Combustion Synthesis Of Nano Gamma-Alumina By Using Amino Acids As Fuels And Investigation Of Effective Factors

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ABSTRACT

Nano-crystalline alumina particles were synthesized by combustion method using serine and asparagine as fuels, for the first time. A screening design was conducted to determine how key process factors influence preparation of nano crystalline powders. The screening design in this work utilized to rank effective factors on crystalline size of alumina powders. The product was characterized by XRD, BET, and SEM. Nano crystalline γ-alumina powders with crystal sizes between 3.95nm and 6.71nm were obtained by combustion synthesis. The specific surface areas of samples are between 22.17m2/g and 75.21m2/g. Results of statistical analysis illustrate that fuel to oxidizer ratio is the most effective factor for decreasing the average crystal size.
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INTRODUCTION

Alumina is one of the most important ceramic materials presenting exceptionally high resistance to chemical agents, as well as giving an excellent performance as catalyst or catalytic support for many chemical reactions[1,13]. It is widely used for structural, microelectronic and membrane applications. Various chemical methods such as spray pyrolysis[14], precipitation[19], sol-gel[17], hydrothermal[18] and combustion synthesis have been employed to synthesize ultrafine Al_2O_3 powders.

Combustion synthesis is particularly a simple, safe and rapid production process wherein the main advantages are energy and timesaving. This quick, straightforward process can be used to synthesize homogeneous, high-purity, crystalline oxide ceramic powders including ultrafine alumina powders with a broad range of particle size.

The basis of the combustion synthesis technique comes from the thermochemical concepts used in the field of propellants and explosives[2]. The success of the process is due to an intimate blending among the constituents using a suitable fuel or complexing agent(e.g., citric acid[4], urea[16], glycine[3], etc.) in an aqueous medium and an exothermic re-

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dox reaction between the fuel and oxidizer(nitrates). Actually, the mechanism of the combustion reaction is quite complex. The main parameters that influence the reaction include: type of the main fuel, fuel to oxidizer ratio, the amount of excess oxidizer, ratio of fuels, pH of the solution, and rate of calcination[3,4,5,20]. In general, a good fuel should not react violently or produce toxic gases, and must act as a complexing agent for metal cations[6]. In this research two amino acids, serine($HOCH_2CH(NH_2)COOH$) and asparagines($NH_2COCH_2CH(NH_2)COOH$), were used as fuels. The effectiveness of important factors on the crystal size of combustion synthesized γ-alumina powders are investigated by using two-levels factors in a screening design. The powders obtained through combustion synthesis have been characterized by X-ray diffraction, BET, and SEM.

EXPERIMENTAL

Design of experiments

A two level screening design was utilized for investigating and sorting the effective factors on combustion synthesis of alumina powders. The first step is selection of factors. The seven important factors studied are: the ratio of excess oxidizer, type of fuel, fuel to oxidizer ratio, type of secondary fuels, secondary fuel to the main fuel ratio, pH of the starting solution, and rate of calcination. The second step is determination of high and low levels for each factor. Ammonium nitrate(NH_4NO_3) was used as excess oxidizer(combustion aid)[7]. The molar ratio of the ammonium nitrate to aluminum nitrate(main oxidizer) was selected, as the first factor and amounts of 0.25 and 0.5 were its low and high levels respectively. The initial composition of the solution containing aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$ and asparagine was derived from the total oxidizing and reducing valences of the oxidizer and fuel using the concepts of propellant chemistry[8]. Carbon, hydrogen and aluminum were considered as reducing elements with the corresponding valences of +4, +1 and +3, respectively. Oxygen was considered as an oxidizing element with the valence of-2, the valence of nitrogen was considered to be 0. The total calcu-

TABLE 1 : Factors and levels

Factor	Allocated letter	High Level	Low Level
Molar ratio of the excess oxidizer to aluminum nitrate	A	0.5	0.25
Fuel to oxidizer ratio	B	1.5×St.	St.
Type of main fuel	C	Asparagine	Serine
Type of added fuel	D	Urea	Ammonium acetate
Molar ratio of added fuel to the main fuel	E	0.2	0
pH of the starting solution	F	4	2
Calcination rate	G	$20^0C/mins$	$10^0C/mins$

lated valences of metal nitrates by arithmetic summation of oxidizing and reducing valences was -15. The calculated valence of asparagine was +15. The stoichiometric composition of the redox mixture demanded that 1(-15)+n(+8)=0, or n=0.833mol. This calculation was done for mixture of aluminum nitrate and serine, so the stoichiometric composition of the redox mixture demands that 1(-15)+n (+13)=0, or n=1.154mol. Selected levels for fuel to oxidizer ratio were stoichiometric amount(St.) and 1.5×St.. As mixtures of fuels can influence the final product size[5], we used mixtures of amino acids with Urea and ammonium acetate. In this study type of main fuels was a qualitative factor and asparagine and serine were its high and low levels respectively, type of added fuel was another qualitative factor with assumption that urea is its high level and ammonium acetate is its low level, and molar ratio of added fuel(Urea or ammonium acetate) to the main fuel(serine or asparagine) was introduced as one of the quantitative factors. The amounts of 0 and 0.2 were selected as low and high levels respectively. Other factors investigated were pH of the starting solution and rate of calcinations. The amounts 2 and 4 were chosen as low and high levels for the pH, which was adjusted by adding ammonium hydroxide or nitric acid to the solution. The $10^0C/mins$ and $20^0C/mins$ were selected levels for the calcination rate. The factors studied and the amounts used for high and low levels are shown in TABLE 1 used in design of experiments.

The combination of factors and levels accord-

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TABLE 2 : Screening design table

Sample	Factor						
	A	B	C	D	E	F	G
1	0.5	1.5	Asparagine	Urea	0.2	4	20°C/mins
2	0.5	1.5	Serine	Urea	0	2	10°C/mins
3	0.5	1	Asparagine	Ammonium acetate	0.2	2	10°C/mins
4	0.5	1	Serine	Ammonium acetate	0	4	20°C/mins
5	0.25	1.5	Asparagine	Ammonium acetate	0	4	10°C/mins
6	0.25	1.5	Serine	Ammonium acetate	0.2	2	20°C/mins
7	0.25	1	Asparagine	Urea	0	2	20°C/mins
8	0.25	1	Serine	Urea	0.2	4	10°C/mins

ing to screening design is shown in TABLE 2.

Preparation of samples

All of the materials used were supplied from Merck Company and were analytical graid. Eight samples were prepared according to combination of factors and levels showed in TABLE 2. In the first step 0.04mol of $Al(NO_3)_3.9H_2O$ was dissolved in 100ml distilled water. The amounts of serine or asparagine with amounts of urea or ammonium acetate and consequent amounts of ammonium nitrate under vigorous stirring(rpm=1000) were added to the solution. Then pH of the solution was adjusted with addition of ammonium hydroxide solution or nitric acid if required. The obtained solution then heated on a hot plate and was stirred until the solution was boiled at 100^0C. When almost 90% of water evaporated, a yellowish and transparent gel was obtained. Then the obtained gel was transferred to porcelain

## TABLE 3 : Bragg's angle, 2θ, and average crystallite size of samples

Sample	B^0	B^{rad}	$2\theta^0$	Average crystal size D(nm)	Y_i (Response)
1	2.417	0.042184608	67.000	3.95	Y_1
2	1.809	0.030089476	66.872	5.29	Y_2
3	1.724	0.030089476	66.893	5.55	Y_3
4	1.861	0.032480577	66.780	5.14	Y_4
5	2.185	0.038135444	66.921	4.37	Y_5
6	2.241	0.039112828	66.648	4.26	Y_6
7	1.432	0.024993114	66.946	6.71	Y_7
8	1.750	0.030543261	66.830	5.47	Y_8

crucible and it was heated in a muffle furnace up to 400^0C and ignited in this temperature. At this stage a blackish voluminous fluffy solid product was obtained. It was calcined according to TABLE 2 up to 900^0C and remained in this temperature for 2 hr. White and very fine powders were obtained. The powders were analyzed by X-ray diffraction(XRD) and average crystal sizes were selected as response of the experiments. X-ray diffraction was performed on calcined powders for phase characterization, at a rate of 1^0/min, using nickel filtered CuKα radiation in the range of $2\theta=25-80^0$, on a Philips X-ray diffractometer,(model X'Pert). The surface area of the powders were measured using multipoint BET method(QUANTACHROME AutosorbI, Micro meritics instrument) assuming a cross sectional area of $0.16nm^2$ for the nitrogen molecule. The porosity and the microstructure of the products were examined by means of scanning electron microscopy (Philips XL30).

RESULTS AND DISCUSSION

XRD data

In this research we selected two amino acids as fuels. These fuels have amine groups. Amine group, which could complex with metal cations and decomposes at a relative low temperature giving ammonia (NH_3). The redox reaction eq.(1) between ammonia and the oxides of nitrogen(NO_x) from the decomposed nitrates give water and Nitrogen:

$$4xNH_{3(g)} + 10NO_{x(g)} \rightarrow (5+2x)N_{2(g)} + 6xH_2O_{(g)} + 2xO_{2(g)} \quad (1)$$
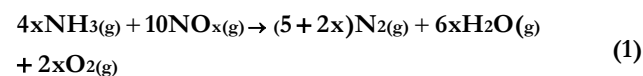
The energy released from the redox reaction accelerated the phase formation of γ-alumina[9].

The XRD patterns of the powders calcined at 9000^0C for 2 hr are shown in figures 1 to 8.

The peak broadening method was obtained to calculate the average crystallite size. The full width at half maximum(FWHM) of the peak was measured and the average crystallite size values were estimated using the following equation of Scherrer [11]:

$$D = \frac{0.9\lambda}{\sqrt{B^2 - b^2} \times \cos\theta} \quad (2)$$
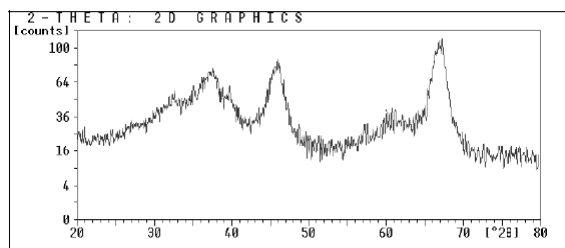
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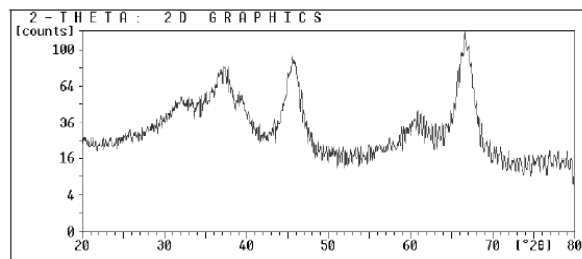

Figure 1 : XRD pattern of sample number 1

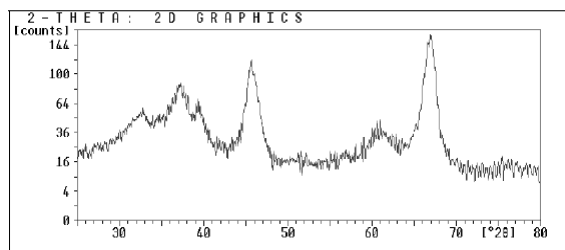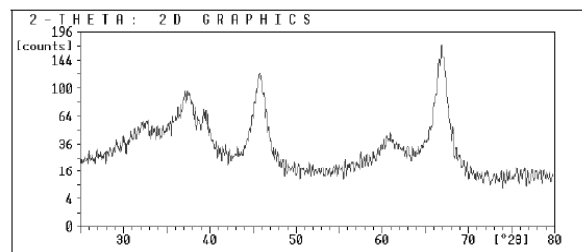**Figure 2 : XRD pattern of sample number 2**

Figure 3 : XRD pattern of sample number 3

Figure 4 : XRD pattern of sample number 4

Figure 5 : XRD pattern of sample number 5

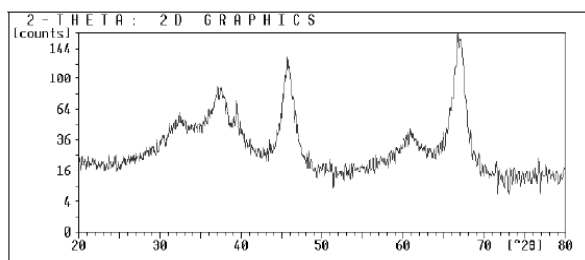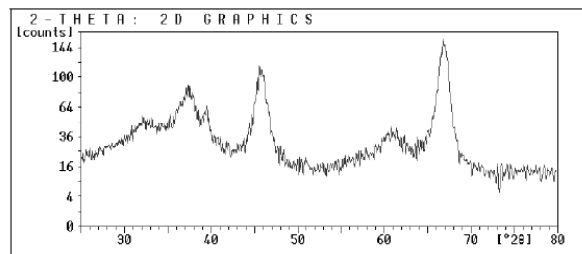**Figure 6 : XRD pattern of sample number 6**
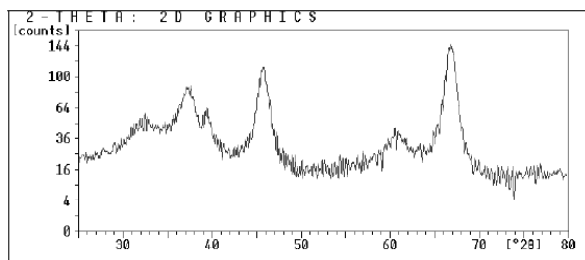

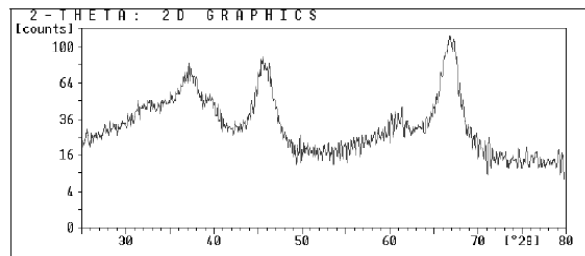**Figure 7 : XRD pattern of sample number 7**

Figure 8 : XRD pattern of sample number 8

Where D is the average crystallite size, λ the wavelength of the radiation, θ the Bragg's angle and B and b are the FWHMs observed for the sample and standard, respectively. Silicon powder was used to measure the instrumental peak broadening. Terms B and 2θ were obtained from each XRD pattern and PC-APD(X_manager) software that uses information of ICDD(international center of diffraction data) to recognize alumina phases. The average crystallite size for each sample was calculated from above formula. Results are shown in TABLE 3. Crystal sizes are responses of experiments and average crystal size of sample i in TABLE 3 is shown by Y_i.

Investigation of TABLE 3, illustrates that sample 1 has the smallest average crystallite size(3.95nm) and sample 7 has the largest one (6.71nm). It should be mentioned that these results are almost the least average sizes have been obtained

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TABLE 3 : Bragg's angle, 2θ, and average crystallite size of samples

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6	2.241	0.039112828	66.648	4.26	Y_6
7	1.432	0.024993114	66.946	6.71	Y_7
8	1.750	0.030543261	66.830	5.47	Y_8

TABLE 4 : Result of average calculations and term E_f for factors

Factor	L_+	L_-	E_f
A	4.9825	5.2025	-0.22
B	4.4675	5.7175	-1.25
C	5.1450	5.0400	0.105
D	5.3550	4.8300	0.525
E	4.8075	5.3775	-0.57
F	4.7325	5.4525	-0.72
G	5.0150	5.1700	-0.155

TABLE 5 : Factors, comparison of averages, and optimum condition to produce smaller particles

Factor	Comparison (smaller is better)	Optimum condition
A	$L_+ < L_-$	Increasing of the factor quantity
B	$L_+ < L_-$	Increasing of the factor quantity
C	$L_- < L_+$	Using Serine
D	$L_- < L_+$	Using Ammonium acetate
E	$L_+ < L_-$	Increasing of the factor quantity
F	$L_+ < L_-$	Increasing of the factor quantity
G	$L_+ < L_-$	Increasing of the factor quantity

TABLE 6 : Ranking of factors (screening) based on sorting the $|E_f|$ values

Ranking of the factors	$|E_f|$
1. Fuel to oxidizer ratio	1.25
2. pH of the starting solution	0.72
3. Molar ratio of added fuel to the main fuel	0.57
4. Type of added fuel	0.525
5. Molar ratio of the excess oxidizer to aluminum nitrate	0.22
6. Calcination rate	0.155
7. Type of main fuel	0.105

by combustion synthesis. XRD patterns show that sample 1 and 5 have more amorphous particles than the others. Also the crystallinity of samples 2,3,6,and 7 is better than the other samples. Furthermore, samples 2 and 3 include mixture of δ and γ phases, and samples 6 and 7 are completely γ-alumina. Other samples are mixture of some amorphous particles and more-alumina crystalline powders. The results show that when XRD profile has broaden peaks the crystallite size is small and the crystallinity is poor but when the peaks are narrow the corresponding crystals are large. The mentioned software and XRD patterns illustrate all samples synthesized in this work are γ-alumina.

The effect of changing the level for anyone factor, E_f is determined by subtracting the average responses(crystal size) when the factor is at its high level(L_+) from the average value when it is at its lower case level(L_-).

$$E_f = \frac{\left(\sum Y_i\right)_{\text{high level}}}{4} - \frac{\left(\sum Y_i\right)_{\text{low level}}}{4} \qquad (3)$$

$$E_f = L_+ - L_- \qquad (4)$$
$$E_A = (Y_1+Y_2+Y_3+Y_4)/4 - (Y_5+Y_6+Y_7+Y_8)/4 \qquad (5)$$
$$E_B = (Y_1+Y_2+Y_5+Y_6)/4 - (Y_3+Y_4+Y_7+Y_8)/4 \qquad (6)$$
$$E_C = (Y_1+Y_3+Y_5+Y_7)/4 - (Y_2+Y_4+Y_6+Y_8)/4 \qquad (7)$$
$$E_D = (Y_1+Y_2+Y_7+Y_8)/4 - (Y_3+Y_4+Y_5+Y_6)/4 \qquad (8)$$
$$E_E = (Y_1+Y_3+Y_4+Y_8)/4 - (Y_2+Y_4+Y_5+Y_7)/4 \qquad (9)$$
$$E_F = (Y_1+Y_4+Y_5+Y_8)/4 - (Y_2+Y_3+Y_4+Y_7)/4 \qquad (10)$$
$$E_G = (Y_1+Y_4+Y_6+Y_7)/4 - (Y_2+Y_3+Y_5+Y_8)/4 \qquad (11)$$

Results of calculations are shown in TABLE 4.

As we are looking for the production of smaller particles the least average is considered as aim of calculations. By utilizing this concept optimum condition of factors to produce smaller particles is obtained and it is shown in TABLE 5.

Sorting of the amounts of E_f without consideration of their signs leads to ranking of factors based on their influence on the combustion synthesis of alumina. Results are shown in TABLE 6.

Factor B(fuel to oxidizer ratio) is the most important factor responsible for reducing the average diameter value of γ-alumina. Other effective factors are F(pH of the solution) and E (molar ratio of added fuel to the main fuel) respectively. The effect of D(type of added fuel) is positive, so in comparison with urea, ammonium acetate fuel is more suit-
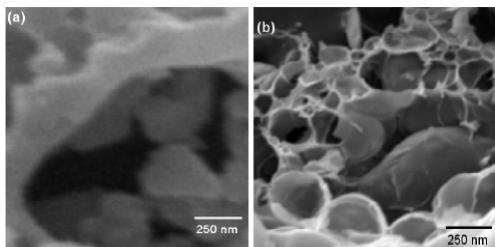
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Figure 9 : The SEM photographs of the sample 1(a) and sample 6(b)

able. The effects of A, G, and C are less and the least effective factor is C(type of the main fuel).

BET data

The specific surface areas of sample 1 and 6 were calculated according to the Brunnauer-Emmet-Teller(BET)procedure(model Autosorb I QUAN TACHROME, Micromeritics instrument)[10] by using the data of adsorption of nitrogen on the samples at 77^0k assuming a cross sectional area of 0.16nm2 for the nitrogen molecule. Results show that the specific surface area of sample 1 is 22.17m^2/g and the specific surface area of sample 6 is 75.21m^2/g. So the specific surface area of sample produced by serine-nitrate combustion is more than the sample that is the product of asparagines-nitrate combustion. The amounts of surface area of samples show that these samples are suitable for using as catalyst support or adsorbent.

SEM Data

An electron microscope(Phillips XL30) was used to take SEM view of the samples 1 and 6 (magnification is 50000). The SEM photographs of the mentioned samples are given in figure 9. It was clearly observed from these photographs that sample 6 has more porosity and surface area than sample 1. The porosity range of sample 6 is 50-250nm and could be used as molecular sieve or catalyst support[12,15].

CONCLUSION

(1) In this research nano γ-Al$_2$O$_3$ powders with crystallite sizes between 3.95nm and 6.71nm were successfully synthesized by using serine and aspatragine as new flues. These results show that serine-nitrate and asparagine-nitrate combustion synthesizes have outstanding potential for producing nano crystalline alumina powders in comparison with other conventional fuels.

(2) Using a screening design, the order of effective factors and the optimum combination of their levels required for preparing γ-Al$_2$O$_3$ with consideration of smaller crystal sizes was obtained, so the most effective factor was fuel to oxidizer ratio.

(3) The specific surface area of powders was measured and the results show specific surface area of sample produced from serine-nitrate combustion is more than sample prepared from asparagine-nitrate combustion.

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