ELSEVIER

Low-temperature synthesis of β-aluminas by a sol–gel technique

V. Jayaraman, T. Gnanasekaran, G. Periaswami [*]

Materials Chemistry Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

Abstract

New intermediates observed in the process of preparing sodium β-aluminas by a sol–gel method using metal alkoxides as precursors are described. Results of studies to optimise the conditions for the preparation by changing parameters such as calcination temperatures and initial concentration of isopropoxides are reported. Based on IR, TG/DTA and XRD studies, different steps in the process leading to the formation of β-aluminas are discussed. These studies show that the formation of β-alumina starts at as low a temperature as 1273 K possibly through a modified cubic-close-packed γ-alumina structure stuffed with sodium ions and completes at 1473 K.

1. Introduction

Solid electrolytes such as β- and β''-alumina play a major role in the development of high-temperature alkali metal batteries [1]. Conventional methods of synthesising these materials suffer from two major shortcomings: (a) inclusion of impurities during ball milling giving rise to significant electronic conductivity and reduced ionic transport number of the solid electrolyte and (b) loss of sodium oxide as well as grain growth during high-temperature sintering leading to higher resistance and poor mechanical strength [2]. In order to overcome these problems, novel methods, such as sol–gel processing [3,4], solution

spray-drying, freeze-drying [5], co-precipitation [6] etc. are being developed as alternatives.

The sol–gel method for producing ceramics is an emerging route which shows high promise. Preparation of β-alumina by this method would have the following advantages over the conventional powder route: (i) being a solution method, molecular level mixing of reactant species is ensured which results in a high degree of homogeneity, (ii) yields high surface area powders which can be sintered at lower temperatures compared with conventional procedures and (iii) gives relatively high purity products because of the absence of grinding and milling steps. In this study, an alkoxide based sol–gel technique was used to prepare sodium–β-aluminas. The preparation procedure and various steps in the process leading to the formation of β''-alumina are discussed in detail in this paper.

---

[*] Corresponding author.

2. Experimental

Aluminum isopropoxide and sodium isopropoxide were used as precursors in this study. Sodium isopropoxide was prepared by reacting sodium metal with dry isopropanol at 300 K. Aluminum isopropoxide was prepared by reacting aluminum metal in the form of turnings with dry alcohol under prolonged reflux conditions in the presence of a catalyst, mercuric chloride and a radical initiator, carbon tetrachloride [7]. Dry isopropanol needed for this work was prepared as described in Ref. [7].

Aluminum isopropoxide and sodium isopropoxide were taken in 5:1 molar ratio in dry isopropanol. The mixture was thoroughly stirred at room temperature using a magnetic stirrer. A hydrolysis solution was prepared by taking 6 mol of water per 1 mol of alkoxide. This was diluted by dry isopropanol along with a small quantity of acetic acid. This solution was added drop by drop (-0.3 to 0.5 ml/min) to the stirred alkoxide mixture through a dropping funnel. The gel obtained was dried by distilling away the excess isopropanol under vacuum. A portion of the resultant gel powder, hereafter called the as-dried gel powder, was heated first at 473 K and then at 773 K for 24 h at each temperature. Subsequently, the samples were calcined at 1173 K for 5 h followed by a similar treatment at 1473 K for another 5 h. These samples were subjected to surface area measurement (Monosorb surface area analyser of M/s Quanta Chrome, USA) and particle size analysis (M/s Malvern Instruments model M3.0, UK). Surface area determination was done using the BET method with nitrogen and helium mixture.

Another portion of the as-dried gel sample was subjected to thermogravimetric analysis (thermal Analyser model STA 1500 of M/s Polymer Laboratory, USA) with a view to understand the processes leading to the formation of the phases and intermediates. Thermal characteristics of these phases and intermediates were compared with those formed during heating of gibbsite (γ-aluminum trihydroxide) and pseudoboehmite (hydrated γ-aluminum oxyhydroxide). For this purpose, gibbsite and pseudoboehmite were prepared as described in Ref. [8] and subjected to thermal analysis. All the thermal analyses were carried out with a heating rate of 10 K/min in air. Further, to characterise the intermedi-

ates corresponding to various thermal events observed in the thermogram, as-dried gel samples were heated isothermally at 378, 503, 593, 773, 973, 1273 and 1473 K for different durations (24, 46, 22, 20, 6, 4 and 5 h respectively) till a constant weight was obtained at each set temperature. The products obtained from each heat treatment were analysed by X-ray diffractometer (M/s Siemens model D-500, Germany) using Cu Kα radiation. As-dried gel and the products obtained after heat treatment at 773, 1273 and 1473 K were analysed by infrared spectroscopy (M/s Digilab FTIR, model FTS 15/90, USA). For infrared studies the samples (1 wt% in KBr) were normalised for path length and concentration.

The influence of the initial composition of the alkoxides taken on the final products obtained was also studied. For this purpose, the initial composition of alkoxide mixture was varied so as to obtain the Na_2O to Al_2O_3 ratio of 1:8 to 1:3 in the final product. Elemental analysis of the products was done by atomic absorption spectrometry (aa/ae spectrophotometer model 751 of M/s Instrumentation Laboratory, USA). As-dried gel powder for each composition was heated at 473 and 773 K for 24 h at each temperature followed by calcination at 1173 and 1473 K for 5 h at both temperatures. The products calcined at 1473 K were analysed for their phase content by XRD.

3. Results and discussion

Fig. 1 shows the infrared spectra of the as-dried gel and gels heat treated at 773, 1273 and 1473 K. The as-dried gel showed a broad peak at 3410 cm^{-1} corresponding to H–OH stretch, a sharp peak at 1590 cm^{-1} corresponding to H–O–H bend, a peak at 1420 cm^{-1} due to C–H bend and a broad peak ranging between 1000 and 450 cm^{-1} corresponding to Al–O vibrational modes. The peak at 1590 cm^{-1} indicates the presence of free water molecules on the surface and in the pores of the gel powder. The humps around 2950 cm^{-1} are due to the C–H stretch of the isopropoxy groups. These humps are not discernible due to the broad H–OH stretch. When the gel was heat treated at 773 K there was a significant reduction in the intensities of the H–OH stretch, H–O–H bend and C–H bend indicating the
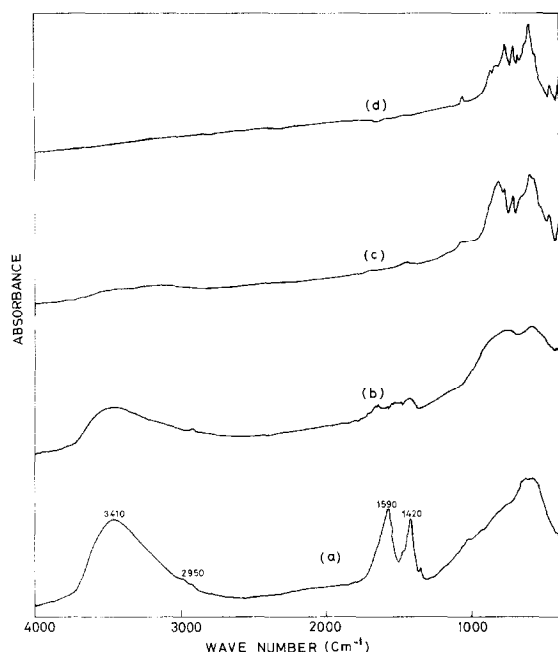
Fig. 1. Infrared spectra of as-dried gel and heat-treated samples (Na$_2$O:Al$_2$O$_3$ = 1:5). (a) As-dried gel and heated at (b) 773 K, (c) 1273 K and (d) 1473 K.

removal of free water and isopropanol present in the pores. For the sample heated at 1273 K, complete disappearance of C–H peaks and further reduction in intensities of O–H peaks were seen. For the sample calcined at 1473 K, complete absence of these peaks was observed except for those due to Al–O vibrational modes. This sequential loss of water, alcohol and structural rearrangement was further investigated by thermal analysis experiments.

The particle size and surface area of the samples heated at different temperatures are given in Table 1. The as-dried gel had 67% of the particles within ≤ 20 μm size and a surface area of 366 m^2/g. This

indicates the fine nature of the particles obtained by the sol–gel method. The surface area remained almost constant when heated at 473 K (347 m^2/g). When the sample was heat treated at 773 K, the surface area was reduced by roughly 55% (153 m^2/g). This significant reduction in surface area points to agglomeration of the intermediate phases formed. The sample heat treated at 1173 K exhibited an area of 4 m^2/g. This large reduction in surface area indicates the sintering of samples. A marginal reduction in surface area was observed when the sample was calcined at 1473 K and this sample had only 15% of the particles with ≤ 20 μm size.

Thermograms of the as-dried gel powder, pseudoboehmite and gibbsire are given in Fig. 2. The as-dried gel sample exhibited four weight loss steps initiating at 360, 389, 595 and 680 K. The first weight loss (≈ 20%) was due to the desorption of adsorbed moisture and isopropanol; this weight loss was accompanied by an endothermic peak in the DTA trace shown in Fig. 2. In the third weight loss step, an exothermic DTA peak was observed at 644 K. Weight loss at this step was 12%. Thermal analysis patterns of pseudoboehmite and gibbsire, as seen from Fig. 2, are significantly different from the pattern observed for the as-dried gel powder. Both gibbsite and pseudoboehmite do not show the exothermic peak at 644 K. Also gibbsire exhibits a characteristic endothermic peak at around 625 K which is due to the conversion of aluminum trihydroxide to aluminum oxyhydroxide [8]. The exothermic peak at 644 K observed for the as-dried gel sample could be due to burning of the unreacted isopropoxy groups present in the macro-molecular gel network. This process was confirmed by a separate experiment wherein the carbon dioxide liberated in the burning process was estimated. Around 600

Table 1
Surface area and particle size analyses as a function of heating temperature

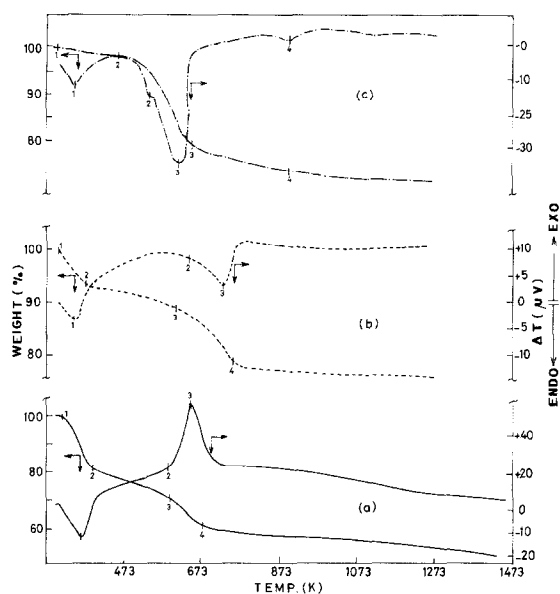| Heat treatment temperature (K)	Duration (h)	Surface area (m^2/g)	Particles with size (%)		
			≤ 20 μm	20–50 μm	50–100 μm
300	–	366	67	23	10
473	24	347	a	a	a
773	24	153	25	28	47
1173	5	4	a	a	a
1473	5	1	15	32	53

a Not measured.

Fig. 2. Thermal analysis traces of (a) as-dried gel ($Na_2O:Al_2O_3$ = 1:5), (b) pseudoboehmite and (c) gibbsite.

treated at 773 and 1273 K (Fig. 1) show that the complete decomposition of alkoxy groups occurs around 873 K.

The second weight loss step seen in the TG trace of the as-dried gel was gradual and extended from 389 K to 595 K. This step accounts for a weight loss of 13% and was not accompanied by a clear thermal event. The weight loss could be due to dehydroxylation of aluminum trihydroxy or oxyhydroxy groups and this is expected to be an endothermic process. However, the slight positive slope in the DTA base line in this temperature range indicates the onset of the burning process of the isopropoxy groups at around 400 K itself. Decomposition of the isopropoxy groups would further augment the weight loss. Another process of a gradual weight loss (− 10%) was observed between 680 and 1473 K without an accompanying thermal event. This weight loss is attributed to the completion of the conversion of residual hydroxy and oxyhydroxy intermediates to oxides. These weight loss steps and the associated processes are given in Table 2.

The X-ray diffraction patterns of various samples heat treated under isothermal conditions are given in Fig. 3. The sample heated at 378 K showed intense reflections at d values of 2.81, 2.16 and 1.99 Å (corresponding 2θ values are 31.80, 41.90 and 45.55°). Low-intensity peaks were observed at d values 4.75, 3.27, 1.84 and 1.40 Å (corresponding 2θ values are 18.70, 27.25, 49.50 and 66.85°). When the sample was heated at 503 K, the intensity of the peak at 41.90° decreased considerably compared to the sample heat treated at 378 K. Also, the low-intensity peak at 49.50° was absent. When the sample was heated to 593 K, the peak at 41.90° was totally absent. On further heat treatment at 773 K, the peak at 18.70° was also absent. The difference in the

mg of the as-dried gel powder was taken in a closed vessel with a provision to pass oxygen. The sample was heated to 873 K from 573 K in steps of 25 K and the outlet gas containing carbon dioxide was passed through barium hydroxide solution. To ensure completion of the combustion process, the heating at 873 K was continued for 2 h after no more visible precipitation could be observed. The amount of carbon dioxide liberated was calculated by weighing the total barium carbonate precipitate. The weight loss corresponding to this carbon dioxide release was 11% which closely matches with the 12% weight loss observed in the thermogravimetric analysis. This result in conjunction with the observations about C–H bend bands in IR spectra of the samples heat

Table 2
Weight loss with associated processes at various temperatures

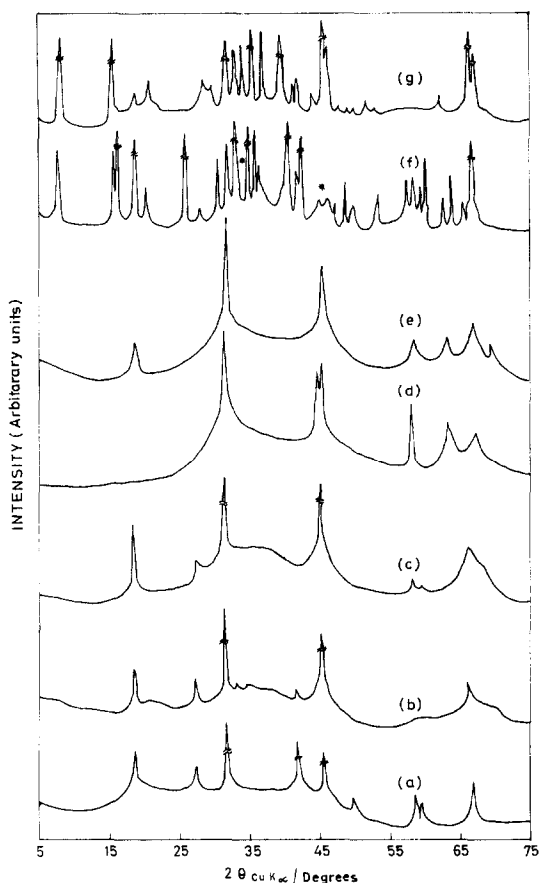| Temperature (K)	Weight loss (%)		Associated process
	this step	cumulative	
360	20	20	desorption of sorbed moisture and isopropanol
389	13	33	dehydroxylation of aluminum trihydroxy or oxyhydroxy groups
595	12	45	burning of isopropoxy groups
680	10	55	conversion of residual hydroxy and oxyhydroxy intermediates to oxides

Fig. 3. X-ray diffraction patterns of samples heat-treated at (a) 378 K, (b) 503 K, (c) 593 K, (d) 773 K, (e) 973 K, (f) 1273 K and (g) 1473 K ($Na_2O:Al_2O_3 = 1:5$).

patterns observed at 378 K and those observed at temperatures up to 773 K could be due to the decomposition of the unreacted alkoxy groups present in the gel matrix which was inferred from IR and thermal analyses. Further, heat treatment of the sample at 973 K, resembled γ-alumina in its pattern to a certain extent. The peak at 18.75° (4.73 Å) could be due to a small shift in the (111) reflection (4.56 Å) of γ-alumina. The peaks at 31.85° (2.81 Å) appear as 100% intensity and 45.50° (1.99 Å) as 60% intensity against 20 and 100% respectively for the JCPDS (10425) pattern. Also the peak at 66.90° (1.39 Å) was low in intensity. These differences in the peak intensities and the shift in the peak position could be due to stuffing of sodium ions in the open γ-alumina network forming a modified γ-alumina intermediate. When the sample was heated to 1273

K, the basal plane reflections (002/003) and (004/006) of β- and β''-alumina started appearing along with other prominent reflections, viz. (220) and (017), indicating the formation of β-aluminas at temperatures as low as 1273 K. This could be due to the conducive cubic-close-packed arrangement of the sodium, aluminum and oxygen atoms in the intermediate formed in this preparation technique resulting in the formation of β-aluminas. The XRD pattern of the sample calcined at 1473 K showed reflections (01, 11) and (02, 10) corresponding to β''-alumina along with reflection (017) corresponding to β-alumina. The intergrowth of them around d values 2.71–2.57 and 2.01–1.94 Å is shown in Fig. 3 (marked with $*$). By calculating the intensities of reflections (104) and (012) using Johnson's formula [9], the percentage of β-alumina present in the sample was calculated. This value was around 70%.

Yamaguchi et al. [4] in their preparation of β-alumina using alkoxides did not observe crystallisation of β-alumina. This could be due to the use of non-polar solvent (benzene) and sub-stoichiometric quantities of water (0.5 mol/mol of alkoxide) which would result in partial hydrolysis of alkoxides. Curing of sol for 100 h could have resulted in complete gelation. In the present studies, 6 mol of water was used per 1 mol of alkoxide which leads to greater hydrolysis and condensation of alkoxide molecules. This process resulted in the formation of gel when the hydrolysis mixture was added to the alkoxides and thus did not require any curing time. Probably, this process facilitates the formation of crystalline intermediates at low temperatures (378 K) which results in the formation of sodium ion stuffed modified γ-alumina. Subsequently, on heating at 1473 K, this intermediate γ-alumina gives rise to an intergrown β, β''-alumina product.

Dongare and co-workers [10] prepared β-alumina by a pyrolysis reaction of aluminum isopropoxide and sodium isopropoxide. In their studies, the alkoxides (dissolved in isopropanol) were heated slowly from room temperature to 1373 K. They observed an endothermic peak between 373 and 803 K which was attributed to the decomposition of aluminum isopropoxide. They also observed an exothermic peak between 973 and 1373 K without any weight loss. This was attributed to the formation of β-alumina. Similar exothermic peak between 1273 and 1473 K
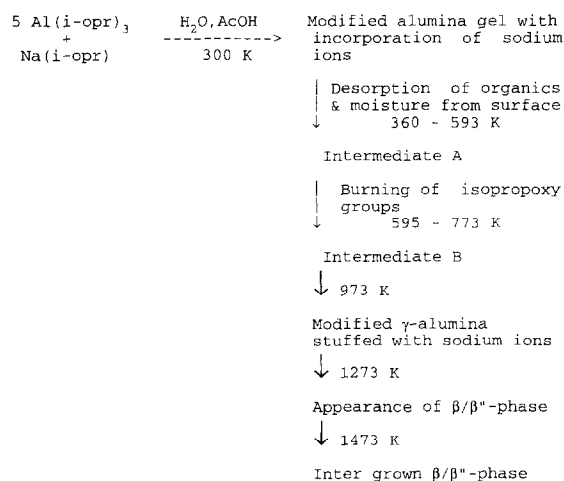
Table 3
Composition of precursors and final products

Initial ratio of $Na_2O : Al_2O_3$	Observed phases
1 : 8	α-alumina + β-alumina
1 : 7	β-alumina
1 : 5	β-alumina + β''-alumina
1 : 3	β, β''-alumina + $NaAlO_2$

was also observed by Yamaguchi and co-workers [4]. In the present studies, we did not observe any exothermic peak around 1373 K. This indicates that a γ-alumina like phase stuffed with sodium ions proposed to be formed in the present process, probably does not require major rearrangement for forming γ-alumina phase.

The effects of the initial composition of the alkoxide taken on the final products obtained are given in Table 3. At the composition corresponding to the Al_2O_3/Na_2O ratio of 8, both α and γ-aluminas were obtained. When the ratio was 7, γ-alumina was obtained exclusively. An intergrowth of β with β''-aluminas was observed when the ratio was 5, as discussed above (Fig. 3). At higher concentrations of sodium isopropoxide, along with β-aluminas, sodium aluminate was also obtained.

Based on the above observations, a reaction sequence leading to the formation of β-aluminas is presented inScheme 1.

```
5 Al(i-opr)₃      H₂O,AcOH      Modified alumina gel with
      +          ------------>   incorporation  of  sodium
 Na(i-opr)          300 K        ions

                          |  Desorption  of  organics
                          |  & moisture from surface
                          ↓        360 - 593 K

                          Intermediate A

                          |  Burning of  isopropoxy
                          |  groups
                          ↓        595 - 773 K

                          Intermediate B

                          ↓ 973 K

                          Modified γ-alumina
                          stuffed with sodium ions

                          ↓ 1273 K

                          Appearance of β/β"-phase

                          ↓ 1473 K

                          Inter grown β/β"-phase
```

Scheme 1.

4. Conclusions

The various steps in the alkoxide based sol–gel route for the preparation of β and β-alumina have been identified and the processes taking place at various steps have been studied using different techniques. Hydrolysis mixture with excess of water facilitates the formation of crystalline intermediates at 378 K. These intermediates lead to the formation of a modified cubic-close-packed γ-alumina structure with stuffed sodium ions at 973 K. This proposed γ-alumina intermediate leads to crystallisation of intergrown β- and β''-alumina around 1473 K.

Acknowledgements

References

[1] J.L. Sudworth and A.R. Tilley, The sodium–sulphur battery (Chapman and Hall, New York, 1985).

[2] J.T. Kummer, Progr. Solid State Chem. 7 (1972) 141.

[3] V. Chandry and R.M. Cannon, Mater. Sci. Res. 11 (1978) 443.

[4] S. Yamaguchi, K. Terabe and Y. Iguchi, Solid State Ionics 25 (1987) 171.

[5] D.J. Green and S. Hutchison, Mater. Sci. Monog. 6 (1980) 964.

[6] A. Pekarsky and P.S. Nicholson, Mater. Sci. Res. 15 (1980) 1517.

[7] A.I. Vogel, A text book of practical organic chemistry, 3rd Ed., ELBS (1971).

[8] A. Van Zyl, M.M. Thackery, G.K. Duncan and A.I. Kingon, Mater. Res. Bull. 28 (1993) 145.

[9] D.W. Johnson Jr., S.M. Granstraff Jr. and W.W. Rhodes, Ceramic Bull. 58 (1979) 849.

[10] M.K. Dongare and A.P.B. Sinha, Bull. Mater. Sci. 11 (1988) 281.