Hydrated aluminium sulfate precipitation by enzyme-catalysed urea decomposition

Ferhat Kara*, Gülcan Sahin

Department of Ceramic Engineering, Anadolu University, Iki Eylül Kampüsü, Eskisehir, Turkey

Abstract

Hydrated basic aluminium hydroxide precipitates were obtained from aluminium sulphate solution at room temperature and at 92°C by using urea. Enzyme urease was used to decompose urea at room temperature. It was observed that precipitates obtained at room temperature were much finer than those obtained at 92°C but they had similar chemistry. On calcination at 1200°C, each precipitate obtained at room temperature converted to a discrete α-Al_2O_3 crystal whereas that obtained at 92°C converted to a rather densely packed agglomerate of α-Al_2O_3 crystals. As a result of this, α-Al_2O_3 powder obtained from 25°C precipitates showed much better sintering behaviour. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Powders-chemical preparation; Sintering; Urea

1. Introduction

Powder characteristics such as particle size and shape and agglomeration play a major role in preparation of ceramics, especially for high performance applications. Powders having spherical morphology, fine particle size, narrow particle size distribution and no agglomeration are needed to obtain homogeneous microstructure and thus high mechanical properties.

Homogeneous precipitation by urea has been used to obtain uniform particles of aluminium hydroxide with controlled morphology.[1–4] In this method, upon heating a solution containing aluminium ions and dissolved urea to over 70°C, urea decomposes to CO_2 and NH_3. NH_3 reacts with water producing hydroxyl ions which causes a uniform rise in pH of the solution until the solubility limit of aluminium sulfate hydrate is exceeded. Uniform rise in pH prevents the occurrence of very high local supersaturation (as in the case with the additions of a base) allowing nucleation homogeneously throughout the solution. Then, the nucleates grow uniformly with no further nucleation forming uniform size precipitates.

Decomposition of urea in a reasonable time requires temperatures over 85°C. However, the decomposition reaction can take place at room temperature with a trace amount of enzyme urease.[5] Very recently, Simpson et al.[6] published the results of the first study on precipitation of basic aluminium sulfate at room temperature by urease catalysed decomposition of urea. They successfully obtained precipitates with sizes in the range of 20–600 nm.[6] The precipitates were amorphous. Their investigation on the effect of urease amount on the decomposition kinetic of urea in a solution containing 0.16 M aluminium acetate, 0.19 M sodium sulfate and 0.12–0.56 M urea revealed that at least 4.8 units urease per mL of the solution was required to complete the reaction in the given time frame of 25 h.[6] Other studies concerning precipitation of hydrated basic aluminium sulfate by urea in the literature [1–4] deals with precipitation by the thermal decomposition route of urea above 80°C. In this study, precipitation of aluminium sulfate hydrate by urea decomposition at 92°C (thermal decomposition) and at room temperature (urease catalysed decomposition) was investigated. Precipitate morphologies and characteristics were compared.

2. Experimental

Chemicals used in this work were analytical reagent grade from Merck (Darmstadt, Germany). 16.6 gr

* Corresponding author.

$Al_2(SO_4)_3.16 H_2O$ was dissolved in 1 l of distilled water in a beaker. Then, 30 g urea was added and dissolved. pH of this solution was 4. This is referred to here as the standard solution. The beaker covered by an aluminium foil was put in a still water bath and temperature of the solution was raised to 92°C and kept there for 3 h for precipitation.

For precipitation experiments at room temperature, 100 mg urease powder, containing 5 units/mg, was added to the above solution and kept at ambient for 24 h. Urease amounts of 3, 15 and 500 mg was also used to find out the effect of urease concentration. The precipitates obtained in these ways were filtered, washed three times with distilled water and once with ethanol and dried in an oven at 60°C. The dried precipitates were then calcined at 1200°C for 2 h.

In order to see the effect of cation concentration on the precipitation behaviour at room temperature, up to six times more aluminium sulphate and urea (by keeping the aluminium/urea ratio constant) than the standard solution was added to 1 l of distilled water. In these experiments, urease amount was kept constant at 100 mg.

Morphology and crystallinity of the dried and calcined precipitates were examined by scanning electron microscopy (SEM) (CamScan S4, Cambridge, UK) and by X-ray diffraction (XRD) (Rigaku D-Max 2200, Tokyo, Japan), respectively. Thermal decomposition behaviour of the precipitates were analysed by simultaneous thermogravimetric-differential thermal analysis (TG-DTA) (Linseis, Selb, Germany). Comparison of the sintering behaviour of the as-calcined precipitates were carried out by dilatometry (Linseis, Selb, Germany). Samples for dilatometry were prepared by isopressing as-calcined powders at 300 MPa. They were then heated to 1525°C with a heating rate of 10°K/min and kept at this temperature for 10 min.

3. Results

Precipitation at 92°C was completed within 3 h and pH of the solution after the completion was 7. Precipitation at room temperature took longer. No study was undertaken to find the minimum time necessary for complete precipitation but it was completed after 24 h and pH of the solution after the completion was 8. The precipitates produced at both temperatures were easily filterable. Precipitation was not observed with urease concentration of 3 and 15 mg.

There were various experimental observations during room temperature precipitation to be noted. If urease was dissolved in water and added to the standard solution, no precipitation was observed. If, on the other hand, it was added in the powder form, it does not dissolve and remains at the top of the solution (see

Section 4) and precipitation results. However, at higher (up to six times) solution concentrations than the standard, urease powder was mostly dissolved when added to these solutions and no precipitation was observed. Only limited precipitation was seen when the solution concentration was twice as high as the standard solution.

Fig. 1(a) and (b) shows morphology of the precipitates obtained at 92°C and at room temperature, respectively. The size of the precipitates obtained at 92°C varied between 1 and 3 μm and they were agglomerated rather extensively [Fig. 1(a)]. Precipitates obtained at room temperature had a rather fine size, mainly around 0.3–0.5 μm although few had sizes up to 1 μm [Fig. 1(b)]. Agglomeration was also observed at room temperature but the agglomerates seemed comparatively loose. That is, not much growth was observed at the neck regions of the precipitates in comparison to the precipitates obtained at 92°C. When the amount of urease was increased to 500 mg, the precipitate size was observed to increase slightly.

Fig. 2 shows XRD traces of the precipitates. Both precipitates were amorphous. Simultaneous thermal analyses (TG-DTA) of the precipitates are given in Fig. 3. Decomposition behaviour of both precipitates is
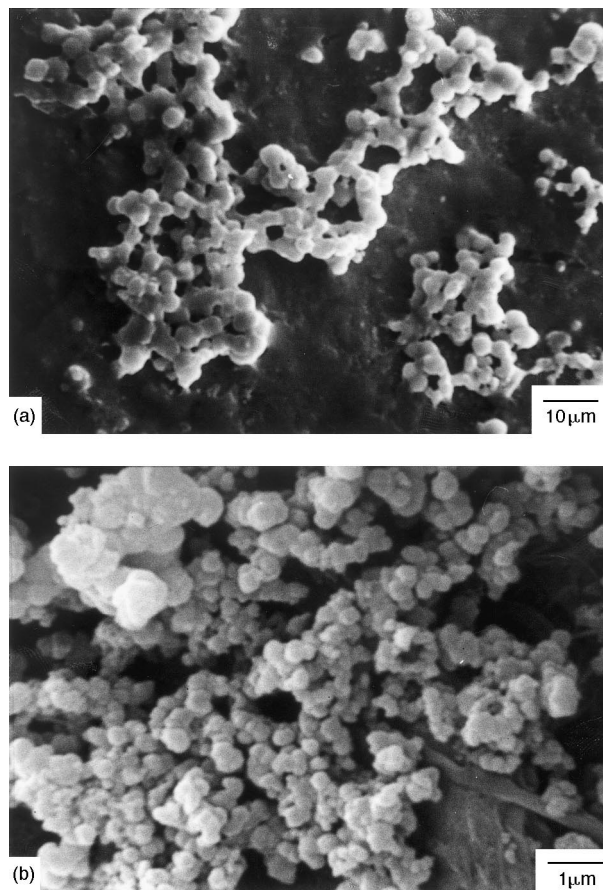

Fig. 1. SEM micrographs of precipitates obtained at (a) 92°C and (b) room temperature.

esentially similar. There is a large weight loss starting above 50°C up to 500°C with the total weight loss of about 35% at 500°C. Peak temperature of the weight loss is 136°C as shown in DTA curve. In the room temperature precipitates, there is another endothermic effect at ≈250°C. On heating above 900°C, there is a sudden weight loss with a sharp endothermic peak. This peak is located at ≈917°C for room temperature precipitates and at ≈937°C for 92°C precipitates. A small weight loss is also noticable around 11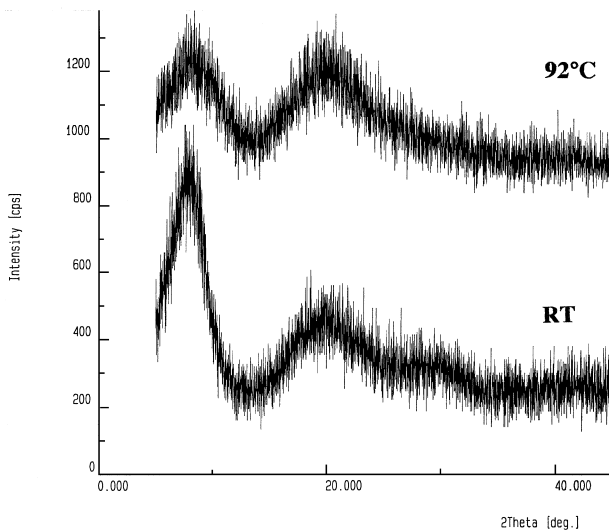50°C. The amount of sudden weight loss above 900°C is around 18%. Total weight loss is about 55%. α-alumina forms above 1200°C indicated with an exothermic peak in the DTA trace.

Morphology of the precipitates after calcining at 1200°C for 2 h is given in Fig. 4. Fig. 4(a) shows the morphology of the calcined precipitates produced at 92°C while Fig. 4(b) shows that produced at room temperature. Primary particle size of α-Al₂O₃ crystals seen in Fig. 4(a) and (b) is around 0.2 μm mainly with round morphology but some vermicular particles are also visible.

Shrinkage behaviour of the α-Al_2O_3 particles shown in Fig. 4 was compared in Fig. 5. It is clearly visible from this figure that α-Al_2O_3 particles obtained from room temperature precipitates shows much better sintering behaviour than those obtained from 92°C precipitates. Total shrinkage of α-Al_2O_3 particles obtained from room temperature precipitates after 10 min sintering at 1525°C was almost 19% and that obtained from 92°C precipitates was only about 9%.

4. Discussion

4.1. Precipitation

In homogeneous precipitation by the decomposition of urea with the effect of temperature (over 80°C), precipitates nucleate and grow throughout the solution with no secondary crystallisation.[7] Therefore, the number of nuclei formed initially determines the particle size. Increasing urea concentration at constant aluminium ion

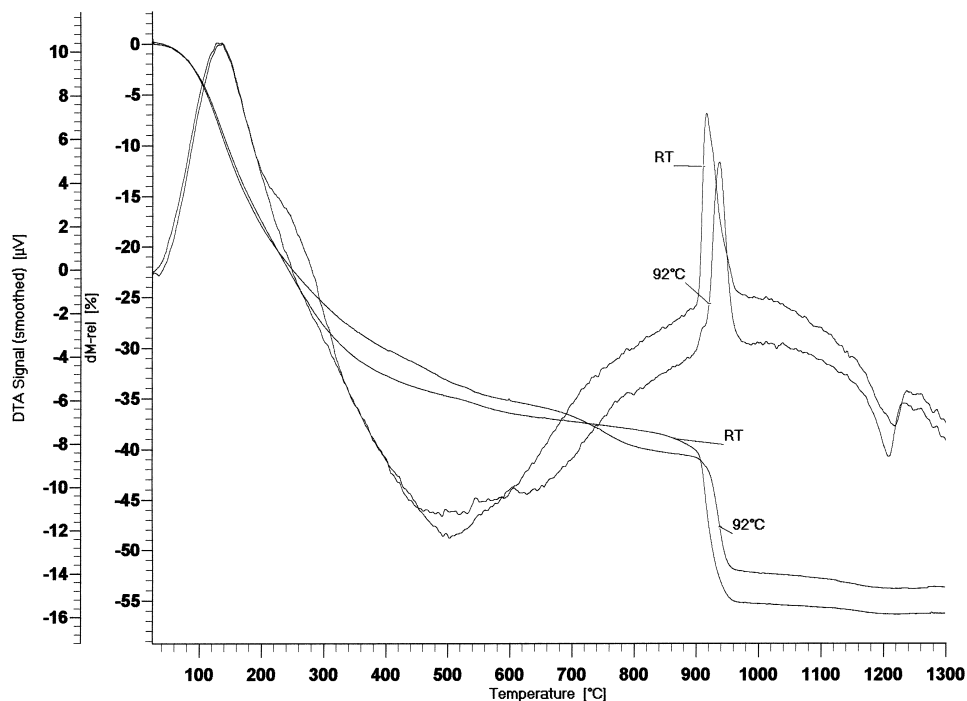Fig. 2. XRD traces of the precipitates (RT = room temperature).

Fig. 3. TG-DTA traces of the precipitates obtained at room temperature (RT) and 92°C.
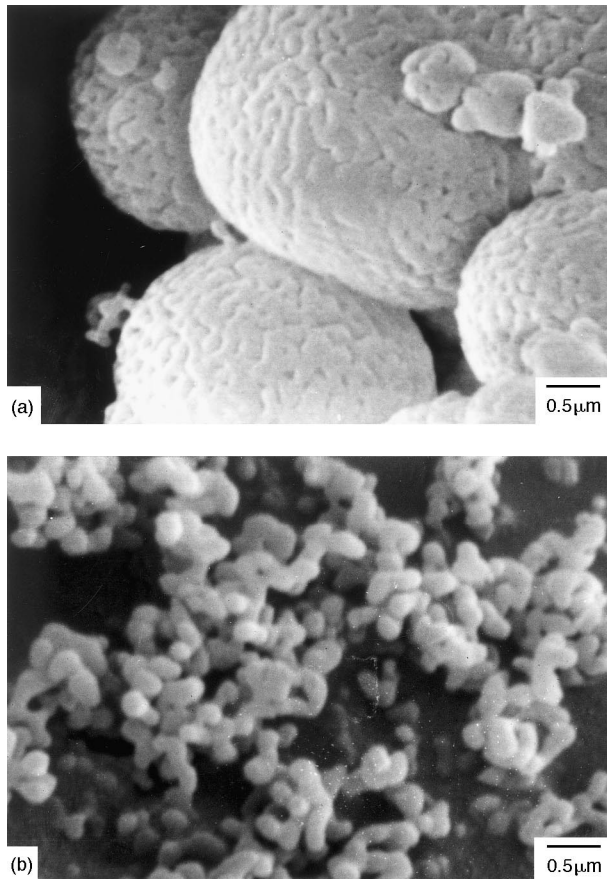
Fig. 4. SEM micrographs of precipitates after calcination at 1200°C for 2 h. (a) Precipitates produced at 92°C and (b) precipitates produced at room temperature.

concentration was observed to decrease the particle size of the precipitates from aluminium sulphate solutions.[4] This was explained to be due to more urea decomposition (i.e. higher hydroxyl ion production) for a given time causing somehow more nuclei.[4]

The way in which precipitates were formed was rather different at room temperature than that at 92°C. Urease powder added to the standard solution was observed to form a web-like foamy structure, with time, on the top of the beaker. This foam decomposed urea where it interacted, that is, at the top of the beaker. This is supported by the observation that pH at the top of the beaker was higher than that at the bottom during precipitation. In this way, precipitation should take place at the top of the beaker and this was observed experimentally in this work. Then, precipitates settled out to the bottom.

In such a precipitation phenomenon, precipitation does not occur homogeneously but it takes place progressively, probably with multiple nucleations. That is, urea is decomposed at the top of the beaker to produce hydroxyl ions which react with aluminium ions to form precipitates. These precipitates, forming clusters, start settling down with limited growth because of the unavailability of hydroxyl ions at the deeper regions. More urea and cation travel to the top for reaction and further precipitation. This type of progressive precipitate formation could be the reason for much smaller precipitate size at room temperature than at 92°C. When the solution was stirred during precipitation by a magnetic stirrer, no foamy structure was formed at the top of the beaker and no precipitation was observed.
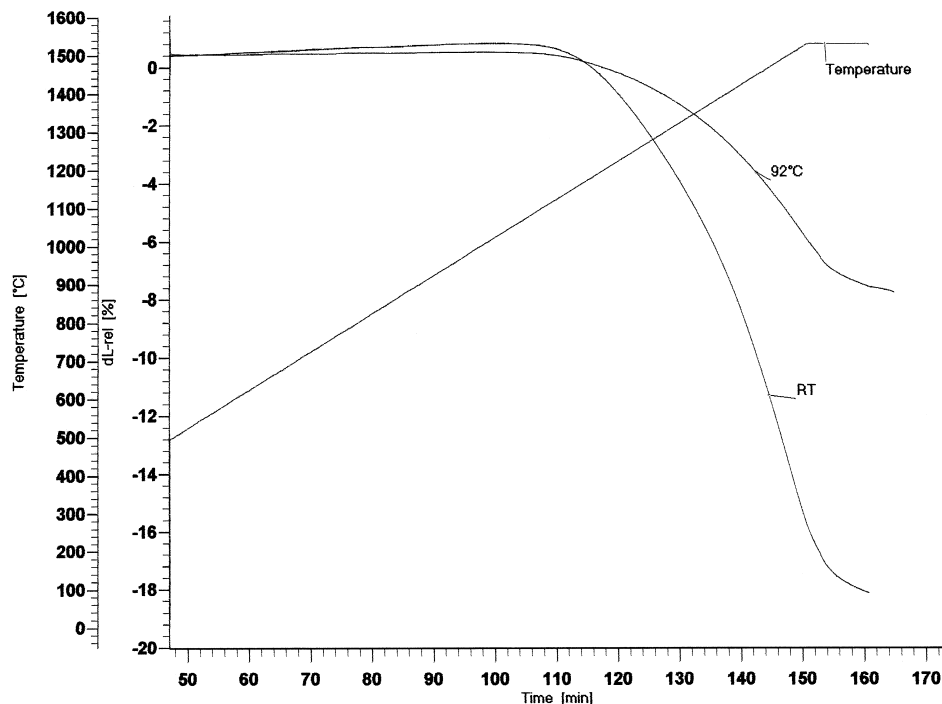

Fig. 5. Comparison of shrinkage behaviour of α-Al$_2$O$_3$ powders obtained by calcining room temperature (RT) precipitates and 92°C precipitates.

When the enzyme was dissolved in water, then added to the solution, no precipitation observed. That is, it was inactive and did not catalyse urea decomposition. Simpson et al.[6] observed that a minimum of 4.8 units of urease per ml solution of 0.16 M aluminium acetate–0.19 M sodium sulfate were required for it to catalyse urea decomposition within the given time frame of 25 h. Considering that the concentration of urease used in this work, when dissolved, is 0.5 unit per ml standard solution, its inactivity is not surprising. Simpson et al.[6] pointed out that higher urea/urease ratio inhibits the enzyme because of increased relative ammonium ion concentration. Similarly, the presence of Na+ and Al3+ in the solution was also thought to inhibit the enzyme.[6] The metal cations bind to the active site of the enzyme and prevent the enzyme from binding to the substrate.[6] Dissolving and inactivity of the enzyme at higher solution concentrations may be due to a similar effect of the cations.

4.2. Thermal decomposition behaviour

Relatively low peak temperature (136°C) of the weight loss in DTA trace in Fig. 3 indicates that it is due to the removal of molecular water. This reveals that precipitates are significantly hydrated. Continued weight loss with temperature is a result of the loss of hydration water of aluminium sulfate, which was stated to be largely completed by 400°C.[8–10] Although it occurs with a decreased rate, water removal continues above 400°C. Decomposition of various aluminium hydroxide phases takes place in the range 250–550°C.[1]

Sudden weight loss occuring above 900°C with associated sharp endotermic peak in DTA trace is due to desulfurisation (Fig. 3). About 18% weight loss indicates that the particles contain 18% SO_3. Similar SO_3 levels were also reported by Sacks et al.[1] and Cornilsen and Reed.[11] Small weight loss around 1150°C is associated with the removal of residual sulfate.[1]

In Fig. 3, a second endothermic peak seen as a shoulder in the DTA trace of room temperature precipitate and corresponding higher weight loss rate in the TG trace is also noticeable between 200 and 300°C. Decomposition behaviour during thermal analysis is dependent on factors such as heating rate, sample bed packing and particle size. For the same heating rate and sample bed packing characteristics, small particles decompose more easily and/or at a lower temperature due to easier heat transfer and lower diffusion distance for the volatiles. Therefore, the minor differences in DTA and TG traces can be attributed to the smaller particle size of the room temperature precipitates.

4.3. Morphology of precipitates

Rather more extensive agglomeration of precipitates at 92°C than at room temperature can be explained to be due to higher mobility of particles at higher temperatures due to thermal vibrations, causing higher probability of particle impact and coalescence. When the precipitates are agglomerated, further precipitation takes place at the neck regions of the agglomerates. This makes them rather strong. On the other hand, unavailability of the reactants while the agglomerates settle down during room temperature precipitation can be the reason for their comparatively loose structure.

Generally, when precipitates derived from aluminium sulphate are calcined, very fine α-Al_2O_3 crystallites (0.2–0.3 µm in size) are formed[1,2] as also seen in Fig. 4. Therefore, if the precipitate size is much larger than α-Al_2O_3 crystallite size, then upon calcination it is not surprising to see that each precipitate particle becomes an agglomerate of α-Al_2O_3 crystallites as shown in Fig. 4a. If the precipitates are also agglomerated, then the calcined powder becomes agglomerates of agglomerated primary particles [Fig. 4(a)]. Therefore, for agglomerate free powders to be produced (without milling), unagglomerated precipitates with a particle size close to α-Al_2O_3 crystallite size need to be produced. As the precipitate size produced at room temperature is close to α-Al_2O_3 crystallite size, upon calcination, each precipitate converts into an α-Al_2O_3 crystallite as shown in Fig. 4(b). Comparatively loosly agglomerated structure of the room temperature precipitates is also reflected in the calcined precipitate structure [Fig. 4(b)]. Powder in Fig. 4(a) will need extensive milling operations for the elimination of agglomerates. Better quality in terms of sintering of the powder obtained from the room temperature precipitates is reflected in the dilatometer test of the as-calcined precipitates (Fig. 5).

5. Conclusions

Precipitation by enzyme urease catalysed urea decomposition at room temperature produces very fine precipitates of aluminium sulfate hydrate compared to those produced by thermal decomposition of urea at 92°C. For successful precipitation at room temperature, at the urease amount studied here, it was important that urease remained undissolved and undisturbed in the solution. Higher solution concentrations caused urease to dissolve and thus prevented the occurrence of precipitation.

As-produced precipitates were amorphous with similar chemical structures as understood by their thermal decomposition behaviour.

Precipitates having sizes close to the size of α-Al_2O_3 crystallites forming after calcination is advantageous for obtaining powders without much agglomeration and for much better sinterability. Larger precipitates, even unagglomerated, become agglomerates of primary α-Al_2O_3 crystals after calcination.

References

1. Sacks, M., Tseng, T-Y. and Lee, S. Y., Thermal decomposition of spherical hydrated basic aluminium sulfate. *Am. Ceram. Soc. Bull.*, 1984, **63**, 301–310.
2. Blendell, J. E., Bowen, H. K. and Coble, R. L., High purity alumina by controlled precipitation from aluminium sulfate solutions. *Am. Ceram. Soc. Bull.*, 1984, **63**, 797–802.
3. Nagai, H., Hokazono, S. and Kato, A., Synthesis of aluminium hydroxide by a homogeneous precipitation method I. Effect of additives on the morphology of aluminium hydroxide. *Br. Ceram. Trans.*, 1991, **90**, 44–48.
4. Nagai, H., Oshima, Y., Hirano, K. and Kato, A., Sintering behaviour of aluminium oxides derived from aluminium hydroxides with various morphologies. *Br. Ceram. Trans.*, 1993, **92**, 114–119.
5. Ishihara, K., Muramoto, N., Fujii, H. and Shinohara, I., Preparation and permeability of urea-responsive polymer membrane consisting of immobilized urease and poly(aromatic carboxylic acid). *J. Appl. Polym. Sci.*, 1978, **22**, 1991–2009.
6. Simpson II, R. E., Habeger, C., Rabinovic, A. and Adair, J. H., Enzyme catalyzed inorganic precipitation of aluminium basic sulfate. *J. Am. Ceram. Soc.*, 1998, **81**, 1377–1379.
7. Akinc, M., Ceramic powder synthesis: homogeneous precipitation by urea. In *Proceedings of Fourth Euro Ceramics—Vol. 1, Developments in Processing of Advanced Ceramics*, ed. P. Duran and J. F. Fernandez. Faenza Editrice Iberica S.L, Castellon de la Plana, 1993, pp. 3–13.
8. Sato, T., Ozawa, F. and Okima, S., Thermal decomposition of aluminium salts-hydrates of the chloride, nitrate and sulphate and of ammonium alum. *J. Appl. Chem. Biotechnol.*, 1978, **28**, 811–822.
9. Johnson, D. W. and Schnettler, F. J., Characterisation of freeze-dried Al_2O_3 and Fe_2O_3. *J. Am. Ceram. Soc.*, 1970, **53**, 440–444.
10. Johnson, D. W. and Gallagher, P. K., Kinetics of the decomposition of freeze-dried aluminium sulfate and ammonium aluminium sulfate. *J. Am. Ceram. Soc.*, 1971, **54**, 461–465.
11. Cornilsen, B. C. and Reed, J. S., Homogeneous precipitation of basic aluminium salts as precursors for alumina. *Am. Ceram. Soc. Bull.*, 1979, **55**, 1199–1204.