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Preparation of high pure α-Al_2O_3 nanoparticles at low temperatures using Pechini method

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Abstract

A Pechini process was successfully used to synthesize alpha-alumina (98.95% mass fraction) at relatively low calcination temperature (925 °C). The synthesis of these nanoparticles was carried out using a polymer prepared from citric acid and ethylene glycol by the melt blending method. This polymer worked as a chelating agent for aluminum cations. The final products were produced after a dual-stages thermal treatment. The resulting α-alumina consisted of nanoparticles of 8–16 nm in diameters with a surface area (~8 $m^2 g^{-1}$). The mass fraction of α-alumina was dependent on the concentration of aluminum salt and polymer precursor's solutions, while the surface area of the final product was dependent on the mass fraction of θ-alumina.

Keywords: α-Alumina; Pechini method; Citric acid; Ethylene glycol; Nanoparticles

1. Introduction

Alumina is an advanced ceramic that has a wide range of applications in various industrial areas. α-Alumina (corundum) is a thermodynamically stable polymorph of Al_2O_3 [1,2]. Synthesis of ceramic powders on the nanometer scale has a significant importance from the advanced ceramic technological point of view.

Several methods have been adopted for the synthesis of nanosized alumina materials, which includes mechanical milling, sol–el method, hydrolysis and precipitation, hydrothermal method, combustion synthesis, and electrospinning method [3]. Such conventional methods result nanosized particles that may be accompanied with different disadvantages such as uncontrolled crystalline growth, composition inhomogeneities, nonuniformity of grain size and high operating costs. The utilization of sol–gel technique gave rise to the production of ultra fine powders, highly homogeneous, with controlled chemical purity and crystallinity [4]. Modified sol–gel method (Pechini) is more commonly used to avoid the disadvantages of the conventional method and to achieve better control of nanoparticle properties [5].

Pechini method is based on a chelation process between metal cations in the form of chlorides, nitrates, carbonates, or hydroxides with a hydroxyl carboxylic acid e.g. citric acid. It is believed that the crosslinked resin may provide more homogeneous mixing of the cations and less tendency for segregation during charring and calcination [6].

Previously, Shiau and Fang [7] prepared α-alumina using citrate process with α-alumina seeding. Later, Hernández and González [8] studied the effect of the heating source on the features of α-alumina prepared using Pechini method.

The aim of the present work was to clarify the effects of synthesis conditions on the formation temperature of α-alumina nanoparticles using Pechini method. The effects of citric acid-to-salt ratio and solution concentration on the properties of the final products were tested. In order to achieve this aim, thermal analysis (TG-DTA), X-ray diffraction (XRD), nitrogen gas adsorption at the liquid nitrogen temperature, Fourier transform infra-red (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques were employed.

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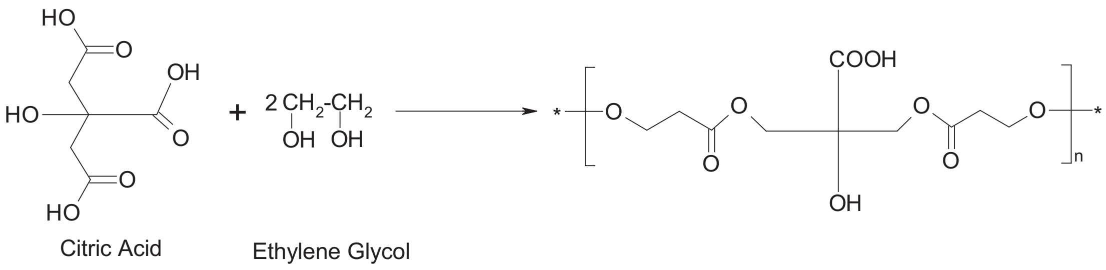
2. Experimental

2.1. Polymer preparation

In a three-neck round-bottom flask fitted with a thermometer and condenser, 100 mL (0.1 M) solution of anhydrous citric acid (CA, Sigma–Aldrich, assay ≥99.5%) was mixed with equivalent volume (0.2 M) solution of ethylene glycol (EG, Sigma–Aldrich, assay ≥99.0%). The reaction was maintained at moderate temperature 100–150 °C to obtain a clear transparent color of viscous polymer. The synthesis of the polymer was carried out according to the following equation:



The acidity of the prepared viscous polymer was measured via titration against solution of 0.05 N NaOH. One gram of the prepared viscous polymer was equivalent to 11.69 μmol NaOH. The FT-IR spectrum of the prepared viscous polymer (Fig. 1) shows OH broad band at 3200–3600 cm^{-1}. Also, the spectrum indicates the presence of a C═O ester group at 1730 cm^{-1} and ethereal band of ethylene oxide at 1000–1200 cm^{-1}.

The average molecular weight of the prepared polymer was measured by gel permeation chromatography (GPC) using a Waters 600E system controller (Millipore Waters Chromatography, Milford, MA) equipped with the Shodex KB800 series of columns (two of KB80M and one of KB802.5), a refractive index detector (Waters, Model 410), and a Waters Model 730 data module. The chromatographically determined average molecular weight of the polymer (892 g/mol) was higher than the theoretically calculated weight (272.2 g/mol). The polydispersity index was equal to 1.1.

2.2. Alumina preparation

Five different alumina powders were prepared using the polymerizing-chelating synthesis process. For all of the prepared samples, 20 g of the previously made viscous polymer was heated to 80 °C with stirring. The required volume of an aluminum nitrate nonahydrate (Sigma–Aldrich, assay ≥98.0%) solution with desired concentration was added to the polyester. Stirring was continued for another hour, during which time the metal salt reacted with free carboxylic groups, and consequently the pH of the medium decreased. The solutions were then slowly heated to 140 °C and maintained at this temperature until removal of water was almost complete (2.5 h). The clear gels obtained from this process were transferred to an electrical furnace and dried at 150 °C overnight, yielding solid resins of high porosity. The resulting resins were ground in an agate mortar and subjected to a pyrolysis process at 450 °C (heating rate 5 °C/min) for 4 h in glazed alumina crucibles. Finally, the pyrolysis product was subjected to a calcination process at 925 °C (heating rate 5 °C/min) for 4 h in the presence of purified air.

The prepared materials are listed in Table 1 and named according to their synthesis differences. Alumina samples were prepared using a variety of CA-to-Al^{3+} molar ratios, as well as different concentrations of the aluminum nitrate solution at a constant CA-to-EG molar ratio. The samples were named AlR_C-R_A, where R_C is the CA:Al^{3+} ratio and R_A is the $Al(NO_3)_3 \cdot 9H_2O$ concentration.

2.3. Analytical methods

Differential thermal analyses coupled with thermogravimetric analysis (TGA) of the solid resins were recorded on SDT Q600 Simultaneous DSC/TGA Analyzer manufactured by TA Instruments, Inc. (USA). The run was carried out in air at a heating rate of 10 °C/min. The crystalline structure of the prepared powders was analyzed by X-ray diffractometry (X-Pert PRO, PAN analytical, Netherlands) using Cu Kα radiation in the angular region of $2\theta = 4–70°$. For phase identification purposes, automatic JCPDS library search and match were used. The mass fraction of α-alumina in the calcined products was estimated with respect to the relative intensity of the (1 0 4) reflection [2]. The surface area of different samples of the prepared α-alumina was determined from the adsorption of nitrogen gas at liquid nitrogen temperature (−195.8 °C) using NONA3200e (Quantachrome, USA). Prior to such measurements, all samples were perfectly degassed at 150 °C and 10^{-4} Torr overnight. FT-IR spectra (KBr disc method) were recorded on an ATI/Unicam Infinity 961M instrument. The alumina texture was examined using a scanning electron microscope (SEM)-JEOL JSM-5300 (30 keV). High resolution transmission electron microscopy images (HRTEM) were recorded on a JEOL JEM-2100 electron microscope at 200 kV. The alumina sample was dispersed in absolute ethyl alcohol via sonication for 10 min. A drop of the dispersion medium was spread and dried on copper-carbon coated grid.

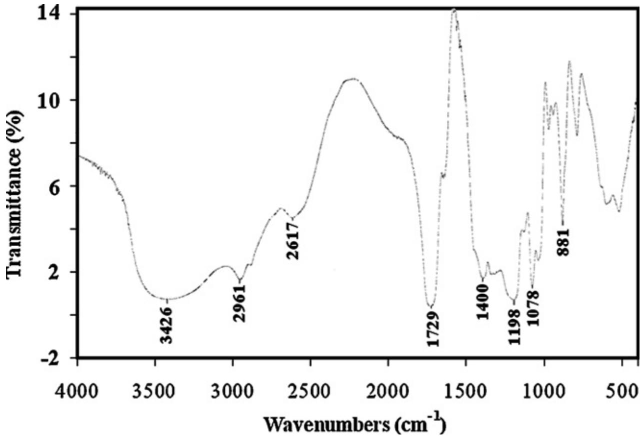


Fig. 1. FT-IR spectrum of the as-prepared polymer.

3. Results and discussion

3.1. Thermal analysis (DSC-TGA)

All of samples showed the thermal behavior that usually found in polymerized complex resins.

According to the data listed in Table 1 the weight loss increased as the CA/Al^{3+} molar ratio increased.

Numerous research efforts had been carried out to prepare α-alumina at lower temperatures than 1200 °C. The aim of these researches was to decrease the grain growth of the α-alumina, which causes a regression in the sinterability and the mechanical features of the product [9].

According to Fig. 2, broad significant exothermic peaks of maxima around 560 °C can be observed. Such broad exothermic peak may be related to successive reactions including the elimination of many of the organic species involving the hydrocarbon, polymer charring, and the pyrolysis of the organics [8]. With respect with the TG curves (not shown here) no significant weight loss was observed for temperatures higher than 600 °C. Such observation indicated the complete combustion of the organic resin. No distinguish peak for the thermal elimination of ethylene glycol was observed in the DSC curves, which indicates the carrying out of full polymerization reaction [8].

Distinguished exothermic peaks due to the transformation of alumina phases into alpha phase were appeared in a narrow range of temperatures 908–920 °C (Fig. 2). The DSC curves clarified that the dilution of the solution of aluminum salt retards the formation of α-alumina to 910 °C (0.16 mol/L, Fig. 2a) to 920 °C (0.05 mol/L, Fig. 2e).

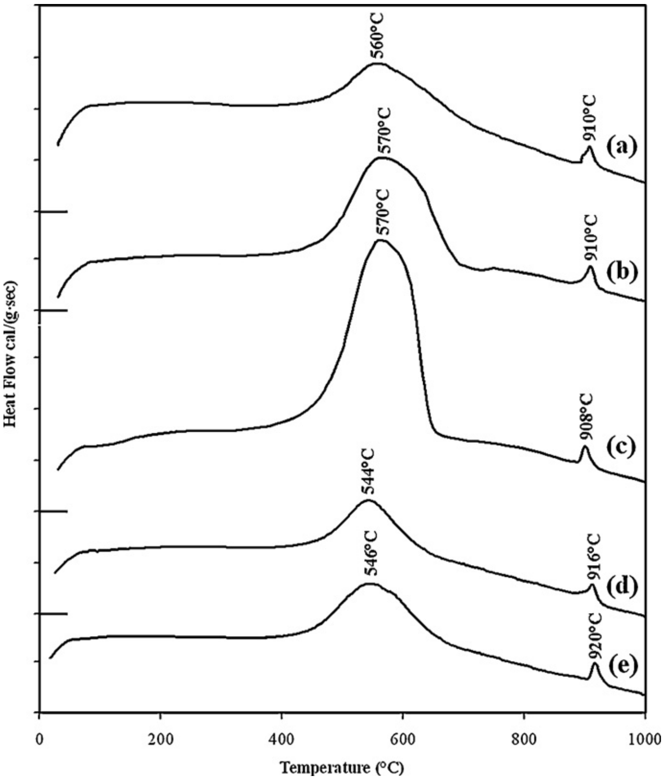


Fig. 2. DSC curves for resins of (a) Al1-16, (b) Al2-12, (c) Al3-8, (d) Al1-8, and (e) Al1-5 samples.

3.2. X-ray diffraction analysis (XRD)

The XRD patterns of most of the calcined samples at 925 °C (Fig. 3) show highly crystalline and good agreement with the reference XRD pattern of α-Al_2O_3 powder (JCPDS file 42-1468, Fig. 3f). XRD patterns of the samples clarified the presence of monoclinic θ-alumina as a minor phase (JCPDS file 35-0121, Fig. 3c–e) as indicated from the small reflections at *d*-spaces 2.73 and 2.31 Å.

Table 1
Amounts, concentrations and ratios of reactants, % weight loss of dried resins according to TGA, mass fraction of α-alumina and the BET surface area (S_{BET}) of prepared α-alumina samples.

Material	CA	EG	Al salt solution		CA/Al^{3+}	Wt loss	α-Al_2O_3	S_{BET}
	(g)	(mL)	(mol/L)	(mL)	(molar ratio)	(%)	(%)	($m^2\ g^{-1}$)
Al1-16	0.19	0.11	0.16	500	0.01	26.21	98.95	7.91
Al2-12	0.19	0.11	0.12	500	0.02	32.25	95.91	8.76
Al3-8	0.19	0.11	0.08	500	0.03	53.14	83.39	10.1
Al1-8	0.19	0.11	0.08	1000	0.01	27.59	81.02	12.12
Al1-5	0.19	0.11	0.05	1500	0.01	28.18	75.96	13.71

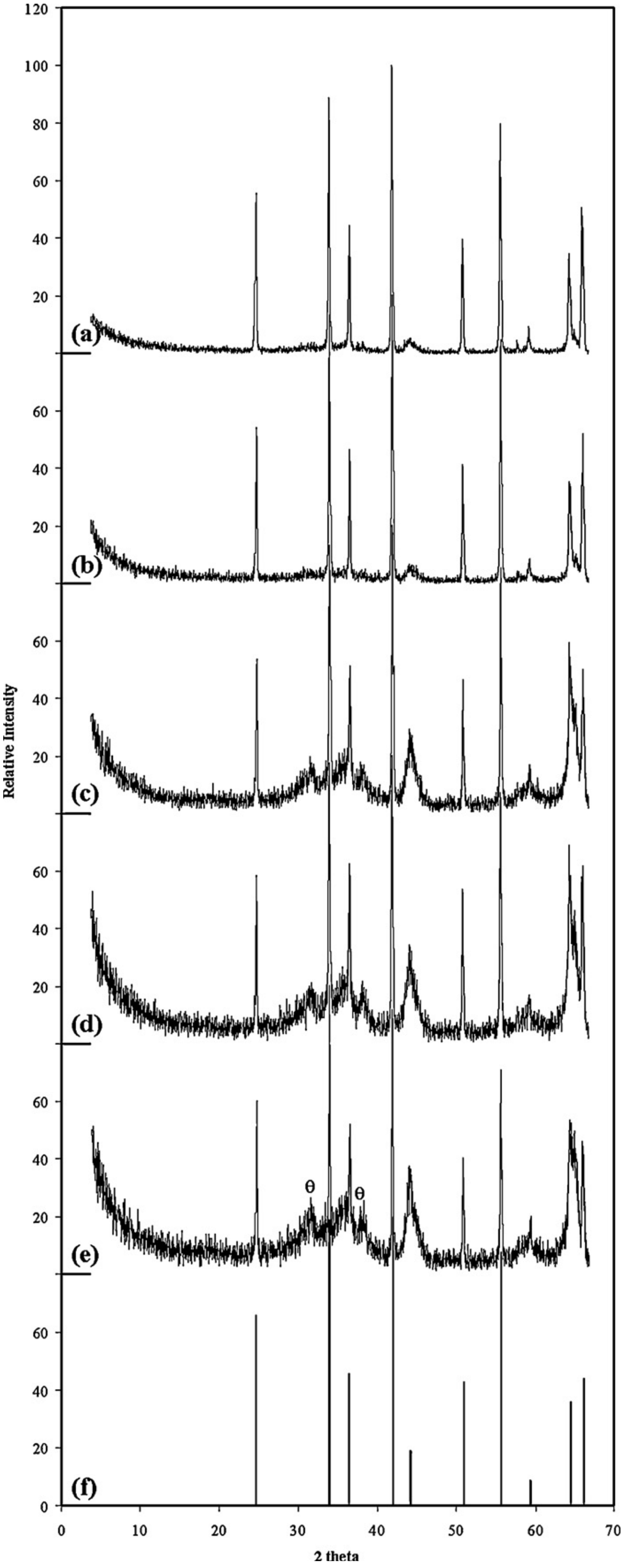


Fig. 3. X-ray diffraction patterns of (a) Al1-16, (b) Al2-12, (c) Al3-8, (d) Al1-8, and (e) Al1-5 samples compared with (f) α-alumina (JCPDS files no. 42-1468).

Table 1 shows that the mass fraction of α-alumina decreased slightly from 98.95% to 95.91% as the CA/Al^{3+} molar ratio increased from 0.01 to 0.02; respectively. For another increase in the CA/Al^{3+} molar ratio to 0.03, the mass fraction of α-alumina decreased strongly to 83.39%. In spite of the relatively high synthesis temperature with respect to the previously published data 800 °C [2] but the recently prepared powders showed distinct high mass fraction of α-alumina 98.95% in comparison with the low synthesized samples, 58% [2].

The concentration of the solution of the start aluminum precursor showed strong influence on the mass fraction of α-alumina. Whereas, the fraction of α-alumina decreased from 98.95% to 81.02% as the concentration of aluminum precursor decreased from 0.16 to 0.08 mol/L; respectively.

All of the prepared samples showed high crystallinity with respect with the previously prepared α-alumina using Pechini method without seeding at the same preparation temperatures, i.e. 900–950 °C [7,8].

The high mass fraction of α-alumina in Al1-16 and Al2-12 samples (98.95 and 95.91% respectively) may be attributed to the low temperature at which the phase of α-alumina formed (910 °C, Fig. 2).

3.3. Nitrogen adsorption–desorption technique

The results of surface area obtained from nitrogen adsorption–desorption at −195.8 °C are listed in Table 1. Results showed that the mass fraction of θ-alumina caused an increase in the surface area of the materials, whereas Al1-5 sample that has mass fraction of α-alumina of 75.96%, showed the highest value for the surface area, i.e. ~14 $m^2\ g^{-1}$.

3.4. Fourier transform infrared spectroscopy (FT-IR)

IR spectrum of Al1-16 presents strong and well defined bands corresponded to Al–O bonds. Whereas, Fig. 4 clarified two strong bands at 609 and 651 cm^{-1} which are characteristics for octahedral AlO_6 stretching modes. While, the lowest energy band (around 460 cm^{-1}) could be assigned to AlO_6 bending modes [10]. The maxima that are observed at 1611 and

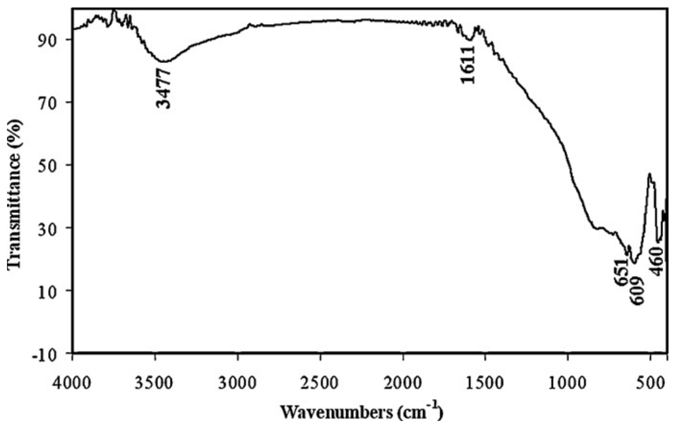


Fig. 4. FT-IR spectrum of the Al1-16 sample.

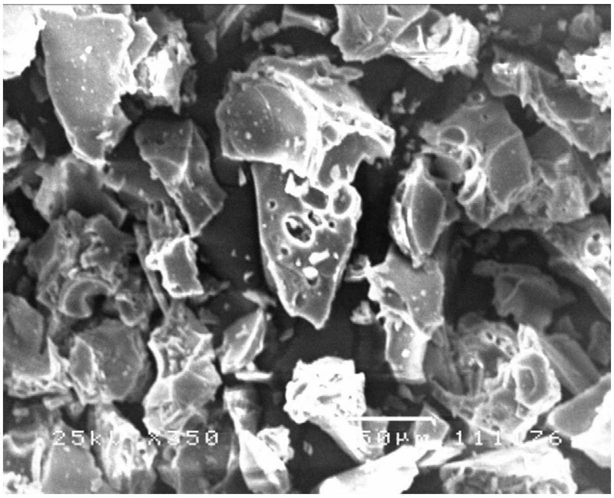


Fig. 5. SEM photograph of the Al1-16 sample.

$3477\ cm^{-1}$ may be resulted from the water deformation vibrations and OH stretching mode successively.

The IR spectrum of Al1-16 confirmed the interpretation of related XRD pattern (Fig. 3a), whereas it indicated the presence of α-Al_2O_3 (octahedron AlO_6 only) as the major phase (∼99%).

3.5. Electron microscopy

The SEM micrograph of Al1-16 (Fig. 5) showed sharp and irregular-shaped particles. These high density agglomerates showed porous morphology. The HRTEM micrograph of Al1-16 (Fig. 6) showed that the material is constituted by irregular-shaped particles of 8–16 nm diameters. The present preparation method resulted nanoparticles of obvious small dimensions regarded the previous published particle size for α-alumina crystals prepared using lineal polymer (95 nm) [1] or using seeding of alumina nanoparticles 50–60 nm [11].

3.6. Effect of synthesis method on final product

The molecular structure of the citric acid presents three carboxylic groups and one hydroxyl group; while the smaller molecule of ethylene glycol displays only two hydroxyl groups. The subsequent esterification and polymerization reactions will only be possible between the carboxylic group of citric acid and hydroxyl group of ethylene glycol giving rise to polymer of long chain structures [8].

As it well known, in the chelation reaction, it is important to consider the number of reactive sites in the polymer that have able to bond with the metal cations. In the synthesized polymer the free carboxylic groups of citric acid will be the only reactive sites and will be directed in different directions around long hydrocarbon chain to avoid the strain effect.

In case of low CA/Al^{3+} molar ratio and high concentrated aluminum precursor solution, such as Al1-16 sample, the bonding of metal ion to insufficient and strained free carboxylic groups is therefore considered softer because of the inability to form stable chelated complexes. This structure corresponds to the creation of small agglomerates during the thermal treatment, and decrease the temperature required for the transformation of other phases of alumina into α-alumina.

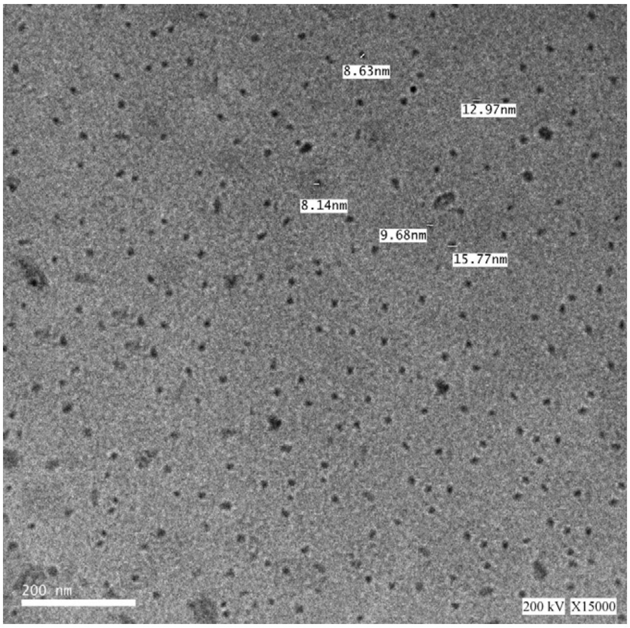


Fig. 6. HRTEM micrograph of the Al1-16 sample.

4. Conclusion

α-Al_2O_3 were successfully prepared by Pechini process. The diameters of the particles are found to be in the range of 8–16 nm by TEM study. XRD analysis of the calcined Al1-16 sample at 925 °C confirms the formation of pure α-alumina phase. This sample was prepared using lowest value of citric acid to aluminum salt molar ratio (0.01) and highest concentration of aluminum precursor solution (0.16 mol/L). This very dilute reactant solution may be considered as principal reason for the crystals nano-size and the low transformation temperature with respect to the previous published tries using Pechini method [8]. SEM image shows that the α-alumina has high density and irregular morphology.

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