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Estimation of formation mechanism of spherical fine ZrO_2–SiO_2 particles by ultrasonic spray pyrolysis

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Spherical fine ZrO_2–SiO_2 (1 : 1) particles were synthesized from a hydrolysed mix-solution of $Si(OC_2H_5)_4$ and $ZrOCl_2 \cdot 8H_2O$ by ultrasonic spray pyrolysis, and the formation mechanism of the particles discussed. All of the resultant particles identified as t-ZrO_2 and amorphous SiO_2 with an atomic order dispersion were spherical, and mainly of diameter 0.8 to 1.0 μm. It was estimated that the three-dimensional ladder siloxane chains containing an equimolar Zr^{4+} homogeneously dispersed were formed by hydrolysis, and an atomized droplet itself converted into an isolated ZrO_2–SiO_2 (1 : 1) particle without aggregation.

1. Introduction

Ultrasonic spray pyrolysis is one of the useful techniques for synthesis of fine particles of oxides or multi-component oxides. The technique is that the small droplets of the mother solution are atomized by an ultrasonic mist generator, immediately dried, decomposed, and oxidized by passing through a few furnaces maintained at different temperatures. The technical features of the method are that the complex oxides are easily produced from the mix-solution of multi-component metal salts; the diamter of the oxide particle is primarily determined by controlling the concentration of the mother solution, and aggregation of fine particles during evaporation and decomposition is hindered.

In the preparation of $CoLaO_3$ catalyst fine particles by this method, Imai *et al.* [1, 2] revealed that the particles were spherical (0.4–1 μm), porous, and consisted of a network of hollows. The specific surface area of the particles was found to increase by the addition of reagents such as NH_4Cl and polyvinyl alcohol, where these reagents operate to reform the deposition of the finer particles during drying, and to prevent the sintering of the ultra fine particles in the pyrolysis.

In their study of powder synthesis using this method, the group of Kato and Mizutani reported the synthesis of the Y_2O_3-stabilized ZrO_2 powders with a mean diameter of about 0.24 μm [3]. Spherical and uniform ZnO particles having a mean size of 0.15 μm were obtained [4], and spherical fine particles of SiO_2 were prepared from a partially hydrolysed tetra-ethyl-ortho-silicate (TEOS) solution catalysed with NH_4OH [5].

Kamiya *et al.* [6] reported the details of the preparation of glass fibres of the ZrO_2–SiO_2 system from metal alkoxides of $Zr(OC_3H_7)_4$ and TEOS, and discussed the formation mechanism of metaloxane chains and two- or three-dimensional network polymers produced by the hydrolysis of the metal alkoxides.

Ono *et al.* [7] investigated ultrafine particles of the ZrO_2–SiO_2 system produced by the spray ICP (inductively coupled plasma) in relation to particle growth and phase change induced by heat treatment, where the resultant powders were composed of roundish ultrafine particles 10 to 20 nm in size, and their components were tetragonal ZrO_2 (t-ZrO_2) and amorphous SiO_2 (a-SiO_2).

In the preparation of glass ceramics of the ZrO_2–SiO_2 system by the sol–gel process from metal alkoxides, Nogami [8] investigated the crystal growth of ZrO_2 and crystallite size dependence of the t- to m-ZrO_2 transformation.

We reported in a previous paper [9] that the spherical fine ZrO_2–SiO_2 (1 : 1) particles being of equimolar composite were mono-dispersively obtained by ultrasonic spray pyrolysis from the mix-solution of the $ZrOCl_2 \cdot 8H_2O$(ZOC), TEOS, C_2H_5OH and H_2O system. Furthermore, TEM observation revealed that the inner particles were homogeneous, no matter what size the particle diameter, without forming a hollow structure. In the present work, the characterization and formation mechanism of equimolar ZrO_2–SiO_2 particles produced by this method and the mutual interaction between ZrO_2 and SiO_2 in the powders were investigated.

2. Experimental procedure

The details of the apparatus for ultrasonic spray pyrolysis preparation and the procedure for the preparation of the atomized mother solution were described in the previous paper [9].

The equimolar solution of ZOC dissolved in hot C_2H_5OH and TEOS was mixed by magnetic stirrer agitation at room temperature and four parts of

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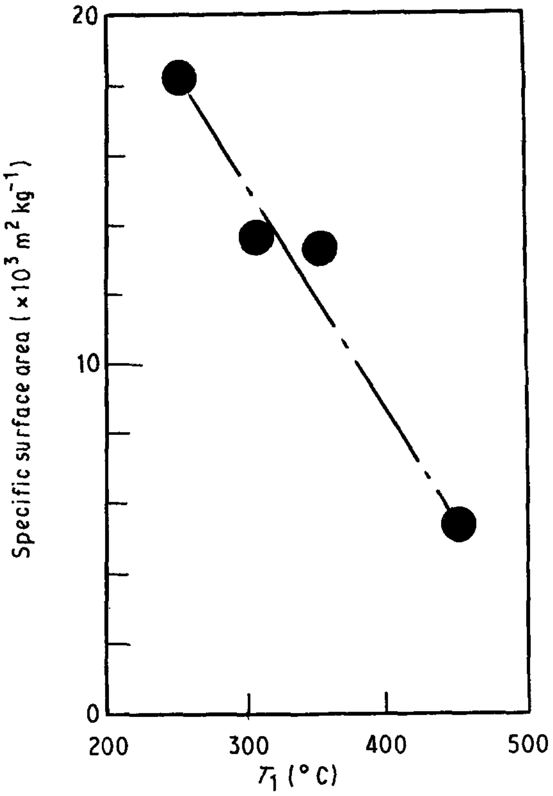

Figure 1 Variation of specific surface of ZrO_2–SiO_2 particles plotted against furnace temperature T_1 (T_2 = 900° C).

distilled water (the molar ratio of H_2O to ZOC and TEOS, r = 288) were added in order to advance the formation reaction of metalosiloxane polymer which was assumed to be composed of siloxane polymer and Zr^{4+}. The mother solution prepared as above was then atomized by an ultrasonic vibrator, and introduced successively into two furnaces (low temperature T_1, high temperature T_2), with nitrogen and oxygen carrier gases, at a flow rate of 3 cm^3 sec^{-1}, wherein the exhaust gas was aspirated. The resultant particles were collected by a CH_3OH trap, where the alcohol was agitated by the magnetic stirrer in order to improve the collection efficiency. The particles were subjected to specific surface area measurement by BET nitrogen adsorption technique, X-ray powder diffraction (XRD) pattern and infrared absorption spectra (FT-IR) using the photo acoustic method without KBr mixing. The geometrical characteristics were examined directly by using SEM operated at 25 or 10 kV and TEM.

3. Results and discussion

3.1. Particle characterization

Fig. 1 shows the variation of specific surface area of ZrO_2–SiO_2 (1 : 1) particles plotted against T_1. T_2 was maintained at 900° C. The specific surface area gradually decreased with an increase of temperature, this decrease was elucidated by the SEM observation shown in Fig. 2 pictured at an accelerating voltage 10 kV in order to observe the surface state of the particles. Fig. 2 indicates that the surface state of particles prepared at a lower temperature was very rough, whilst those prepared at higher temperatures had smooth surfaces. Therefore, the decrease of specific surface area was ascribed to the shrinkage of the particles and the lowering of surface roughness, these phenomena occurring simultaneously. This means that the migration of a surface atom took place in the direction in which the surface free energy was minimized under the thermal-equilibrium state (by Wulff's principle).

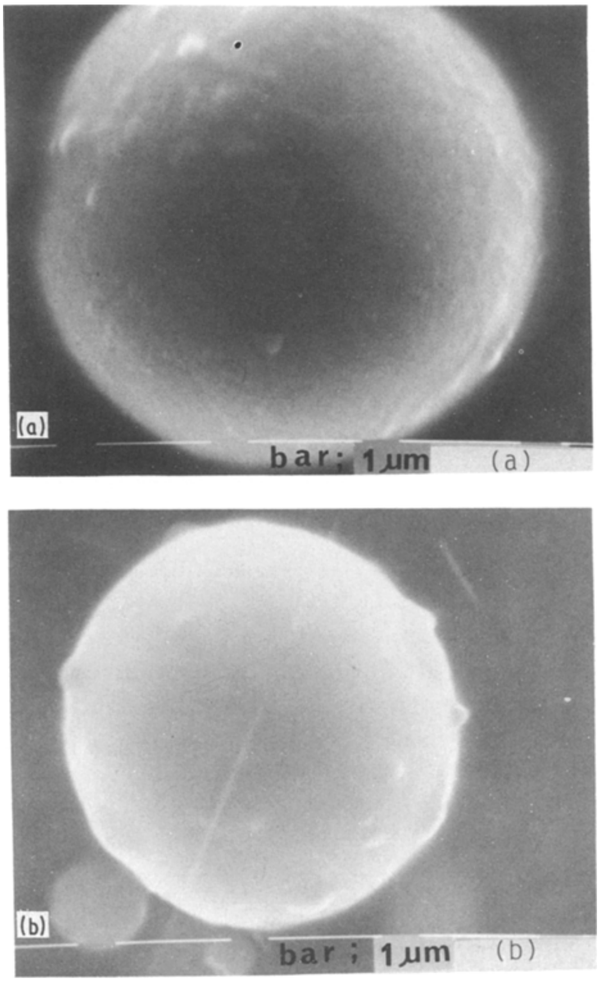

Figure 2 SEM microphotographs of ZrO_2–SiO_2 particles prepared at (a) T_1 = 250° C, T_2 = 900° C, (b) T_1 = 350° C, T_2 = 900° C.

Additionally, we can see as spots the small volcano-like projections formed by the effluent gas emitted from an inner part of the particles.

In the preparation of $CoLaO_3$ catalyst fine particles by pyrolysis, Imai *et al.* reported that the BET specific surface area of the resultant particles decreased with an increase of the furnace temperature, corresponding to T_1 of our work, set for the decomposition of the mixed metal salts [1]. Therefore, we expected that the specific surface area of the resultant particles was strongly affected by the furnace temperature set for the thermal decomposition, namely the lower temperature furnace, which was perhaps related to the effluent velocity of the gas emitted from the inner part of the particles. On the other hand, the high temperature furnace is perhaps concerned mainly with the crystallization of the particles and/or ordering of bond length.

Fig. 3 shows the representative particle size distribution calculated from SEM photographs (T_1 = 350° C, T_2 = 900° C). The inset in Fig. 3 shows the maximum and minimum diameters of prepared particles

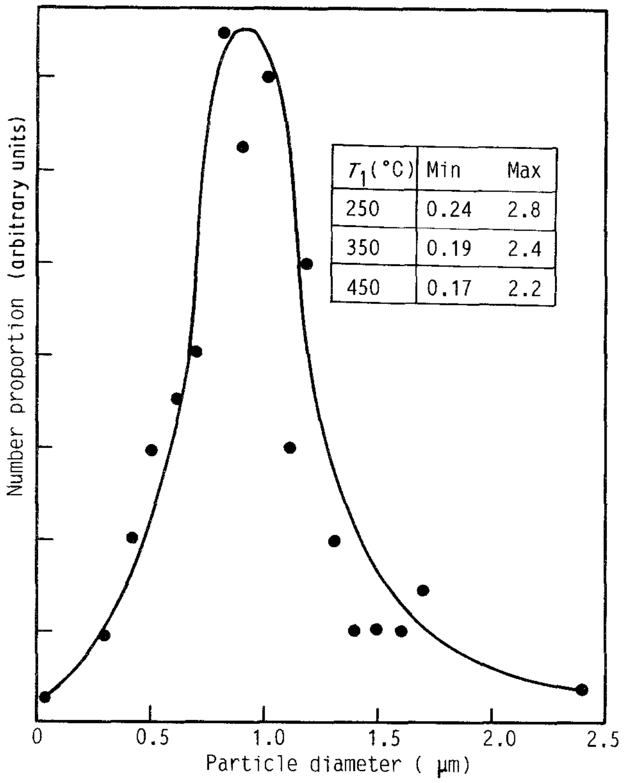

Figure 3 Particle size distribution of ZrO_2–SiO_2 particles. T_1 = 350° C, T_2 = 900° C. The inset shows the minimum and maximum size.

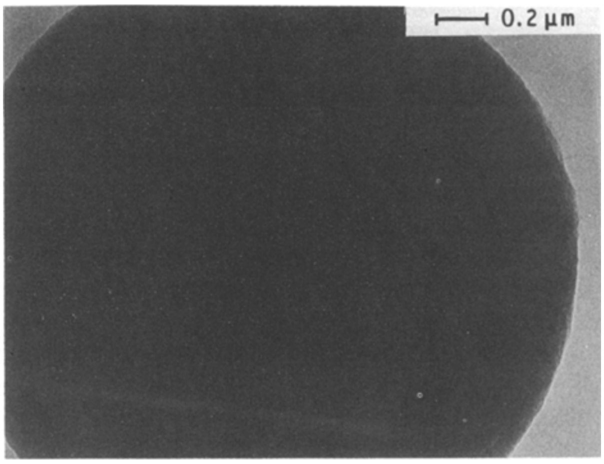

Figure 4 TEM microphotograph of a ZrO_2–SiO_2 particle prepared at T_1 = 350° C, T_2 = 900° C.

(T_1 = 250 to 450° C) calculated from SEM photographs, T_2 is maintained at 900° C. The centre peak per number of particles is between 0.9 and 1.0 μm, the proportion of the particles having a diameter of 0.8 to 1.0 μm is about 42%. The minimum and maximum diameters tend to decrease slightly with an elevation of furnace temperature, this calculation also indicates that particle shrinkage has taken place.

The frequency of the present ultrasonic vibrator is 1.67 MHz, measurement by dust (coulter) counter revealed that the diameter of the generated mist is 0.3 to 10 μm, having a centre peak of about 3 μm in the case of distilled water [10].

The mean size of the ultrasonically atomized mists is determined by the equation derived by Lang [11]

$$d = 0.34\left(\frac{8\pi\gamma}{\varrho f^2}\right)^{1/3} \tag{1}$$

where γ and ϱ are the surface tension and density of the solution respectively, and f is the frequency of the ultrasonic atomizer. In order to ascertain the measurement of the dust (coulter) counter, we will try to calculate a mean size by applying Equation 1. If $\gamma_{H_2O}^{30^\circ C} = 71 \times 10^{-3}\,\mathrm{N\,m^{-1}}$, $\varrho_{H_2O}^{30^\circ C} = 0.99 \times 10^3\,\mathrm{kg\,m^{-3}}$, and $f = 1.67 \times 10^6$ Hz, the droplet size is calculated to be $d_{calc} = 2.94\,\mu m$. Therefore, the measurement of the dust (coulter) counter is surely justified.

If we assume that the hydrolysis of TEOS does not occur in the preparation process of the atomized mother solution, the mean size of atomized mists d' can be roughly estimated by

$$\frac{d'}{d_{H_2O}} = \frac{(\gamma'/\varrho')^{1/3}}{(\gamma_{H_2O}/\varrho_{H_2O})^{1/3}} \tag{2}$$

where $d_{H_2O} = d_{calc} = 2.94\,\mu m$.

Generally, the surface tension of a solution containing inorganic salts is almost unchanged while that of a solution having surface active substances such as alcohol and fatty acids is remarkably decreased. Thence, it is assumed that the mother solution is simply composed of 20 wt % ethanol solution and the surface tension γ' is $36 \times 10^{-3}\,\mathrm{N\,m^{-1}}$ [12]. The density of the mother solution is estimated as $\varrho' = 0.96 \times 10^3\,\mathrm{kg\,m^{-3}}$ if $\varrho_{TEOS} = 0.935 \times 10^3\,\mathrm{kg\,m^{-3}}$ [12]. Thus d' is estimated as 2.3 μm. If we assume that one ZrO_2–SiO_2 (1 : 1) particle is formed from one droplet then the mean size of the spherical oxide particle is calculated by

$$d_{ZrO_2\text{-}SiO_2} = \left(\frac{M_{ZrO_2\text{-}SiO_2}}{M_{ZOC\text{-}TEOS}}\,\frac{C}{\varrho_{ZrO_2\text{-}SiO_2}}\right)^{1/3} d_{drop} \tag{3}$$

where M is the molecular weight of each compound, C the concentration of the mother solution, and d_{drop} the mean diameter of the droplets. From Equation 3, $d_{ZrO_2\text{-}SiO_2} = 0.49\,\mu m$ is estimated when $C = 1.3 \times 10^2\,\mathrm{kg\,m^{-3}}$, $\varrho_{ZrO_2\text{-}SiO_2} = \varrho_{ZrSiO_4} = 4.56 \times 10^2\,\mathrm{kg\,m^{-3}}$ (cf. $\varrho_{SiO_2} = 2.2$, $\varrho_{ZrO_2} = 5.6$), $M_{ZrO_2\text{-}SiO_2} = 183.3$, $M_{ZOC\text{-}TEOS} = 530.3$, $d_{drop} = 2.3\,\mu m$.

Strictly speaking, the resultant oxide particles are not zircon crystals ($ZrSiO_4$) [9], but a rough calculation is done in order to see the formation mechanism qualitatively. The mean particle size calculated from Equation 3 is about one-half of the value derived using the SEM photographs. This discrepancy is clarified by considering two factors.

The first factor is the possibility that the resultant particles are not perfectly dense but slightly porous. However, this factor was disproved by the high magnification TEM microphotograph, shown in Fig. 4, of representative particles prepared at T_1 = 350 and T_2 = 900° C. The particles obtained are almost all spherical independent of the diameter size and one spherical particle is composed of only one primary particle.

Generally, the particles prepared by the spray pyrolysis method are used to form a hollow structure, agglomerates and/or various more or less spherical geometrical shapes [1, 3, 4, 13]. In this work, all of the obtained particles are spherical and monodisperse, which means that the TEOS solution was not only

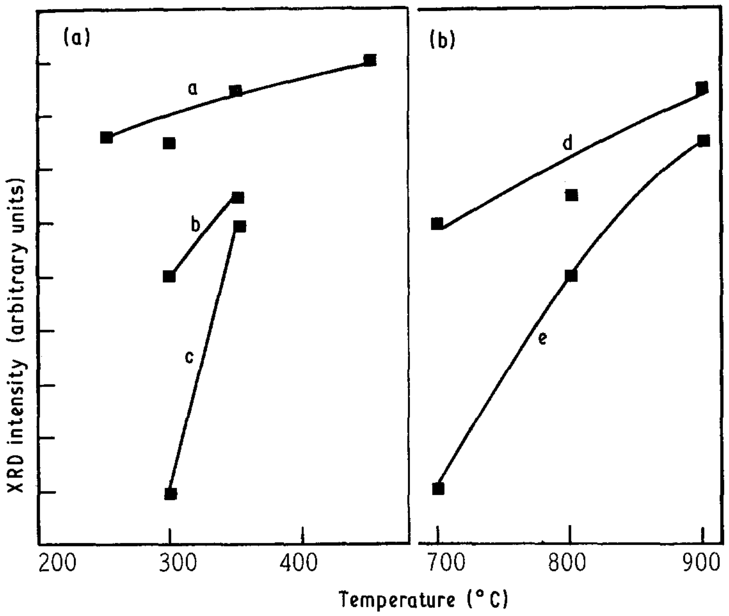

Figure 5 Variation of peak intensity of (1 1 1) plane of t-ZrO_2 plotted against furnace temperatures. (a) T_1 is variable (b) T_2 is variable. (a) T_2 = 900° C, (b) T_2 = 800° C (c) T_2 = 700° C, (d) T_1 = 350° C, (e) T_1 = 300° C.

atomized itself, but some reaction occurred by mixing with ZOC. Therefore, the second factor is selectively discarded. The assumption that the hydrolysis of TEOS does not occur in the preparation process of the mother solution is misleading that is, we expect that the mix solution of the equimolar ZOC and TEOS was rapidly hydrolysed by an addition of distilled water and conducted to the network formation of siloxane polymer and Zr^{4+}. Incidentally, in the synthesis study of spherical SiO_2 particles by ultrasonic spray pyrolysis, Nogami *et al.* [5] reported that the atomized starting solution composed of TEOS without preliminary hydrolysis treatment with a NH_4OH catalyst did not produce particles, perhaps because of its considerable vapour pressure. Moreover, it was stated that a poorly hydrolysed solution of TEOS produced the non-spherical particles.

On the other hand, in the formation of SiO_2 by thermal decomposition of TEOS vapour, Honjyo *et al.* reported that the resultant SiO_2 was composed of granular, film-, pillar-shaped particles and/or aggregates [14]. The discrepancy was recognized between two groups, but we are able to conclude that the spherical particles of ZrO_2–SiO_2 (1 : 1) are not obtained without being propagated by the hydrolysis of TEOS. The hydrolysis formation mechanism of the network of the siloxane polymer will be discussed later in this paper.

XRD and IR studies revealed that the resultant particles were characterized as t-ZrO_2 crystal and a-SiO_2 [9]. Fig. 5 shows the variation of peak intensity of the (1 1 1) plane of t-ZrO_2, being the highest peak, plotted against furnace temperatures.

The peak intensity increased with an increase of temperature, so that it was seen that the crystallinity of the particles was gradually developed by pyrolysis at the higher temperature. The development of crystallinity is more strongly affected by elevating the temperature of the higher furnace than the lower one.

In the preparation of ZrO_2–SiO_2 particles by the spray-ICP technique, Ono *et al.* [7] stated that t-ZrO_2 itself converted to m-ZrO_2 above 400° C without coexisting SiO_2 and was completed at 1200° C. For a 1 : 1 mixture of ZrO_2 and SiO_2, prepared by this technique, t-ZrO_2 was maintained below 1400° C. On the other hand, for 1 : 1 mechanical mixture of ZrO_2 and SiO_2, which is different to an atomically homogeneous mixing, t-ZrO_2 was converted to m-ZrO_2 above 400° C.

In this work, as we could not find m-ZrO_2, it was seen that the resultant oxides were composed of the particles in which homogeneous mixing of atomic order between zirconium and silicon was successfully attained. This means that the resultant particles were not composed of the compound formed from the mixture of separate ZrO_2 and SiO_2 particles. Namely, the hydrolysis of TEOS fully proceeded in the mixing process of ZOC, TEOS and H_2O, and equimolar distribution of the siloxane polymer and Zr^{4+} may be effectively accomplished.

In the previous paper [9], the infrared spectra of ZrO_2–SiO_2 (1 : 1) composite particles were shown, where the identification of the spectra assigned to the respective Zr–O and Si–O bond was carried out and the variation of signal intensity with an elevation of furnace temperature was briefly stated. Further, the absorption peak assigned to the Si–O–Zr bond was not formed.

Fig. 6 shows the intensity variation of highest peaks of Zr–O (896 cm^{-1}) and Si–O (1090 cm^{-1}) with furnace temperature (T_1). The other absorption peak intensities also varied in a similar manner to the highest peak. With an increase of temperature, the intensity was increased, the bond characters of Zr–O and Si–O were improved, and the transformation from an amorphous state to a pseudo-crystal-like SiO_2 gradually took place. However, this was not seen in the result of XRD, where SiO_2 was amorphous over the whole temperature range. The variation of the Zr–O peak supports the result of XRD.

3.2. Formation mechanism of a spherical ZrO_2–SiO_2 (1 : 1) particle

Prior to a discussion about the formation mechanism of spherical ZrO_2–SiO_2 particles produced by the ultrasonic spray pyrolysis, we pay attention to the

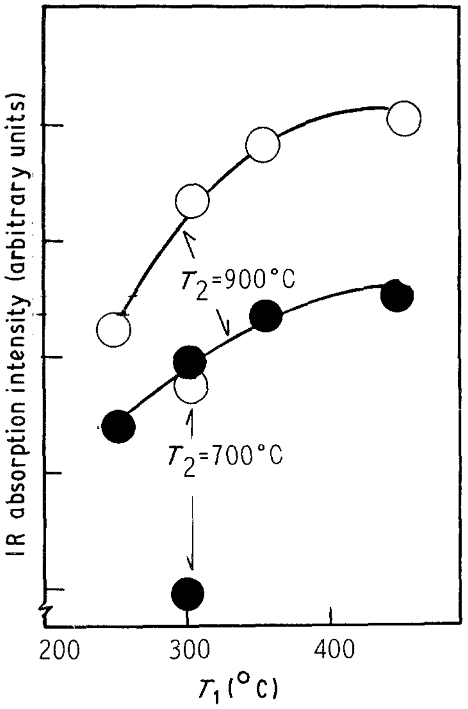

Figure 6 Variation of IR absorption peak intensities of Zr–O (●) ($896\,cm^{-1}$) and Si–O (○) ($1090\,cm^{-1}$) plotted against furnace temperature (T_1).

siloxane polymers produced in the course of hydrolysis of TEOS, as it is easy to guess that the formation mechanism of siloxane polymers is closely related to that of the mixed polymer of Zr^{4+} and siloxane.

Shimohira *et al.* [15] investigated the conditions leading to the formation of uniform sized spherical SiO_2 particles by the reaction of TEOS in an aqueous alcoholic solution in the presence of a NH_4OH catalyst. Numerous small particles having irregular shapes and size from 10 to 20 nm were formed in the very early stages of the process (1 min), and the aggregates changed from an irregular shape into perfect spheres and grew larger exhausting immediately the supply of small particles. In the final step of the hydrolysis (after 10 min), slow growth of spheres was observed by the adhesion of solute $Si(OH)_4$ species on their surfaces. Furthermore, Azuma *et al.* [16] reported that SiO_2 diameters were changed by the reaction temperature and the mole ratio H_2O/TEOS, NH_3/TEOS of the solution. The combustion of organic matters in SiO_2 occurred at about 400° C, and the dehydration from the silanol group at nearly 450° C. Yoldas [17] studied the formation mechanism of the hydrolysis and polymerization reaction, and revealed clearly that the product polymer was composed of a three-dimensional network structure. From viscosity measurement of the TEOS solution containing H_2O and C_2H_5OH preliminarily hydrolysed with NH_4OH catalyst at 55° C in a nitrogen atmosphere, Nogami *et al.* [5] reported that the spherical fine particles were obtained in the case of the intrinsic viscosity of the atomized droplets being 0.009 to $0.019 \times 10^5\,l\,kg^{-1}$, and nonspherical and aggregate particles were obtained in the other intrinsic viscosity.

In a range of $pH > 7$, it was uniformly concluded that the colloidal SiO_2 particles were produced by the hydrolysis of TEOS [18]. On the other hand, for a $pH < 7$, Bechtold *et al.* [19, 20] proposed the formation mechanism of the ladder polymers of three siloxane chains in the region of $1.73 < r < 5.20$.

In an investigation on the type of siloxane polymers produced in the course of hydrolysis of TEOS in the presence of HCl catalyst, Kamiya *et al.* [21] prepared four solutions in the TEOS–H_2O–C_2H_5OH–HCl system and found that the siloxane polymer showed a linear type in the case of the molar ratios of water to TEOS r being 1.0 and 2.0, and the type corresponded to the three-dimensional or spherical polymer for a solution with r of 20. The linear type appeared in the earlier stage of the reaction, and became three dimensional in the terminal stage for the intermediate value of $r = 5.0$.

The condensation process of TEOS was also studied by Makihara *et al.* using the trimethylsilylation (TMS) method at various reaction temperatures and at various concentrations of HCl or NH_3 [22]. The rate of disappearance and/or appearance of monomer, dimer and cyclic tetramer increased with an increase of reaction temperature. The rate of disappearance of monomer increased with a decrease of the pH of the solution, while the rate of polymerization of the oligomer (average molecular weight $\bar{M}_w > 1000$) decreased with a decrease of pH. It was assumed that, in a low pH range, the growth of particles proceeded by the linking of particles of similar size, and in a high pH range by the incorporation of the monomer or dimer into a larger particle.

Now, we will again discuss the condensation process of a ZOC–TEOS–C_2H_5OH–H_2O system which occurred during the production of atomized droplets. From a preliminary experiment, it was revealed that TEOS solution tends to float on the distilled water on mixing because it is water repellent but can be mixed homogeneously by the addition of ZOC dissolved in hot ethanol.

When H_2O was added to the TEOS–ZOC–C_2H_5OH system, an exothermic reaction was seen. These facts perhaps support the progress of the condensation reaction by hydrolysis in ZOC–TEOS–C_2H_5OH–H_2O system. It is not clear how the condensation reaction progresses, however; more detailed investigation is required on the viscosity measurement of the solution.

From a qualitative viewpoint, it is not justifiable to consider that the surface oxide layer formed in an earlier stage of pyrolysis was broken by the violent evaporation of H_2O solvent molecules and a fragment having various geometrical shapes formed, because the resultant ZrO_2–SiO_2 particles were almost spherical. Therefore, it is assumed that water molecules tend to bind together on the surface of the siloxane polymer complex and Zr^{4+} condensed because it is water repellent, ethanol molecules are uniformly dispersed also within the inner part of the complex, and a large number of water molecules are quickly evaporated without breaking the atomized particles in an earlier stage of pyrolysis.

It was assumed that the mother solution exhibits a strong acidity because of the ZOC dissolved in C_2H_5OH, the acidity effectively catalysed the

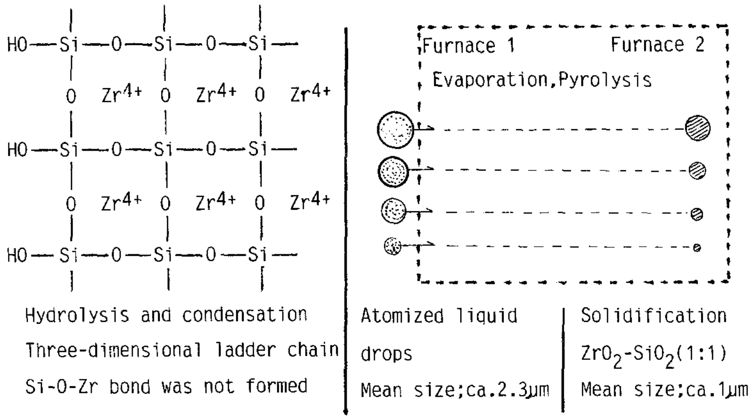

Figure 7 Schematic representation of formation mechanism for ZrO_2–SiO_2 (1 : 1) particles.

hydrolysis reaction of TEOS, the formation reaction of an oligomer with the same molecular weight was accelerated, and the polymer consisting of siloxane and Zr^{4+} was grown in the form of a three-dimensional or spherical polymer. In this work, the molar ratio $r(=288)$ is very large compared with that used by other researchers [21, 22]. It is uncertain whether the mechanism of condensation proceeds in a similar manner. However, it is estimated that a complex polymer with the same molecular weight was rapidly produced, and followed by the successful synthesis of spherical fine ZrO_2–SiO_2 (1 : 1) particles. Propagation of the condensation of TEOS also contributed to the lowering of the number of H_2O and C_2H_5OH molecules vapourized during the pyrolysis and resulted in the formation of spherical particles.

This discussion enables us to postulate the formation mechanism of spherical fine ZrO_2–SiO_2 (1 : 1) particles by ultrasonic spray pyrolysis as shown in Fig. 7. That is, the formation mechanism of the particle by the present method was considered to be as follows. Three-dimensional ladder siloxane chains containing the equimolar Zr^{4+} were formed by the hydrolysis and condensation reactions of TEOS with the aid of high acidity and a large molar ratio r. The complex chain structure polymer was atomized into spherical droplets having an average mist diameter of about 2.3 μm, and resulted in the formation of ZrO_2–SiO_2 (1 : 1) particles having a mean size of about 1 μm by gentle pyrolysis using two furnaces with a long heating zone. Then, one droplet may be converted into one oxide particle.

4. Conclusions

The mix-solution of silicon alkoxide (TEOS) and zirconium salt (ZOC) with an ethanol solvent was hydrolysed in the presence of a very large amount of water under a strong acidity. The prepared mother solution was sprayed into two furnaces having a long heating zone in the shape of small droplets with an ultrasonic atomizer. The resultant ZrO_2–SiO_2 (1 : 1) particles were spherical, mono-disperse and mainly 0.8 to 1.0 μm in diameter, and identified as t-ZrO_2 and a-SiO_2. The surface roughness, the crystallinity of the particles, and the bond character of Zr–O–Zr and Si–O–Si were improved with an increase of furnace temperature, and the small volcano-like projection formed by the effluent gas left behind in the inner part was observed in spots on the surface of the particle. The experimental results obtained strongly support the progress of the hydrolysis and condensation reaction of TEOS. The formation mechanism of spherical ZrO_2–SiO_2 (1 : 1) particles was discussed in connection with that of the siloxane polymer of TEOS. It was estimated that the three-dimensional ladder siloxane chains containing uniformly dispersed equimolar Zr^{4+} was formed by the hydrolysis of TEOS, and the atomized droplets with an average size of 2.3 μm converted into ZrO_2–SiO_2 (1 : 1) particles with a mean size of about 1 μm with 1 : 1 matching by ultrasonic spray pyrolysis.

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