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Preparation and characterization of nanoscale Y-TZP powder by heterogeneous azeotropic distillation

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A heterogeneous azeotropic distillation process was effectively used to dehydrate hydrous zirconia and therefore prevent the formation of hard agglomerates in the preparation of nanoscale zirconia powder. The mechanism of azeotropic distillation to prevent hard agglomerate from forming was studied by investigating the interaction of hydrous zirconia with *n*-butanol. The prepared powder was sintered to 99.5% of theoretical density by slow-sintering (average grain size of ~200 nm), 97.5% by fast-sintering (average grain size of ~120 nm) at 1250 °C.

1. Introduction

The reduction of particle size is a very promising and important approach to lowering sintering temperature and obtaining fine grain size for advanced ceramics because densification depends inversely on the fourth power of particle size [1]. Considerable effort has been put in to develop wet chemical synthesis methods since they offer convenient routes for obtaining ultrafine and high-purity ceramic powders. By wet chemical routes, however, the fine particles were often found to be agglomerated on drying and calcination, which is very detrimental for full densification. The state of agglomeration is therefore particularly important for ceramic powders synthesized by wet chemical methods.

It is generally accepted that soft agglomerates do not impede densification, but hard ones lead to incomplete densification and develop strength-limiting processing flaws. The agglomerate strength has been proposed to be determined by the extent to which water molecules and/or hydroxyl groups incorporated in the co-ordinated structure that are able to form strong oxygen bridges between adjacent particles [2].

Among a variety of methods which have been used to avoid the formation of hard agglomerates, ethanol or other organic solvent washing for water removal has been a widely used method [3]. Ethanol washing was speculated to remove all non-bridging hydroxyl groups and co-ordinated water and therefore reduce/eliminate hard agglomerates [4]. Kaliszewski and Heuer [5] investigated the interaction of ethanol with hydrous zirconia during drying using Fourier transform infrared (FT–IR) spectroscopy and concluded that ethanol washing resulted in the formation of surface ethoxyl groups which had a direct influence on strength reduction of the resulting agglomerates.

The process of reflux and distillation has been recently reported to dehydrate hydrous gels in powder preparation [6, 7]. In the present paper, heterogeneous *n*-butanol azeotropic distillation method used in the preparation of ultrafine Y-TZP powders is described, and the mechanism was studied by using mass spectroscopy and FT–IR spectroscopy. The results in this work demonstrate that the method is applicable to the control of hard agglomerates in the preparation of ultrafine zirconia powder and is expected to be suitable for a variety of single or multicomponent ceramic powders prepared by aqueous chemical methods.

2. Experimental procedure

2.1. Preparation of hydrous zirconia gel by azeotropic distillation

The well-stirred stoichiometric solution mixing of $ZrOCl_2 \cdot 8H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ (3 mol % Y_2O_3) was sprayed through a nozzle into concentrated ammonia solution at a rate of about 25 ml min^{-1} while maintaining the pH of the solution at 11. After complete precipitation, the Cl^--containing hydroxide precipitate was washed several times with distilled water until no reaction for Cl^- ions (with $AgNO_3$) were observed.

The washed gel was vacuum-filtrated to remove as much excessive water as possible and then was mixed with *n*-butanol under vigorous mechanical agitation because they are not mutually wettable at the room temperature. The suspension was transferred to a flask for distillation in an apparatus as in Fig. 1. The volume of water removed and the azeotropic temperature of the suspension could be readily and continuously monitored during distillation. By heating the suspension to its azeotropic point (93 °C) for water–*n*-butanol system, the water, no matter how associated, began to be carried away by *n*-butanol in the form of an azeotrope and separated after cooling in the water trapper. The boiling point should be kept at 93 °C for a few hours until the water was completely removed.

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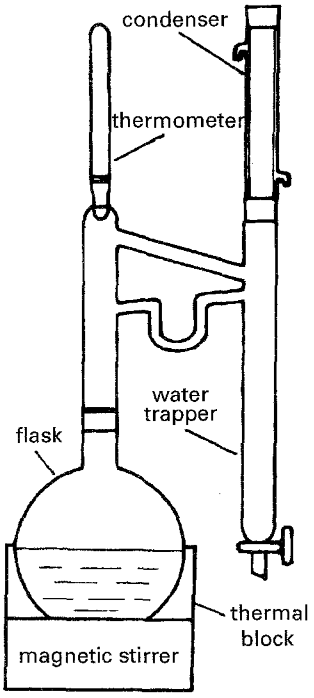

Figure 1 Schematic representation of azeotropic distillation apparatus.

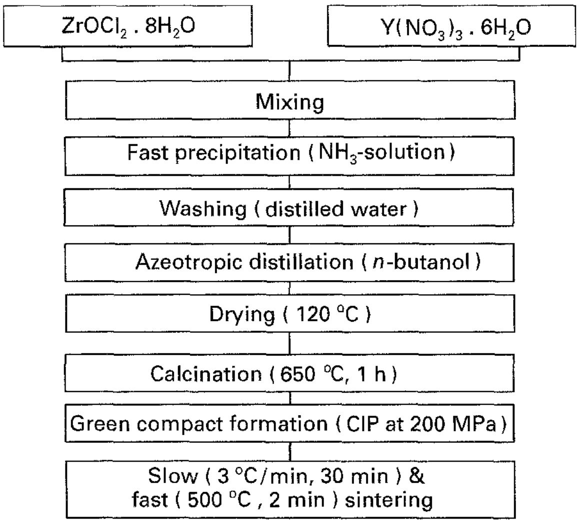

Figure 2 Scheme for powder preparation and sintering of nanoscale Y-TZP powder.

After that, the suspension's boiling point will continue to rise to the boiling point of *n*-butanol (117 °C). The mixture was further refluxed at 117 °C for 30 min.

2.2. Powder preparation and sintering

The whole Y-TZP powder preparation and sintering processes are schematically shown in Fig. 2. The distilled gel was oven-dried at 120 °C and the product was an extremely soft and friable powder. It was calcined at 650 °C for 1 h. The friable powder was granulated by using polyvinyl alcohol (PVA) as binder which was evenly distributed with an agate mortar and was pressed into green pellets having the dimensions (diameter × height):18 × 3 mm(large-size sample) (first compacted by cold pressing at 35 MPa and followed by cold isostatic pressing at 200 MPa) or 10 × 1 mm (small-size sample) (cold pressing at 250 MPa).

Characterization of powder sinterability was performed by two different methods. The first method was a slow-rate sintering using 18 × 3 mm samples at a heating rate of 2 °C min^{-1} to 700 °C followed by a hold of 10 min, 3 °C min^{-1} to the preset sintering temperature with a hold of 30 min, 3 °C min^{-1} cooling down to ambient temperature. The second one using 10 × 1 mm because of size limitation of the furnace sample-holder was a fast-rate sintering method. It was performed in a specially designed fast firing furnace system with the heating rate of 500 °C min^{-1} for both heating and cooling. The samples were held at the sintering temperature for 2 min.

2.3. Characterization of synthesized powder and sintered bodies

Particle size and morphology, specific surface area and the thermal behaviour of the powders were characterized by transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) and differential thermal analysis (DTA) methods. Shrinkage of 35 MPa pressed sample (5 mm dia. × 12 mm) was measured with a Netzsch 402ES/3 dilatometer at a heating rate of 10 °C min^{-1} in air up to 1400 °C.

Transmission FT-IR spectra of powders were recorded by a Nicolet FT-IR 5DX spectrometer in vacuum when samples were heated to 100, 200, 300 and 380 °C, respectively. A combintion of DTA–TG (TG, thermogravimetric analysis) analysis and mass spectroscopy was used to study the interaction of *n*-butanol with surface hydroxyl groups of hydrous zirconia during heating. DTA–TG and mass spectroscopy were coupled so that the mass spectroscopy would monitor the "off" gases of the powder as it was heated. Parameters for the mass spectroscopy were: mass scan speed 1 s a.m.u.$^{-1}$; mass filtering time 0.03 s. A Faraday cup was used to record ion current signals. The following mass numbers were preset to detect positive ions: H_2O^+ ($m/z = 18$), CO_2^+ ($m/z = 44$), $C_4H_8^+$ ($m/z = 56$), $C_4H_{10}O^+$ ($m/z = 74$), $C_8H_{18}O^+$ ($m/z = 130$). The DTA–TG–mass spectroscopy analysis was performed in argon at a heating rate of 10 °C min^{-1}.

The densities of large-size samples were measured by Archimedes' method in water, small-size samples by specific gravity bottle in water due to their small dimensions. The grain size of the sintered specimens was determined by TEM using ion milled samples.

3. Results

3.1. Synthesized powder

The morphology of prepared powder is shown in Fig. 3. TEM verified that the powder was composed of 10 to 20 nm particles. The powder has a BET area of 53.5 $m^2 g^{-1}$ and thereby a calculated equivalent BET diameter of 18.7 nm which is in agreement with the average size from the TEM image, signifying the loose aggregate nature of the powder. The synthesized powder has a low apparent density of approximately 10% theoretical density.

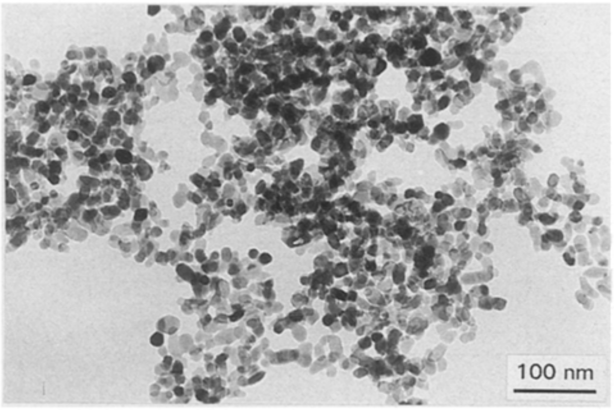

Figure 3 TEM micrograph of prepared Y-TZP powder treated by distillation.

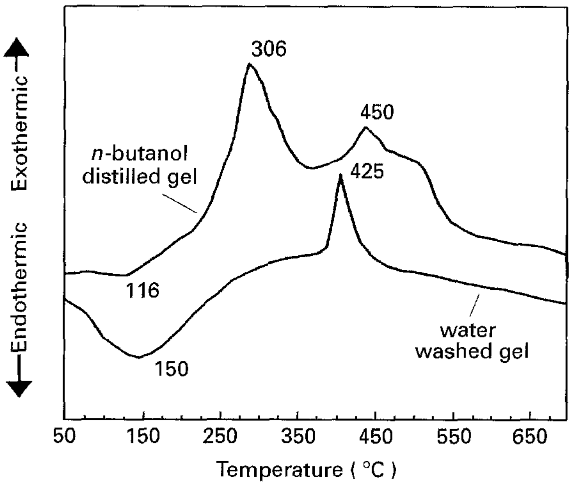

Figure 4 DTA curves of the water-washed and *n*-butanol distilled gels.

The strong dewatering effect of *n*-butanol distillation was supported by the DTA data of both water-washed gel and distilled gel before calcination in Fig. 4 which showed their different water desorption behaviours. The water-washed gel had a large endothermic peak at 150 °C due to the desorption of physisorbed water along with the dehydration of the gel but the distilled gel had only a very small peak of the same kind at 116 °C, indicating a high degree of dehydration caused by distillation. The organic burnout exothermic peak at 305 °C, was shown on the distilled gel which was followed with another exothermic peak at 450 °C, 25 °C higher than that of water-washed gel. The exotherm around 450 °C of both samples showed the onset of crystallization of hydrous zirconia from amorphous to tetragonal [7].

3.2. Particle surface characterization by TG–DTA–mass spectroscopy and FT–IR spectroscopy

The FT–IR spectra of distilled powder are shown in Fig. 5. The broad absorption bands from 3800 cm^{-1} to 3000 cm^{-1} are caused by an O–H stretch, broadened due to hydrogen bonding between the various hydroxyl groups. The band at 1626 cm^{-1} corresponds to the bending stretch of absorbed and coordinated water molecules, decreasing with increase in temperature and disappearing at 200 °C. The band at 1544 cm^{-1} is due to bending stretch of bridging hydroxyl groups. There are evidences of strong *n*-butanol interaction with particle surface on the spectra. Two peaks at 1105 cm^{-1} and 1050 cm^{-1} which remain discernible at 300 °C are caused by C–O stretching of $-O-CH_2-C_3H_7$ on the particle surface. Bands at 2900 cm^{-1} are due to C–H stretching and retained even at 380 °C. These three bands indicate the *n*-butanol molecules are in a state of strong chemical adsorption on the surface of colloid particles.

Fig. 6 shows the mass spectra of distilled powder. CO_2^+ peaks are clearly shown at 130, 193 and 500 °C, respectively. It was important to find that the $C_4H_8^+$ peak was found at 400 °C in Fig. 6(a) due to the release of butene ($CH_3(CH)_2CH_3$), but there are no peaks of $C_4H_{10}O^+$ and $C_8H_{18}O^+$ detected. It can be seen that the hydrous gel was quite well dehydrated by the distillation process since there was no H_2O^+ peak found in Fig. 6(a). There was only a small H_2O^+ peak found at about 100 °C in Fig. 6(b) after liquid N_2 was introduced to reduce the partial pressure of water in vacuum system. However, the reason for the absence of $C_4H_8^+$ peak under this condition needs further study.

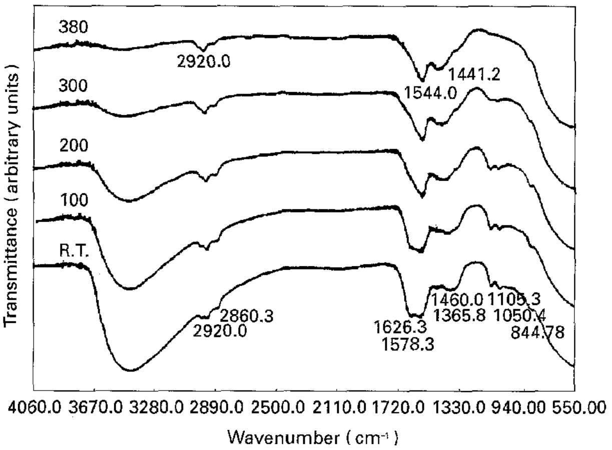

Figure 5 FT–IR spectra of the powder processed by *n*-butanol distillation at room temperature, 100, 200, 300 and 380 °C.

3.3. Densification behaviour of the powder compact

Fig. 7 is the shrinkage curve of green compact from room temperature to 1400 °C. The compact commenced to display remarkable shrinkage at 900 °C with a maximum shrinkage rate at 1200 °C. Table I lists the sintered densities as a function of sintering temperature by both slow and fast sintering. Relative density was based on a 6.04 g cm^{-3} theoretical density. Samples at 1200 °C have reached densities over 95% by both sintering methods, and the average grain sizes are ~150 nm and ~100 nm for slow and fast sintering, respectively. Samples by slow sintering were sintered to 99.5% at 1250 °C with a grain size of ~200 nm (Fig. 8(a)) and dropped to 97.2% at 1300 °C with coarsened grains of ~300 nm. By fast sintering

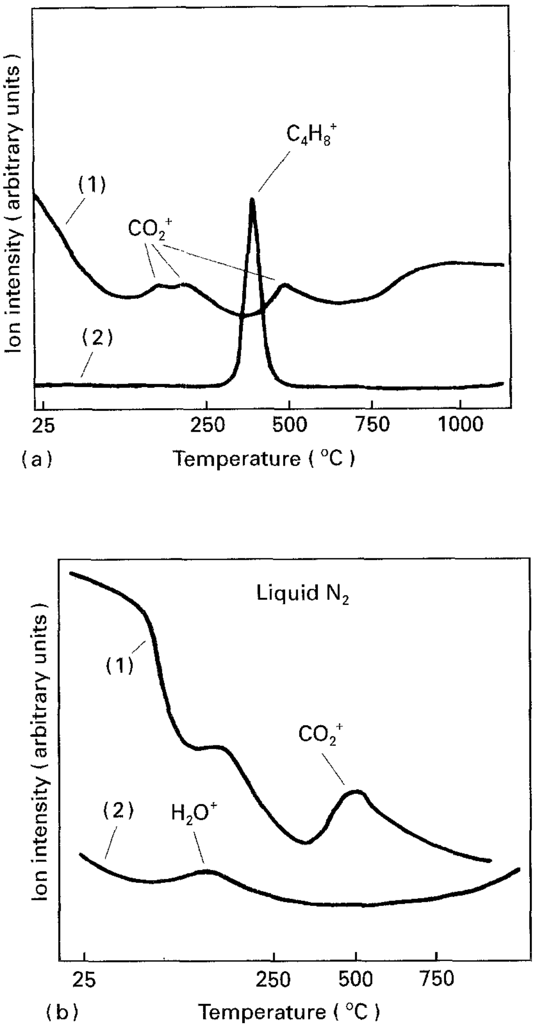

Figure 6 DTA–TG coupled mass spectra of the distilled gel at atmosphere of (a) argon ((1) CO_2^+ ($m/z = 44$); (2) $C_4H_8^+$ ($m/z = 56$)): (b) argon (liquid N_2 introduced in system) ((1) CO_2^+ ($m/z = 44$) ; (2) H_2O^+ ($m/z = 18$)).

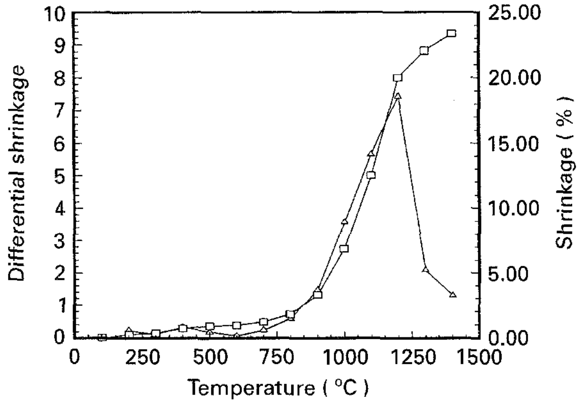

Figure 7 Shrinkage curve of the green compact prepared by distilled powder (△); shrinkage (□).

TABLE I Sintered densities versus sintering temperature of Y-TZP powder sintered by fast and slow sintering methods

Sintering methods and densities (% TD)	Sintering temperature (°C)			
	1200	1250	1300	1350
Fast sintering	96.5	97.5	97.5	98.0
Slow sintering	96.0	99.5	97.2	96.2

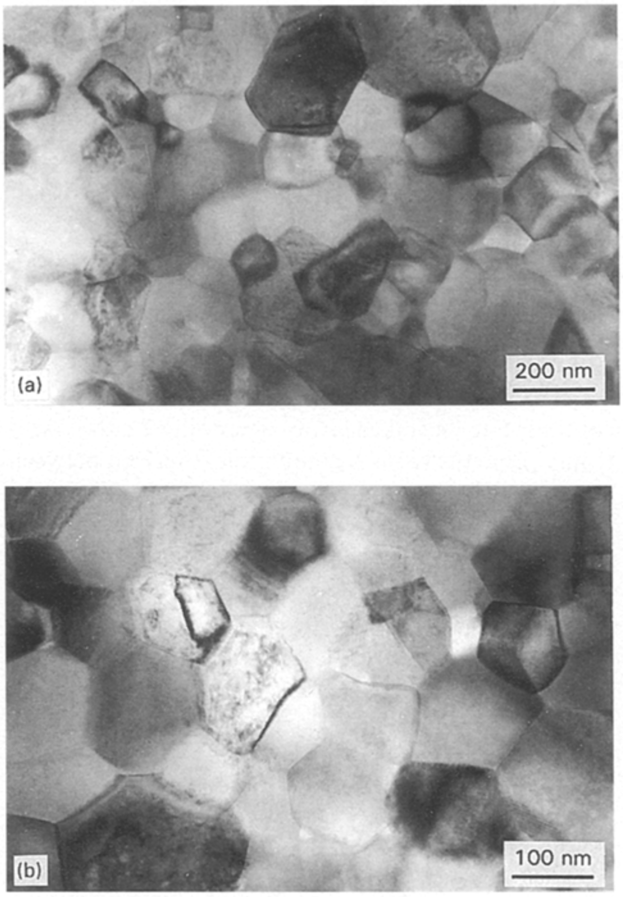

Figure 8 TEM micrograph of sintered bodies at 1250 °C by (a) slow and (b) fast sintering methods.

the samples achieved 97.5% at 1250 °C with a mean grain size of ~120 nm (Fig. 8(b))

4. Discussion

4.1. Azeotropic distillation process

The aim of distillation is to effectively dehydrate the hydrous powder and thus eliminate the potential for building up of hard agglomerate on drying and further calcination. The dehydration process is postulated to be that the terminal hydroxyl groups and physically adsorbed water molecules on particle surface were removed via distillation by forming water–organic solvent binary azeotrope. Therefore the selection of the organic solvent to act as a "water carrier" is pivotal to the effectiveness of the process, which should be determined by such a principle that the water composition in the azeotrope can be as high as possible. *n*-Butanol was selected in this work because of its highest water content in the azeotrope (44.5 wt %) among several practicable water–organic binary systems [8].

As only about 10 wt % of water is miscible in *n*-butanol at room temperature, and thus the aqueous particle surface is not wettable with *n*-butanol, strong mechanical or ultrasonic agitation are needed to facilitate the mixing of the hydrous gel and *n*-butanol. The water was gradually extracted from the gel as the distillation proceeded. A highly dispersed and stabilized suspension was finally formed after reaching the azeotropic point when water remained in the system

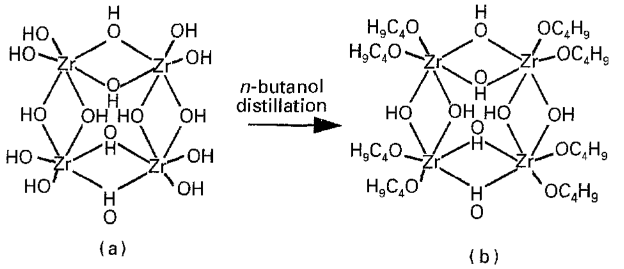

Figure 9 The proposed hydrous zirconia structure (a) before and (b) after *n*-butanol distillation.

continued to be taken away according to the azeotropic principle, with a compatible interface between terminal butoxyl groups on the particle surface and *n*-butanol solvent being formed. Butoxyl groups on the gel surface will be unable to lead hard agglomerate since they are less likely to interact to form bridging between particles.

4.2. Interaction of *n*-butanol with hydrous particle surface

The chemical structure of zirconium hydroxide gel proposed by Zaitsev [9] and that after *n*-butanol distillation suggested by other authors are shown in Fig. 9(a) and (b) respectively. Butanol interaction with hydrous zirconia during distillation results in the replacement of terminal hydroxyl groups with butoxyl groups. After distillation, the surface in Fig. 9(b) is completely or partially covered by butoxide species. The experimental phenomenon first provided the basis for such a proposed structure in Fig. 9(b); the *n*-butanol miscibility with water-washed gel was quite poor before distillation but as the boiling temperature gradually approached the azeotropic point, a well-dispersed gel–butanol suspension developed. This is because the surface hydroxyl groups were gradually substituted by butoxyl groups during distillation and a compatible interface between hydrous zirconia with *n*-butanol was formed.

As is generally recognized [4], non-bridging hydroxyl groups are bonded to the zirconium ions with excess water being physically adsorbed onto the gel. During heating for drying and calcination, adsorbed water was first to be removed. Non-bridging hydroxyl groups on adjacent particles will interact, if they are close enough, to produce the following condensation reaction which is the basic mechanism for hard agglomerate formation

$$\mathrm{ZrOH} + \mathrm{HOZr} \rightarrow \mathrm{ZrOZr} + \mathrm{H_2O} \qquad (1)$$

Distilled powder behaves differently. By reference to Kaliszewski's proposed mechanism of prevention of hard agglomerate formation by ethanol washing of hydrous zirconia [5], a similar mechanism of *n*-butanol interaction with hydrous zirconia by azeotropic distillation could be proposed. Fig. 10 illustrates how distilling hydrous gel reduces or avoids hard agglomerates. It was clear that the excess *n*-butanol existing between particles does not create any appreciable attractive force between them. Since the surface hydroxyl groups had already been replaced with butoxyl groups by distillation process (Fig. 10(b1)), the possibility of a condensation reaction between two terminal hydroxyl groups (Fig. 10(a2)) is greatly reduced. Furthermore, the terminal butoxyl groups might also act sterically to prevent the particles from closely approaching each other.

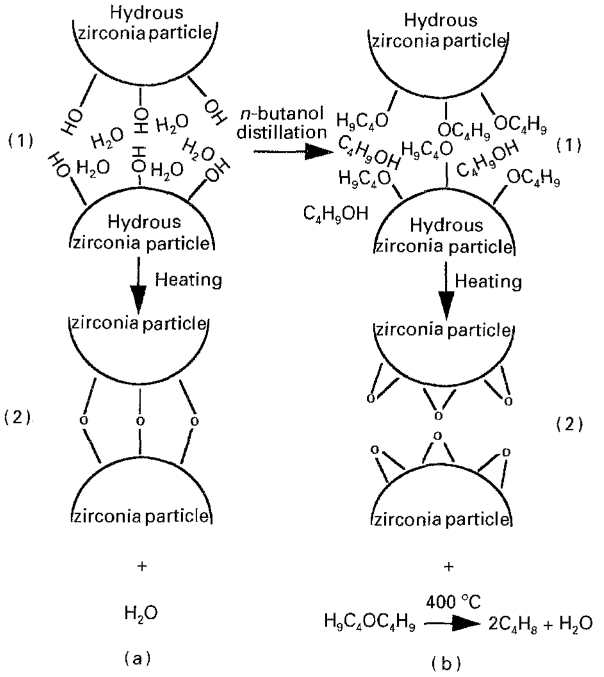

Figure 10 Proposed mechanism for hard agglomerate formation in (a) water-washed gel and (b) *n*-butanol-distilled gel.

As the heating temperature is increased, removal of the terminal butoxyl groups, which occurs preferentially between the neighbouring groups on the same particle, since the close approach of particles is inhibited, involves a reaction similar to that involved in catalysed ethylene production [10] because zirconia itself is a well-known dehydration catalyst for alcohols [11]. As a result, two butoxyl groups on the same particle react to finally form butene molecules and water. Thus, chemical bonding between particles does not occur as in the water-washed case. This important reaction product, butene, was indeed captured by mass spectroscopy (Fig. 6) while the initial *n*-butanol molecules and intermediate product, $C_4H_9OC_4H_9$ molecules, were not found.

The reduction or elimination of chemical bonding as shown in Equation 1 between particles after distillation prevents hard agglomerates from forming and results in a friable and sinterable ultrafine powder compared with the water-washed case.

4.3. Sinterability of the distilled powder

The prepared powders were sintered to over 99% at as low as 1250 °C by slow sintering. Haberko [12] reported that the water-washed powder attained 85.7%, and ethanol-washed powder achieved 98.8% with the grain size of about 0.7 μm sintered at 1300 °C for 3 h [12]. It is obvious that due to the reduction of hard agglomeration in distilled powder, low sintering temperature with good sinterability and small grain size in the sintered bodies was obtained. Finer grain size was obtained by fast sintering because it provided the benefit of quickly bypassing the lower temperature region where grain growth would surpass densification, while at the higher temperature region, densification would exceed grain growth.

5. Conclusions

Azeotropic distillation effectively dehydrated hydrous zirconia gel and thus reduced the formation of hard agglomerates. Studies on the interaction of *n*-butanol with hydrous zirconia indicated that distillation treatment greatly reduced the possibility of Zr–O–Zr bonding between adjacent particles and thus reduced hard agglomerates. The powder derived from azeotropic distillation process could be sintered at 1250 °C to 99.5% by slow sintering with a grain size of about 200 nm, to 97.5% by fast-sintering with a grain size of about 120 nm.

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