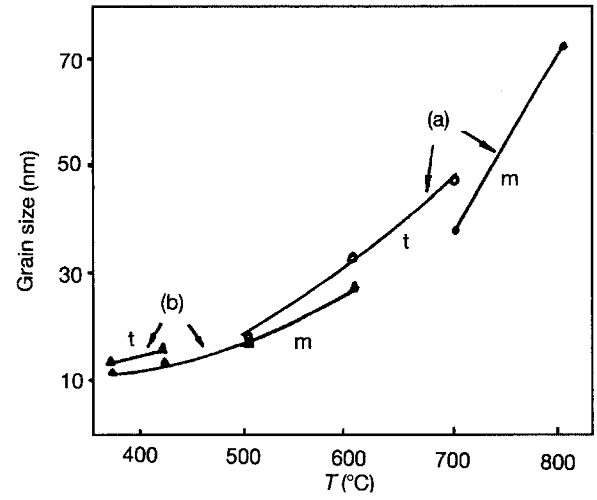


Figure 10 Temperature dependence of crystallite size of calcined powders of (a) particulate and (b) gel precipitates "t", tetragonal phase; "m", monoclinic phase.

5. Conclusions

1. Spherical basic zirconium sulphate particles were obtained by homogeneous precipitation through controlling $[SO_4^{2-}]/[Zr^{4+}]$ and $[\text{urea}]/[Zr^{4+}]$, and the cooling method. The precipitates were $Zr_2(SO_4)(OH)_6 \cdot 6H_2O$ or $Zr_2O_2(OH)_2(SO_4) \cdot 6H_2O$.
2. Uniformly sized spherical primary particles formed during temperature holding but much finer secondary particles may occur during cooling. The formation of uniformly sized primary particles was the result of first nucleation and that of secondary particles resulted from secondary nucleation during cooling.
3. $[Zr(OH)_n]^{4-n}$ complexes in the mixed solutions could prevent the formation of particulate precipitation and lead to the formation of gel hydroxide precipitation.
4. Spherical particles could only be obtained in the presence of SO_4^{2-}, and not with NO_3^- and Cl^-.

References

1. E. A. BARRINGER and H. K. BOWEN, *Ceram. Eng. Sci. Proc.* **5** (1984) 295.
2. *Idem., J. Amer. Ceram. Soc.* **65** (1982) c-199.

3. B. FELEY, Jr., E. A. BARRINGER and H. K. BOWEN, *ibid.* **67** (1984) c-133.
4. B. FELEY, Jr., P. WHITE and H. K. BOWEN, *Amer. Ceram. Soc. Bull.* **64** (1985) 1115.
5. E. MATIJIVIC, *Ann. Rev. Mater. Sci.* **15** (1985) 483.
6. R. BRACE and E. MATIJIVEC, *J. Inorg. Nulc. Chem.* **35** (1975) 3691.
7. L. GORDON, M. L. SALUTSKY and H. N. WILLARD, "Precipitation from Homogeneous Solution" (Wiley, New York, 1959).
8. J. E. BLENDELL, H. K. BOWEN and R. L. COBLE, *Amer. Ceram. Soc. Bull.* **63** (1984) 797.
9. M. D. SACKS, T. Y. TSENG and S. Y. LEE, *ibid.* **63** (1984) 301.
10. J. L. SHI, J. H. GAO and Z. X. LIN, *Solid State Ionics* **32/33** (1989) 537.
11. J. L. SHI, Z. X. LIN and T. S. YEN, *Ceram. Int.* **18** (1992) 155.
12. G. C. GARVIE, *J. Phys. Chem.* **69** (1965) 1238.
13. Y. MURASE AND E. KATO, *J. Am. Ceram. Soc.* **66** (1983) 196.

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