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A new chemical route for the synthesis of nano-crystalline α-Al_2O_3 powder

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Abstract

Nano crystalline α-Al_2O_3 powders have been prepared by pyrolysis of a complex compound of aluminium with triethanolamine (TEA) and sucrose. The soluble metal ion-TEA complex with sucrose forms the precursor material on complete dehydration. The single-phase α-Al_2O_3 powder has resulted after heat treatment at 1150°C. The precursors and the heat treated final powders have been characterized by X-ray diffractometry (XRD), differential thermal and thermogravimetric analysis TG/DTA, Infrared spectroscopy (IR) and transmission electron microscopy (TEM). The average particle sizes as measured from X-ray line broadening and transmission electron microscopy studies are around ~20 nm. The powder which has crystallite sizes of the same order with the particle size indicates the low agglomeration of crystallites. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Calcination; Powders-chemical preparation

1. Introduction

In recent years there has been an increasing interest in the synthesis of nano crystalline metal oxides.[1–5] Such nano crystals are important for a variety of applications including fabrication of metal ceramic laminate composites and as a reinforcement phase in polymer and brittle matrix composites. Corundum (α-Al_2O_3) is one of the most important ceramic materials. Nano crystalline α-alumina powder has considerable potential for a wide range of applications including high strength materials, electronic ceramics and catalysts.[6,7] In particular, high quality nanocrystals of corundum are used as electronic substrates, bearing in watches, and other fine precision equipment. Conventional methods for synthesizing α-Al_2O_3 powder involve solid state thermally driven transformations from the hydrates of aluminium oxide.[8] The extent of conversion to the corundum structure depends on the temperature and the time of thermal treatment. Total conversion occurs on heating above 1230°C.

Ramanathan et al.[9] has prepared α-Al_2O_3 powder at 1400°C using urea and $AlCl_3$ as the precursors. Borsella et al.[10] synthesized α-Al_2O_3 fine powder from gas phase precursors at 1200–1400°C. Ding et al.[11] have synthesized α-Al_2O_3 at 1250°C via the reaction $2AlCl_3 + 3CaO \rightarrow Al_2O_3 + 3CaCl_2$. Hong et al.[12] have prepared ultrafine α-Al_2O_3 by the sol-gel process at 1100°C. Zhongqing et al.[13] synthesized ultrafine α-Al_2O_3 powder at 1200°C. Hayashi et al.[14] have prepared α-Al_2O_3 fine powder using ammonium aluminium carbonate hydroxide (AACH) as starting material at 1050°C. Fanelli and Burlew[15] have reported synthesis of a fine particle transition alumina (χ-Al_2O_3) by the treatment of aluminium sec-butoxide in sec-butanol.

However, due to high temperatures and pressures being the prerequisites of the reaction process the direct formation of α-Al_2O_3 via hydrothermal process has not been commercially exploited.

In the present paper, we report a novel chemical route for the preparation of nano crystalline (average particle size around ~20 nm), single phase α-Al_2O_3 powder. In the route, TEA is used for the formation of a metal–TEA complex and sucrose is used as a fuel and to keep the metal–TEA complex in a polymeric network. The route involves the dehydration of the solution of a metal ion–TEA complex, followed by pyrolysis of the sucrose imbedded metal ion–TEA complex. To ensure this, the amount of sucrose in the starting solution has been optimized. Complete dehydration of the resulting solution to dryness produces a voluminous, organic based,

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black, fluffy mass. The dried carbonaceous mass is ground to a fine powder to produce the precursor material. Heat treatment of the precursor material results in the nanosized α-Al_2O_3 powder. α-Al_2O_3 powder also has been formed using only TEA (in the absence of sucrose), but the agglomerations are very frequent in the process. To avoid this situation sucrose is used in this process. Another important point to note that a mesoporous structure of carbonaceous material has been formed easily in the presence of sucrose, which controls agglomeration and particle size.

2. Experimental procedure

The chemicals required are $Al(NO_3)_3.9H_2O$ (E. Merck India Limited, 98%), Triethanolamine (Qualigen Fine Chemicals, India), sucrose (E. Merck India Limited) and HNO_3 (S.D. Fine Chemicals, India). A requisite amount of $Al(NO_3)_3.9H_2O$ has been mixed with an equal amount of deionised water (i.e. 1 g of aluminium nitrate is mixed with 1 g of deionized water) to prepare a pasty like mass. This material is then added to triethanolamine (TEA) to make a viscous solution. At the beginning TEA forms a precipitation (due to the formation of Al^{3+}-hydroxide.) with metal ions. This precipitation dissolves and a clear solution is obtained by heating at about 150°C. After dissolving the precipitation, a sucrose solution is added to this resulting solution at a metal to sucrose ratio 1:4. Then a few drops of HNO_3 have been added to maintain the pH at 3–4. The clear solutions of TEA complexed metal nitrates with sucrose are evaporated on a hot plate at 180°C. The continuous heating of these solutions causes foaming and puffing. During evaporation the nitrate ions provide an in situ oxidizing environment for TEA which partially converts the hydroxyl groups of TEA and sucrose to carboxylic acids. When complete dehydration occurs, the nitrates themselves are decomposed with the evolution of brown fumes of nitrogen dioxide leaving behind voluminous, organic based, black, fluffy powders i.e. precursor powders. The precursor powders, after grinding, have been calcined at various temperatures to get a series of Al_2O_3 powders. The heat treatments of the precursor materials (in air, 1 h) have been facilitated at 800, 900, 1000 and 1100 and 1150°C at a heating rate of 8–10°C/min. These powders are characterized by X-ray diffraction, infrared spectroscopy, transmission electron microscopy and various thermal analyses.

3. Results and discussion

Thermogravimetric and differential thermal analysis (TG–DTA) (Model DT-40, Shimadzu Co., Kyoto, Japan) have been performed in air at a heating rate of 5°C/min. The DTA curve (Fig. 1) indicates that the α-Al_2O_3 precursor decomposes exothermally, with sharp peaks at 534 and 362°C. These exotherms can be assigned to the major decomposition of the metal (TEA) complexes and metal sucrose polymeric network respectively. From the graph it is also observed that the metal–TEA precursor powder exhibited weight loss up to 600°C, and above 600°C the weight becomes almost constant. Below 600°C, the metal complex, along with unreacted amine, decomposes. The whole thermal process is associated with the evolution of a large amount of gasses (such as CO, CO_2, NH_3, NO_2, and water vapor) that is reflected in the TGA curve.

The X-ray diffraction (Model PW 1710 and PW 1810, Philips Research Laboratories) studies of the precursor and calcined powders after subsequent heat treatment have revealed (Fig. 2) that precursor powders are

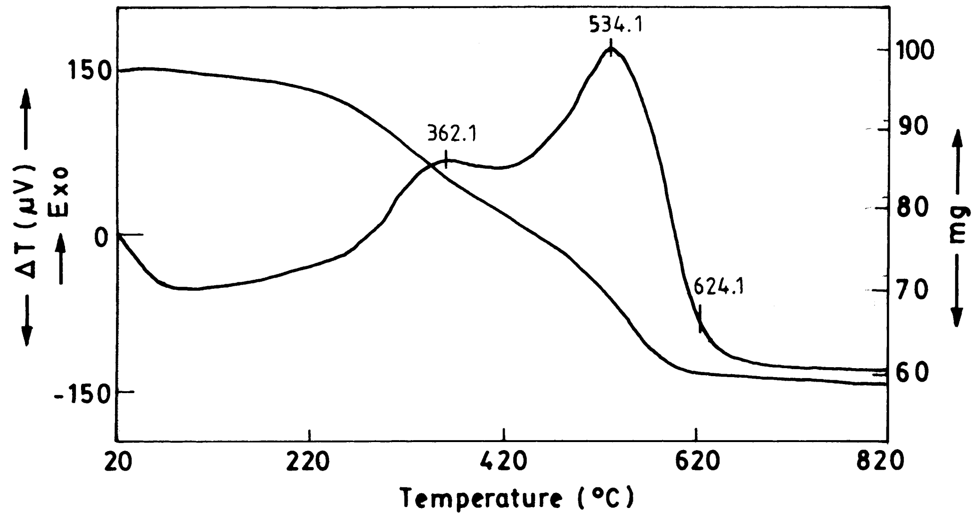

Fig. 1. Simultaneous TG-DTA curves of the α-Al_2O_3 precursor powder (TS_4).

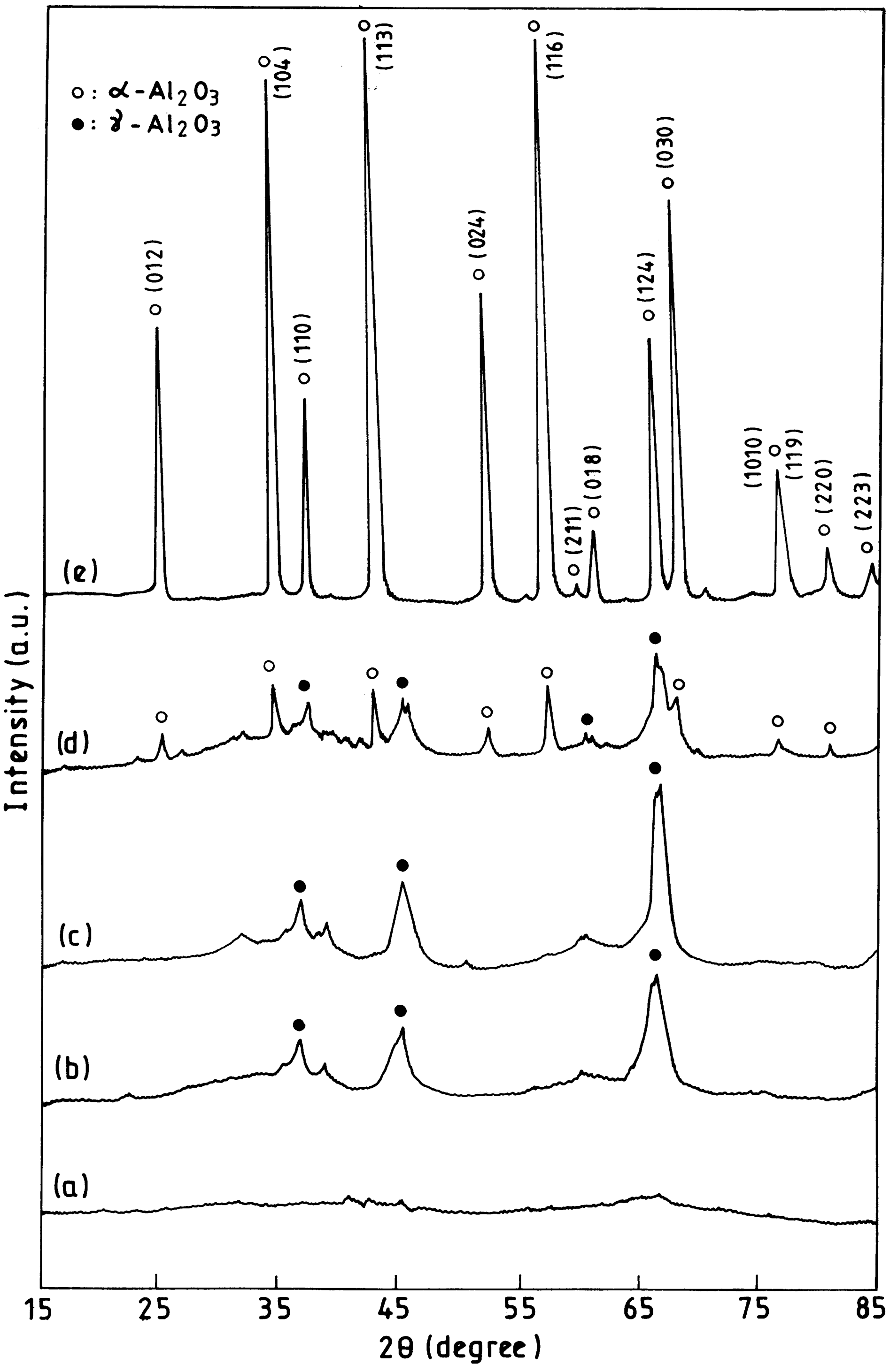

Fig. 2. Room temperature X-ray diffractograms (using CuK_α radiation, $\lambda = 0.15418$ nm) of the calcined powders heat-treated at (a) 800°C, (b) 900°C, (c) 1000°C, (d) 1100°C and (e) 1150°C.

always amorphous. Diffraction peaks corresponding to γ-Al_2O_3 have been found for the samples calcined at 800°C. No significant change in the structure has been found after heat-treatment temperature up to 1000°C. A small amount of α-Al_2O_3 has been detected after calcining at <1050°C, coexisting with the major phase γ and δ phase. The phase transformation of γ-Al_2O_3 to δ-Al_2O_3 and θ-Al_2O_3 at 800–1000°C could not be confirmed because of the similar XRD patterns exhibited by these phases. At last single-phase α-Al_2O_3 has been observed in the sample calcined at 1150°C (2 h). The crystallite size of heat treated powder has been obtained from X-ray line broadening studies using Scherrers' equation.[16] It is the average value calculated from d_{104}, d_{113}, and $d_{030,}$ and their values are close.

The IR spectra (Perkin-Elmer 883 infrared spectrophotometer) of the precursor powder are shown in Fig. 3. The IR spectrum of the precursor powder shows the strong absorption bands at around 1600 cm^{-1}, which can be attributed to the various, vibrational modes of the carboxylate ions,[17] formed due to the reaction of decomposed TEA with metal ions. The bands appearing at 1005 and 800 cm^{-1} could be attributed to the presence of some undecomposed nitrate ions in the precursor material. Apart from these bands two or three-weak bands appeared in the region 700–400 cm^{-1}, which could be the results of some trace amounts of metal oxides forming during the evaporation process.

The finer details of the particles and their morphology were investigated by using transmission electron microscopy (TEM) (Model Philips TM-300 Philips Research Laboratories). The bright field (BF) electron micrograph of the α-Al_2O_3 powders produced at 1150°C (for 1 h) (Fig. 4a) has reflected the basic powder morphology, where the smallest visible particle could be identified with the crystallite and/or their aggregates. The micrograph exhibited a sharp distribution of the particles, with an average particle diameter of 20 nm and corresponding selected area electron diffraction (SAED) pattern (Fig. 4b) confirms the crystallinity of the sample. This value is consistent with the value of the crystallite size (20 nm) calculated from Scherrers' equation for the same powder heat treated under similar conditions.

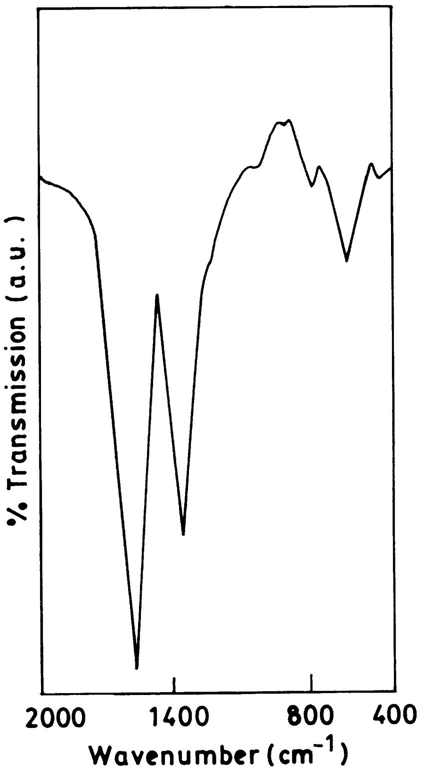

Fig. 3. IR spectra of the precursor powder (TS_4).

The chemical process starts from homogeneous distribution of metal ions in solution. The solution after complete evaporation decomposes into a fluffy black mass, which is effectively a mesoporous carbonaceous material, supported by TEM micrograph (Fig. 5) and the surface area measurement by N_2 gas absorption whose value is 180–200 m^2/g. It is interesting to note that without metal complexes, the sucrose or polyhydroxy

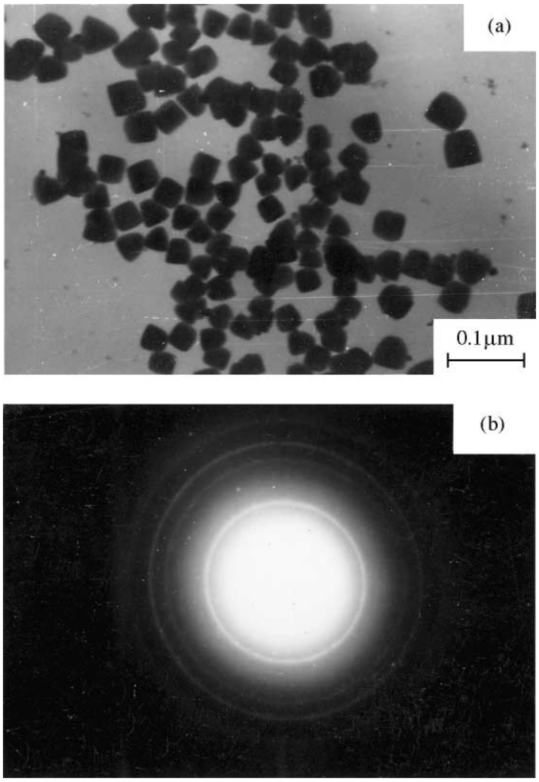

Fig. 4. (a) Bright field TEM micrograph and (b) SAED pattern of α-Al_2O_3 powder heat-treated at 1150°C.

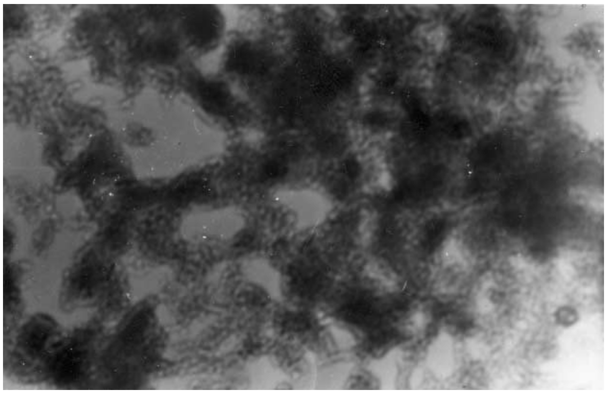

Fig. 5. TEM micrograph of the carbonaceous material before heat-treatment.

Table 1
Variation of average crystallite, particle size and external formation temperature with sucrose

Preparative route[a]	$Al(NO_3)_3.9H_2O$ taken (mol)	TEA taken (mol)	Sucrose taken (mol)	Formation temperature (°C)	Average crystallite size (nm)	Average particle size (nm)
TS_2	0.02	0.02	0.04	1150	28	45
TS_4	0.02	0.02	0.08	1150	20	21
6-TS_6	0.02	0.02	0.12	1150	20	20

[a] 'T' represents TEA and 'S' represents sucrose.

organic compounds, such as sorbitol, mannitol, etc. with PVA gives similar mesoporous structure. It may be presumed that during decomposition of the metal ion complex in air it produces nescent metal oxides, which is basically a small atomic cluster imbedded in carbonaceous material. The nescent metal oxides on rearrangement produce desired single-phase α-Al_2O_3 at final stage of calcination. The exothermic decomposition of carbonaceous material produced gasses (such as CO, CO_2, NO, NO_2, NH_3, water vapor) that not only helps to disintegrate the agglomerated particle[1] with each other but also helps to dissipate the heat of combustion, thus inhibiting the sintering of nano crystalline powders. Table 1 shows that the variation of particle size and crystallite sizes with respect to variation of sucrose at constant TEA concentration. The table shows that the optimum concentration of sucrose is helpful to produce minimum particle size and crystallite size.

4. Conclusion

The chemical synthesis through aluminium-TEA complex with sucrose is a moderate route for the preparation of nano crystalline α-Al_2O_3 powder having a particle diameter in the range of $\sim$20 nm. The formation of α-Al_2O_3 through the chemical route can be attributed to the homogeneous distribution of cations throughout the liquid phase and afterward formation of metal oxide clusters imbedded in organic mesoporous carbonaceous material, which after calcination gives nanosized α-Al_2O_3 particles. This process for the preparation of nano crystalline α-Al_2O_3 powder offers a cost effective and simpler alternative to the other reported expensive routes.

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