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Alumina Powders from Aluminium Nitrate–Urea and Aluminium Sulphate–Urea Reactions — The Role of the Precursor Anion and Process Conditions on Characteristics

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Abstract: Precursor powders for alumina were prepared by aluminium nitrate–urea (NU-) and aluminium sulphate–urea (SU-) reactions. The role of process conditions on the reactions and characteristics of the resultant powders were studied. NU-reactions resulted in an amorphous gel that upon prolonged refluxing at a higher pH crystallized into boehmite powders of 0·3–0·8 μm size. These were agglomerates having elongated fibrillar morphology. SU-reactions resulted in the direct formation of amorphous powders of 2–7 μm size which were agglomerates of spherical particles. Upon prolonged refluxing at higher pH these powders were also found to undergo crystallization into boehmite, with a little modification of their particle size distribution and morphology. The alpha alumina powders formed by calcination of these precursors at 1673 K exhibited the same size distribution and morphological features as that of the precursors. At 1823 K, NU-based powder compacts sintered to above 95% T.D., while SU-based powder compacts could sinter only to about 85%. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

High density alumina ceramic components with controlled and uniform microstructure required for advanced engineering and structural applications need powders having narrow particle size distribution, fineness and desired morphology, dispersibility, etc.[1] Normal methods of preparation of sinterable alumina powders involve extensive grinding and classification stages. Another method is direct formation of such powders by thermal decomposition of the crystalline hydroxides prepared by chemical reactions under controlled conditions using either organometallic precursors or inorganic precursors.[2–9]

The inorganic precursors are extensively hydrolysed into small polynuclear species in aqueous solutions which undergo further polymerization/condensation into primary particles of hydroxide during the increase of pH. During the formation of primary particles the most important requirement is the maintenance of their colloidal stability against coagulation.

During heterogeneous precipitation little control over shape, size and degree of agglomeration can be exercised because of the rapid changes in solution concentrations and localized discontinuous nature of the ligand introduction and consequent reaction. A better control can be achieved if the reacting species is introduced uniformly throughout the solution in molecular level slowly by the reaction of another source chemical (e.g. evolution of ammonium hydroxide through hydrolysis of urea present in an aqueous solution of aluminium nitrate or sulphate).

Even though some studies on aluminium nitrate–urea and aluminium sulphate–urea reactions have been reported,[7–9] a comparison of the role of the anionic part of the aluminium salt (i.e. sulphate and nitrate) on capability to form insoluble precursor powders, their crystallization into boehmite upon prolonged refluxing, and the powder characteristics of these precursors and the alumina obtained by their calcination have not been reported. This article covers the results of a systematic study of the above aspects. The influence of process conditions on the characteristics of the powders formed has also been studied and reported. The difference in the phenomenon of powder formation has been explained based on colloid stabilizing versus coordinate bond forming powers of the sulphate and nitrate ions of the aluminium salt.

2 EXPERIMENTAL

Aluminium nitrate, aluminium sulphate and urea (GR grade from M/s BDH, UK) were used. Aqueous solutions with desired concentrations of aluminium nitrate–urea and aluminium sulphate–urea were prepared and thermostatted at 373 K in a 3 litre round bottom flask fitted with a reflux air condenser for durations up to 100 h. The concentration of aluminium was varied up to 0·3 M, while the urea added was varied up to three times excess of the amount required for complete precipitation as hydroxide. (Note: 1 mole of Al^{3+} requires 1·5 moles of urea.) The reactions were interrupted at a typical duration and the precursor powders were filtered, washed repeatedly with distilled water and characterized. The characteristics studied were volatile loss upon calcination, type of phase evolved by XRD (Cu Kα radiation, 2θ from 10 to 70°, M/s Dyno Corp., USA), molecular structure by IR (200–4,000 cm^{-1}, M/s Perkin-Elmer), particle size distribution by Sedigraph (M/s Micromeritics Corp., USA), specific surface area by BET (M/s Quantachrome Corp., USA) and morphology by SEM (M/s Cambridge Instruments, UK). The above characteristics of the alumina powders formed by calcination at 1673 K of these precursors were also studied. Typical sintering behaviour of the powder compacts (compacted at 175 MPa) were studied in the range 1823–1873 K. The conditions of preperation and the corresponding sample numbers are given in Tables 1 and 2. (Note: In each figure the data corresponding to the respective sample is marked by the number inside a circle.)

3 RESULTS AND DISCUSSION

3.1 Initial powder formation:

Table 1 shows the details of initial concentrations of reactants, required time of refluxing and resultant pH of powder formation for some of the typical aluminium nitrate–urea and aluminium sulphate–urea reactions (hereafter referred to in the text as NU- and SU-reactions, respectively). These reactions are chosen to demonstrate the role of the anionic part of the aluminium salt and process

Table 1. Initial concentration of reactants, time of refluxing and resultant pH for powder formation and characteristics

			Powder forming conditions			
			Initial		Final	
Sample no.	Concentration of Al^{3+} (M)	Molar ratio of Al^{3+}:Urea	Time h	pH	Time h	pH
0N	0.10	1:1.5	24	6.5	150	7.2
			amorph. gel		cryst. grnlr.	
1N	0.10	1:4.5	4.5	6.5	72	8.8
			amorph. gel		cryst. grnlr.	
2N	0.30	1:4.5	4.5	6.5	72	9.0
			amorph. gel		cryst. grnlr.	
3N	0.10	1:3.0	8.0	6.5	96	8.5
			amorph. gel		cryst. grnlr.	
1S	0.10	1:4.5	3.0	4.2	—	—
			amorph. grnlr.			
2S	0.10	1:4.5	3.0	4.2	72.0	9.0
			amorph. grnlr.		cryst. grnlr.	
3S	0.30	1:4.5	3.0	4.2	72.0	9.2
			amorph. grnlr.		cryst. grnlr.	
4S	0.10	1:3.0	8.0	4.2	96.0	9.0
			amorph. grnlr.		cryst. grnlr.	

N and S refer to NU- and SU-reactions.

conditions on the characteristics of the powders formed. The most important point observed was that NU-reactions result initially in a sudden formation of voluminous gelatinous precipitate, while SU-reactions produced compact granular precipitate (powders). For NU-reactions gelation occurred at a pH of about 6·5, while for SU-reactions powder formation occurred at a pH of about 4·2. These pH values are found to be characteristic of the counter anion and not influenced by the reactant concentrations, unlike the kinetics of gelation or powder formation.

Even though the real situation in the solution is complicated by many processes occurring simultaneously, initial powder formation can be visualized to occur as follows. Urea hydrolyses into carbon dioxide and ammonia (yielding carbonate and hydroxide as ligands) in water at about 353 K and above. The competition between these ligands for aluminium ion decides the compound that is formed. Since aqueous aluminium nitrate and sulphate solutions are acidic, carbon dioxide escapes the system. However, the hydroxide takes part in the polymerization of the hydrolysed aluminium bearing cationic species existing in solution and simultaneously increases the pH. In the case of NU-reaction, because of the poor coordinate bond forming ability of nitrate, it does not interfere in the reaction of hydroxide with the aluminium containing polymeric cation growing into the bigger, charged polymeric species via olation and oxolation involving Al–OH–Al and Al–O–Al bridges. With increasing pH, caused by the increased polymeric size and hydroxide ion concentration, gelation occurs at a pH of about 6·5. Due to widely spread and weak binding characteristics of the oxy- and hydroxy-bridges, the resultant precipitate (gel) is porous and voluminous. In the case of SU-reaction due to the better coordinating ability of sulphate it bonds to the growing polymeric cation at a pH of about 4·2, terminating further polymerization and results in neutral species of composition $Al_4(OH)_{10}SO_4$ as reported by Brosset *et al.*[10] Since this species is neutral, it forms strongly bound, compact primary particles which subsequently agglomerate resulting in granular precipitate.

In the case of the NU-reactions the gelatinous mass formed was difficult to filter because of extensive bridging and upon drying it resulted in a strongly agglomerated mass that required grinding to get a fine powder. However, the granular precipitates formed by SU-reactions are easily filterable.

3.2 Crystallization into boehmite

The precipitates formed by both these reactions were amorphous to X-ray and prolonged refluxing at the reaction temperature with the mother liquor led to the formation of crystalline boehmite. In the case of NU-reactions, crystallization was found to be accompanied by breaking of the gel into a compact powder mass that upon filtering and oven drying could be easily dispersed into fine powder. The final pH of the mother liquor after the prolonged refluxing increases from 7 to 9·0 with increasing urea content (Table 1). The initially formed amorphous powder from SU-reaction, under similar conditions of refluxing, also crystallized into boehmite.

The onset of formation and growth of nuclei leading to crystallization of boehmite from the initially formed precipitates as revealed by XRD is shown in Fig. 1. In both NU- and SU-reactions crystallites grew to a detectable size only after 24 h. In the case of NU-reactions the powder cake obtained at this stage is still jelly-like and upon drying is highly agglomerated and required 72 h of reaction to form fine powder. These powders obtained from NU-reactions completely crystallized into boehmite, while under similar conditions those from SU-reactions underwent only partial

Table 2. Characteristics and sintering data of different alumina powders

Sample no.	S.S.A. ($m^2 \cdot g^{-1}$)	Particle size from S.S.A. (μm)	Particle size from Sedigraph (μm)	Green density (%T.D.)	Sintered density at 1823 K (%T.D.)	Sintered density at 1873 K (%T.D.)
C1N	5	0.3	0.4	48	97	97
C2N	5	0.3	0.8	50	95	96
C3N	4	0.4	0.7	49	96	97
C1S	10	0.15	3.5	41	78	85
C2S	6	0.25	2.2	50	85	90
C3S	8	0.18	3.4	47	78	87
C4S	8	0.18	5.0	43	79	85

Note: 1. Letter 'C' with the Sample no. indicates that the respective precursor is calcined isothermally at 1673 K for 3 h.
2. Powders compacted at 175 MPa.

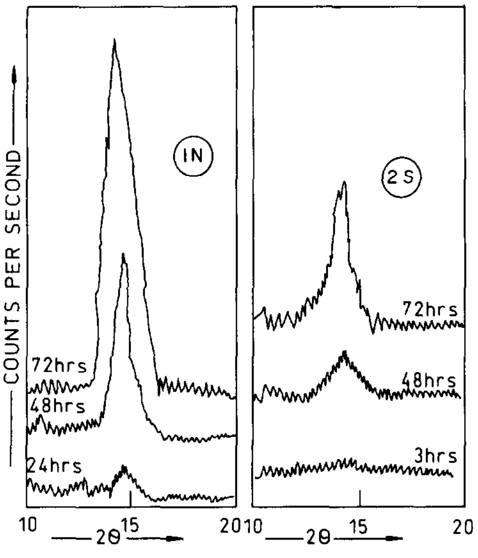


Fig. 1. XRD profiles of < 020 > peak depicting progress of crystallisation of boehmite from the gel or amorphous powder.

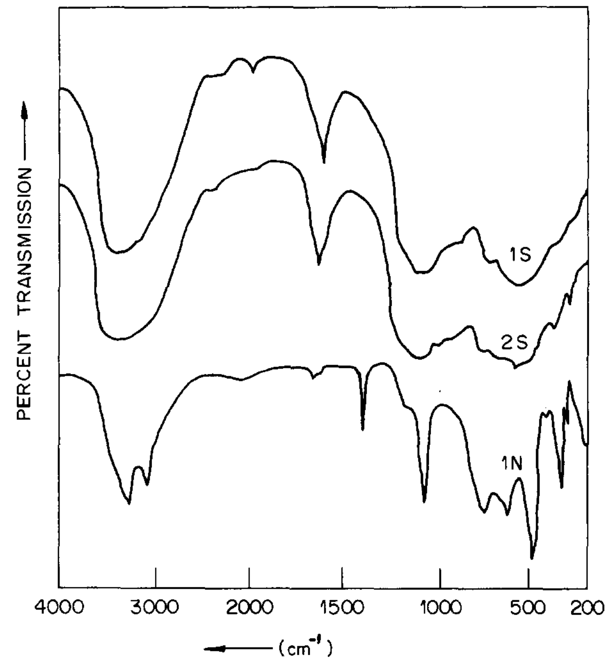


Fig. 2. IR spectra of precursor powders.

crystallization as revealed by IR spectra of typical precursors (Fig. 2). The amorphous sulfato complex powder formed initially exhibited a broad band centred at 600 cm^{-1} and a strong band centred around 1100 cm^{-1}, characteristic of sulphate in agreement with the results of Sacks *et al.* [9] Upon subsequent refluxing for 72 h at higher pH (9·0) the spectrum did not alter much, indicating the presence of a major amount of sulphate in the powder which has undergone partial transformation into boehmite, as revealed by XRD. However, the powder obtained from NU-reactions, under identical conditions of reactions, exhibited sharp peaks (or bands) centred around 370, 470, 610, 750 and 1060 cm^{-1} characteristic of pure boehmite as reported by Clarke and Lannutti and Gadsden.[11,12] For all precursor powders, the broad bands occurring around 3000–3500 and sharp band around 1650 cm^{-1} are attributed to the presence of molecular and structural water. This was further confirmed by the data of loss on calcination at 1673 K (Table 3). The data for powders from NU-reactions (~21 wt%) agreed well with expected loss for boehmite (~17 wt%). However, powders from SU-reactions exhibited a higher percentage of weight loss (32–50 wt%) indicating the incomplete conversion of the amorphous sulphate into boehmite. Thus the kinetics of conversion to boehmite of the initially formed precursor powder from SU-reaction is slower than that from the NU-reaction which could be attributed to the difference between the reactants-gel and the amorphous sulphate complex.

The mechanism of crystallization can be explained as follows: The uniform *in situ* slow evolution of ammonium hydroxide in molecular level throughout the solution results in minimum fluctuation in environmental composition and sufficient time for orderly polymerization to occur leading to the formation of boehmite nuclei. Lower pH favours a high rate of nucleation, while the growth is a much slower process compared to

Table 3. Characteristics of the precursor powders

Sample no.	% wt loss on calc. at 1673 K	Sp. surface area (m^2.g^{-1})	Av. particle size from S.S.A. (μm)	Av. particle size from Sedigraph (μm)
1N	21.0	62	0.03	0.3
2N	21.7	40	0.05	0.9
3N	21.1	37	0.05	0.7
1S	52.0	20	0.12	4.2
2S	32.0	30	0.08	3.0
3S	40.0	27	0.08	3.7
4S	45.0	25	0.09	5.0

hydrolysis of urea. However, as hydrolysis of urea proceeds, when the concentration of hydroxide in the system exceeds a certain value, gelation or powder formation occurs and the nuclei of boehmite are entrapped inside the gel network or the powder formed. Upon subsequent refluxing at the same temperature, the pH further increases to a value of 8–9·2. The gel or amorphous powder, as a result of its unstable state, dissolves and reprecipitates on the existing nuclei of boehmite (>363 K)[13] leading to their growth due to the presence of the following equilibria:

$$Al(OH)_3\ (gel) + OH^- \rightarrow [Al(OH)_4]^-$$

$$Al_4(OH)_{10}SO_4(powder) + 6\,OH^- \rightarrow 4\,[Al(OH)_4]^- + SO_4^{--}$$

Increasing urea content increases pH which leads to the increasing equilibrium concentration of $Al(OH)_4^-$ which makes the kinetics of crystallization faster (Table 1). For the NU-reactions, at a pH of 7 it takes about 150 h, while at a pH of 9·0 it takes about half this time (72 h). Thus the kinetics of crystallization was found to be enhanced by the increase in the amount of urea, i.e. increase of pH. The difference in the crystallization rate of NU- and SU-reactions can be attributed to the difference between the aluminium bearing reactants in the above equilibra. Another process simultaneously occurring during crystallization is the agglomeration of the crystallites to particles, which is influenced by the nature of the counter ions present in the system and their concentrations.

3.3 Particle size distribution, specific surface area and morphology

Prolonged refluxing of the initially formed amorphous powders of SU-reactions in the mother liquor not only results in crystallization but also shifts the particle size distribution to the finer side (Fig. 3). For comparing the powders from SU- and NU-reactions, the typical ones having the same reaction conditions (time of reaction and concentration of reactants) were chosen.

Effect of concentration of aluminium and urea on the particle size distribution of the precursors formed by the reactions are shown in Figs 4 and 5. The powders obtained from NU-reactions exhibited a distribution which is an order of magnitude less (0·3–0·8 µm) than the corresponding powders from SU-reactions (2–7 µm). This can be attributed to the poorer ability of sulphate to provide colloid stability (compared with nitrate) that results in termination of agglomeration of the primary particles formed at a higher size. For both NU- and SU-reaction based powders, decreasing aluminium ion concentration decreased the particle size that could be attributed to the lesser ionic strength of the medium resulting in weaker agglomeration and probability of coalescence of

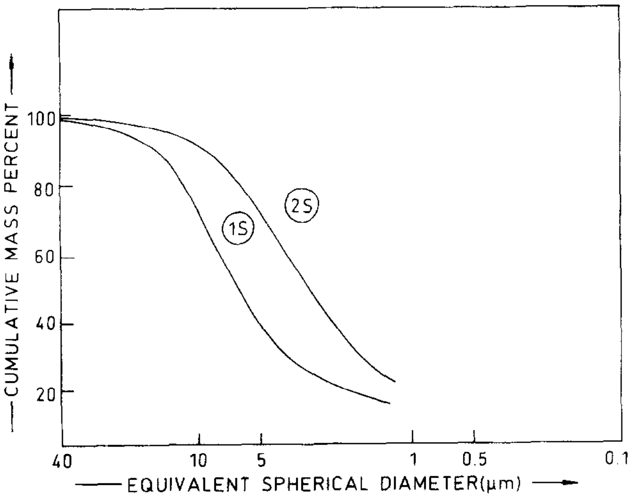


Fig. 3. Particle size distribution of precursor powder from aluminium sulphate (effect of time of refluxing).

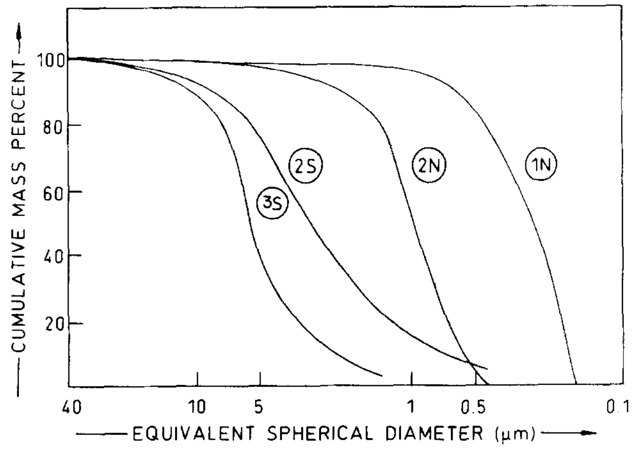


Fig. 4. Particle size distribution of precursor powder from aluminium sulphate and nitrate (effect of aluminium concentration).

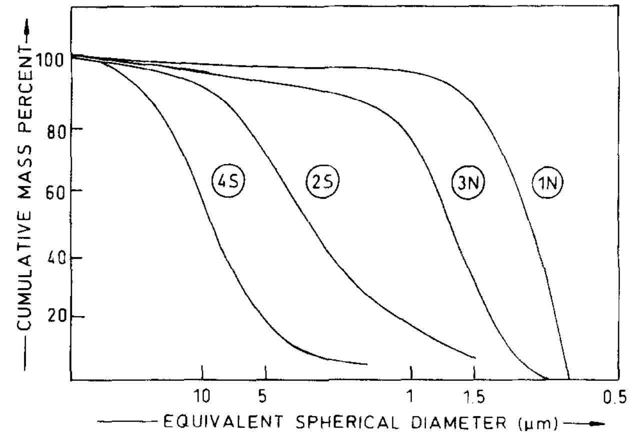


Fig. 5. Particle size distribution of precursor powder from aluminium sulphate and nitrate (effect of amount of urea).

particles, terminating agglomeration at a lower size. Another interesting feature is that the particle size increased with decreasing amount of excess urea. Also, mono sized nature improved with increasing urea content (especially for NU-reaction based powders) (Fig. 4), which could be attributed to the fact that the changeover from nucleation to growth of agglomerates occurs quickly, without much time lapse. Simultaneous nucleation and growth is expected to result in a wider distribution.

For all precursor powders, it is obvious from Table 3 that the average particle size values obtained from specific surface area data are an order of magnitude lower than those obtained from sedimentation technique, which is a clear indication of the fact that the powder particles are porous agglomerates of individual primary particles whose dimensions are of the order of the values obtained from the specific surface area values. The morphological features of the typical precursor powders are shown in Figs 6 and 7. It is clear that the powders from NU-reactions are elongated fibrillar bundles that are characteristic of boehmite structure. It could be said that the open structure of the gelatinous precipitate formed initially in the NU-reactions allowed the compact crystallites

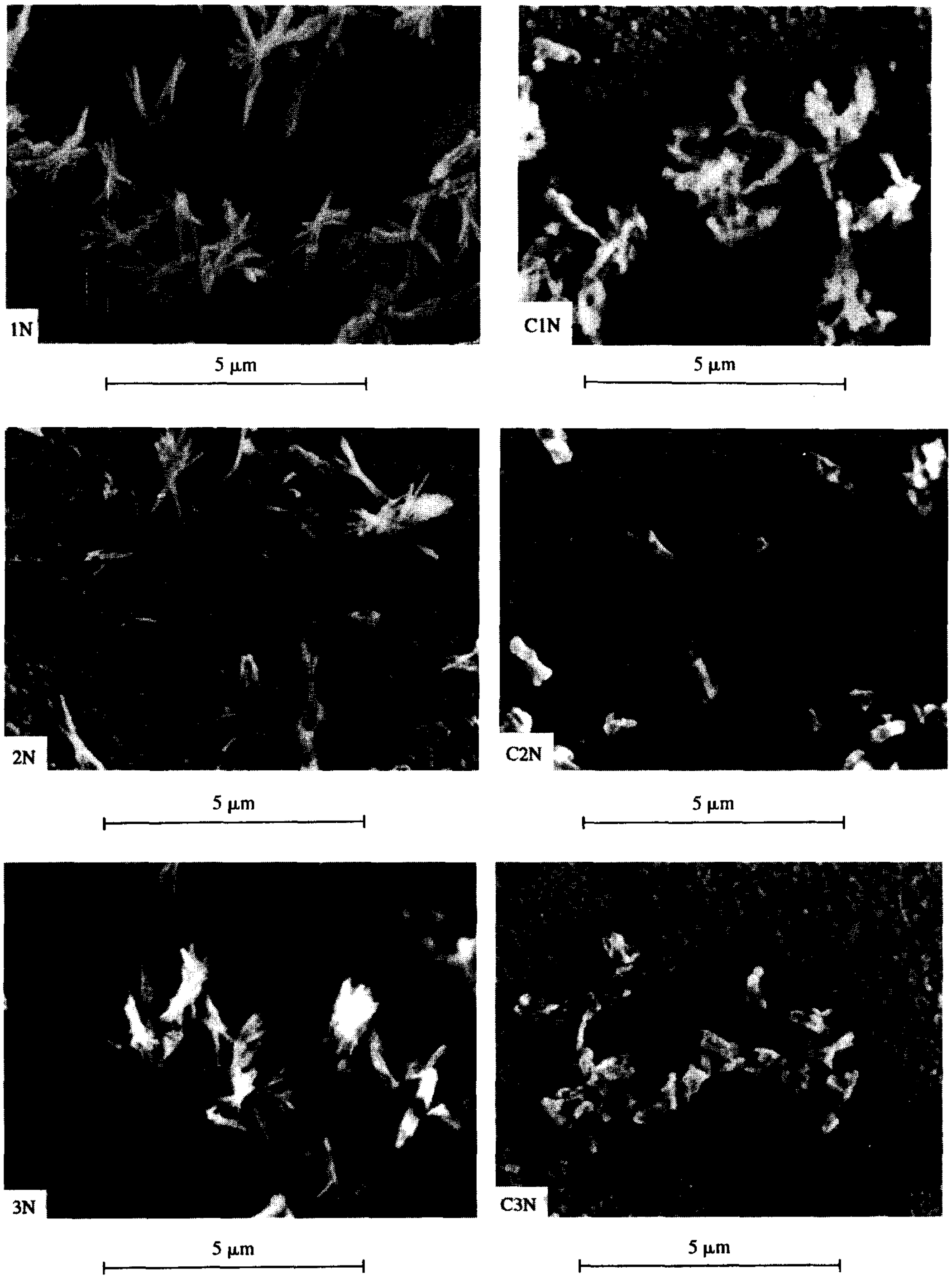


Fig. 6. SEM morphology of precursor and alumina powders from NU-reactions.

of boehmite formed to undergo rearrangement and agglomeration freely, resulting in the evolution of the typical morphology characteristic of the boehmite structure (Fig. 6). The size of the agglomerates is in keeping with that of particle size data.

The amorphous granular precipitates of sulfato complex formed initially by SU-reactions were found to be agglomerates of individual spheres (Fig. 7). Upon subsequent refluxing with the mother liquor, boehmite fibrils started growing from the surface of these agglomerates contributing to the roughening of the surface. Even though the degree and extent of crystallization varied with conditions, the agglomerates formed initially remained intact (Fig. 7) because of the strong binding involved in the compact structure of the initially formed amorphous powder. As a result of this, upon prolonged refluxing at a higher pH, the size and shape do not change. The boehmite crystallites are not free to rearrange and are anchored into the original compact structure. Thus the particle size distribution and morphology does not change much. Thus in the NU-reaction the initially formed gel (open and weakly bonded structure) breaks into crystallites of boehmite that freely agglomerates into particles. But in SU-reaction the

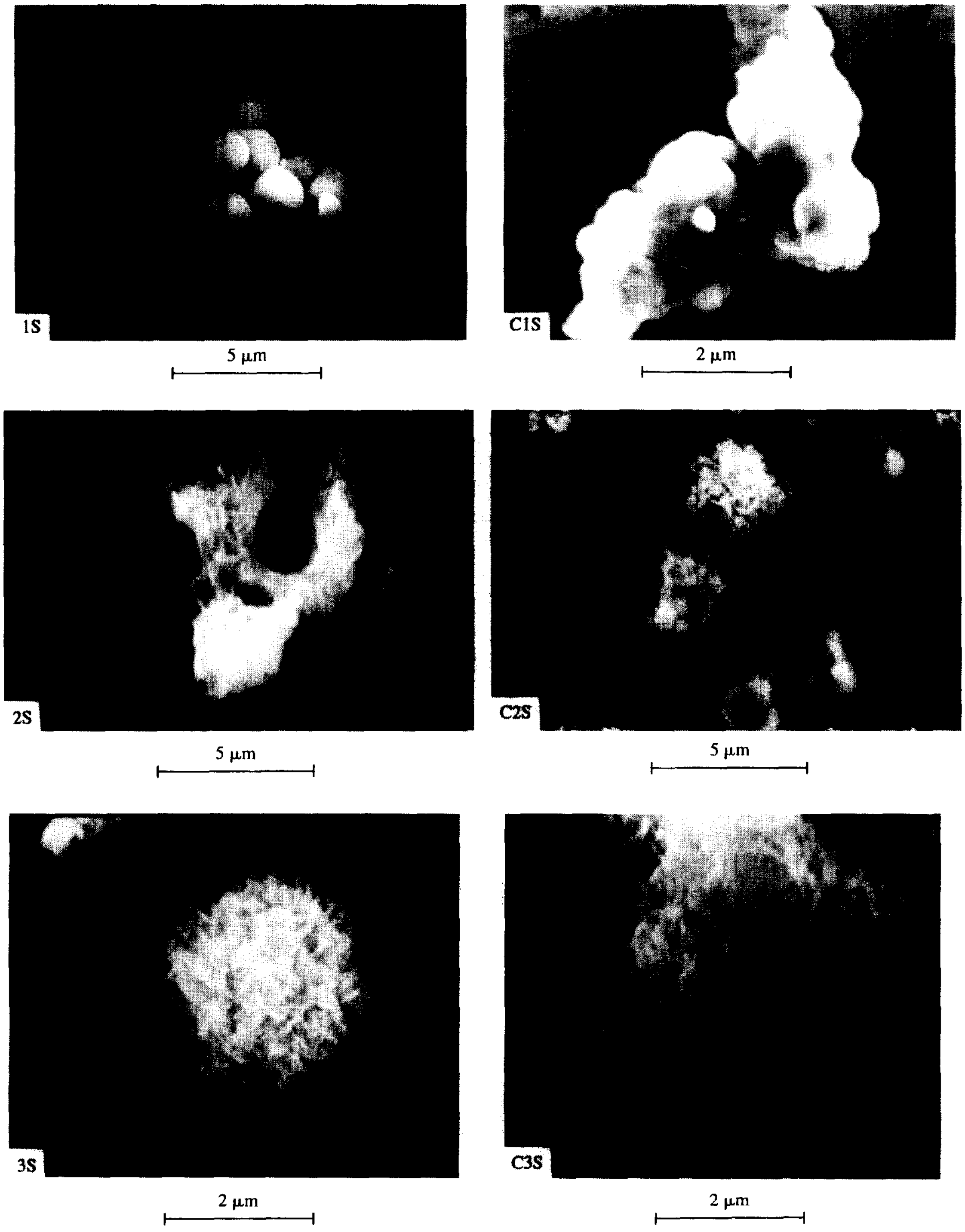


Fig. 7. SEM morphology of precursor and alumina powders from SU-reactions.

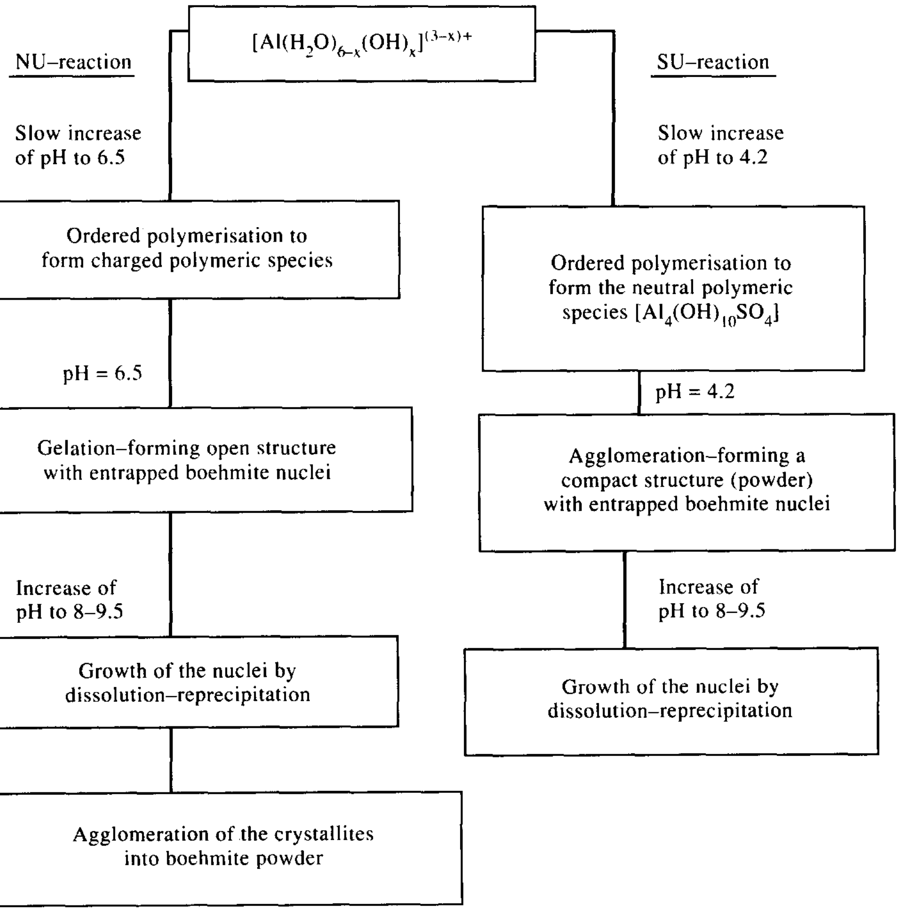
compact and strongly bonded agglomerates formed initially retained their structure during crystallization into boehmite and the crystallization is partial. Thus a schematic of powder formation can be proposed as given in the flowsheet (Scheme 1).

3.4 Calcination and sintering studies

The characteristics of alumina obtained by calcination at 1673 K of the various precursor powders and the sintering data are given in Table 2. It is obvious from Table 2 and Figs 8 and 9 that the particle size distribution of the alumina powders formed are the same as that of the precursors, implying no further agglomeration taking place during calcination at 1673 K while the following reactions occur:

1. $AlO(OH) \rightarrow gamma\text{-}Al_2O_3 \rightarrow alpha\text{-}Al_2O_3$
2. $Al(OH)SO_4 \rightarrow gamma\text{-}Al_2O_3 \rightarrow alpha\text{-}Al_2O_3$

However, the specific surface area decreased and average particle size obtained from it increased. The particle size values are comparable with those of the sedimentation data, particularly for the NU-reaction based powders. This could be attributed to the fact that the crystallites in the porous agglomerates undergo rearrangement to completely eliminate internal porosity and sinter together while calcining at 1673 K. However, alumina from SU-reaction based precursors still exhibited a higher specific suface area data and the particle size calculated from it was substantially lower than that obtained from sedimentation results, indicating the presence of open pores in the particles. The morphological features of the alumina powders obtained by calcination at 1673 K are shown in Figs 6 and 7. It is clear that they retain the features of the respective precursor powders. It is seen from Table 2 that the maximum green density obtained and corresponding compaction pressure required to get defect-free compacts are of the order of 50% theoretical density and 175 MPa, respectively. The green density of the compacts of the alumina powders from SU-reaction based precursors increased with increasing degree of crystallization into boehmite. Also their green strength was found to improve. The bulk density of the typical specimens sintered at 1823 and 1873 K are given in Table 2. The compacts from SU-reaction based powders sintered only to a maximum of about 85%, while those from NU-reaction based powders attained about 95% of theoretical density at 1823 K. This could be attributed to the larger particle size of the SU-reaction based powders.



Scheme 1. Flowsheet showing the steps in powder formation.

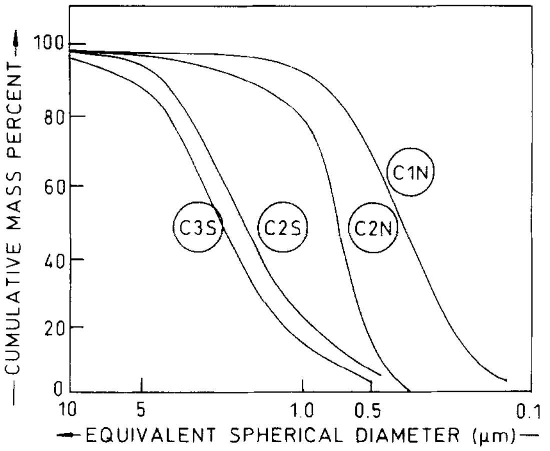


Fig. 8. Particle size distribution of alumina obtained by calcining 4S, 2S, 3N and 1N at 1673 K (effect of amount of urea).

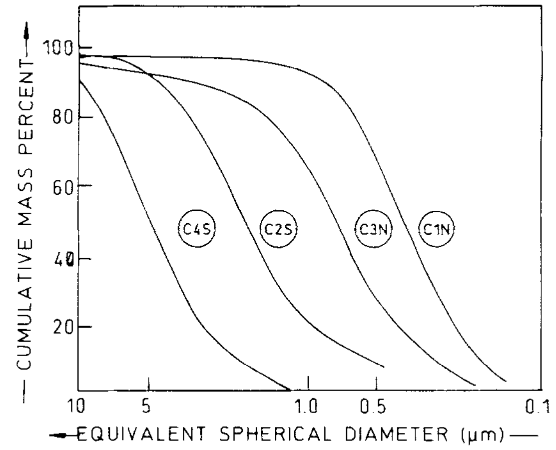


Fig. 9. Particle size distribution of alumina obtained by calcining 3S, 2S, 2N and 1N at 1673 K (effect of aluminium concentration).

4 CONCLUSIONS

Precusor powders for alumina could be prepared by the aluminium nitrate–urea (NU-) and aluminium sulphate–urea (SU-) reactions. NU-reaction results in a gelatinous precipitate that requires longer periods and higher pH to break into a fine powder, while SU-reactions results in direct formation of granular powder. The gelatinous and granular precipitate formed from NU- and SU-reactions initially are amorphous that transform into crystalline boehmite upon prolonged refluxing at higher pH. The transformation is faster with the gelatinous precipitate than with the granular one. The NU-reaction results in powders of submicron size (0·3–0·8 μm), while SU-reaction results in powders of size an order of magnitude larger (2–7 μm). The NU-reaction based powders exhibited a morphology of elongated fibrillar bundles. The initially formed powders of SU-reaction are agglomerates of spheres, while subsequently crystallized ones have plates of boehmite grown on their surface. All the precursor powders are porous agglomerates as revealed by specific surface area data. These precursors upon calcination at 1673 K form α-alumina having the same prticle size distribution and morphology. However, the specific surface area decreases because of the internal sintering of the particles. The compacts of alumina from NU-reaction sintered to 95% T.D., while those from SU-reaction sintered to about 85% T.D. only at 1823 K.

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