

Specific Surface Area Increment of Alumina Nanoparticles Using Mineral Fuels in Combustion Synthesis

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Abstract

Ammonium carbonate and ammonium sulfate have been proposed and used as two new fuels for synthesizing gamma alumina nanoparticles. The prepared samples have been characterized by X-ray diffraction (XRD), N_2 adsorption (BET) and Transmission electron microscopy (TEM). A comparison has been made between the properties of the nanoparticles synthesized by these two fuels and other conventional fuels. These two mineral fuels showed to be suitable for replacing organic fuels in combustion synthesis because they reduce the size and increase specific surface area of alumina nanoparticles effectively.

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1. Introduction

In recent years, increasing attention has been focused on the development of nanocrystalline Al_2O_3 powders. Because of low cost, fine particles size, high specific surface area and high activity of the surfaces, the γ -alumina finds wide applications in industry as absorbent, catalyst, catalytic support, coating and soft abrasive [1-3].

There are variety chemical routes for production of ultrafine Al_2O_3 powders such as sol

gel, hydrothermal process and control precipitation [2-5]. But all these routes need high pressure, high temperature, long processing time or they suffer from high price of raw materials [6]. As the contrary solution combustion synthesis is easy, safe and rapid production process wherein the main advantages are energy and time savings [7].

This technique involves the exothermic chemical reaction between salts of desired metals

(usually nitrates) and some organic fuels [8, 9]. This process has the advantage of choice of a wide variety of fuels; therefore fuel plays an important role in determining the crystallite size, specific surface area, morphology, phases, degree and nature of agglomerates [10].

Urea seems to be the most convenient one to be employed in this route to produce alumina nanostructures, 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 the oxides during combustion [11, 12]. So, other organic fuels such as glycine [7, 8], ammonium acetate [12], sucrose [13], citric acid [14], acetylacetone [6], serine and asparagines [15, 16] have been used to improve ultrafine and specific surface area of alumina nanoparticles. Using these organic fuels γ -alumina with crystallite sizes in the range of 4- 16nm and specific surface area in the range of 21- 96m²/g have been reported.

It seems that application of fuels containing amino groups can successfully prepare nanoparticles of alumina by solution combustion synthesis [1, 15]. Recently, Norouzbeigi and Edrissi [1] 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 13nm and specific surface area between 21 and 70m²/g. They could optimize condition to prepare highest possible specific surface area (122.6m²/g) using series of taguchi L_{16} statistical design. This amount of specific

surface area is still smaller than those values reported by other techniques such as sol gel, hydrothermal processing and control precipitation [2-4]. In spite of simplicity and rapidity of the combustion synthesis, this process suffers from low specific surface area of the products while most of the industries need powders with high specific surface area. So, it is necessary to explore techniques to improve the specific surface area of the products. The type of the fuel is known to be one of the parameters affecting on specific surface area of the particles.

In this work ammonium carbonate (NH_4)₂CO₃ and ammonium sulfate (NH_4)₂SO₄ have been used as two new mineral fuels in combustion synthesis to produce alumina nano particles with higher specific surface area and finer particle sizes. These mineral fuels have lower price and they are more available compared to often organic fuels.

2. Experimental

Analytical grade of aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O), ammonium carbonate ((NH₄)₂CO₃) and ammonium sulfate ((NH₄)₂SO₄) were used as starting materials. All of the materials used were prepared from Merck Company.

2.1. Preparation of sample (a)

Suitable amount of stoichiometric starting materials solved in minimum amount of deionized water. Ammonium carbonate solution was added drop-wise to the aluminum nitrate solution, under stirring. Then the dish containing as-prepared precursor heated in a pre-heated furnace maintained at 400°C. The material foamed, decomposed and generated large volume of gases. Then spontaneous ignition occurred and

underwent smoldering combustion with enormous swelling, producing a yellowish foamy, voluminous mass. The voluminous foamy mass was easily crushed to the powder and named sample (a).

2.1. Preparation of sample (b)

Ammonium sulfate solution was added to aluminum nitrate solution under stirring. The prepared solution filtrated and dish containing precursor heated in a pre-heated furnace maintained at 500°C. The material solution boiled, foamed, decomposed and generated large volume of the gases. Then spontaneous ignition occurred and underwent smoldering combustion with enormous swelling, producing a white foamy voluminous mass. The voluminous mass was calcined at 900 °C for 2h, and named sample (b).

The crystallinity and phase identification of prepared powders were determined by using D4 Bruker X-ray diffractometer with Cu-K α as the radiation source and Ni as the filter. The specific surface areas (BET) and pore size distributions of prepared powders were determined by nitrogen adsorption at 77 K, using adsorption analyzer (BEL Japan, Inc). TEM analysis was performed using EM208S philips 100kV to determine the accurate particle size of the samples.

3. Results and discussion

The XRD patterns of samples (a) and (b) are shown in Fig 1. It is observed that the both samples are in the gamma phase and pure

crystalline in nature. Broadening of the peaks clearly show the nano- size nature of crystallites.

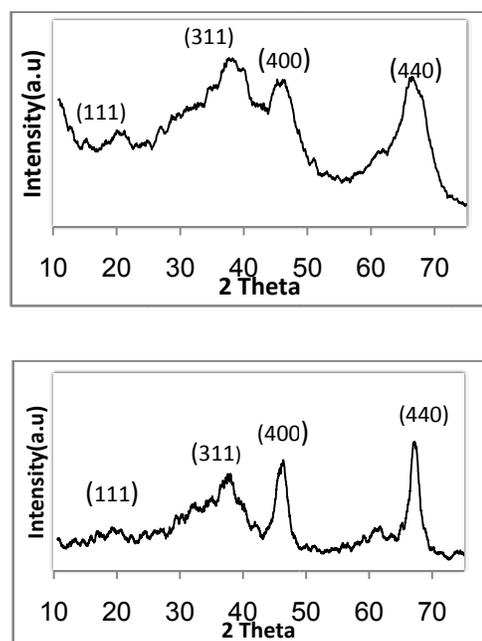


Fig. 1. XRD patterns of samples (a) and (b)

The crystallite sizes were calculated using the Scherer equation. Where k is a constant ~ 0.9 , λ is the wave length of the X- ray, β is the full width of diffraction peak at half maximum (FWHM) intensity and θ is Bragg angle.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

The calculated crystallite size of samples (a) and (b) were found to be almost 2.5 and 6.7 nm, respectively.

Table 1. Crystallite size, phase and specific surface area of alumina nanoparticles prepared by different fuels.

Fuel	Crystallite size (nm)	Specific surface area(m^2/g)	Phase	Calcination temperature($^{\circ}C$)
Urea [11]	50	–	α	–
Urea [13]	98	8.0	α	–
Glycine [7]	90.3	15.1	α	1100
Glycine [8]	9.6–18	–	α	1200
(using variety pH)	–	39–96	γ	800
Citric acid [14]	63–113	4.5–9.2	α	–
Acetylacetone [6]	93–111	–	α	1000
Serine, asparagine [15]	3.95-6.71	22–75	γ	900 $^{\circ}C$
Four amino acids[1]	7.2–13	21–70	γ	900 $^{\circ}C$
Ammonium carbonate*	2.5	357.08	γ	–
Ammonium sulfate*	6.7	176.32	γ	900 $^{\circ}C$

* This work

Using ammonium carbonate leads to production of ultrafine alumina with crystallite size about 2.5 nm. This size is lower than those values reported for production of alumina nanoparticles by other researchers using organic fuels. Table 1 summarizes crystallite size, phase and specific surface area of alumina nanoparticles prepared by other researchers using organic fuels in compared with our results.

S. Cava et al. [17] could prepare alumina nanoparticles calcined at 900 $^{\circ}C$ with crystallite size of 6.7nm using polymeric precursor($(NH_4)Al(SO_4)_2$), but they carried out several steps of polymerization, milling and heat treatment, whereas our combustion synthesis process is rapid and simple.

The specific surface area, average pore volume and pore radiuses of samples (a) and (b) were measured according to the Brunauer-Emmet-Teller (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 molecules.

The BET measurement showed that the specific surface area of sample (a) was found to be $357.08 \text{ m}^2/g$, pore volume was $0.296 \text{ cm}^3/g$ and pore size lower than 2nm with narrow distribution, so it can be concluded that sample (a) contains micropore alumina nanoparticles [18]. 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 micropore distribution from the adsorption isotherm for sample (a) [19].

The nitrogen adsorption/desorption isotherm and pore size distribution from MP method of as-synthesized sample (a) are shown in Fig. 2. The specific surface area using ammonium carbonate in combustion synthesis was found be higher than that value reported using control precipitation ($190 \text{ m}^2/g$)[3]. using ammonium carbonate as a new mineral fuel in combustion synthesis leads to production of alumina nanoparticles with higher specific surface area and finer particle sizes other than organic fuels [Table 1].

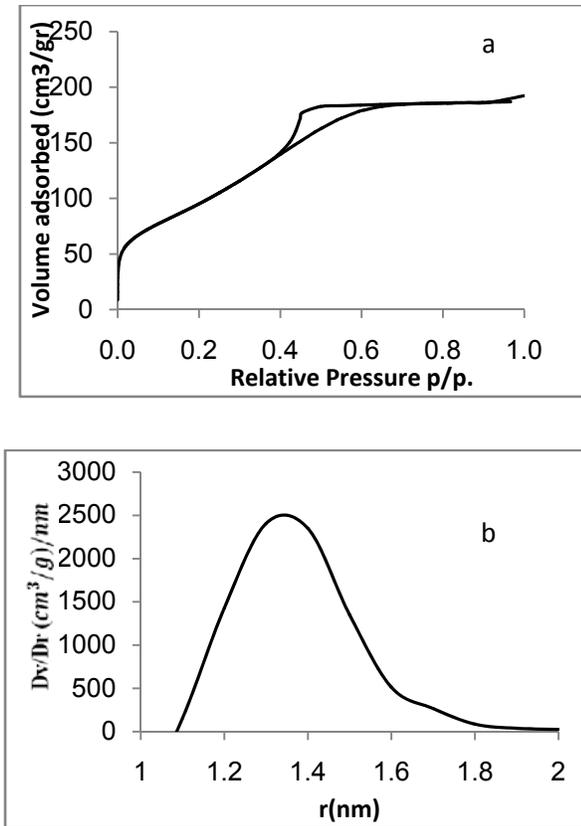


Fig. 2. a. Adsorption/desorption isotherm and b. pore size distribution of the sample (a)

Using non-stoichiometric amount of urea can produce alumina nanoparticle with the specific surface area of more than $400 \text{ m}^2/\text{g}$ but this amount of urea is unable to trigger a combustion reaction and the resulting powder would be amorphous [20, 21].

Alumina is conventionally obtained by precipitation or by treating different aluminum hydroxides (bohemite, bayerite, etc) to obtain various transition phases. In all these ways it is possible to obtain rather high specific surface area (in the range of $300\text{-}400 \text{ m}^2/\text{g}$) but the pore size distributions are often wide or even bimodal. Many alumina applications would benefit from use of mesoporous materials with high specific surface area and narrow pores distribution [20]. As it is

seen in Fig. 2 hysteresis loop occurs at relatively low pressures (around 0.5). It suggests a narrow pore size distribution [4], which is confirmed in Fig 2.

The Figs. (3, a) and (3, b) show the nitrogen adsorption/desorption isotherm and pore size distribution from BJH method of sample (b).

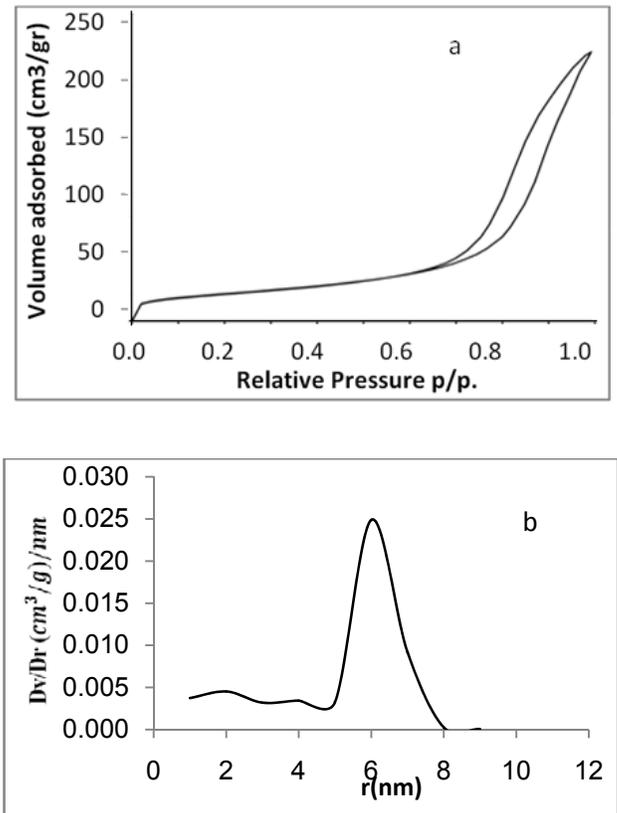


Fig 3. a. Adsorption/desorption isotherm and b. pore size distribution of the sample (b).

The specific surface area and average pore volume of sample (b) were measured to be $176.32 \text{ m}^2/\text{g}$ and $0.684 \text{ cm}^3/\text{g}$ respectively. This value is higher than those values reported for production of alumina nanoparticles by other researchers using organic fuels and optimum condition (taguchi), while alumina was prepared in optimum condition by taguchi with more

complexity condition other than this work [Table 1, [1].

It observed that the mineral fuels generally produce higher surface. There different parameters affecting on properties of nanoparticle synthesized by solution combustion, the chemical nature of type fuel, fuel to oxidizer ratio and pH of the solution [1, 9]. These parameters play in a little complex manner in changing the properties of the compound. But it is observed that mineral fuels generally result to higher specific surface area. Though the attention can be made on these type of fuels to synthesize alumina nano particles with higher specific surface area. But the exact effect of each parameter determined by number of synthesizing experiments under different condition.



Fig. 4. TEM photograph of sample a.

In order to determine the accurate crystallite sizes of samples (a) and (b), TEM analysis was performed. The TEM image of sample (a) is shown in Fig 4. It is clearly seen that the particles are nearly spherical in shape and they have sharp distribution with particle size about 5 nm. This result is agreement to the value obtained from XRD analysis (2.5nm).

The TEM image of sample (b) is shown in Fig 5.

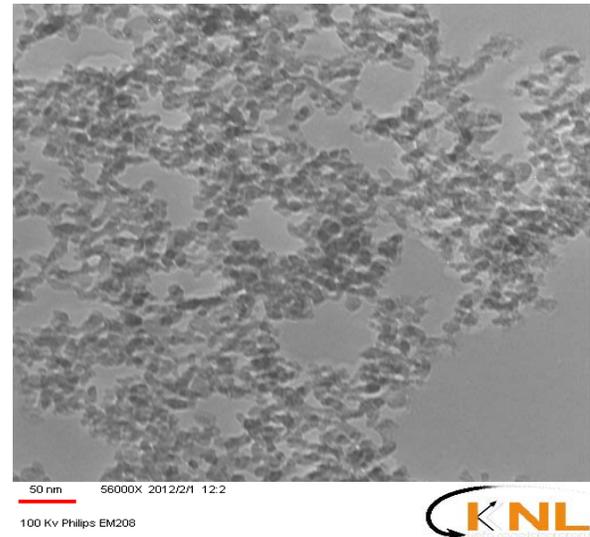


Fig. 5. TEM photograph of sample (b).

It is clearly seen that the particles have size about 10 nm with sharp distribution. This result is in agreement with the value obtained from XRD analysis (6.7nm).

4. Conclusions

Nano-sized porous γ -aluminas have been successfully synthesized by two new mineral fuels in combustion synthesis. The ammonium carbonate have been successfully utilized to produce microporous γ -alumina with particle size about 5 nm, specific surface area about $357.08\text{m}^2/\text{g}$ and average pore volume $0.296\text{cm}^3/\text{g}$ with narrow pore size distribution. The ammonium sulfate has been successfully utilized to produce mesoporous γ -alumina with particle size about 10nm, specific surface area about $176.32\text{m}^2/\text{g}$ and average pore volume $0.684\text{cm}^3/\text{g}$. The specific surface areas obtained in our study were found to be higher than those values results of reported for organic fuels in combustion synthesis.

Therefore, mineral fuels can propose as new groups of fuels to produce alumina nanoparticles

with better properties. These fuels are suitable replacing for organic fuels in combustion synthesis.

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