Journal of the European Ceramic Society 21 (2001) 589–594

www.elsevier.com/locate/jeurceramsoc

Effects of attrition milling on precursors of Al_2O_3 and 12Ce–TZP powders

Stefano Maschio [a], Alessandro Piras [a], Chiara Schmid [b,*], Elio Lucchini [b]

[a] *Università di Udine, Dipartimento di Scienze e Tecnologie Chimiche, Via Cotonificio 108, 33100 Udine, Italy*
[b] *Università di Trieste, Dipartimento di Ingegneria dei Materiali e Chimica Applicata, Via A. Valerio 2, 34127 Trieste, Italy*

Received 30 March 2000; received in revised form 21 August 2000; accepted 31 August 2000

Abstract

The influence of attrition milling on the chemical precursors of alumina and tetragonal zirconia polycrystal (12 mol% CeO_2) is studied, with particular attention to the morphology, the specific surface area, the crystallographic form and the sinterability of powders obtained by (i) calcining the pristine precursors and (ii) milling the pristine precursors and then performing the calcination. It has been demonstrated that in the latter case the specific surface area is reduced but the sinterability is increased with respect to the former one. This behaviour is due to the destruction, by the attrition milling, of the porous microstructures and of the large aggregates in the "as-prepared" materials. The influence of milling is more evident in the alumina precursor, since it contains a high quantity of organic matter and therefore exhibits a very porous microstructure with a high specific surface area. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Calcination; Milling; Sintering; ZrO_2

---

1. Introduction

Powder production is an important step in the synthesis of ceramics for structural as well as functional materials. As an example, catalytic performance in the reduction of gas emission from combustion processes used for energy transformation is heavily determined by the quality of the powders. In the case of structural material a good sintering behaviour is required, whereas for catalytic applications, a high surface area is preferable. Alumina and tetragonal zirconia polycrystals represent two of the most studied materials in these respects.[1–6]

α-Alumina has several applications due to its high hardness, elastic modulus and strength as a monolithic structural material.[1,2] Powders of γ-alumina are often used as catalytic supports due to the high surface area often associated with this crystal phase.[7–10]

Tetragonal zirconia polycrystals (TZP) are important structural ceramics since the transformation toughening which is associated with the tetragonal/monoclinic polymorphism imparts high toughness to dense sintered bodies.[11–13] The catalytic properties of zirconia powders are also interesting since it has been demonstrated that they can be used for redox reactions at moderate temperature when ceria is used as the added oxide.[14–16]

Due to the wide range of applications, both alumina and zirconia have received much attention from researchers and many papers are present in the literature, many of these being devoted to powder synthesis and to the production of dense materials (for alumina see Refs. 1 and 2; for zirconia see Ref. 17).

The best routes to obtain powders with specific properties still remain matters of discussion: depending on the application, either stable surface area after high temperature treatment, or good sinterability are required. The difficulty depends on the high number of parameters that must be controlled during the powder production, in particular when the so-called "chemical routes" are followed. In all cases, the performance (dense sintered body or high surface area material) depends strongly on the long milling processes after the precursor calcination. These mechanical treatments reduce the aggregates to particles of small dimensions, but sometimes also introduce impurities due to the wear of the milling media. On the other hand, it is often impossible to reduce the milling time without paying a high cost in terms of powder performance.

---

* Corresponding author. Tel.: +39-40-676-3765; fax: +39-40-572044.
E-mail addresses: schmid@univ.trieste.it (C. Schmid), stef.maschio@dstc.uniud.it (S. Maschio).

PII: S0955-2219(00)00259-4

With this in mind, we have investigated the possibility of introducing a short milling process just after the first step of the powder preparation, and before the calcination, in order to see if it is possible to avoid or shorten the prolonged milling after calcination. We were not able to find papers concerning the effects of mechanical treatment on chemical precursors *before* rather than *after* calcination.

In this work, we have produced γ-Al_2O_3 and α-Al_2O_3 by denitration of aluminium nitrate nonahydrate and 12Ce–TZP by coprecipitation of zirconyl chloride penthahydrate and cerium nitrate tetrahydrate. The products were divided each into two batches: one was characterised as prepared ("as-prepared" samples), the other one was attrition milled and then characterised ("milled" samples).

2. Experimental procedure

2.1. Alumina precursor preparation

Aluminium nitrate nonahydrate (Aldrich Chem. 98%) was melted at 75°C to form a clear liquid. A water solution with ten percent by weight of tartaric acid was added in order to avoid the explosive removal of nitrates. The solution was then aged in an oven at 200°C for 12 h to expel as much water as possible.

The cake was cooled down to room temperature, manually crushed and sieved through a 200 μm sieve.

2.2. 12Ce–TZP precursor preparation

Preparation of 12Ce–TZP powders was performed by co-precipitation. Mixtures of $ZrOCl_2{\cdot}8H_2O$ (99.0% Aldrich Chem.) and $Ce(NO_3)_3{\cdot}6H_2O$ (99.9% Aldrich Chem.) were dissolved into distilled water to give a 0.5 M solution. The solution was poured while stirring into concentrated ammonia (28 wt%) at room temperature. The product was washed with de-ionised water and with acetone–toluene–acetone.[18]

Both the precursors were then heated at 80°C in an oven for 12 h and sieved through a 63 μm sieve; they were then divided into two batches: the first one was characterised as-prepared; the second one was attrition milled and then tested. The milling conditions were: 1 h in a plastic jar at 300 rpm; α-alumina spheres for the alumina precursor and 3yttria–zirconia spheres for the 12Ce–TZP precursor were used as milling media. For both cases the sphere's diameter was 5 mm; 30 g of powder were added to 500 g of milling media slurrying with 50 cm^3 of ethanol as dispersing medium. Drying was performed in an oven at 80°C for 24 h.

Simultaneous thermal analysis (STA) diagrams were obtained on Netzsch STA 409 equipment at a heating rate of 10 K/min up to a temperature of 1250°C. On the basis of this information, further calcinations of alumina precursors were done at 850, 910 and 1050°C for 2 h; while 12Ce–TZP precursors were calcined at 700°C always for 2 h.

X-ray diffraction data were recorded on an XRG 300 Inel Powder Diffractometer equipped with a CPS 120 detector. Monochromated Co$K_{\alpha 1}$ radiation was used with settings 35 kV and 20 mA.

A Sorptomatic Carlo Erba BET instrument using nitrogen as percolating gas was used for the determination of specific surface areas. Powders morphology, after calcination, was examined by a Cambridge Stereoscan Scanning Electron Microscope (SEM). Sintering was performed on uniaxially pressed (200 MPa) cylindrical specimens (diameter 11 mm and height 4 mm) using a muffle furnace heated by $MoSi_2$ elements. The density of the sintered bodies was measured with the Archimedes method using de-ionised water as the displacing liquid.

3. Results and discussion

3.1. Alumina precursor

The STA results for the alumina precursors are reported in Fig. 1. The total weight loss of the as-prepared sample (45.5%) is higher than that of the milled one

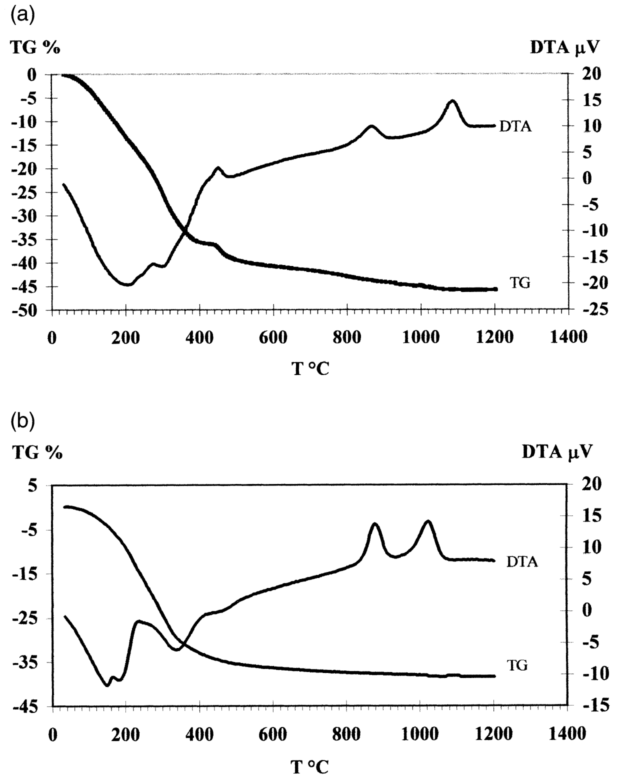

Fig. 1. STA results for alumina precursor: (a) as-prepared; (b) milled. Positive DTA refers to exothermic effect.

(38.5%). This difference can be ascribed to the "washing" effect of the ethanol used as dispersant liquid for the milling. Ethanol facilitates the release of water trapped in the precursor during the drying. It is possible to see that the as-prepared sample has a continuous weight loss also after 620°C (see Fig. 1a). This behaviour is due to the microporosity and the presence of aggregates: both containing non-decomposed material. The reactions proceed more slowly as the high partial pressures of the evolved gases in the cavities inhibit the complete decomposition of the entrapped material. Conversely in the case of the milled sample, most of the micropores and of the aggregates are broken and therefore the material is in direct contact with the surrounding free atmosphere and can decompose more easily.

The DTA curves also show differences. Apart from the endothermic peaks due to the emission of entrapped water, two peaks are evident. The former is due to the crystallisation of the γ-phase, the latter to the transformation to α. In the as-prepared sample, γ begins to crystallise at 807°C, the maximum being at 866°C; whereas in the milled sample, the onset and peak temperatures are respectively 842 and 877°C. In the case of the transformation to the α-phase, the peak maximum falls at 1080°C for the as-prepared sample and at 1021°C for the milled one. In the as-prepared powder the γ-crystallisation begins early and it is reasonable to argue that the entire amount of the alumina is crystallised in the γ-form. For the milled powder, with a higher γ-crystallisation temperature some alumina may remain in the amorphous form. This directly crystallises to the α-form (see the floor between the two peaks in Fig. 1b, which is higher than the base line: this can be attributed to a superimposed effect due to α-formation); this results in an earlier α-crystallisation peak. It was decided to choose for the further calcination step three different temperatures: 850°C when γ-Al_2O_3 is forming; 910°C when γ-Al_2O_3 has formed but no α is present; 1150°C when the transformation $\gamma \rightarrow \alpha$ is completed.

In Table 1, the specific surface area of the alumina samples calcined at the various temperatures is presented. The decrease of this parameter with increasing heating temperature can be explained by considering that the high temperatures promote the coarsening and densification process. The sudden fall of the specific surface between the calcination temperatures of 910 and 1150°C is due especially to the alumina $\gamma \rightarrow \alpha$-transition.[19,20] The most striking difference between the as-prepared and milled precursors is the marked reduction of the specific surface area for the latter, for all three calcination temperatures. This behaviour can be related to the morphology of the precursor after the oven treatment at 200°C. The addition of tartaric acid induces microporosity in the material that favours powders with a high specific area also after calcination. If the precursor is submitted to an energetic milling before the heating, the activity of the powder for coarsening is increased.[21] Indirect evidence for the milling effects was seen in the results of the thermogravimetric analysis.

Table 1
Specific surface areas and X-ray results for alumina precursors calcined for 2 h at different temperatures

Alumina precursors	T (°C)	Specific surface area ($m^2\ g^{-1}$)	X-ray results
As-prepared	850	149	γ
	910	137	γ
	1150	55	α
Milled	850	122	γ
	910	92	$\gamma+\alpha$
	1150	31	α

In Table 1 the results of the X-ray analysis of the alumina precursors calcined at 850, 910 and 1150°C are also reported. The X-ray results confirm that, for powders treated at 910°C (that is between the two crystallisation peaks), in the as-prepared case only γ crystals are detected, whereas in the milled both α and γ are present.

The examination of the SEM micrographs (Fig. 2) showed the presence in the non-milled samples of coarse particles. In Fig. 2a the appearance of the as-prepared

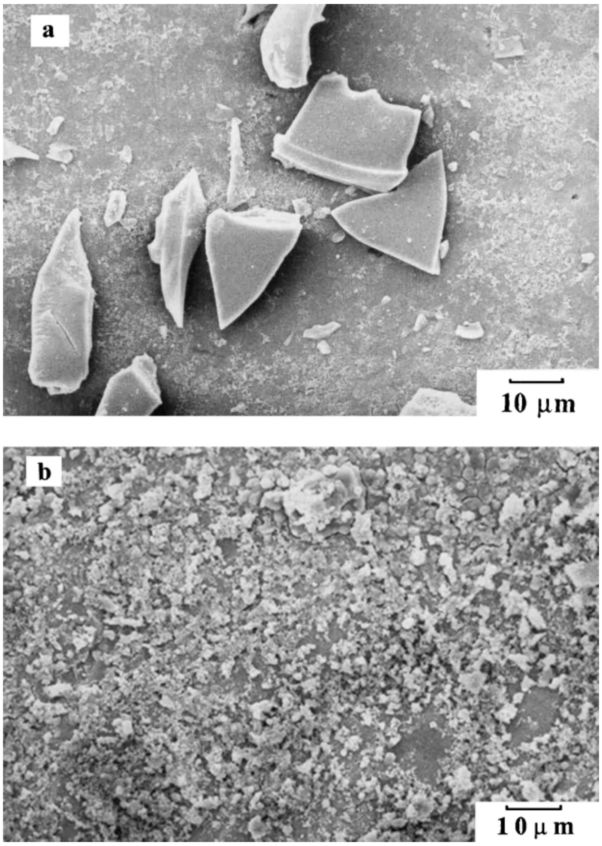

Fig. 2. SEM pictures for alumina precursors: (a) as-prepared; (b) milled.

precursor calcined for 2 h at 850°C is shown. This morphology can be explained by considering that the ageing at 200°C does not decompose the tartaric acid that bonds together the particles forming large lumps that remain also after calcination. If the precursor is milled before the heating at high temperature, the large lumps are broken or reduced. In Fig. 2b the appearance of the milled powder heated at 850°C for 2 h is presented: finer particles are evident. Consequently the milled powder has a higher sinterability with respect to the as-prepared one.[22,23]

In Table 2 the densities of alumina bodies obtained with as-prepared and with milled precursors, sintered at 1550°C for 1 h are reported.

3.2. 12Ce–TZP precursor

In Fig. 3 the STA of 12Ce–TZP precursors are reported. The STA measurements show very little difference in the weight loss between the as-prepared and the milled samples; also the tetragonal crystallisation temperatures (peaks at about 450°C) match (see Fig. 3a and b, respectively). This different behaviour with respect to the alumina precursors is probably due either to the modest quantity of micropores in the coprecipitated hydroxides and/or to the different decomposition product (aqueous vapour).

Table 2
Densities of sintered samples obtained from alumina precursor powders (1550°C for 1 h)

Alumina precursors	d_r%
As-prepared	80
Milled	97

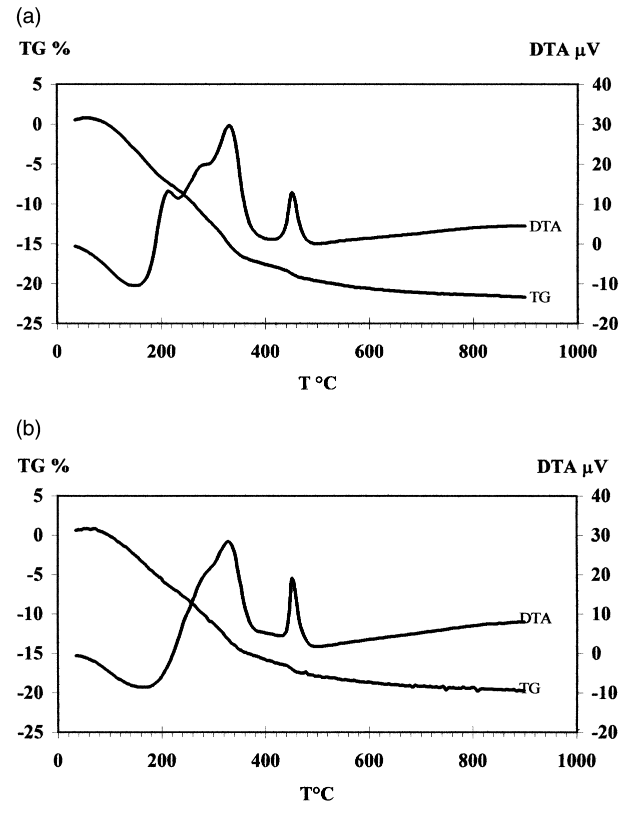

Fig. 3. STA results for 12Ce–TZP precursors: (a) as-prepared; (b) milled. Positive DTA refers to exothermic effect.

Surface areas and crystal phases of the calcined (700°C 2 h) 12Ce–TZP powders are reported in Table 3. Both products have tetragonal symmetry and their surface areas are quite similar. Milled powders have lower values. As for alumina, also in this case, powder morphology is different as reported in Fig. 4: the as-prepared product (Fig. 4a) contains large agglomerates while the milled one (Fig. 4b) shows small particles.

Table 3
Specific surface areas and X-ray results for 12Ce–TZP precursors calcined at 700°C for 2 h

12Ce–TZP precursors	T (°C)	Specific surface area (m^2 g^{-1})	X-ray results
As-prepared	700	48	Tetragonal
Milled	700	36	Tetragonal

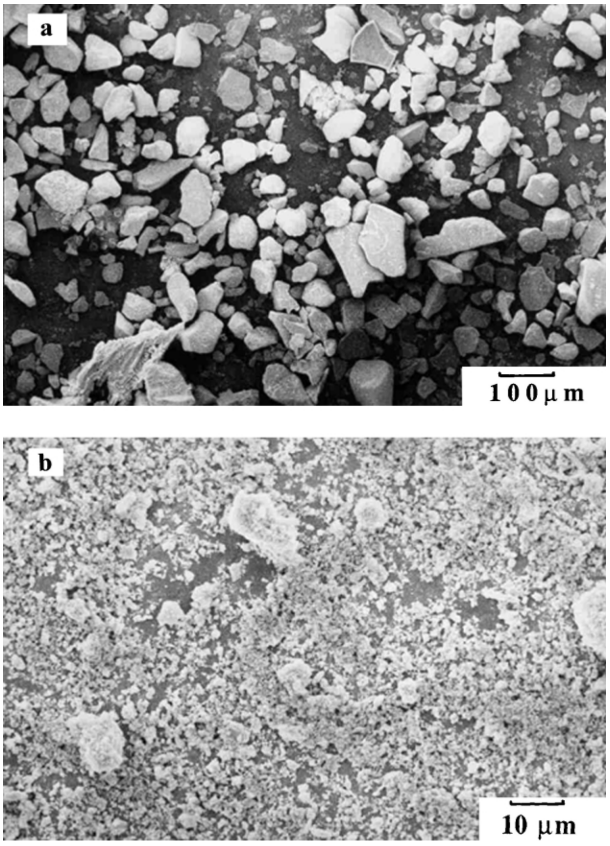

Fig. 4. SEM pictures for 12Ce–TZP precursors: (a) as-prepared; (b) milled.

Table 4
Densities of sintered samples obtained from 12Ce–TZP precursor powders (1450°C for 1 h)

12Ce–TZP precursors	d_r%
As-prepared	85.0
Milled	98.5

Table 5
Comparison, for both the materials, between densities of sintered bodies obtained with milling step *before* and *after* the calcination one

	d_r%		
Materials	*Milled*→calcined	Calcined→*milled*	Firing conditions
Alumina	97.0	92	1550°C, 1 h
12Ce–TZP	98.5	94	1450°C, 1 h

As a consequence the milled sample exhibits a higher sinterability with respect to the as-prepared one. In Table 4 the densities of 12Ce–TZP bodies obtained with as-prepared and with milled precursors fired at 1450°C for 1 h are reported.

We have also prepared sintered samples with both the materials (alumina and 12Ce–TZP) in the traditional way, that is making the milling step after calcination. The sintering times and temperatures were the same used for the milled samples (1 h at 1550°C for alumina and 1 h at 1450°C for zirconia), as well as the milling step (1 h attrition milling at 300 rpm in ethanol). In Table 5 the comparison of the densities obtained in the two ways is reported. It is evident that performing the same milling step before calcination produces higher densities in the sintered bodies. It is possible to obtain finer powders (and also higher densities) operating the milling after calcination, but this involve longer times and consequently increase the probability of introducing contamination in the powder, as well as increasing the cost of the operation.

4. Conclusions

On the basis of these results, it is possible to argue that the alumina precursor containing a high quantity of organic phase develops, after calcination, a microstructure with a high quantity of micropores and a high specific surface area. Besides, by limiting the decomposition temperature, only the γ-phase is obtained. These features are useful for catalytic applications.

A short attrition milling before calcination reduces the specific surface area with respect to the as-prepared precursors, but in this case the presence of large aggregates is avoided. Therefore the powders obtained with this procedure and calcined at temperatures where the α-form is stable can be used for the production of high-density sintered bodies. The behaviour of the coprecipitated 12Ce–TZP is similar to that of alumina.

The specific surface area of the milled and calcined precursors is lower than that of the as-prepared samples, but the difference is not very large. The mechanical treatment also in this case increases the powder sinterability.

Using the same milling and firing conditions, it has been shown that milled and then calcined powders consistently yield bodies with higher density than powders calcined and then milled. From this point of view the milling of precursors *before* the thermal decomposition is useful as it is less time-consuming, more economic and reduces the contamination from the milling media.

References

1. Dorre, E. and Hubner, H., *Alumina*. Springer, Berlin, 1984.
2. Gitzen, W. H., *Alumina as a Ceramic Material*. The Am. Ceram. Soc. Pub, Columbus, OH, 1970.
3. Spriggs, R. M., Mitchell, J. B. and Vasilos, B., Mechanical properties of pure, dense aluminium oxide as a function of temperature and grain size. *J. Am. Ceram. Soc.*, 1964, **47**(3), 323–327.
4. Garvie, R. C., Hannink, R. H. and Pascoe, R. T., Ceramic steel. *Nature*, 1975, **258**, 703–704.
5. Swain, M. V., Shape memory behaviour in partially stabilized zirconia ceramics. *Nature*, 1986, **332**, 234–237.
6. Butler, E. P., Transformation toughened zirconia ceramics. *Mater. Sci. Technol.*, 1985, **1**(6), 417–432.
7. Church, J. S., Trimm, L. D. and Cant, N. W., Stabilization of aluminas by rare earth and alkaline earth ions. *Appl. Catal.*, 1993, **101**, 105–116.
8. Marecot, P., Fakche, A., Pirault, L., Mabilon, C. G., Prigent, M. and Barbier, V., Effect of the preparation procedure on the properties of three-way automotive platinum-rhodium/alumina-ceria catalysts. *J. Appl. Catal. B: Environ.*, 1994, **5**, 43–50.
9. Shyu, J. Z. and Otto, K., Characterization of Pt/γ-alumina catalysts containing ceria. *J. Catal.*, 1989, **115**, 16–24.
10. Braun, S., Appel, L. G., Zinner, L. B. and Schmal, M., Thermal behaviour of aluminas with different morphologies. *Br. Ceram. Trans.*, 1999, **98**(2), 81–85.
11. Evans, A. G. and Heuer, A. H., Review — transformation toughening in ceramics: martensitic transformation in crack-tip stress field. *J. Am. Ceram. Soc.*, 1980, **63**(5–6), 241–248.
12. Swain, M. V., Limitation of maximum strength of zirconia-toughened ceramics by transformation toughening increment. *J. Am. Ceram. Soc. Commun.*, 1985, **68**(4), C97–C99.
13. Gupta, T. K., Lange, F. F. and Berchtold, J. H., Effect of stress-induced phase transformation on the properties of polycrystalline zirconia containing metastable tetragonal phase. *J. Mater. Sci.*, 1978, **13**, 1464–1470.
14. de Leitemburg, C., Trovarelli, A., Zamar, F., Maschio, S., Dolcetti, G. and Llorca, J., A novel and simple route to catalysts with high oxygen storage capacity: the direct room-temperature synthesis of CeO_2–ZrO_2 solid solutions. *J. Chem. Soc., Chem. Commun.*, 1995, 2181–2182
15. Trovarelli, A., de Leitemburg, C. and Dolcetti, G., Design better cerium-based oxidation catalysts. *Chemtech*, 1997, **27**, 32–37.
16. Trovarelli, A., Zamar, F., Llorca, J., de Leitemburg, C., Dolcetti, G. and Kiss, J. T., Nanophase fluorite type structured CeO_2–ZrO_2 catalysts prepared by high energy mechanical milling. *J. Catalysis*, 1997, **169**, 490–502.
17. A. H. Heuer and L. W. Hobbs (eds.), *Advanced in Ceramics Vol. 3, Science and Technology of Zirconia*, American Ceram. Soc., 1981.

18. Chiu, Bi.-Shiu, Hsu, W. Y. and Duh, J. G., Dehydration of synthesized calcia-stabilized zirconia from a coprecipitation process. *J. Mater. Sci. Lett.*, 1986, **5**, 931–934.
19. Ozawa, M. and Kimura, M., Effect of cerium addition on the thermal stability of gamma alumina support. *J. Mater. Sci. Lett.*, 1990, **9**, 43–45.
20. Ismagilov, Z. R., Shkrabina, R. A. and Koriabkina, N. A., New technology for production of spherical alumina supports for fluidized bed combustion. *Catal. Today*, 1999, **47**, 51–71.
21. Rahaman, M. M., *Ceramic Processing and Sintering*. Marcel Dekker, New York, 1995, pp. 50–51.
22. Kellet, B. J. and Lange, F. F., Thermodynamics of densification: I sintering of single particle arrays, equilibrium configuration, pore stability and shrinkage. *J. Am. Ceram. Soc.*, 1989, **72**(5), 725–734.
23. Kellet, B. J. and Lange, F. F., Thermodynamics of densification: II grain growth in porous compacts and relation to densification. *J. Am. Ceram. Soc.*, 1989, **72**(5), 735–741.