

Synthesis of γ -Al₂O₃ nano particles by different combustion modes using ammonium carbonate

F Bustan Afruz & M J Tafreshi*

Faculty of Physics, Semnan University, Semnan, Iran

*E-mail: mj.tafreshi@gmail.com

Received 26 February 2013; revised 10 December 2013; accepted 10 March 2014

Gamma-alumina nanoparticles have been successfully synthesized by different modes of combustion using ammonium carbonate as well as effective material. Thermodynamic calculations predicted the capability of ammonium carbonate as compared with some other fuels in production of nanoparticles with improved properties by combustion process. The proposed reactions involved in synthesizing process were verified by TG analysis. The synthesized samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), N₂ adsorption (BET), Transmission electron microscopy (TEM) and Dynamic light scattering (DLS). For all modes of combustion, γ -alumina nanoparticles were obtained with crystallite size in the range 2.0-2.5 nm. But DLS and BET analyses showed that conventional volume combustion synthesis mode is advantageous over other modes, with respect to the higher specific surface area and narrower agglomerate size distribution of the products. Specific surface area for synthesized samples was found to be in the range 328.0-392.8 m².g⁻¹. Ammonium carbonate was found to be a suitable material for the production of alumina fine particles with high specific surface area.

Keywords: γ -Al₂O₃, Nanoparticles, Ammonium carbonate, Different modes of combustion

1 Introduction

Alumina is widely used in industry in refractories, mechanical parts, abrasives and insulators. Especially, because of its large surface area, low cost, thermal stability, good mechanical strength and volatile acidity and in its γ -phase it has been utilized as a carrier for catalyst in petroleum and refining petrochemical industries¹. Gamma alumina nano particles have been synthesized by various techniques such as: sol gel^{2,3}, flame spray pyrolysis⁴, control precipitation⁵, hydrothermal¹ and combustion synthesis⁶⁻⁹. Among these techniques, combustion synthesis is particularly an easy, safe and rapid production process and the main advantages are energy and time savings^{10,11}.

Three different modes (solid, liquid or gas) of reactants have been used for combustion synthesis¹²⁻¹⁴. The list of materials produced by gas-phase combustion is relatively short and low effectiveness of this technology currently dictates high cost of the final products¹³. Solid state combustion (SSC) can occur in two modes: linear or self-propagating high temperature synthesis (SHS) and bulk or volume combustion synthesis (VCS). In both of the cases, the reactants are pressed into a pellet, typically cylindrical in shape, the pellet is then ignited by an external

source locally (SHS) or uniformly¹² (VCS). It is not an easy task to produce nanomaterials by conventional SHS, where the typical scale of heterogeneity for the initial solid reactants is at the order of 10-100 μ m. This feature, coupled with high reaction temperatures (>2000 K), makes it difficult to synthesize nano size structures with high surface area. Therefore, only the VCS mode of synthesis is suitable for weakly exothermic reactions that require activation by preheating or electric field¹².

The combination of combustion and solution approaches leads to the so-called solution combustion synthesis (SCS) method. The SCS method of preparing oxide materials is a fairly recent development as compared to SSC and SHS techniques¹⁴. This technique involves the exothermic chemical reaction between salts of desired metals (usually nitrates) and some organic fuels^{15,16}.

The production of alumina nano structures has been reported by solution combustion synthesis, using different organic fuels^{6-10,16-18}. Among these fuels, urea seems to be the most convenient one to be employed in this route to produce alumina nano structures, but using urea as fuel directly yields α -alumina powders with high crystallite size, low specific surface area and hard agglomerates, because

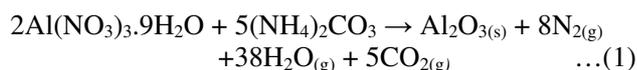
of the formation of stable polymeric intermediates that prevent the dissipation of heat and thereby sintering during combustion¹⁶.

So, other fuels such as, ODH (oxalyldihydrazide⁶), sucrose⁷, serine, asparagine⁸ and glycine¹⁵ with low exothermicity have also been examined by different researchers to produce smaller alumina nano structures with higher surface area and finer agglomerates. They could produce γ -alumina with crystallite size in the range 4-19.8nm and specific surface area in the range 4.3-96 m².g⁻¹. Recently, Norouzbeigi and Edrissi⁹ have used four amino acids (glutamine, histidine, lysine and arginine) as main fuels to improve the specific surface area of prepared alumina nanoparticles by solution combustion synthesis. They could prepare γ -alumina with crystallite size between 7.2 and 13 nm and specific surface area between 21 and 70m².g⁻¹. Our theoretical prediction shows that it is possible to improve more the properties of γ -alumina nano structures by exploring new materials which can contribute in combustion reactions via different modes. Comparing the properties of the alumina nano particles prepared via different modes of combustion has rarely been studied.

In the present work, ammonium carbonate [(NH₄)₂CO₃] has been used as a well effective mineral material in combustion synthesis to produce alumina nano structures. Ammonium carbonate is lower priced as compared to organic fuels and it can be used in variety modes of combustion synthesis to produce alumina nano structures with smaller crystallite size and higher surface area because it produces lower amount of energy and releases higher amount of gas.

2 Thermodynamic Calculations

Aluminium nitrate nonahydrate Al(NO₃)₃.9H₂O (Merck) and ammonium carbonate (NH₄)₂CO₃ (Merck) were used as starting materials. The theoretical stoichiometric overall reaction for the formation of Al₂O₃ can be presented as follows:



Using the thermodynamic data for the various reactants and products listed in Table 1, the enthalpy of combustion was approximately calculated by the following equation:

$$\Delta H_c = (\sum n\Delta H_p) - (\sum n\Delta H_r) \quad \dots(2)$$

Table 1 — Thermodynamic data of various reactants and products [16]

Compound	ΔH_f kcal/mol
Al(NO ₃) ₃ .9H ₂ O _(s)	-857.59
(NH ₄) ₂ CO ₃ _(s)	-942.2
N _{2(g)}	0
Al ₂ O _{3(s)}	-399.09
H ₂ O _(g)	-57.796
CO _{2(g)}	-94.051

where ΔH_c , ΔH_p and ΔH_r are the enthalpies of combustion, products and reactants, respectively. The calculated enthalpy of combustion for production of alumina by using stoichiometric ratio of ammonium carbonate is -227.5 kcal/mol. Its absolute value is less than those reported^{10,17} for ammonium acetate (-389 kcal/mol), glycine (-415 kcal/mol) and urea (-440 kcal/mol). Urea and glycine are two most popular and attractive fuels for producing highly uniform, complex oxide ceramic powders with precisely controlled stoichiometry¹³.

In addition, the moles of gaseous released by ammonium carbonate are 51 moles which are higher than the values reported^{10,17} for ammonium acetate (34 moles), glycine (19 moles) and urea (41 moles). Therefore, it is suggested that ammonium carbonate can reduce the enthalpy of combustion due to releasing of higher amount of gas and prevents sintering of particles and renders the soft and fluffy products with fine agglomerates and high surface area. It has been reported that characteristics such as particle size, surface area, extent and nature of agglomeration are primarily governed by enthalpy and the amount of gases that escape during combustion^{6,8,19}. Generally, a larger amount of gas phase products leads to a smaller size and higher surface area in synthesized solid particles¹⁵. The gas evolution also helps in limiting the inter particle contact and hence, resulting in more easily friable product with a very high surface area¹⁹.

3 Experimental Details

3.1 Solid state combustion

This experiment was carried out in VCS mode. For that, suitable amount of ammonium carbonate and aluminum nitrate with stoichiometric ratio were crumbled in mortar as a dry. Ammonium carbonate decomposed by water of companied aluminium nitrate and foamed, released CO₂ gas, the mixture reacted and then in short time it dried spontaneously.

This process helped us to produce a homogenous mixture (named a).

3.2 Solution combustion

It was observed that producing alumina with ammonium carbonate by conventional solution combustion synthesis modes is a little difficult because, precipitation was formed when ammonium carbonate solution was added in stoichiometry ratio to aluminium nitrate. Therefore, this process was performed in two modes: gel combustion synthesis and conventional VSC (volume solution combustion) synthesis and the precursors were prepared in different ways involving gel and solution to produce alumina nano structures. For gel combustion mode, suitable amount of stoichiometric starting materials dissolved in minimum amount of deionized water to prepare separate solutions with stoichiometric ratios. Ammonium carbonate solution was added drop-wise to the aluminium nitrate solution, under stirring. The formed colloidal precipitant dissolved by continuous stirring and the solution became clear. This dissolving continued until 85% of ammonium carbonate was consumed. Thereafter, by adding the remained 15% of ammonium carbonate the precipitation started and solution gradually changed to gel. Gel was stirred for 2 h and it was aged at room temperature for two days, then it dried at 35°C for several hours (named b). For VSC mode, 85% of ammonium carbonate solution was added into aluminium nitrate solution under stirring to prepare a transparent solution. Then the solution was filtered (named c).

The fourth precursor (d) prepared when acid was used to dissolve the gel in precursor b. For that, part of the precursor b was dissolved with 30 ml nitric acid (1 molar, Merck) under stirring, and then the solution was filtered. Then dishes containing precursors (a, b, c and d) were introduced one by one to pre-heated furnace maintained at 400°C. The materials underwent foaming followed by decomposition generating large volume of gases like CO₂, N₂, NO₂ and H₂O. Then, spontaneous ignition occurred and

underwent smoldering combustion in all the cases with enormous swelling producing a foamy and voluminous mass. The foamy and voluminous masses were easily crushed to produce the powders (a-1, b-1, c-1 and d-1) for characterization. The brown colour of the fumes evolved during the combustion reaction of samples²⁰ can be attributed to NO₂. The powders (b-1, c-1 and d-1) were found to be yellowish due to the captured NO₂ gas but the sample a-1 was found to be white. Table 2 summarizes the conditions at which powders were synthesized by different modes of combustion. All the samples were found to have almost same pH values which are given in Table 2.

3.3 Characterization

The crystallinity and phase identification of synthesized powders were determined by using D4 Bruker X-ray diffractometer with Cu-K α as the radiation source and Ni as the filter. To confirm the results obtained from X-ray diffraction regarding phase and nature of products, Fourier transform infrared spectroscopy (FTIR) performed in the range 400-3900 cm⁻¹ by using Shimadzu 8400 spectrophotometer. Thermogravimetric (TG) analysis was carried out in an atmosphere of air with TGA Q50 V6.3 system in the temperature range between 25°C and 600°C at a heating rate of 20°C/min to assess the weight loss due to conversion of precursors. BET surface area and pore size distribution of synthesized powders were determined by nitrogen adsorption at 77 K using BET, BJH and MP methods, respectively by adsorption analyzer (BEL Japan, Inc). The agglomeration particle size distribution was measured by Dynamic Light Scattering (DLS) method on a Malvern Instruments Analyzer. TEM analysis was performed using EM208S Philips 100 kV to determine the accurate crystallite size of the samples.

4 Results and Discussion

4.1 Proposed chemical reactions

Aluminium nitrate loses 2.5 molecules of water from the outer coordination sphere below 80°C

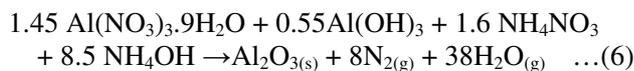
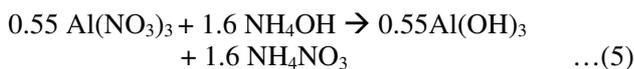
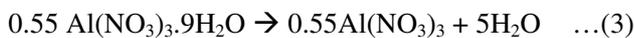
Table 2 — Conditions for synthesizing samples by different modes of combustion

Precursors	As-synthesized powder	Type of synthesis (mode)	Ammonium carbonate Composition	pH of precursors
a	a-1	Solid (VCS)	St	—
b	b-1	Solution (Gel)	St	5.71
c	c-1	Solution (VSC)	Non St	4.71
d	d-1	Solution (VSC)	St by adding nitric acid	4.11

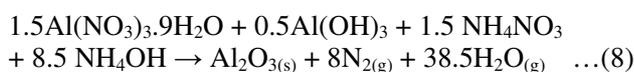
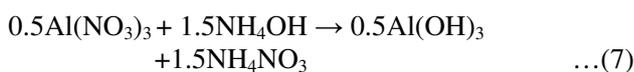
St: Stoichiometric

without breaking the structure of the nitrate groups. So, 5 moles of water release 2 moles of used non-hydrate aluminium nitrate according to reaction given in Eq. (1). The mechanism of the dehydration of aluminium nitrate may be explained by assuming the following formula²⁰ to the initial hydrate $[\text{Al}(\text{H}_2\text{O})_6](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$.

Stoichiometric amount of ammonium carbonate and aluminium nitrate were crumbled in mortar as a dry. Ammonium carbonate reacts with amount of H_2O by reaction given in Eq. (3), then amount of ammonia reacts with aluminium nitrate without water and alumina sample (a-1) is produced by combustion according to reaction given in Eq. (5).



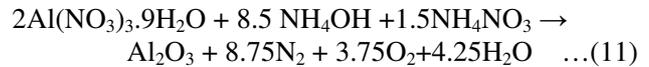
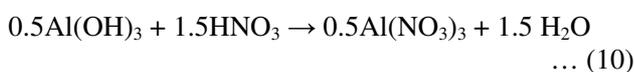
when ammonium carbonate dissolved in water, it decomposed to ammonia and carbon dioxide (reaction given in Eq. 3). 15% of ammonium carbonate changed the transparent solution to the gel (reaction given in Eq. 6). Obtained gel combusted and Al_2O_3 was produced by reaction (given in Eq. 7).



The following chemical reaction occurred during preparation of sample (c-1):



when the precipitated $(\text{Al}(\text{OH})_3)$ was dissolved in nitric acid through reaction (given in Eq.9), Al_2O_3 was produced by combustion of sample (d) through reaction (given in Eq.10).



Using nitric acid for dissolving precipitants through releasing an enormous amount of gases, leads to increasing surface area, so it predicts that the surface area of sample d-1 should be more than that of sample b-1.

4.2. Physico-chemical characterization

Thermogravimetry (TG) analysis was performed on one of the samples. The TG/DTG curves on dried precursor (sample a) are shown in Fig. 1. Two weight losses are observed on TG/DTG curves. The first weight loss is observed between 25°C and 100°C which is related to the removal of water and CO_2 . With decomposition of $\text{Al}(\text{NO}_3)_3$ at 170°C , auto-ignition step starts in narrow temperature range 200 - 260°C . The expected weight loss corresponding to the complete conversion of the precursor to Al_2O_3 in case of precursor powder during auto-ignition is about 70%. The less difference in weight loss may be attributed to remaining NO_2 contamination, which can be inferred from the fact that the remaining NO_2 is combustible gas.

The total mass-loss determined for the production of Al_2O_3 from sample (a) was 85.9%. Calculation of theoretical mass-loss based on the stoichiometry of the initial materials in reaction given in Eq. (4) shows that 89% of them have changed to gas, which is found to be in good agreement with results of TG analysis. In addition, rapid slope weight loss at 200 - 260°C associated with the rapid auto ignition, another crucial factor, is fast cooling due to the rapid evolution of the gases during auto ignition. Such a vigorous process not only helps to disintegrate the agglomerated

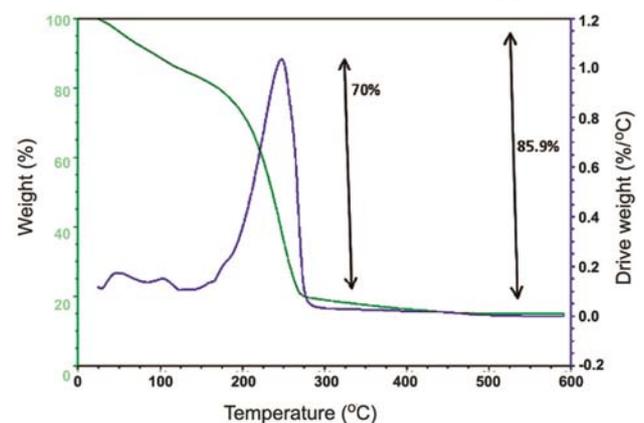


Fig. 1 — TG / DTG curves of dried precursor (sample a)

particle with each other to obtain nanoparticles, but also helps to dissipate the heat of combustion thus inhibiting the sintering of nano crystalline powder¹⁴. Therefore, this process has considerable potential for producing alumina powders with high surface area, small crystallite size and high chemical purity.

The XRD patterns of as-synthesized powders are shown in Fig. 2. It is observed that all the samples are in gamma phase and pure crystalline in nature. The broadening of the XRD peaks clearly shows the nano-size nature of crystallites. As it was predicted, the use of ammonium carbonate can produce fine alumina nanoparticles without any need to annealing treatment.

The crystallite sizes were calculated using the Scherer equation.

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where k is a constant ~ 0.9 , λ the wavelength of X-ray, β the full width of diffraction peak at half maximum (FWHM) intensity and θ is Bragg angle. The calculated crystallite sizes were found to be almost same in the range 2.0-2.5 nm. These results show that mode of combustion has less effect on the crystallite size. Figure 3 shows FTIR spectra of as-synthesized powders. The FTIR spectra of the samples a-1, b-1, c-1 and d-1 present a wide pattern extending in the range 400-900 cm^{-1} , the shoulder peaks in this region⁵ are assigned to AlO_4 . Thus, all samples are in γ phase which is found to be in agreement with the results obtained from XRD.

The unresolved wide structure in sample d-1 is typical of complex and disordered crystallographic structure. It is in agreement with XRD patterns (Fig. 2) where the same sample shows less complete structure as compared to other samples. Table 3 presents intensity of peaks corresponding to the presence of NO_2 and hydroxyl groups. The absence of peak at 1380 cm^{-1} in sample (a-1) implies that powder⁵ is free from NO_2 , which was obvious from its white colour.

The highest intensity of peaks corresponding to the presence of hydroxyl groups is for sample d-1. The band around 3500 cm^{-1} becomes larger with more intensity which indicates the formation of more number of OH group by absorbing water molecule on the surface and the intensity of band at 1620 cm^{-1} is the highest since acid helps in opening different

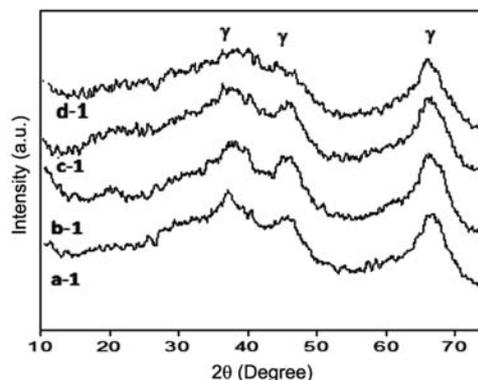


Fig. 2 — XRD pattern of as-synthesized powders prepared by different modes of combustion

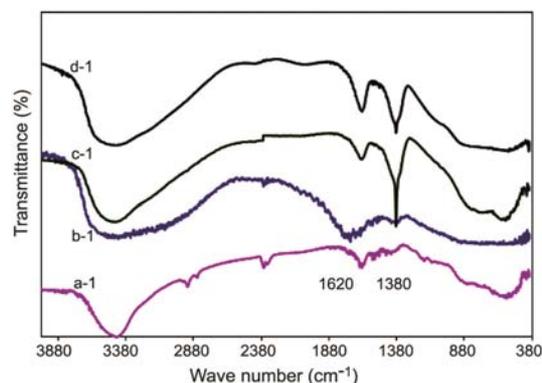


Fig. 3 — FTIR spectra of as-synthesized powders (a-1, b-1, c-1 and d-1)

Table 3 — Intensity of various ions in samples synthesized by different combustion modes

Intensity sample	1380 cm^{-1} NO_2^-	1620 cm^{-1} OH^-	3400 cm^{-1} OH^-
a-1	=	18%	45%
b-1	9%	32%	72%
c-1	92%	20%	75%
d-1	55%	35%	85%

bounding and more number of hydroxyl group to the molecules. Sample a-1 has the lowest intensity of peak corresponding to hydroxyl groups because less amount of water was used to prepare this sample. The water content of the precursor mixture is one of the parameters that influence the reaction¹².

The surface area of as-synthesized powders (a-1, b-1, c-1 and d-1) was calculated according to BET procedure by using the data of adsorption of nitrogen on the samples at 77 K assuming the cross-sectional area of 0.16 nm^2 for the nitrogen molecule. Considering that the BJH method is only used to

calculate the mesopore distribution from the desorption isotherm, the MP method which is an extension of the t-plot procedure was applied to calculate the microprose distribution from the adsorption isotherm². The pore size distributions from MP method of as-synthesized powders are shown in Fig. 4. The surface area, pore size distribution and average pore volume data for different samples are given in Table 4. These results show the existence of microproses in all the samples. The specific surface area of the entire samples lie above 300 m².g⁻¹ with narrow pores distribution. So far, production of alumina nano structures with ordered crystallographic structures by combustion synthesis with this amount of surface area has not been reported. Edrissi and Norouzbeigi⁹ could optimize condition to prepare the highest possible specific surface area using series of taguchi L₁₆ statistical designed and they obtained 122.6 m².g⁻¹. Using non-stoichiometric, amount of urea has been reported to produce alumina nanoparticles with the surface area more than 400 m².g⁻¹. But this amount of urea was unable to trigger a combustion reaction and the resulting powder was amorphous^{22,23}.

Aluminas are conventionally obtained by precipitation or by treating different aluminium hydroxides (bohemite, bayerite, etc.) to obtain various transition phases. In all these techniques, it is possible to obtain rather high surface area in the range 300-400 m².g⁻¹ but the pore size distributions are often wide or even bimodal. Many alumina applications would benefit from use of mesoporous materials with high surface area and narrow pores distribution²⁴.

The production of nano-sized gamma alumina by control precipitation method using ammonium

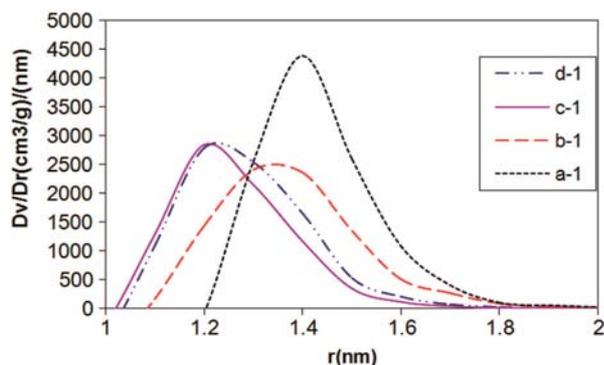


Fig. 4 — Pore size distribution of as-synthesized powders from MP Plot

carbonate has been reported by K.M.Parida⁵ but these particles have shown crystallite sizes in the range of 4.7-5.7 nm, specific surface area 190 m².g⁻¹ and bimodal pores distribution. The specific surface areas for particles in our study are higher and pore size distribution is narrower than those reported by Parida⁵. Similarly, the specific surface area obtained in our study is also larger than those values reported by Yao *et al.*² (178-265 m².g⁻¹) for micropores alumina prepared by sol gel method using ammonium hydroxide. Moreover, we have obtained pure micropores but the particles obtained by Nan Yao *et al.*² contain combination of both micropores and mesopores particles.

Table 4 presents that the samples d-1 and c-1 have higher surface areas as compared with other samples. It seems that the initial amount of water in the precursors has strong effect on reducing flame temperature which in turn causes increasing in specific surface area^{10,24}. As we have surveyed literatures, this can be important reason for change in properties of the synthesized nanoparticles by different modes of combustion. The sample d-1 has the highest surface area due to releasing higher amount of gas during synthesizing process. Generation of extra combustion gases expands the foamy structure more and eventually increases the corresponding surface area⁹. The measured specific surface areas for the samples in crystallite forms can be converted to equivalent particle size according to the following equation:

$$D_{\text{BET}} = \frac{6000}{\rho \times S_{\text{BET}}}$$

where D_{BET} (nm) is the average particle size, S_{BET} is the specific surface area expressed in m².g⁻¹ and ρ is the theoretical density of gamma alumina³ expressed in g.cm⁻³. The average particle sizes calculated from BET were found to be in the range 4.1-4.9 nm which are close to the values obtained from XRD analysis.

Table 4 — Surface area, pore volume and average pore size for samples synthesized by different combustion modes

Samples	specific surface area (m ² .g ⁻¹)	Pore volume (cm ³ .g ⁻¹)	Average pore size (nm)
a-1	328.00	0.328	1.40
b-1	357.08	0.265	1.30
c-1	391.50	0.223	1.20
d-1	392.79	0.256	1.20

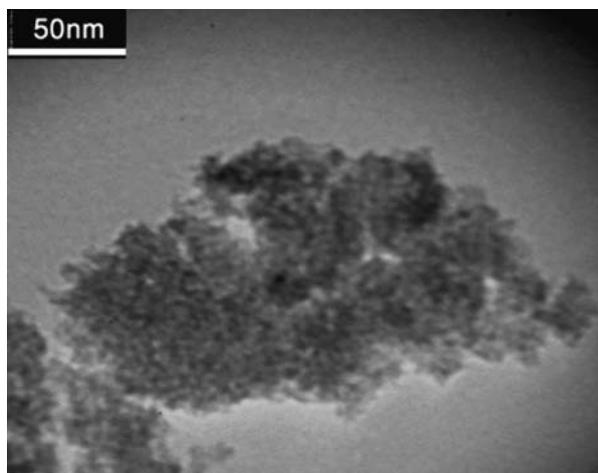


Fig. 5 — Typical TEM photograph of one of the samples

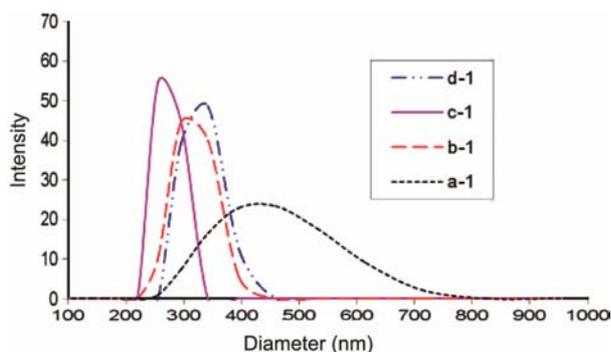


Fig. 6 — Particle sizes distributions of as-synthesized powders

In order to determine the accurate crystallite size of samples, TEM analysis was performed on one of the samples. The TEM image is shown in Fig. 5. It is clearly seen that the particles are nearly spherical in shape and they have narrow distribution and size of particles is about 5 nm. This result agrees more with results of BET measurement rather than those obtained from XRD measurement. The mean agglomerate size of the samples was determined from the particle size distribution measured by DLS method. The particle size distributions of as-synthesized alumina powders are shown in Fig. 6. The solution-based combustion synthesis methods have been advantageous over the solid-state synthesis in terms of better compositional homogeneity of the final products¹⁶. Figure 6 shows that the particle size distribution of samples (b-1, c-1 and d-1) is narrower and more homogeneous than that of sample (a-1) and it is also in accordance with Table 4 which shows that these samples have higher surface area in comparison with sample (a-1) because of homogeneity in initial

materials. The initial reaction media existence in the liquid state allows mixing of the reactants on a molecular level, thus permitting precise and uniform formation of the desired composition on the nano scale¹⁵. The sample c-1 showed the lowest particle size and the most narrow size distribution whereas it has high surface area with ordered crystallographic structure. So, by lowering the particle size, the surface area would be higher. This result agrees well with reports on production of alumina nano structures by combustion synthesis⁹. The lower amount of fuel used in this case (fuel-lean) results in a small enthalpy and hence, the local temperature of the particles remains low, which may prevent the formation of dense structure. Associated gas evolution, results in highly porous structure^{9,10}.

5 Conclusions

Thermodynamic calculations predicted that ammonium carbonate because of its lower enthalpy of reaction and releasing more number of gas molecules, during synthesizing reaction in comparison with some conventional organic fuels should be capable of producing alumina fine particles with high specific surface area. The reactions involved in combustion reaction using this material were verified by TG analysis. γ -alumina powders with high specific surface area (above $300 \text{ m}^2 \cdot \text{g}^{-1}$) and fine crystallite size (about 5 nm) were synthesized by different modes of combustion using ammonium carbonate, without any need to further annealing treatment. The as-synthesized powders produced by different modes of combustion showed almost similar crystallinity, phase and crystallite size (2.0-2.5 nm) which were confirmed by both XRD and BET measurements. But FTIR analysis showed that there is change in intensity of different functional groups in as-synthesized samples due to change in nature of the combustion modes. BET and DLS analysis showed that specific surface area and agglomerate size of as-synthesized powders are more combustion mode dependent. The samples prepared by solution VCS mode of combustion showed higher specific surface areas as compared with samples prepared by solid state combustion. DLS analysis showed that samples prepared by solution mode have relatively more homogeneity and narrower agglomerate particle size distribution. So, the conventional volume combustion synthesis mode which involves uniform reaction solution preheating prior to self-ignition is better than other modes.

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