

Research Article

Comparative Study of Influence of Anions on Thermal Behavior of Nanosized Alumina

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Abstract: Nanoalumina precursors homogeneously precipitated from aluminum nitrate and aluminum chloride were investigated for their thermal transitions and structural transformations. From both the monovalent anionic salts under identical reaction conditions, alumina precursors derived were same i.e., pseudoboehmite but their thermal behavior was different. Pseudoboehmite prepared from nitrate was amorphous and prone to dehydroxylation and subsequent calcination while pseudoboehmite prepared from chloride had relatively higher crystallinity and delayed dehydroxylation and calcination. In case of nitrate, life duration of gamma alumina was brief i.e., up to 350°C whereas it in case of chloride it showed off at 375 and persisted up to 800°C. Consequently, the complete formation of alpha alumina occurred at 1150°C in the former case while alpha phase was in process of its conversion from theta phase in this temperature regime in the latter case. DSC-TG, XRD, SEM, etc. were carried out for the characterization.

Keywords: Aluminum hydroxide, boehmite, corundum, metastable polymorphs, pseudoboehmite

INTRODUCTION

Alumina hydrates are a common source of alumina. There are two main kinds of alumina hydrate known as aluminum hydroxides and aluminum hydroxydioxides. Alumina trihydrate or aluminum trihydroxide [$\text{Al}(\text{OH})_3 = \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$] exist in three crystalline polymorphs named gibbsite or hydrargillite [$\gamma\text{-Al}(\text{OH})_3$], bayerite [$\alpha\text{-Al}(\text{OH})_3$] and nordstrandite [$\beta\text{-Al}(\text{OH})_3$]. Monohydrated alumina or aluminum oxihydroxide [$\text{AlO}(\text{OH}) = \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$] is available in two crystalline polymorphs. These are boehmite [$\gamma\text{-AlO}(\text{OH})$] and diaspore [$\alpha\text{-AlO}(\text{OH})$]. Thermal dehydroxylation of these alumina hydrates leads to the formation of alpha alumina which involves a number of metastable polymorphs called transitional aluminas designated by Greek letter to identify i.e., alpha, gamma, delta and others. Each one of these has a different crystalline structure and is stable in a peculiar temperature range. By progressive elevation of the temperature, each transition alumina can suffer transformation into another transition alumina, however, all of them recrystallize into $\alpha\text{-Al}_2\text{O}_3$ at higher temperatures which has a very stable crystalline structure and melts at 2050°C (Cardarelli, 2008). The

transition alumina particularly the γ form has fine particle size and huge surface area with enhanced catalytic surface activity find industrial applications as adsorbent, catalyst or catalyst carrier, coating and soft abrasive (Levin and Brandon, 1998). Thermal stability of the transitional aluminas depends on their morphology and crystallite size (Braun *et al.*, 1999) which in turn is influenced by the aluminum hydroxide salt used as starting material (Temuujin *et al.*, 2000).

The preparation of nanoalumina powder by solution technique generally involves two stage processes, the formation of metal salt solution and its subsequent decomposition. It is well known that the morphology of the aluminum hydroxide precipitated and its thermal behavior is affected by many factors such as concentration, kind of metal compounds, precipitation reagents, coexistent ions and temperature, etc. (Unuma *et al.*, 1998; Ramanathan *et al.*, 1996; Nagai *et al.*, 1991; De Hek *et al.*, 1978; Stol *et al.*, 1976). It has been reported (Ada *et al.*, 2003) that aluminum nitrate-urea and aluminum chloride-urea reactions result in a sudden formation of gelatinous precipitates at pH 6.5. The monovalent anions NO_3^- and Cl^- because of their poor coordinate bond forming ability do not interfere with the reaction of hydroxide with

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Table 1: Molar compositions of aluminum salt and urea

Sr. No	Composition symbol	Salt: Urea molar ratio	Aluminum salt M/3l	Urea M/3l
1.	AN	1:3	0.3	0.9
2.		1:5	0.3	1.5
	1:7	0.3	2.1	
	AC	1:9	0.3	2.7

Table 2: Parameters of cold compaction

Sr. No.	Composition	Pre-sintering		Binder (2%)	Pressure (MPa)	Time (seconds)
		Temp/Time (°C/hour)				
1	AN	800/2		PVA	100	3
2	AC	800/2		PVA	100	3

aluminum containing polymeric cation growing into the larger charged polymeric species via olation and oxolation within Al-O-Al bridges

In the present study, alumina nanopowders were produced from aluminum nitrate and aluminum chloride under identical reaction conditions to study the relative effect of monovalent anions on thermal transition and structural transformation of alumina nanopowders during conversion into alpha alumina. Besides, variation in average particle size of nanopowders was also studied.

MATERIALS AND METHODS

The study was finished in year 2016, it was conducted in Pakistan Council of Scientific and Industrial Research PCSIR Laboratories Complex Lahore, Pakistan and registered in The Bahawalpur University, Bahawalpur, Pakistan.

Aluminum nitrate nonahydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fluka) and aluminum chloride $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Fluka) were used as starting materials. Molar ratios of aluminum salts and urea $(\text{NH}_2)_2\text{CO}$ (Merck) are given in Table 1.

The sols were heated at 90°C temperature with constant stirring and volume was maintained to 6 L by adding distilled water. The pH of the sols has been monitored throughout the reaction at definite intervals of time. When pH value reached 7, the reaction was stopped. Gels were washed several times using distilled water. A tray freeze drier of Max series was used to sublime gels at -40°C. Nanopowders collected from freeze drier were consolidated into green bodies. After pre-sintering at 800°C for 2 h, the powders were damped with 2 wt% (related to Al_2O_3) polyvinyl alcohol PVA (Hoechst, Frankfurt) and uniaxially

pressed into 1X0.3" disks. The prerequisites and parameters of cold compaction are given in Table 2.

The green machined compacts were initially dried overnight at room temperature, heated at 100°C for 1 h in the electric oven and finally thermolysed at 800°C for 1 h. The digital electric laboratory oven WE 500HA and high temperature rapid heating electric furnace RHF/3 Carbolite, UK were used. Sintering was carried out up to 1400°C at the heating rate 5°C per minute and soaking time 3 h.

For TDA, specimens with 50 mm length and 20 mm width were fired up to 1600°C @ 20°C per minute in Horizontal Orton Dilatometer DIL 2016 STD.

X-ray diffraction measurements were conducted on Siemen's Diffractometer D5000. X-ray tube operated at 40 kV and 30 mA. Data was collected with a scintillation counter in the 10-70° range with a step of 0.05° and a counting time of 60 s/step.

A Hitachi S-3700, Japan SEM equipped with EDS, was used to acquire an image at the accelerating voltage 25 kV, working distance 5 mm, tilt angle 0°. To improve image resolution sample was coated with platinum at 0.1 torr and 20 μA for 2 min which has been found optimum for a thin layer coating.

RESULTS AND DISCUSSION

Hydrolysis-precipitation of aluminum hydroxide:

The hydrolysis-precipitation using aluminum salt and urea as precursors undergoes a change in pH which is plotted as a function of time in Fig. 1. In case of AN3, pH gradually increased from 3 to 5 in about 7.5 h. At this pH, the turbidity appeared in the sol. The increase in pH value, however, was spontaneous in next 1.5 h and reached 6. This lead to flocculation of sol and the content of vessel turned white. The heating and stirring

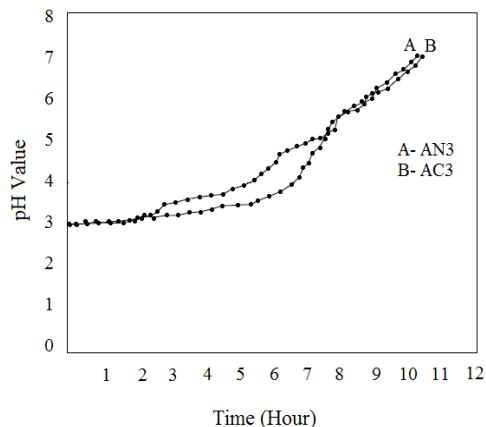


Fig. 1: pH plot of AN3 and AC3

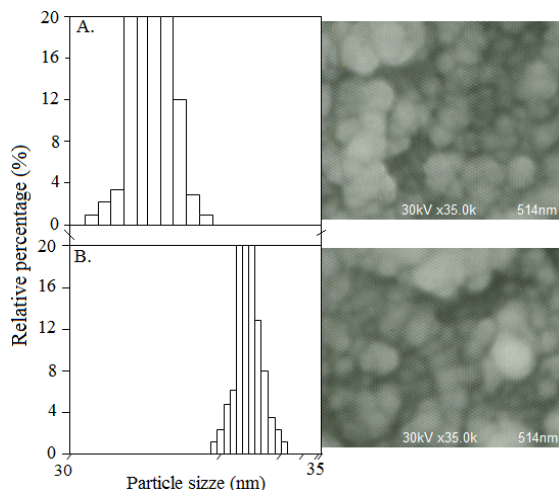
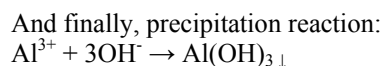
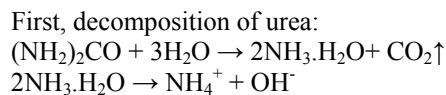


Fig. 2: Particle profile of (A) AN3 and (B) AC3 nanopowders

for further 1 h accomplished the conversion of sol into gel as the pH value reached 7 i.e., neutral. The behavior of AC3 composition is similar to AN3. It also shows two plateaus in pH curve. The time period, however, for the conversion of sol into gel was comparatively little more. There is a difference of about 15 min. The physical appearance of two reaction products was different. AN3 gel was transparent, thick and more colloid thus difficult to filter. Relative to AN3, AC3 gel was opaque, thin and easy to filtrate. The reaction mechanism of the formation of aluminum hydroxide includes:



Particle profile of freeze-dried powders is presented in Fig. 2. The figures revealed that AN3 and

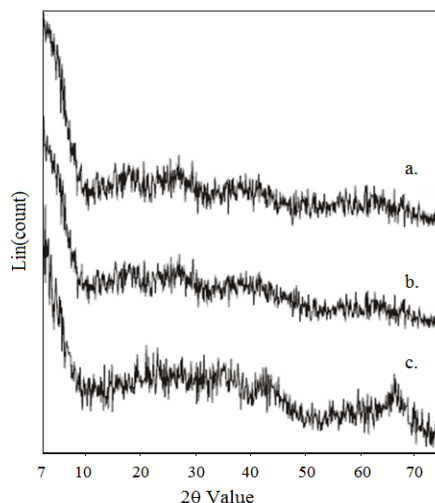


Fig. 3: XRD of AN3 at (a) RT, (b) 125 and (c) 225°C

AC3 nanopowders have 31 nm and 32 nm average particle size, respectively which is quite comparable. However, there was a difference in particle size distribution. AN3 showed narrower particle size distribution while AC3 relatively wider. Scherrer formula was also applied to measure average size of crystallite and data obtained was in agreement.

In case of both the aluminum salts, average particle size increased with increase in the molar concentration of urea and vice versa.

Structural changes and thermal transformations of AN alumina nanopowder:

AN compositions showed the same thermal trend, therefore among these four, AN3 composition was selected for the study of structural changes corresponding to thermal transformations. The XRD diffractogram of AN3 nanopowder presented in Fig. 3a, exhibits that the powder is amorphous. The diffractogram, however, appears more like an array of amorphous haloes. DSC-TG thermogram of AN3 in Fig. 4 shows that the powder undergoes three stages of decomposition with total 45% weight loss. In the first stage, between 30-150°C weight loss is 12% corresponding to a broad endotherm at 150°C which is nevertheless due to the decomposition of volatile compounds. The sample heated at 125°C for 1 h is shown in Fig. 3b. There was no change in diffractogram.

In the second stage, maximum weight loss occurred i.e., 38% in the temperature regime 150 to 360°C along with a large endothermic peak at 250°C. The sample was heated at 225°C for 1 h and diffractogram is shown in Fig. 3c. It seems that haloes tend to organize themselves into bands. These XRD bands are typical of pseudoboehmite. The bands are not sharp and distinct showing that the powder is still predominantly amorphous. The endothermic peak at 250°C relates to dehydroxylation of pseudoboehmite.

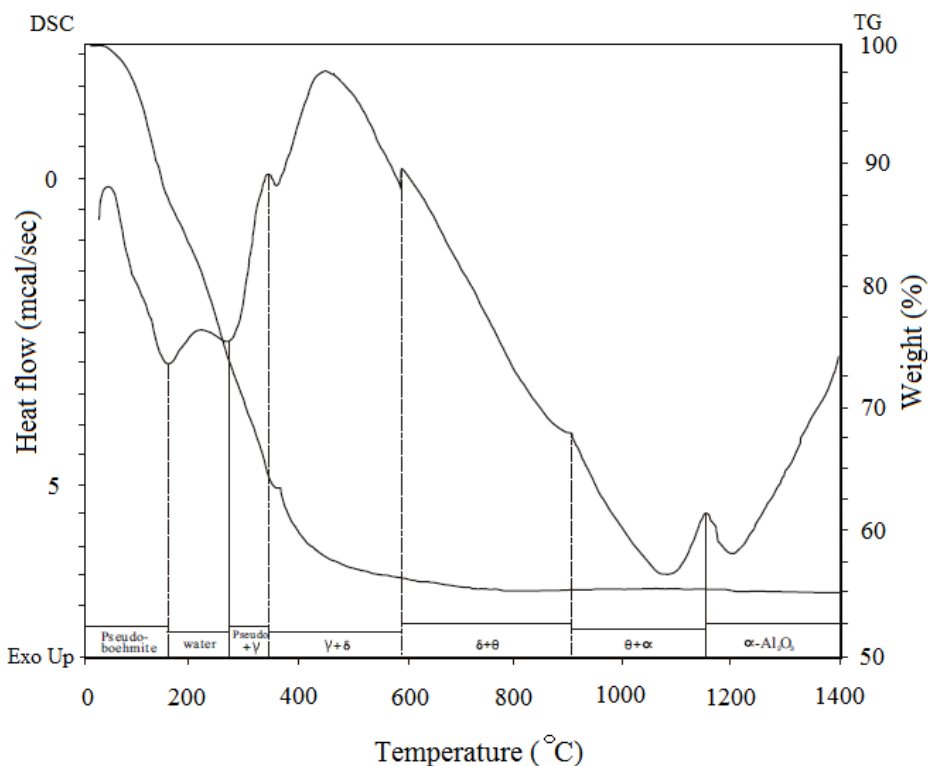


Fig. 4: DSC-TG thermogram of AN3

During thermal transformation, two small endothermic peaks also called humps by Mackenzie (1957) appeared at 360 and 600°C. According to the general pathway of thermal dehydroxylation of aluminum hydroxide (Antos and Aitani, 2004), pseudoboehmite dehydrates on heating into gamma alumina which on further heating into delta then theta and finally into alpha alumina. Therefore, of these two, the low temperature peak corresponding to third and final weight loss of about 2% represents gamma phase while high temperature peak to delta phase of alumina. The medium sized peak at 1150°C accounts for conversion into alpha alumina.

In the temperature region between successive thermal events, two crystalline phases coexist, however their relative proportion varies with temperature (Braun *et al.*, 1999). Based on the fact, the Fig. 4 is charted into various temperature zones in order to compare DSC thermal event with XRD structural change. There are two continuous lines in the figure, below first the powder is exclusively pseudoboehmite and beyond latter alpha alumina. The dotted lines show the transformation of crystalline phases. The area beneath two lines depicts the temperature zone where two crystalline phases coexist. The crystalline phase identification in the present study was carried out on the basis of the principle peak, preceding XRD diffractogram, the relative proportion of crystalline phases and DSC interpretations.

XRD peaks of four aluminas under consideration i.e., gamma, delta, theta and alpha alumina lie close to

Gamma	Delta	Theta	Alpha
4.55		4.52	
		3.55	3.54
	2.87	2.86	
	2.73	2.72	
	2.43	2.44	
2.27	2.28	2.26	
	1.99	2.02	1.99
1.96	1.96	1.96	
1.80		1.80	
		1.77	1.77
1.61		1.62	1.63
		1.57	1.57
	1.54	1.54	1.54
1.51		1.50	
		1.43	1.43
1.40	1.40	1.40	
	1.39	1.38	1.38
1.36		1.36	1.36
1.33		1.33	
1.31		1.31	1.30
		1.28	1.26

each other. This is due to the fact that oxygen anions in the crystal lattices have fixed positions while the distribution of aluminum cations shows the difference in structural arrangements. Relative distribution of cations is cubic closed-packed c.c.p. in gamma, delta and theta and hexagonal closed-packed h.c.p. in alpha alumina thus structural arrangement is quite similar (Levin and Brandon, 1998). Similar d reflexion values of transitional and alpha alumina are given in Table 3.

The sample after heating at 350°C for 1 h is shown in Fig. 5 According to Fig. 4, pseudoboehmite and

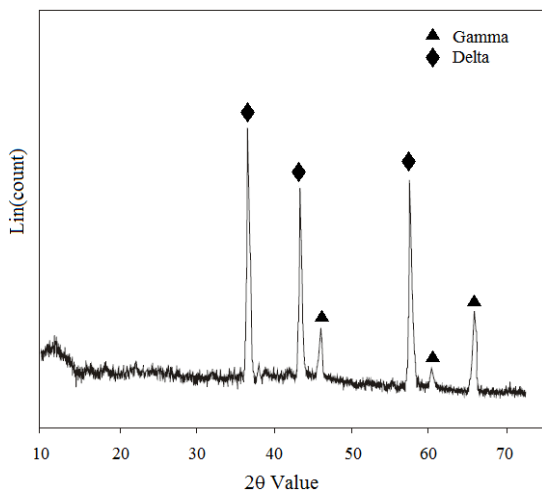


Fig. 5: XRD of AN3 at 350°C

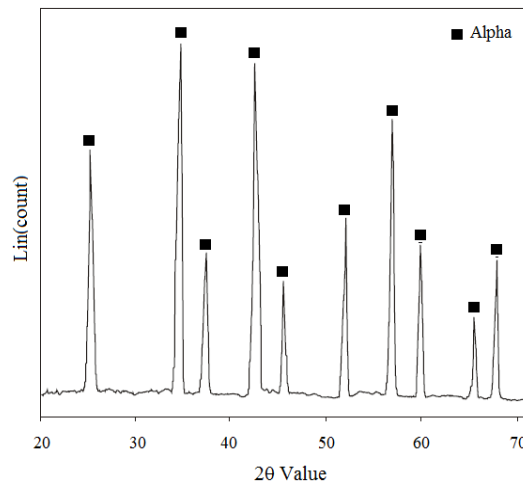


Fig. 7: XRD of AN3 at 1150°C

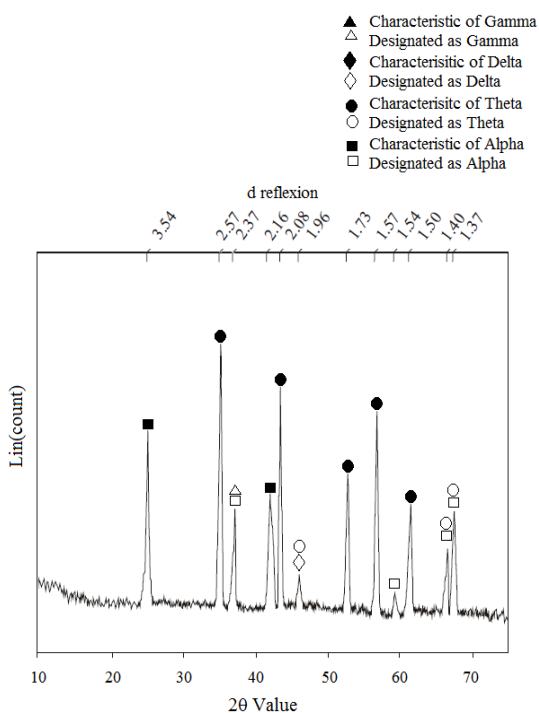


Fig. 6: XRD of AN3 at 800°C

gamma are the two probable phases in this temperature range, however, XRD diffractogram identifies delta as principle phase with minor peaks of gamma. This shows that pseudoboehmite had been completely dehydroxylated and gamma is being transformed into delta alumina.

The sample was heated at a temperature beyond which weight loss is static i.e., 800°C for 2 h. The resulting diffractogram is shown in Fig. 6. In accordance with DSC, delta and theta co-exist at this temperature. Two crystalline phases identified were theta and alpha which seems in succession with the preceding XRD graph. The principle peak with d reflexion 2.57 was identified as theta phase besides

peaks with d reflexion 2.08, 1.73, 1.57 and 1.50. XRD peak with 1.96 d value depicts either of three transitional alumina phases. This peak is designated as theta and/or delta. Gamma phase had been converted into delta phase at 350°C, therefore, is non-existent at 800°C.

The second phase i.e., alpha showed its characteristic peaks at 3.54 and 2.16 d reflexions. The peak with 1.54 d value is marked as alpha in the graph though it has an equal probability of delta and theta phase. This is due to the reason that the crystalline structure of sample at this stage gives an impression that sample is at the initial stage of conversion from theta into alpha phase. In addition, peak with d value 2.37 is also designated as alpha since the gamma is improbable.

The XRD peak with 1.40 and 1.37 d reflexions could be due to one of the transitional aluminas or alpha alumina. Keeping in view relative proportion of theta and alpha phases, the probability of gamma and theta is nil. However, it is difficult to figure out that which of the remaining two phases, the peaks signify to.

The exothermic peak in DSC thermogram at 1150°C accounts for alpha alumina. The diffractogram of the sample obtained after heating at this temperature for 1 h is shown in Fig. 7. It merely shows single crystalline phase i.e., alpha alumina which is in agreement with the DSC thermogram.

Structural changes and thermal transformations of AC alumina nanopowder: Thermal behavior of AC compositions had been same with the shift of thermal event to higher temperature with increase in average particle size. AC3 composition was chosen to explore structural changes on heating.

DSC-TG thermogram of AC3 shown in Fig. 8 is comparable to AN3. TG curve shows 45% weight loss. Up to 150°C temperature, 11.5% weight loss along with a large endothermic peak shows liberation of adsorbed water. Major weight loss i.e., 26.5% from 150 to 375°C

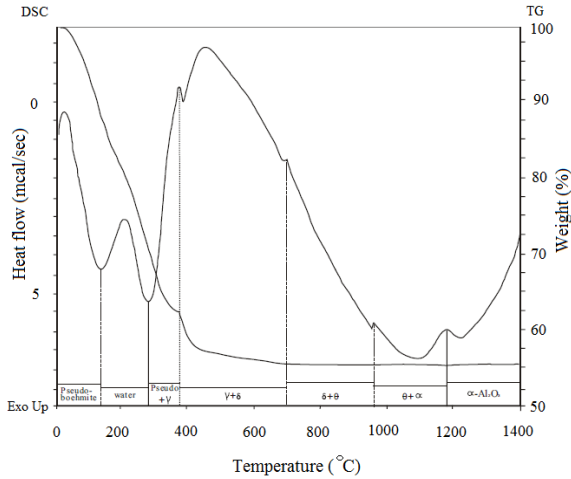


Fig. 8: DSC-TG thermogram of AC3

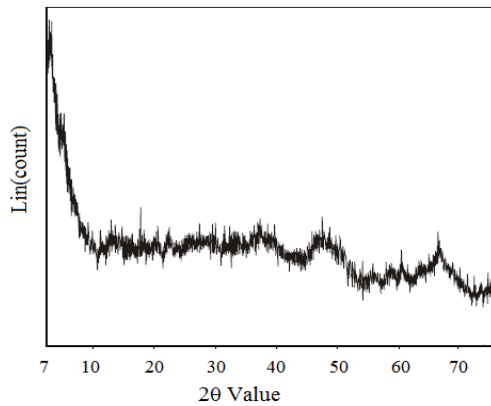


Fig. 9: XRD of AC3 at RT

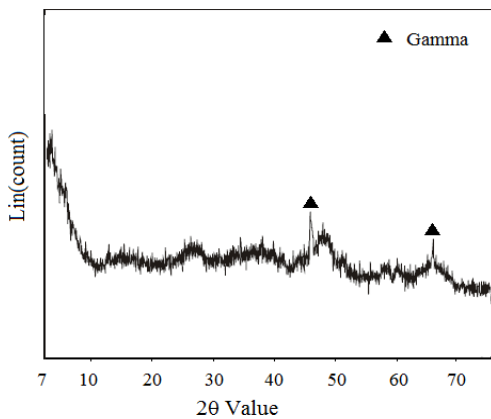


Fig. 10: XRD of AC3 at 375°C

with a large endothermic peak at 280°C is associated with dehydroxylation of pseudo-boehmite.

Remaining 7% weight loss occurred from 375 to 700°C. No further weight loss was observed. First and the foremost exothermic peak at 375°C shows dehydroxylation of pseudo-boehmite into γ-alumina. Two very small exothermic peaks at 700 and 957°C

indicate δ- and θ-alumina, respectively. Last exothermic peak at 1166°C shows transformation into α-alumina.

Comparison of DSC thermogram of AN3 and AC3 shows that peak for the dehydroxylation of pseudo-boehmite is shifted towards higher temperature. The XRD diffractogram of AC3, in Fig. 9 has sharp pseudo-boehmite bands which show that it has higher crystallinity relative to AN3 powder.

Sample after heating at 375°C for 1 h is shown in Fig. 10. It shows several small peaks of gamma phase emerging out of pseudo-boehmite bands. Comparison of Fig. 5 and 11 reveals that dehydroxylation of pseudo-boehmite is completed at a far lower temperature in AN3 than in AC3.

Sample was heated further at 800°C for 2 h and its diffractogram is shown in Fig. 11.

DSC thermogram proposes two phases i.e., delta and theta at this temperature. Theta phase was certainly identified as major phase along with the minor proportion of delta. In addition to these two phases, gamma phase was encountered found in quite fair proportion. Few bands of pseudo-boehmite were also found.

The principle peak with 2.56 besides, peaks with 2.08 and 1.73 d reflexions are characteristics of theta phase. Two peaks with d reflexion 2.73 and 1.60 are characteristics of gamma phase. XRD peaks with d values 1.96, 1.54, 1.51 and 1.33 represent gamma and/or delta phase of alumina.

For peaks with 1.40 and 1.37 d values, the presence of amorphous haloes eliminates the possibility of alpha phase, however; there are equal chances of each of three transitional aluminas.

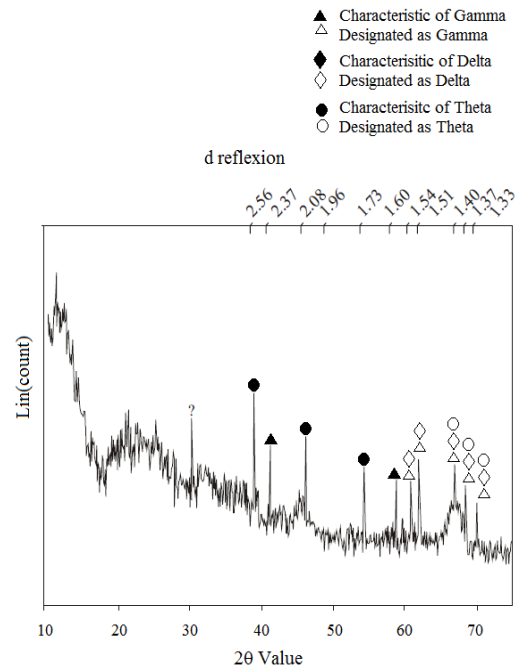


Fig. 11: XRD of AC3 at 800°C

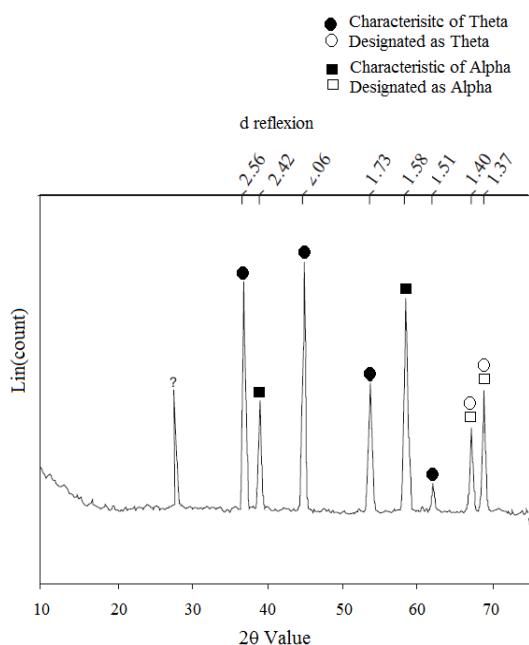


Fig. 12: XRD of AC3 at 1140°C

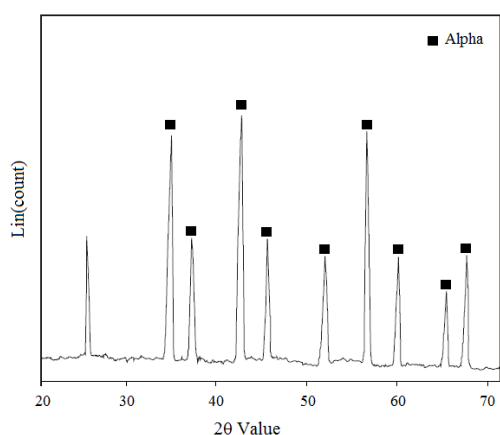


Fig. 13: XRD of AC3 at 1300°C

The peak with 3.46 d reflexion remained unidentified throughout the crystallographic studies.

Comparison of Fig. 7 and 12 reveals that at identical temperature, theta phase just appeared in AC3 whereas it was in the transformation into alpha phase in AN3. It would be worth mentioning that there was no change in physical appearance of AC3 sample while AN3 sample appeared as crumpled crisp mass when collected from furnace after soaking temperature 800°C.

Sample heated at 1140°C for 1 h is shown in Fig. 12. The crystalline phases identified were theta and alpha. The principle peak with 2.06 d reflexion is characteristic of theta phase. Three additional peaks for theta phase appeared with d values 2.56, 1.73 and 1.51. The alpha phase shows its peaks at 2.42 and 1.58 d values.

XRD peaks with 1.40 and 1.37 d values are designated as theta and/or alpha since at such high temperature the existence of gamma and delta phase seems rare.

The sample heated at 1300°C for 1 h shows alpha phase in Fig. 13 which is in accordance with the DSC thermogram.

CONCLUSION

Nanoalumina precursors prepared from aluminum nitrate and aluminum chloride under identical reaction conditions had comparable average particle size but incomparable thermal transitions and structural transformations which relates to the difference in particle size distribution. The precursor in both the cases was pseudoboehmite however, their relative dehydration, dehydroxylation and calcination temperatures were different. Pseudoboehmite obtained from aluminum nitrate has less crystallinity and was more prone to thermal transformations as compared to pseudoboehmite obtained from aluminum chloride. The sequence of thermal transformation was same, i.e., pseudoboehmite → gamma-γ → delta-δ → theta-θ → alpha-α Al₂O₃ though temperature ranges and intensities of transitional aluminas and recrystallization into alpha alumina was not same. In case of nitrate, pseudoboehmite was completely dehydroxylated below 350°C and transformed into gamma alumina. The life of gamma phase was brief, besides theta phase appeared as the major phase. On the other hand in case of chloride, pseudoboehmite was not completely dehydroxylated even up to 375°C. Gamma phase was found existent even up to 800°C. In consequence, alpha phase appeared at 1140°C in nanoalumina produced from aluminum nitrate whereas theta co-existed with alpha up till 1150°C in nanoalumina produced from aluminum chloride.

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