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Preparation and properties of alumina-ceria nano-nano composites

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Alumina-ceria composites were prepared by the calcination in air of gels obtained by homogeneous precipitation from dilute chloride and nitrate solutions, followed by either microwave treatment, autoclave treatment or air-drying. Microwave treatment and air-drying of the gels yielded amorphous powders whereas autoclave treatment yielded well-crystallised boehmite. The phase evolution during calcination was investigated by *in-situ* X-ray diffraction (XRD) and by differential thermal analysis and thermogravimetry (DTA/TG). The structures of the calcined powder were investigated by transmission electron microscopy (TEM) and high resolution TEM. A variety of morphologies was found depending on the processing route. The calcined microwave treated gels consisted of nano-size particles of ceria in nanostructured transition alumina i.e. a nano-nano composite structure suitable for catalysis applications. In comparison, the calcined autoclave treated gels consisted of a coarser composite of large agglomerates of ceria in transition alumina which, however, was more stable against transformation to alpha alumina at high temperature. Boehmite sols made with the autoclave treated gels were suitable for making thin films by dip-coating. *© 1999 Kluwer Academic Publishers*

1. Introduction

Catalytically active membranes are used to synthesise gaseous products from gaseous reactants flowing through them at elevated temperatures, e.g. methane steam reforming to produce syngas ($CO + H_2$) or the synthesis of methanol from syngas. These membranes rely for their efficiency on a fine and uniform dispersion of a catalytically active phases on the surface of porous channels within the membrane. Catalytic converters for car exhausts are similar in structure and function to catalytically active membranes, except that the gas flow is through macroscopic channels parallel to the membrane surface rather than through it, and that they operate under especially demanding conditions with respect to temperature range and fuel/air ratio. Nanoporous materials with nanoscale dispersions of the various phases, i.e. nano-nano composites, should be particularly effective for these applications, providing they can demonstrate sufficient high temperature stability. Methods for producing suitable nanostructures are therefore of current interest, and sol-gel methods in particular appear able to deliver the required nanoscale control over structure and composition. This paper reports results obtained by one of these methods, i.e. homogeneous precipitation, which uses metal salts as starting materials.

A nanostructured γ-Al_2O_3 catalyst support with a dispersed cerium oxide "oxygen storage" component and noble metal (Pt, Pd, Rh) is generally used for car exhaust catalysts [1]. The ceria has a multifunctional role: it acts as an "oxygen storage" component to buffer transient shifts in the fuel/air ratio [2], it acts to stabilise the γ-Al_2O_3 structure and the noble metal dispersion [3], and it has a synergistic effect on the noble metal catalysis of reactions such as that between CO and NO [4]. The oxygen storage capability is required to cover the delay of about one second while the oxygen sensor and energy management system reacts to sudden changes in engine load conditions.

The mechanism by which ceria achieves these beneficial effects is not yet completely clear. However, it is reported that the effectiveness of the ceria increase as the interaction between the ceria and the noble metal particles increases and as the particle size of the ceria decreases [5]. It therefore seems that a nanoscale distribution of ceria in contact with the noble metal particles is required.

With the above requirements in mind, our aim was to find a simple and inexpensive way to make a nanoscale dispersion of cerium oxide in nanostructured alumina (a nano-nano composite). Moreover, the product should also initially consist of boehmite to allow thin coatings to be produced on a suitable substrate by a simple dipping process prior to transformation to transition alumina during calcination. A sol-gel method was used to hydrolyse a mixture of aluminium and cerium salts in

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the presence of urea. This precipitation method yielded a voluminous transparent gel which was calcined to yield a ceramic powder. The properties of the gel and the calcined product were characterised using SAXS, DTA/TG, XRD, TEM and HRTEM techniques and the effect of the processing parameters on the properties of nano-nano composites was discussed.

2. Experimental

2.1. Preparation of the gel

We used the following starting materials: aluminium chloride hexahydrate, $AlCl_3 \cdot 6H_2O$ (Merck, crystalline purified), aluminium nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$ (Baker, analysed, reagent grade), cerium (III) chloride heptahydrate, $CeCl_3{\cdot}7H_2O$ (Janssen Chemica, 99%), urea, CON_2H_4 (Acros, p.a.) and polyvinylpyrrolidone, PVP (Aldrich K-30, special grade).

Salt solutions were prepared with concentrations equivalent to $2 \cdot 10^{-2}$ mol/l of Al_2O_3 and an amount of cerium equivalent to 10 mol % CeO_2 in Al_2O_3. The solutions were filtered to remove undissolved solids. The pH of the solution was adjusted to a value between 3 and 3.5 by addition of the corresponding acid. Additions of PVP (3 g/l) and urea (2 mol/l) were then dissolved in the solutions.

Precipitation was carried out on 5 l volumes of solution by heating the stirred solution in a glass beaker to 86 °C at 1–1.5 °C/min. After ageing at 86 °C for 2 h the resulting hydrosol was cooled to room temperature. A final pH of between 5.7 and 8.2 was obtained depending on the precursor salt used. A small amount of ammonium hydroxide was added to a small sample of the solution to check that precipitation had gone to completion. The clear part of the solution was decanted off and the remainder was centrifuged at 380–450 g to separate about 1200 ml of transparent gel. In most cases the gel was washed with twice its own volume of distilled water to remove most of the anion and organic impurities. To investigate the effects of the washing procedure, some samples of powder were also prepared from non-washed gels for comparison.

2.2. Preparation of powder from the gel

The gel was treated in a number of different ways: drying at room temperature in air, drying in an oven in air, drying in a microwave oven, and crystallisation of the gel in an autoclave.

The air-dried gel was prepared by leaving the gel in glass beaker at room temperature in the laboratory until a solid formed which was than crushed in an agate mortar to produce a fine powder.

The oven-dried gel was prepared by heating the gel in air in an oven at about 80–85 °C for 24 h. The gel dried to yield a very much smaller volume of cracked transparent solids which was then crushed in an agate mortar to produce fine powder.

Microwave-dried gel samples were prepared in a domestic microwave oven. To overcome the tendency of the gel to foam, especially in the case of unwashed gel, a treatment of 500 W for 5 min followed by 20 min at 1000 W was used. The product was a dry solid which was easily broken up to a white powder using an agate mortar. To obtain a reproducible product it was found necessary to process the same amount of gel in each batch.

Autoclave treated gels were prepared in a teflon-lined stainless-steel autoclave vessel using heating rates of about 2 °C/min and treatment temperatures of up to 210 °C with a hold time of 4 h at temperature. After stepwise colling, there were two layers visible in the product. The clear upper layer was discarded. The remaining layer was a gel-like dispersion of boehmite with a slightly basic pH and was light brown in colour. The exact colour and pH depended on the amount of organic impurities present and on the anion species of the precursor salt. This gel was dried in air for 24 h at 80–85 °C to yield a fine boehmite powder.

2.3. Calcination of the powder

Samples for XRD, TEM and HRTEM examinations were calcined in alumina crucibles for 1 h in air at temperatures up to 1400 °C using a heating rate of about 5 °C/min and a cooling rate of about 10 °C/min.

3. Characterisation

The size of the colloidal particles in the gel and the fractal dimension of the gel was measured using small angle X-ray scattering (SAXS) using the method of Teixeira [6]. Samples were also characterised using differential thermal analysis (DTA) and thermogravimetric analysis (TG) (Netsch STA 409) in air using a heating rate of 5 °C/min to a temperature of 1400 °C. The phase composition of samples after calcination at 1000, 1200 and 1400 °C for 1 h was determined by X-ray diffraction (XRD) (Philips PW173) and the crystallite size was estimated from peak broadening using the Scherrer equation i.e. $D_{\mathrm{app}} = K\lambda/(B\cos\theta)$, where $K = 0.9$ and $B =$ peak width obtained using a Voigt peak fitting routine. CuK_α radiation with a graphite filter was used ($\lambda = 1.54060$) and the instrumental broadening was determined using a LaB_6 standard. The evolution of phases during calcination in air was also characterised by *in-situ* X-ray diffraction with a heated specimen stage using various heating rates and dwell times (Siemens D5000).

The microtextural properties of gel, boehmite and calcined powders were examined by transmission electron microscopy (TEM) (Philips EM 400) and high-resolution transmission electron microscopy (HRTEM) (Jeol 4000 EX/II with a point resolution of 1.65 Å at 400 kV). Sample preparation consisted of dispersing the powder in absolute ethanol by ultrasonification, placing a drop of the resulting suspension on a carbon-coated copper grid and allowing the alcohol to evaporate.

4. Results

4.1. Colloidal particle size measurements

A voluminous transparent gel was obtained both for the pure alumina and for the alumina-ceria systems

TABLE I Properties of various alumina and alumina-ceria precursor gels measured by SAXS

	Alumina		Alumina-ceria	
	Nitrate	Chloride	Nitrate	Chloride
Fractal dimension	2.3	2.2	2.4	2.45
Diameter (nm)	4.1	3.7	4.4	4.6

independently of whether chloride or nitrate salts were used. The colloidal particle size in these gels as measured by SAXS is given in Table I and showed that the primary gel particles were all similar in size at about 4 nm. The narrow range of values for the fractal dimension is taken as an indication that the state of aggregation of primary particles within the gel was similar for all gels.

4.2. Phase composition of alumina precursor gels

The phase composition of the washed samples of the undoped alumina precursor gels was deduced from the XRD results. The air-dried samples of alumina precursor gel from the chloride salt yielded poorly crystallised bayerite, $Al(OH)_3$, together with some urea as an impurity. In contrast, more vigorous dehydration processes yielded boehmite instead of bayerite. Microwave treatment of the gel yielded boehmite with a very small crystallite size, and autoclave treated gel yielded well-crystallised boehmite. Alumina precursor gels from the nitrate precursor also yielded well-crystallised boehmite after autoclave treatment, but dehydration by microwave treatment or by air-drying yielded an amorphous product. On calcination in air, boehmite dehydrated at about 400 °C to yield an amorphous product which persisted to temperatures up to about 850 °C. Therefore all gels were amorphous during the intermediate stages of calcination (300–850 °C, approximately) irrespective of whether they were initially amorphous or crystalline. At 850 °C a progressive transformation to γ-Al_2O_3 and θ-Al_2O_3 was observed. At 950 °C crystallisation of α-Al_2O_3 began and after 1 h at 1200 °C only α-Al_2O_3 was present.

4.3. Phase composition of alumina-ceria precursor gels

Washed ceria-doped alumina precursor gels from chloride salts were amorphous after microwave drying but contained boehmite and $CeOHCO_3$ after autoclave treatment. On calcination the evolution in phase composition differed from that of the undoped gel. The microwave treated gel remained amorophous to 900 °C when CeO_2 crystallised—see Fig. 1. Significant amounts of transition alumina were first observed after 1 h at 1200 °C and 1 h at 1400 °C was required to effect the transformation to α-Al_2O_3. The effect of the ceria dopant in the microwave treated material therefore was to impede the development of crystalline forms of alumina. For calcinations in the temperature range 1000 to 1200 °C the product was a nano-nano composite of ceria and transition alumina i.e. both phases were nanocrystalline—see Fig. 5b. After transformation of the transition alumina to α-Al_2O_3 the crystal size increased considerable and the product was a nanocomposite consisting of nanoscale ceria in a coarse-grained α-Al_2O_3 matrix.

The autoclave treated ceria-alumina precursor gel crystallised CeO_2 at about 400 °C and γ-Al_2O_3 at about 500 °C—see Fig. 2. The CeO_2 remained to all higher calcination temperatures and the transition alumina phases δ and θ were also still present after 1 h at 1200 °C, together with trace amounts of α-Al_2O_3. Traces of $CeAlO_3$ were also present after 1 h at temperatures of 1000 °C and above. After 1 h at 1400 °C

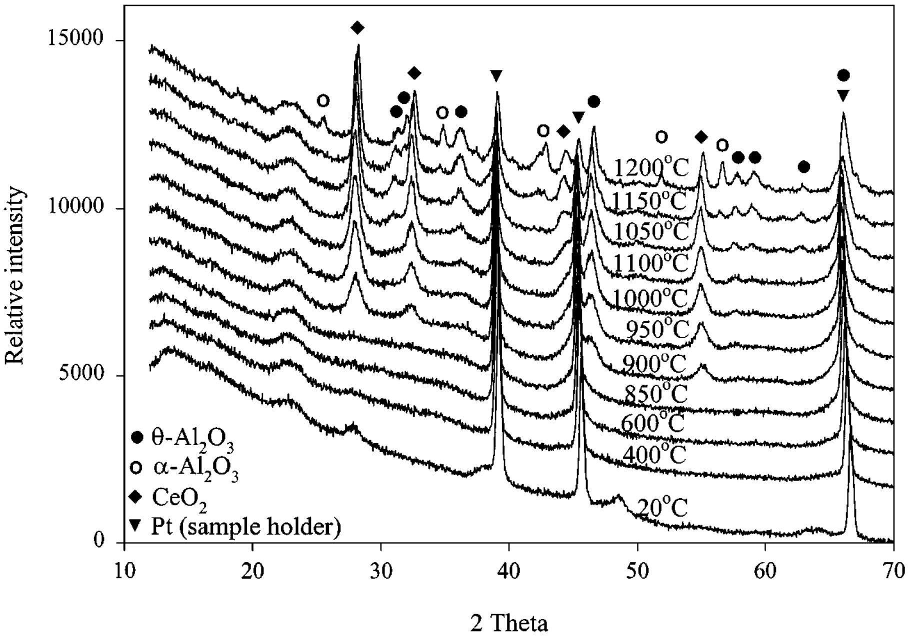


Figure 1 Evolution in phase composition during calcination of microwave treated alumina-ceria precursor gel.

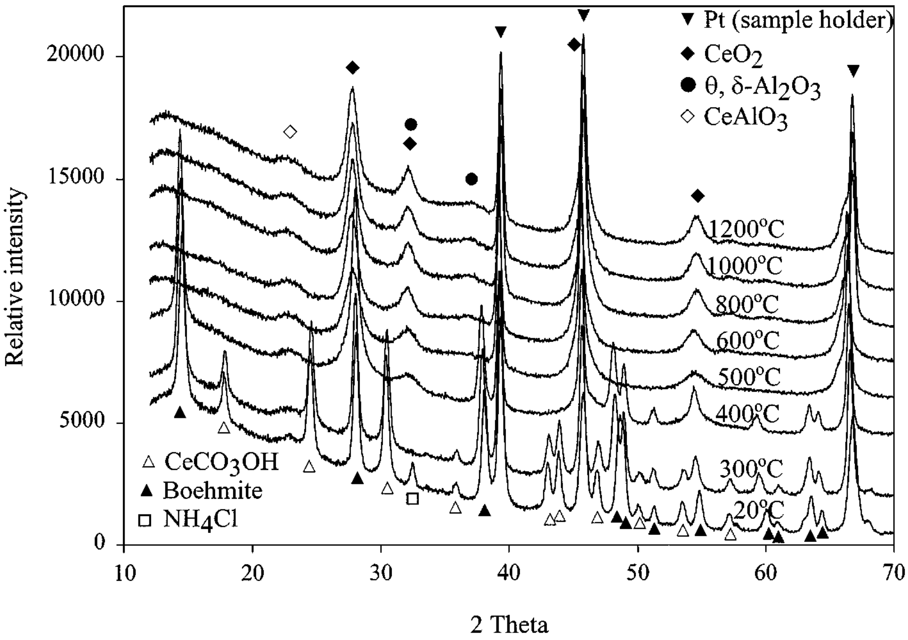


Figure 2 Evolution in phase composition during calcination of autoclave treated alumina-ceria precursor gel.

the alumina was present only as α-Al_2O_3. The effect of the dopant in the autoclave treated gel therefore appears to be to retard the crystallisation of α-Al_2O_3. The crystallite size of alumina was similar to that of the microwave treated samples but the ceria was much coarser, consisting of agglomerates of up to 300 nm diameter.

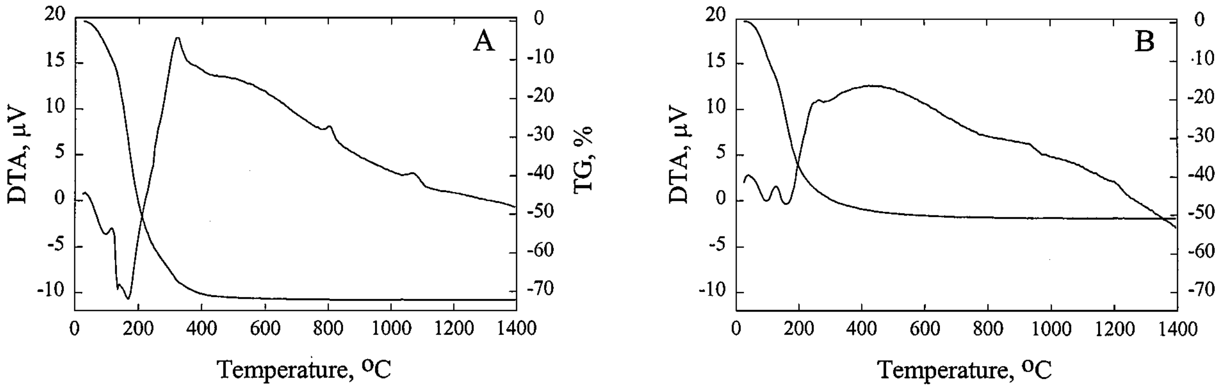
Unwashed ceria-alumina precursor gel contained poorly crystallised $(NH_4)_2CO_3 \cdot H_2O$, $Al_5Cl_3(OH)_{12} \cdot 4H_2O$, and $CeCO_3OH$ after microwave treatment. On calcination the material became amorphous up to 900 °C when $\delta + \theta$-Al_2O_3 crystallised followed by CeO_2 at 1000 °C. Above 1100 °C the transition phases were progressively replaced by α-Al_2O_3 and some traces of $CeAlO_3$ were observed at 1200 °C. A nano-nano composite structure similar to that found in samples from washed gel was found in material calcined at 1000 and 1200 °C—see Fig. 6b. Similarly, a nanocomposite of ceria in coarse-grained α-Al_2O_3 was found after calcination at 1400 °C.

4.4. DTA/TG analysis

The DTA/TG analysis results provided additional information on the nature of the precipitate and its phase evolution during calcination. The alumina and alumina-ceria precursor gels that were air-dried at room temperature exhibited endothermic events at approximately 100 and 180 °C which were attributed to the loss of water by evaporation and by dehydration of aluminium trihydroxide respectively—see Figs 3a and b. The endothermic peaks and corresponding weight losses were larger in the alumina precursor gel than in the alumina-ceria precursor gel. Between 250 and 650 °C a large exothermic band resulting from the gradual and complex decomposition and combustion of organic impurities tended to obscured other events in this temperature range. Nevertheless a small exothermic peak at approximately 280 °C in the alumina-ceria sample appears to correspond to the crystallisation of CeO_2. Crystallisation of γ-Al_2O_3 and α-Al_2O_3 in the alumina sample from the nitrate precursor was indicated by weak but quite narrow exothermic peaks at approximately 800 and 1090 °C respectively. In contrast, the same events in the alumina-ceria sample appear to correspond to very broad peaks in the temperature ranges 900–1000 °C and 1200–1250 °C respectively indicating considerably slower kinetics of phase transformation in the doped materials.

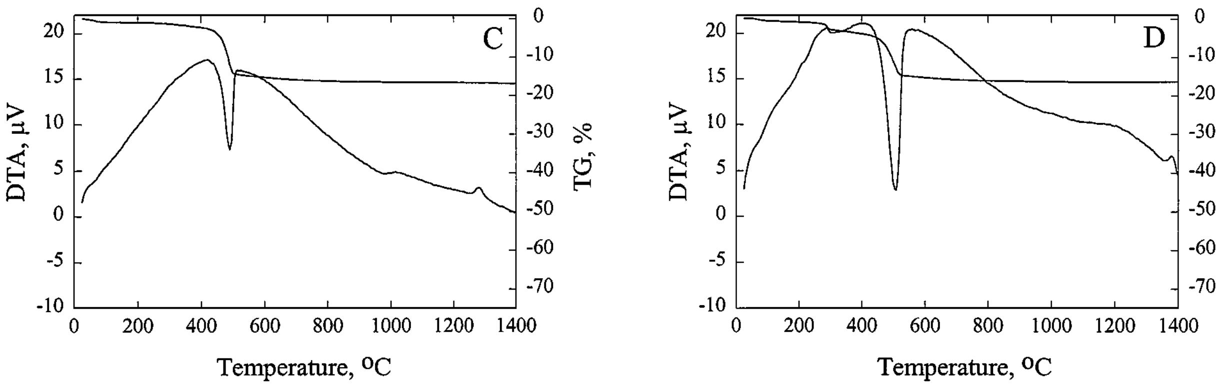
In the DTA/TG results shown in Figs 3c and d for the autoclave treated samples the dehydroxylation of boehmite was very clearly indicated by a large weight loss and a large and well-defined endothermic peak at approximately 510 °C. In the alumina-ceria precursor gels the decomposition of $CeOHCO_3$ and crystallisation of CeO_2 was an additional feature. Gel from the chloride salts was characterised by an endothermic peak and mass loss at approximately 220 °C attributable to the decomposition of $CeOHCO_3$ and the crystallisation of the CeO_2 was indicated by an exothermic peak at approximately 300–320 °C without significant corresponding weight loss. In the same material from the nitrate precursor these two processes appear to occur simultaneously at about 300 °C. These events occurred as relatively small peaks superimposed against the background of a large and broad exothermic peak resulting from the oxidation of organic impurities. The formation of α-Al_2O_3 corresponded to a weak but well-defined exothermic peak at 1280 °C in alumina precursor gels and at 1380 °C in alumina-ceria precursor gels from nitrate salts.

The TG curves from the microwaved samples showed a smooth and continuous weight loss up to 500 °C. The DTA curves from the microwave treated samples were more difficult to interpret—see Figs 3e and f. The endothermic peak at 200–250 °C was probably due to the dehydration of trihydrates but it occurred at a significantly higher temperature than in air-dried samples.



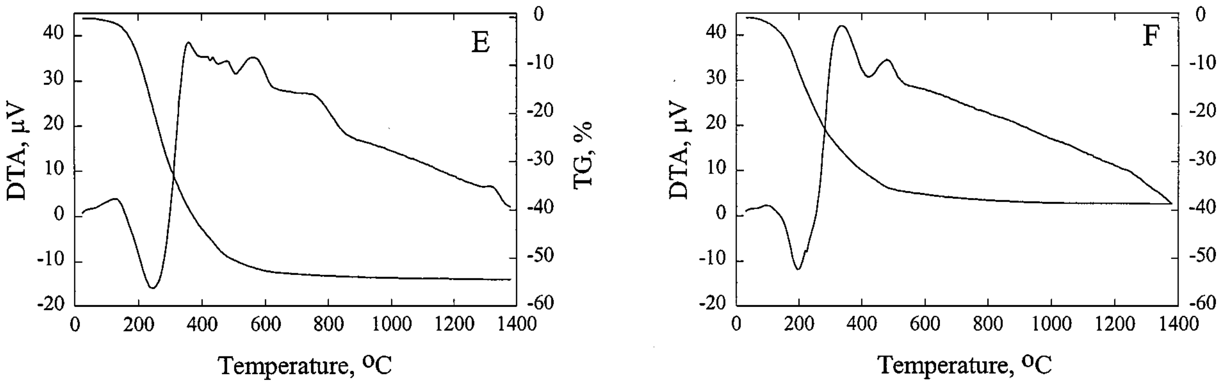
Alumina precursor gel, air-dried, nitrate salt

Alumina-ceria precursor gel, air dried, nitrate salt



Alumina precursor gel, autoclaved, nitrate salt

Alumina-ceria precursor gel, autoclaved, nitrate salt



Alumina precursor gel, microwaved, chloride salt

Alumina-ceria gel, microwaved, chloride salt

Figure 3 DTA/TG analysis of alumina and alumina-ceria precursor gels: air-dried, autoclave treated, and microwave treated.

There is no event identifiable with the dehydration of boehmite but there were exothermic peaks at 350 and 500 °C which we could not correlate to identifiable events but which may be related to the oxidation of organic residues. In samples of unwashed gels there was a well-defined endothermic peak and large weight loss at approximately 340–350 °C which could be attributed to the sublimation of ammonium chloride which formed from the reaction of chloride ions from the metal salts with ammonia from the decomposition of urea. Because ammonium chloride is very water soluble and was easily removed by the washing procedure, this DTA/TG event was not seen in washed gel.

4.5. TEM and HREM results

Although XRD results indicated that the dehydration of alumina precursor gel by microwave drying resulted in the formation of crystalline boehmite, TEM examination revealed that large amounts of crystalline organic impurities were also present which prevented investigation of the morphology and structural characteristics of the boehmite. After removal of the organic impurities by calcination for 1 h at 700 °C the typical whisker-like morphology of boehmite crystals in oriented clusters was found set in a very fine crystalline matrix—see Fig. 4a. After calcination at this temperature, however, the phase present was γ-Al_2O_3 not boehmite and the

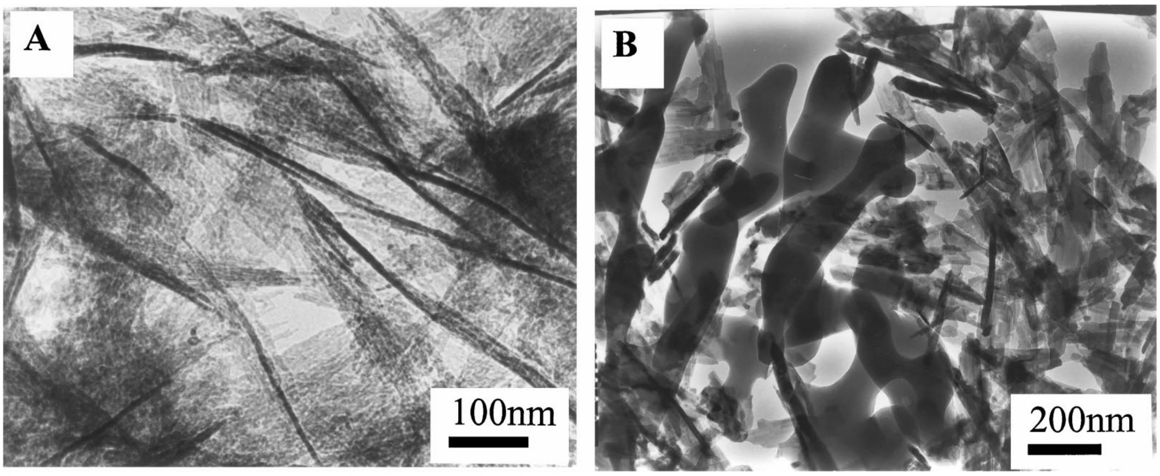


Figure 4 Microwave treated alumina precursor gel after calcination. TEM images show: (a) γ-Al_2O_3 after 1 h at 700 °C (b) finger-like crystals of α-Al_2O_3 growing in a matrix of θ-Al_2O_3 after 1 h at 1200 °C.

crystals were pseudomorphs of boehmite. This indicates that the fine crystalline matrix shown in Fig. 4a was probably also initially boehmite. The coexistence of two boehmite morphologies may be the result of the rapidity of the dehydration process which gave insufficient time for the full development of the usual whisker-like boehmite crystals. The morphology and phase composition changed with increasing of calcination temperature following the characteristic sequence: $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$-$Al_2O_3$. Fig. 4b shows that some increase of crystal size had occurred before crystallisation of θ-Al_2O_3. The transition of θ-Al_2O_3 to α-Al_2O_3 with the growth of characteristic finger-like α-Al_2O_3 crystals in matrix of transition θ-Al_2O_3 is shown in Fig. 4b. The TEM examination confirmed that microwave treatment promoted the formation of boehmite and that the morphology persisted after calcination to yield a fluffy, well-dispersed powder.

In contrast to alumina precursor gels, XRD showed the alumina-ceria samples to be amorphous after microwave drying. Consequently there was no indication of pseudomorphs of boehmite in the alumina-ceria samples after crystallisation by calcination for 1 h at 800 °C—see Fig. 5a. Instead the Al_2O_3-CeO_2 samples showed a very fine and dense crystalline structure. HRTEM showed a uniform distribution of CeO_2 particles of up to about 7 nm in diameter in a matrix of transition alumina. Fig. 5b shows particles of CeO_2 within a matrix of θ and δ-Al_2O_3. Some CeO_2 particles appeared to have transformed to cerium aluminate, $AlCeO_3$. Many CeO_2 particles showed a surface layer, which we assume from XRD results to be $AlCeO_3$, with a layered structure similar to that in turbostratic carbon, as shown in Fig. 7. After transformation to α-Al_2O_3, the CeO_2 particles were 60–70 nm in diameter and were distributed within large α-Al_2O_3 crystals as shown in Fig. 5d.

Non-washed microwave treated alumina-ceria precursor gels showed a less agglomerated nanostructured crystalline product after calcination for 1 h at 800 °C as shown in Fig. 6a and the crystallite size of both the alumina and the ceria was very small at 5–7 nm. After calcination for 1 h at 1200 °C the structure was characterised by a mixture of rod-shaped crystals of θ-Al_2O_3 and of a vermicular structure as shown in Fig. 6b. The crystallite size of CeO_2 was about 30 nm and of Al_2O_3 was about 60 nm. After the transformation of the matrix to α-Al_2O_3, CeO_2 particles of about 50–60 nm diameter were distributed within large α-Al_2O_3 crystals—see Fig. 6d with relatively few CeO_2 particles on the surface of α-Al_2O_3 crystals. The nanocomposite structure obtained in non-washed gel samples after calcination for 1 h at 1400 °C was very similar to that from washed gels—compare Figs 5d and 6d.

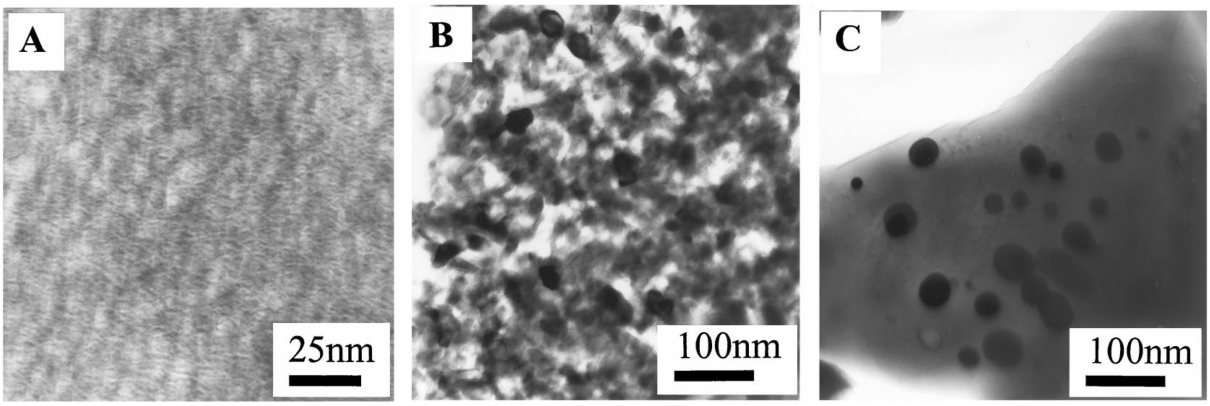


Figure 5 Microwave treated washed alumina-ceria precursor gel after calcination: (a) γ-Al_2O_3 after 1 h at 800 °C, (b) CeO_2 particles in a matrix of θ-Al_2O_3 after 1 h at 1200 °C, (c) CeO_2 particles in a matrix of α-Al_2O_3 after 1 h at 1400 °C.

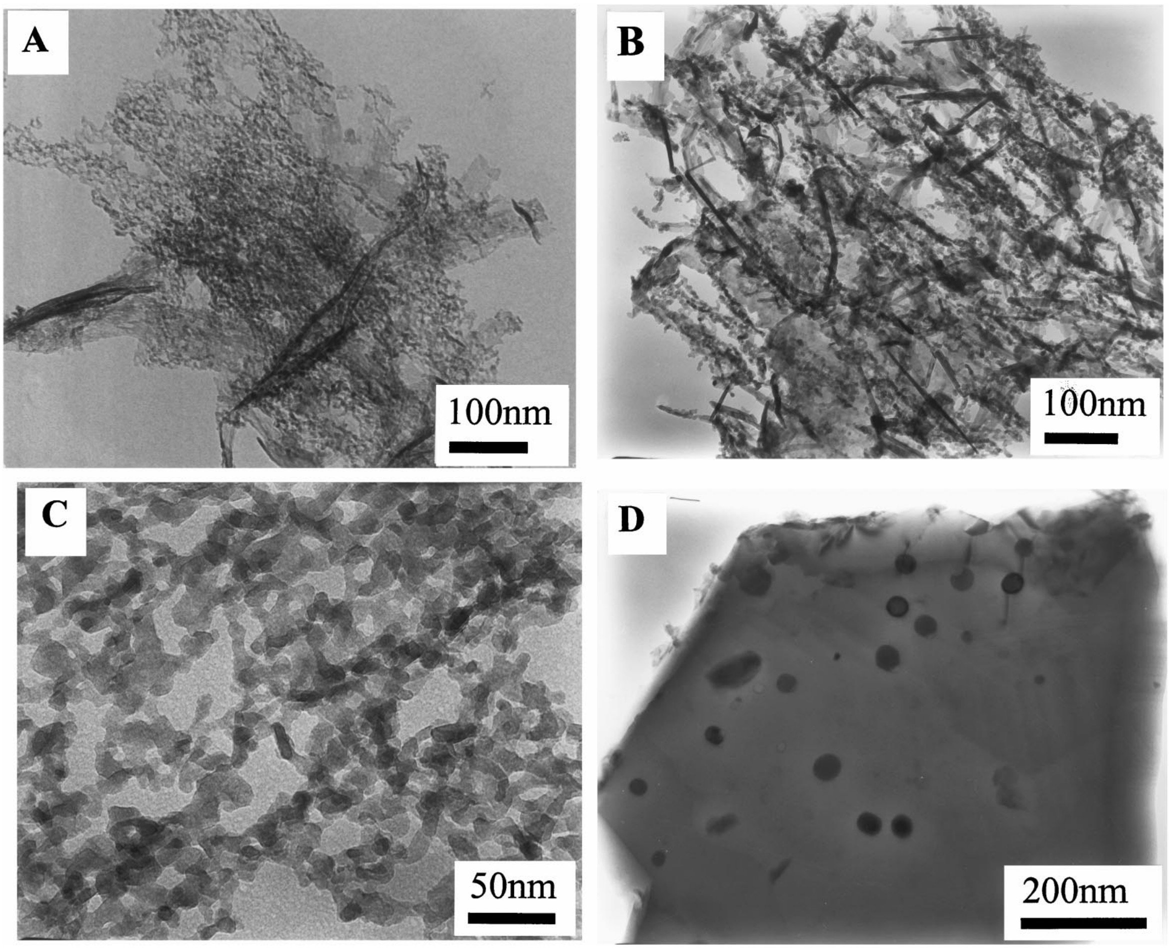


Figure 6 Microwave treated unwashed alumina-ceria precursor gel after calcination. TEM images show: (a) γ-Al_2O_3 after 1 h at 700 °C, (b) rod shaped θ-Al_2O_3 in a matrix of vermicular θ-Al_2O_3 after 1 h at 1200 °C, (c) vermicular θ-Al_2O_3 after 1 h at 1200 °C and (d) CeO_2 particles in an α-Al_2O_3 matrix after 1 h at 1400 °C.

Autoclave treatment of alumina-ceria precursor gels contained well-crystallised platelets of boehmite with a length/width ratio in the range 3–5 as shown in Fig. 8a. The cerium in this material was present as agglomerates of $CeOHCO_3$ of up to 300 nm in size which consisted of non-equiaxed and oriented sub units. After calcination for 1 h at 800 °C the $CeOHCO_3$ agglomerates transformed to polycrystalline CeO_2 as shown in Fig. 8b and the original shape of the boehmite crystals was retained but a fine and uniform porosity appeared within the pseudomorphs. Fig. 8c shows that the twinned θ-Al_2O_3 crystals produced by calcination for 1 h at 1200 °C still retained the boehmite pseudomorph shape, but with larger pores, whereas the CeO_2 had transformed to dense polycrystalline particles in the same samples. After 1 h at 1400 °C a composite between CeO_2 and α-Al_2O_3 was formed as with the other gels, but because the CeO_2 agglomerates were up to 300 nm in diameter, the structure cannot be termed nanocomposite in this case.

5. Discussion

The evolution in the phase composition and morphology of the alumina and alumina-ceria powders during calcination showed significant dependence not only on the starting materials—i.e. on chemical composition—but also on the processing routes used for precipitates of the same composition. The evolution in phase composition as a function of temperature also depended on the kinetics of the phase transformation process: phase transition temperatures recorded by DTA/TG and in-situ XRD were always higher than those apparent from samples held for 1 h at the calcination temperature. The quoted phase transition temperatures are therefore only indicative, but they can be used to compare materials measured in the same way. The homogeneous precipitation process typically produced a very uniform precipitate with primary particle sizes of about 4–5 nm for all samples investigated. However the results obtained for different processes for subsequent removal of water from the gel and the further dehydration of aluminium trihydroxide demonstrated the potential of processing methods for modifying the structural and textural properties of the powders.

In autoclave treated alumina samples, easy crystallisation and the preservation of relatively large boehmite pseudomorphs during dehydration and their retention even after the crystallisation of transition alumina demonstrated the importance of the processing route for the powder morphology. In alumina-ceria powders the formation of well-developed boehmite crystals in autoclave treated samples resulted in an early phase separation with correspondingly large polycrystalline agglomerates of $CeOHCO_3$ as shown in Fig. 8a. The delayed transformation of this material to α-Al_2O_3,

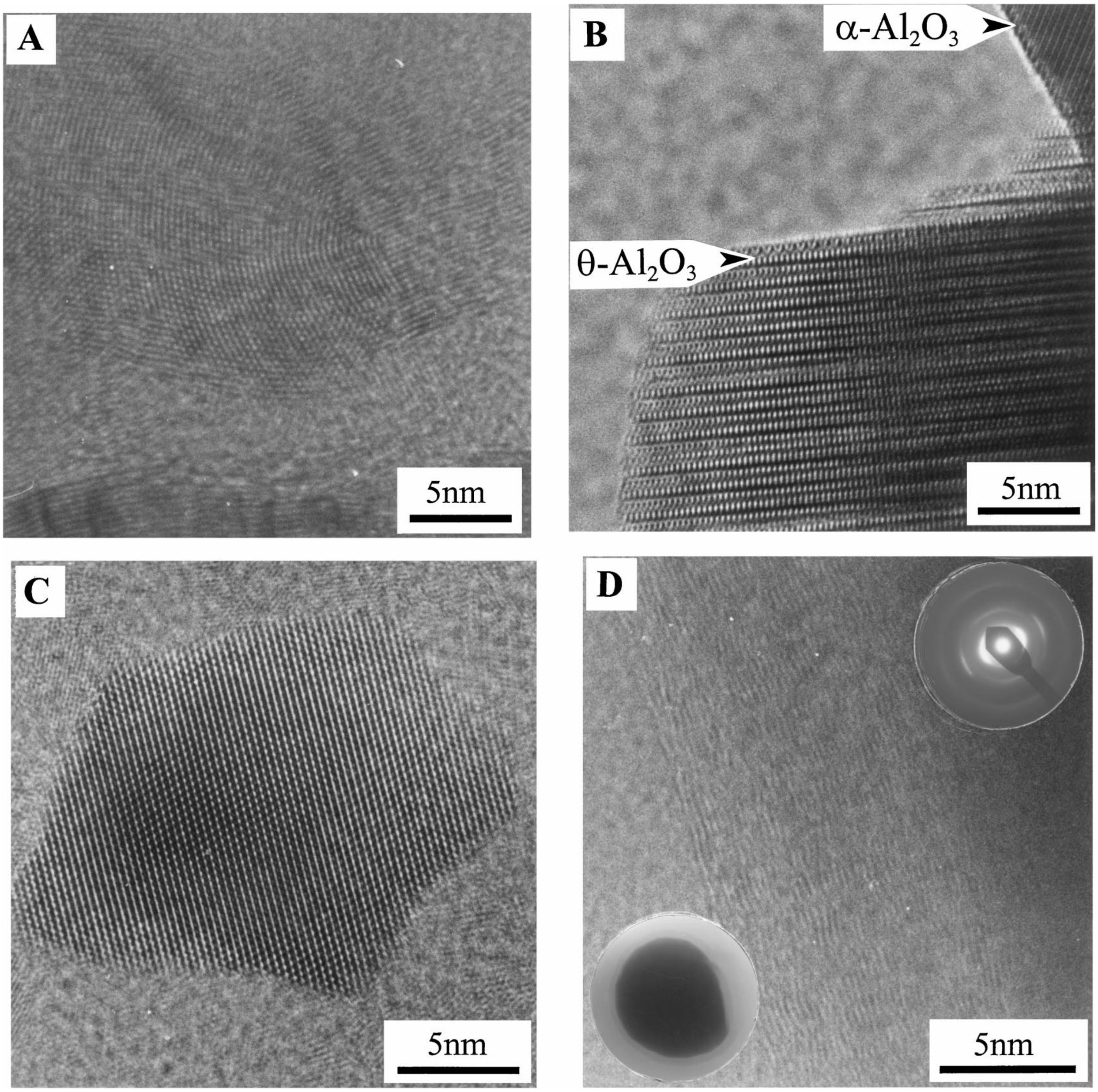


Figure 7 HRTEM pictures of microwave treated alumina-ceria precursor gel after calcination for 1 h at 1200 °C: (a) turbostratic structure with strong curvature of planes, (b) twinned monoclinic θ-Al_2O_3 with *c*-axis in the viewing plane and *c*-spacing of 1.18 nm, in contact with α-Al_2O_3, (c) two overlapping ⟨110⟩ orientated CeO_2 particles; the {111} spacing is 0.31 nm, (d) 10 nm thick turbostratic layer, believed to be cerium aluminate with *d*-spacing of 0.38 nm, surrounding a 50 nm CeO_2 particle (insert, left).

which required 1 h at 1400 °C, is an indication of the enhanced thermal stability of these well-formed crystals. In contrast, the microwave treated samples of pure alumina produced very fine boehmite, Fig. 4a, and in alumina-ceria microwaved samples boehmite formation was suppressed altogether, presumably by the presence of ceria, and the material remained amorphous up to 900 °C when CeO_2 crystallised thereby ensuring a true nanoscale distribution of Ce until crystallisation of transition alumina at about 1200 °C. The resulting nano-nano composite structure consisted of equal sized crystals of alumina and ceria.

Evidence for the importance of the processing route on the evolution of phase composition is less clear. A characteristic feature of the phase evolution during calcination was that the transition alumina phases always crystallised from an amorphous phase. XRD analysis showed that in some cases the amorphous phase was initially present and that in other cases the amorphous phases developed during the early stages of calcination where DTA/TG showed that formation of the amorphous phase was associated with the dehydration of boehmite. The fact that all powders had an amorphous structure prior to the crystallisation of the transition aluminas does not, however, allow us to conclude that all powders, even of the same composition, necessarily had the same amorphous structure. The possibility that different kinds of nearest-neighbour ordering were retained in the amorphous structure during calcination, which were characteristic of differences in the dehydration mechanisms in the different initial structures, cannot be excluded. A better characterisation of the amorphous products than was possible in this work, perhaps with specific surface area, catalytic activity, surface chemistry etc., would however be needed to test this hypothesis.

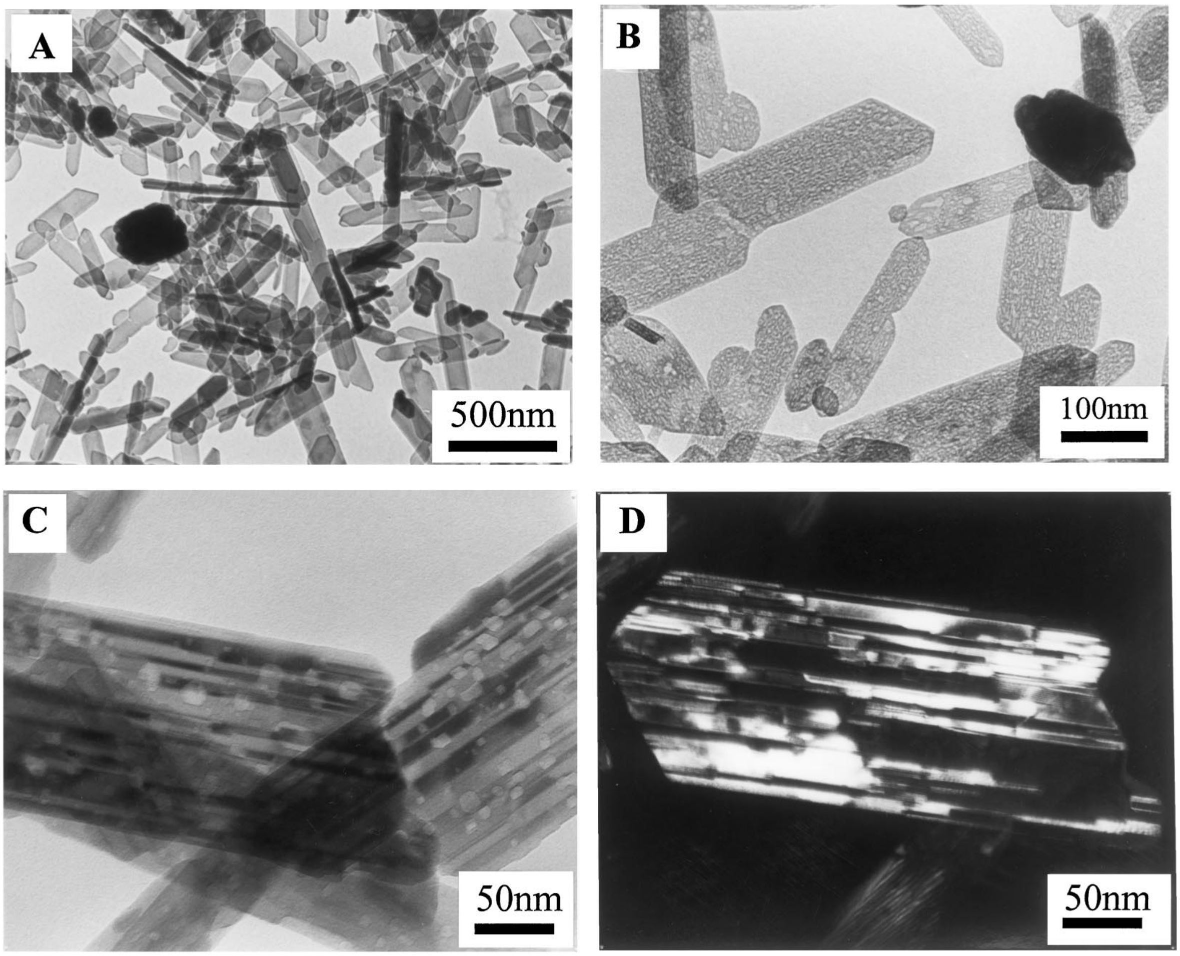


Figure 8 Autoclave treated alumina-ceria precursor gel. TEM images show: (a) agglomerates of $CeOHCO_3$ in a boehmite matrix (b) CeO_2 agglomerates in γ-Al_2O_3 boehmite pseudomorphs after calcination for 1 h at 800 °C, (c) θ-Al_2O_3 pseudomorphs with equiaxed pores after 1 h at 1200 °C, (d) 1 h at 1200 °C detail of finely twinned θ-Al_2O_3 (dark field).

6. Conclusions

Alumina-ceria powders produced by homogeneous precipitation were shown to exhibit a variety of morphologies depending on the processing route. To produce a nano-nano composite suitable for catalysis applications, microwave drying was found to be most appropriate because it minimised phase separation before the crystallisation of the transition alumina. To achieve a composite containing transition alumina with good thermal stability against transformation to α-Al_2O_3 however, autoclave treatment was found to be more appropriate; this resulted in an early phase separation and a coarser microstructure. In the case of the autoclave treated material, the intermediate product was boehmite which allowed easy production of thin films by a dipping technique. In contrast, the microwave treated material did not form boehmite and would therefore be more suited for use in bulk form rather than thin films.

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