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Chemical control in precipitation of spherical zirconia particles

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Monodisperse spherical zirconia particles are precipitated by hydrolysis of alcoholic solutions of zirconium alkoxides in the presence of long-chain carboxylic acids. The particle size can be finely tuned from 0.1 to 2.5 μm by controlling the concentration of zirconium alkoxide, the water/zirconium ratio, the nature of alcohol from ethanol to butanol, the nature of carboxylic acid from caproic to oleic acid and its concentration. The relationships between the induction time before nucleation, the particle size and all the above parameters are tentatively explained on the grounds of the solubility of the carboxy-alkoxide derivatives and their tendency to form micelles. Calcination of precipitated powders between 300 and 600 °C produces mixtures of varying composition from cubic to monoclinic phases of small crystallite sizes, and brings out the loss of surface area and organic content. Different conditions of drying powders lead to variously ordered microstructures.

1. Introduction

The increased reliability of ceramics depends on a lot of expertise and the observance of numerous quality criteria in the multiple manufacturing steps from powder synthesis, including calcination and milling, through processing and sintering. The use of submicrometre, unagglomerated and ultra-pure powder is generally considered as a good start in this regard [1, 2]. Extensive researches to produce zirconia powders have been initiated on wet-chemical processes with the aim of controlling the morphology [3]. Among them, the hydrolysis of zirconium alkoxides in alcoholic solution has attracted a great deal of interest for its ability to generate submicrometre spherical particles [4–7]. However, such particles are so reactive that they tend to agglomerate during synthesis and calcination. Hydroxypropylcellulose added to a titanium alkoxide solution before hydrolysis minimizes the agglomeration and improves the density and the homogeneity of the green body [8].

The control of the kinetics, induction period and growth, is important to shape the particles regarding mean size and particle size distribution, presence of multiplets and tendency to agglomerate. Conventional parameters to determine the kinetics are: concentration of reactants, water/metal molar ratio, nature of the alkyl group of the alkoxide and of the alcohol, presence of seeds [5, 7, 9].

The solubility and reactivity of alkoxides toward hydrolysis and subsequent reactions can be modified readily by exchanging some of the alkoxy groups with carboxylic acids or polyalcohols [10, 11]. Coordinating ligands formed by the complexation of metal alkoxides can also change their solubility, reactivity and global colloidal properties [12].

Long-chain carboxylic acids are known for their activity in colloid systems. Adsorbed on mineral surfaces, they facilitate the dispersion of powders in organic liquids. Reacted with metal salts, they form tensio-active soluble metal soaps and micelles in organic solvents [13]. Mixed with organic solvent and water, they are able to stabilize microemulsions [14].

The present paper describes the synthesis of zirconia powders by the hydrolysis of alcoholic solutions of zirconium alkoxides, in the presence of long-chain carboxylic acids, as morphology controllers.

2. Experimental procedure

2.1. Preparation of powders

A long-chain carboxylic acid is added to an anhydrous propanol solution of zirconium tetra-n-propoxide, $Zr(OC_3H_7)_4$. The solution is allowed 10 min to react. An identical volume of propanol containing water is quickly introduced into the zirconium solution, under intense agitation, at 25 °C. All the solutions have been filtered through Millipore filters (0.2 μm pore size) to avoid uncontrolled seeding and nucleation. All the glass equipment is kept under a dry nitrogen stream. After strong initial mixing, the agitation is slowed down or stopped to reduce the risk of agglomeration, particularly during nucleation. $Zr(OC_3H_7)_4$ is used as received from Dynamit Nobel. Carboxylic acids are analytical-grade products from various sources. Although most of the trials are carried out in dry propanol in the presence of oleic acid, ethanol, isopropanol and butanol were also used as well as various carboxylic acids. All the concentrations are related to the solution after initial mixing of the two reactive solutions. Concentration limits are the following:

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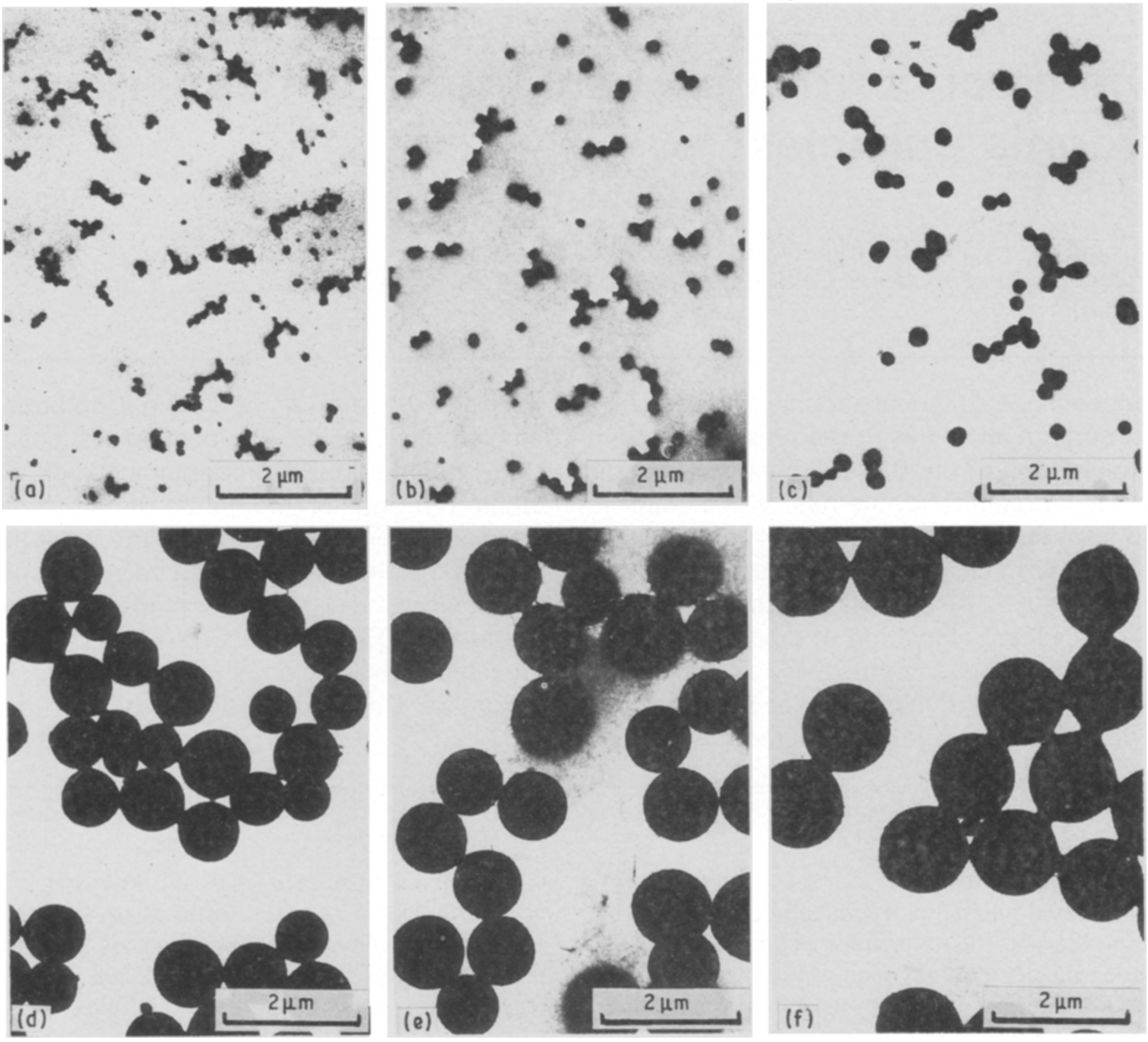


Figure 1 Effect of the nature of carboxylic acids on size and shape of particles. [$Zr(OC_3H_7)_4$] = 0.1 M, [H_2O] = 0.35 M, [carboxylic acid] = 0.016 M. (a) Caproic acid (C6), (b) caprylic acid (C8), (c) capric acid (C10), (d) lauric acid (C12), (e) palmitic acid (C16), (f) stearic acid (C18).

$Zr(OC_3H_7)_4$, 0.1 to 0.2 M; H_2O, 0.3 to 0.6 M; carboxylic acid, 0.01 to 0.05 M. After mixing, an induction time is observed before sudden precipitation. The suspension is then allowed 2 h to age. The powder is then centrifuged and washed with propanol. The settled compact is dried at room temperature.

2.2. Characterization of powders

Particle size and shape are determined from a propanol suspension, after ultrasonic treatment, by counting particles on transmission electron microscope (TEM) pictures. Calcination of powders is performed between 300 and 600 °C. Thermogravimetric (TGA), differential thermogravimetric (DTG) and differential scanning calorimetric (DSC) methods are used to follow up the loss of organic material and the crystallization during calcination. Identification of crystalline phases is based on powder X-ray diffraction patterns, with a copper cathode ($K\alpha$ = 0.15405 nm). Detection and weight fraction of crystalline phases are determined from peak intensities at the following spacings (in nm) and angles (2θ) respectively: monoclinic (0.316, 28), (0.220, 41), (0.202, 44.8); tetragonal and/or cubic (0.295, 30.2); tetragonal (0.213, 43). Data should be considered as rough estimations as it is known that quantification of phases is rather difficult, particularly with a small crystallite size. The latter is estimated from the Scherrer linewidth of the diffraction peak. Pore size distribution and surface area are determined by nitrogen adsorption according to procedures described elsewhere [15].

3. Results and discussion

3.1. Effect of carboxylic acid and alcohol nature

On the one hand, Fig. 1 shows the influence of increasing the chain length of the carboxylic acid from caproic (C6) to stearic (C18) on the particle size, from 0.1 to 1.3 μm, under conditions described in the caption. In this set of experiments, a sharp variation as a function of the number of carbons is observed. With carboxylic acids between C6 and C10, particles are small (0.1 to 0.25 μm) and sphericity is not well developed, whereas large (0.85 to 1.3 μm) and spherical particles are generated with carboxylic acids between C12 and C18. It has also been shown that propionic acid behaves quite similarly to caproic acid.

On the other hand, the induction time before precipitation decreases from 300 to 48 sec when the chain length of carboxylic acid increases from C6 to C18, as shown in Fig. 2. Oleic acid, which is a C18 acid with an unsaturated chain, produces almost the same effect as stearic acid. It has been selected as reference acid in most trials.

Besides carboxylic acids, the nature of the alcoholic solvent has an important effect on induction time and particle size, as can be seen in Fig. 2. Hydrolysis of $Zr(OC_3H_7)_4$, in the presence of oleic acid and by changing successively the nature of the alcohol from ethanol, isopropanol and propanol to butanol, increases the particle size from 0.5 to 2.7 µm and the induction time from 2 to 1320 sec.

These two sets of experiments can only be tentatively explained by a speculative approach as the complexity of the system needs more in-depth research work to be clearly understood.

First, it is obvious that carboxylic acids react with $Zr(OC_3H_7)_4$ to produce a zirconium carboxy-alkoxide derivative, according to the equation

$$Zr(OC_3H_7)_4 + RCOOH \rightarrow Zr(OC_3H_7)_3(OOCR) + C_3H_7OH$$

An increase of the amount of carboxylic acid close to stoichiometry relatively to zirconium, in anhydrous alcohol solution, leads to precipitation. No precipitation occurs when the acid/zirconium molar ratio is kept between 0.1 and 0.5. In the presence of water, the metal–alkoxy bond is hydrolysed but not the metal–carboxy bond due to the higher acidity of the carboxylic acid compared with that of water.

Secondly, it is expected that the solubility of the alkoxy precursors and of the evolving species during hydrolysis is modified as a function of the alcohol and carboxylic acid nature. On the one hand, it is quite clear that not only the extent of hydrolysis but also an increase of the number of carbons in the carboxylate group accelerate the nucleation and precipitation by increasing the mean molecular weight of the hydrolysate. On the other hand, metal carboxylates are known to form micelles in the presence of water molecules. One could believe that, in the core of such micelles or nuclei toward which the polar groups ($ZrOCH_2$–, ZrOOC–, ZrOZr, ZrOH) are oriented, water molecules are attracted and more readily available for hydrolysis and early precipitation.

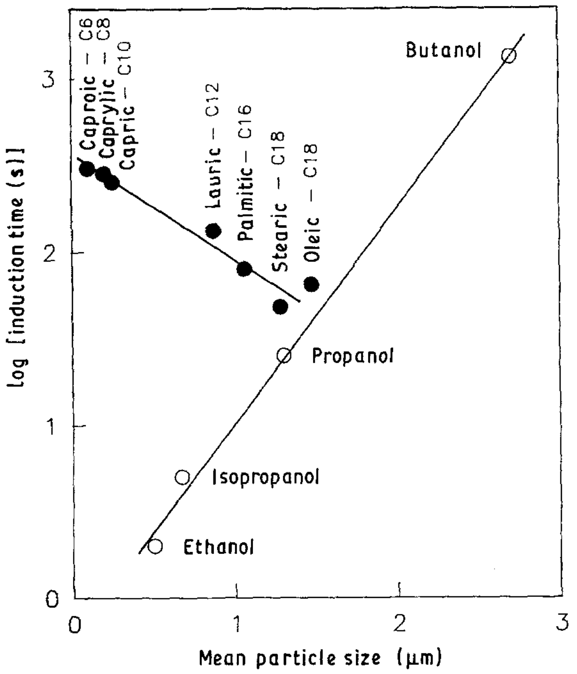


Figure 2 Effect of the nature of alcohol and carboxylic acids on induction time and particle size. $[Zr(OC_3H_7)_4] = 0.1$ M, $[H_2O] = 0.35$ M; (●) nature of carboxylic acid, [acid] = 0.016 M; (○) nature of alcohol as solvent, [oleic acid] = 0.032 M.

Fig. 2 shows the increase of induction time and particle size when the solvent is modified from ethanol, isopropanol and propanol to butanol, at constant oleic concentration. In this case, the solubility factor can be put forward. Indeed, the solubility of carboxylic acids increases with the length of the alkyl group of the alcohol because the organophilic content increases, or conversely because the protic content decreases. As a consequence, the tendency to generate micelles is reduced, the rate of hydrolysis is down and the number of nuclei is low.

3.2. Effect of reactant concentrations

Fig. 3 shows that the particle size can be perfectly controlled and increased from 0.2 up to 1.8 µm, either by reducing the water concentration or by increasing the acid concentration. Fig. 4 illustrates the evolution of induction time as a function of particle size, when

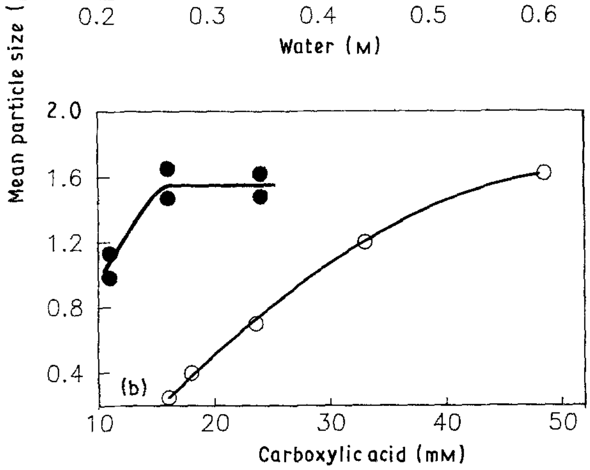


Figure 3 Mean particle size as a function of water and carboxylic acid concentration. $[Zr(OC_3H_7)_4] = 0.1$ M. (a) Water concentration, [oleic acid] = 0.016 M. (b) Carboxylic acid concentration, $[H_2O] = 0.35$ M; (●) oleic acid (C18), (○) capric acid (C10).

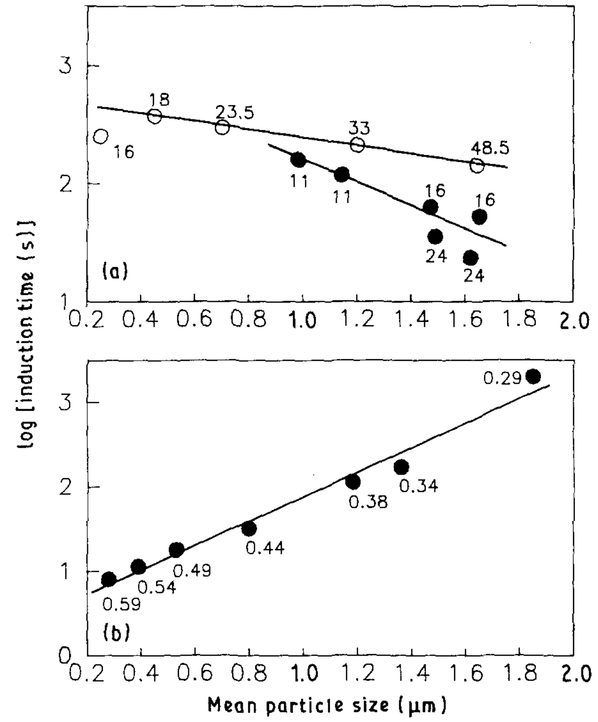


Figure 4 Induction time as a function of particle size, at variable acid and water concentrations. (a) Concentrations of (●) oleic and (○) capric acids expressed in mM as index; $[H_2O] = 0.35$ M. (b) Water concentration expressed in M as index, [oleic acid] = 0.016 M.

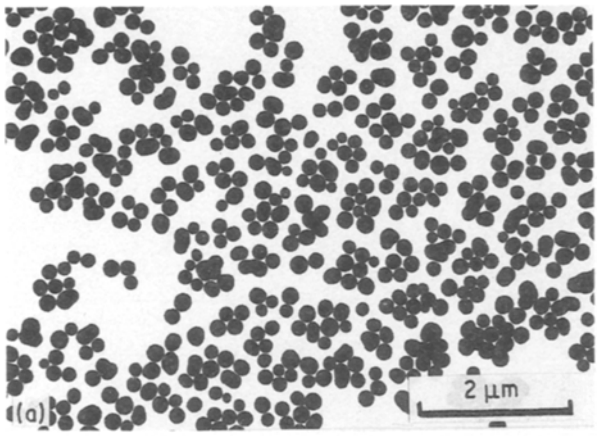
the acid or the water concentration is changed. These observations need some comments:

1. An increase of either water or acid concentration reduces the induction time. The former accelerates the hydrolysis rate, whereas the latter contributes to the heaviness and insolubilization of the evolving species.

2. Hydrolysis in the presence of a high concentration of water is rapid and brings about the production of large quantities of nuclei and small particles after complete precipitation. This is consistent with the La Mer theory on nucleation and growth mechanisms in saturated solution. Monodispersity is obtained more favourably in dilute solution when a burst of nuclei occurs and nuclei grow individually without further delayed nucleation. Ogihara *et al.* [9] show that the growth mechanism is not controlled by diffusion but is rather based on surface reaction with polynuclear-layer growth. The growth rate is independent of the initial particle size, and the particle size distribution is not modified but only the mean size changes.

3. Increases of acid or water concentration have opposite effects on the size of the spherical particles. This is somewhat puzzling with respect to the generally observed phenomena according to which the quicker reaction gives the smallest particles. A possible explanation could be related to surface charges of nucleating particles and to the tendency of particles to agglomerate in the early stages of precipitation. At the very beginning of the hydrolysis, small primary particles nucleate and agglomerate due to their high surface energy [9]. It is probable that the coalescence of primary particles is eased by the suppression or at least by the dilution of superficial charges formed during the hydrolysis due to the presence of oxygenated groups (carboxylate, alkoxylate or zirconate anions). The introduction of a lot of carboxylic acid or an increase of the length of the alkyl chain could play that role and be a part of the explanation. In support of this and in order to get the same particle size, more capric acid is needed than oleic acid to compensate for the higher molecular weight of the latter.

TEM pictures of particles with varying sizes obtained by changing the water concentration are given in Fig. 5. Doublets and a broad particle size distribution are more easily produced when the hydrolysis is



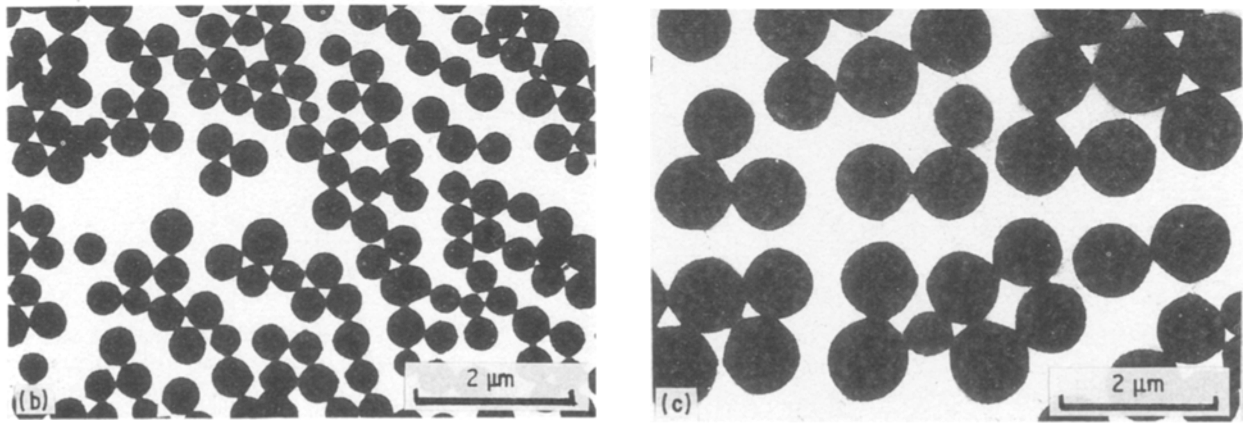


Figure 5 Spherical particles produced by hydrolysis of $Zr(OC_3H_7)_4$ (0.1 M) at various water concentrations, in presence of oleic acid (0.016 M) at 25 °C. (a) $[H_2O] = 0.62$ M; (b) $[H_2O] = 0.50$ M; (c) $[H_2O] = 0.35$ M.

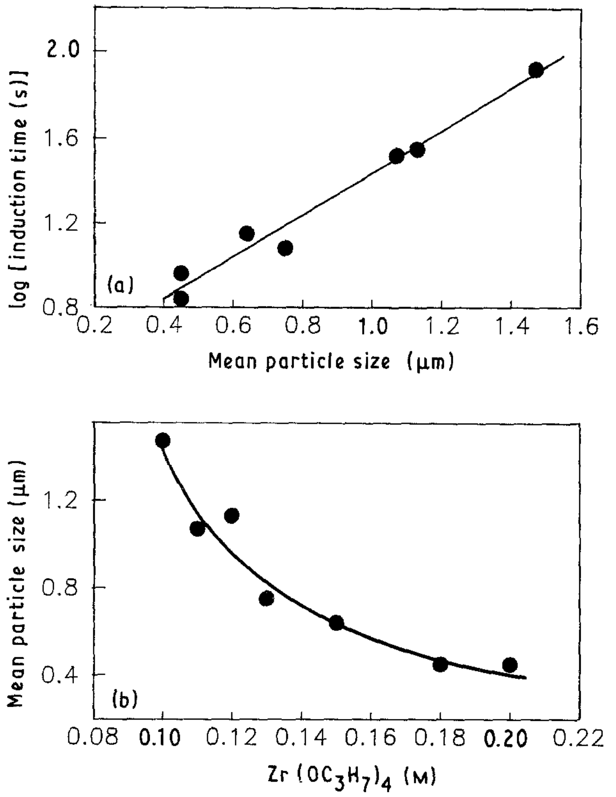


Figure 6 Influence of the total concentration of reactants on (a) induction time and (b) particle size, all the molar ratios being constant. $[H_2O]$:[oleic acid]:$[Zr(OC_3H_7)_4]$ = 3.5:0.16:1.

rapid and when the induction time becomes comparable with the time needed to mix the two solutions. After 2 h reaction time, the yield of precipitation is more than 95% at high water concentration (0.6 M) and as low as 50% at low water concentration (0.3 M) in the experiments of Fig. 3. A reaction temperature at 50 °C instead of 25 °C has only a marginal effect on the kinetics and the particle size.

The effect of increasing the concentrations from 0.1 to 0.2 M of all reactants while keeping the molar ratios constant, on induction time and mean particle size, is illustrated in Fig. 6. In this set of experiments, the mean particle size is plotted as a function of carboxylic acid concentration and the induction time as a function of mean particle size. It is possible to precipitate unagglomerated, monodisperse spherical particles at 0.2 M $Zr(OC_3H_7)_4$. Again the particle size can be fine-tuned.

3.3. Effect of calcination on porosity and crystallographic phases

A powder precipitated from a mixture of composition 0.1 M $Zr(OC_4H_9)_4$, 0.35 M H_2O, 0.008 M oleic acid in ethanol, at room temperature, was washed, decanted and dried. This powder was calcined in a quartz tube ventilated with air, between 300 and 600 °C, for 4 h. The TGA, DTG and DSC analyses show that oleic acid is burnt out between 230 and 350 °C, while a sharp crystallization peak occurs at 440 °C. Loss of material is no longer observed above 400 °C. In this condition, the total loss of weight is 37%. The surface area linearly decreases from 300 to 4 $m^2 g^{-1}$ with calcination temperature between 300 and 500 °C. After calcination at 500 °C, there is no more pore volume left inside the particles. A reduction of the particle size of about 20% is observed.

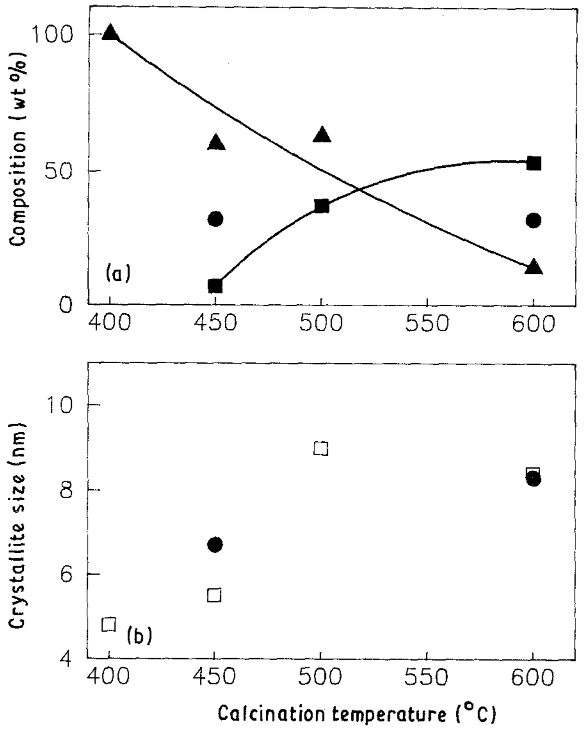


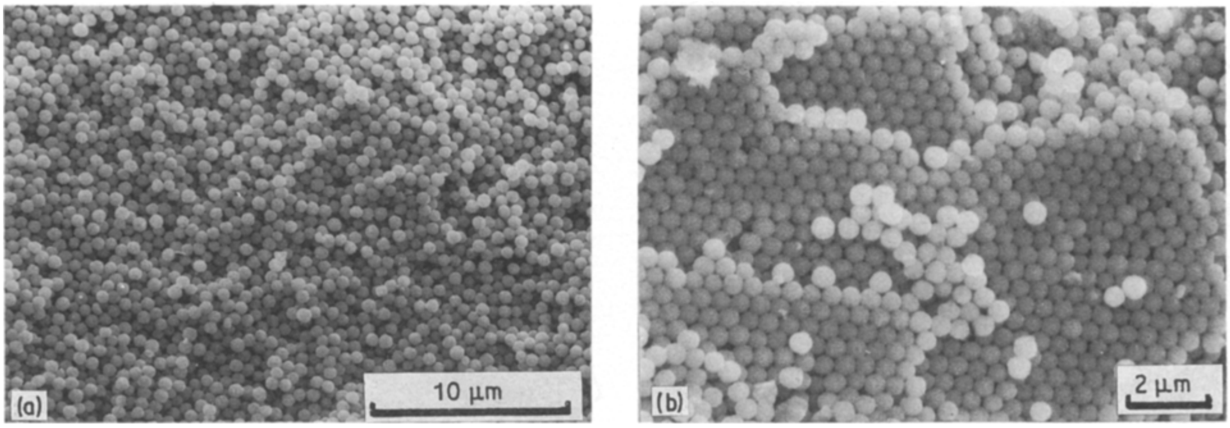
Figure 7 (a) Crystalline phase composition and (b) crystallite size as a function of calcination temperature: (●) monoclinic, (■) tetragonal, (▲) cubic, (□) cubic and/or tetragonal.

The composition of the crystalline phases in powders is illustrated in Fig. 7. It shows that the first crystalline phase to appear around 400 °C is cubic, though some minor amount of amorphous phase may still be present. With increasing temperature, the cubic phase is partly replaced by the tetragonal phase. Although no monoclinic structure has been detected at 500 °C calcination temperature, the volume fraction of the monoclinic phase is constant at 450 and 600 °C. Stability of the cubic phase must only be possible with a small crystallite size. Fig. 7 shows that the estimated crystallite size of all the phases increases from 5 to 9 nm with calcination temperature. These values are somewhat smaller than those obtained, in the range of 8 to 16 nm, by Srinivasan *et al.* [16] with zirconia produced from aqueous phase precipitation.

3.4. Processing of particles

Monosized spherical particles are potentially attractive because they can lead to highly organized microstructures with improved properties. The quality of the compact still depends strongly on the processing method – dry pressing, slip casting, settling or spray drying. Fig. 8 illustrates three configurations of microstructure obtained according to various processing conditions.

The first two pictures are of powders calcined at 500 °C under air, from powder suspensions dried under various conditions. Fig. 8a shows calcined powder from alcoholic suspension quickly evaporated in



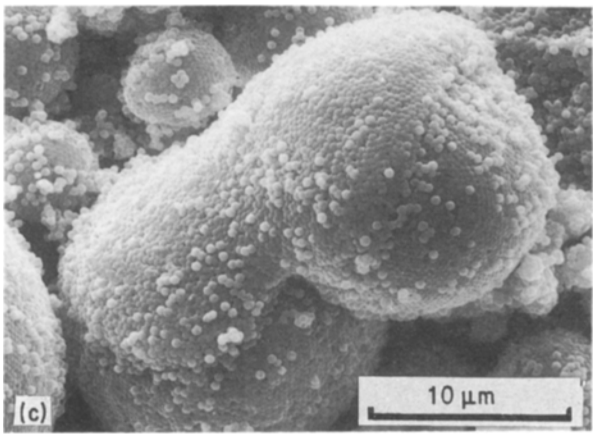


Figure 8 Various examples of microstructures: (a) powder quickly dried in a rotating dryer and calcined at 500 °C, (b) powder slowly dried from settled suspension and calcined at 500 °C, (c) amorphous non-calcined powder spray-dried after substitution of alcohol by water.

a rotating dryer. Fig. 8b shows calcined powder from a slowly dried compact produced with settled particles. The third picture (Fig. 8c) represents the amorphous non-calcined powder which was spray-dried after precipitation and replacement of most of the alcohol by water. Obviously the control of colloidal properties of the particles, as well as the use of appropriate drying technology, can determine their potentiality.

4. Conclusions

The introduction of long-chain carboxylic acids in the hydrolysis of alcoholic solutions of zirconium alkoxides has enabled the precise control of the induction time of nucleation and the mean diameter of the almost monosized spherical particles. In practice the particle size can be controlled between 0.1 and 2.5 µm and the induction time between less than 2 sec and 20 min or more. As a general rule, the particle size is proportional to the induction time. Therefore, the smallest particles are quickly nucleated and precipitated when the alkoxide and water concentration are increased. This is also the case when the nature of the alcohol is changed from butanol to ethanol. On the other hand, an increase of the acid concentration or of the chain length from C6 to C18, at constant molar concentration, shortens the induction time as expected, but leads to larger particles. The solubility of the carboxy-alkoxide derivatives, the tendency of long-chain metal carboxylates to form micelles and the dilution of superficial charges by the bulky acids during the early coalescence of the primary particles have been put forward to tentatively explain the experimental observations. The presence of carboxylic acids is also probably responsible for the production of a small crystallite size and the presence of the unstable cubic phase, after calcination at 400 °C.

The modification of the powder processing conditions has led to interesting microstructures with potential applications. Finally, this work deserves further fundamental study with a colloid-minded approach at each manufacturing and processing step.

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