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ORIGINAL RESEARCH PAPER

Preparation of γ-Al_2O_3 and Prioritization of Affecting Factors on the Crystallite Size Using Taguchi Method

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Abstract

In this work, boehmite sol was prepared by a previously applied and validated method; hydrolysis of aluminum chloride hexa-hydrate. In order to obtain precise results**,** the effect of pH after adding precipitating agent, aging time, peptizing temperature and ultrasonic vibration time on the crystallite size of final precipitate were investigated in a narrow range. The preparation conditions applied in the production step of nanocrystalline boehmite affected on the desired alumina phase. Experiments were set based on the statistical design of experiments (Taguchi method). Furthermore the influence of calcination on crystallization and phase transformation of the precipitate was investigated using X-ray diffractometry (XRD) and simultaneous thermal analysis (STA) techniques**.** To evaluate the results, the obtained data were statistically analyzed. Considering the statistical analysis of experiments, the pH after adding precipitating agent is the major parameter affecting crystallite size. In contrast, aging time has the smallest effect on the crystallite size. In addition, Transmission electron microscopy (TEM) of the samples revealed that the particle size of the powders was well distributed in the nano-size range. Taguchi prediction on the crystallite size was 2.096±0.139 nm (with confidence interval of 95%) which confirmed by a verification experiment (2.064 nm).

Keywords: *Boehmite; γ-alumina; precipitation; aging time; ultrasonic vibration; Experimental design*

1. Introduction

Gamma alumina is one of technological important materials in industrial applications. It is widely used as absorbent, catalyst supports and catalysts in form of nanopowder or thin-film coatings due to high specific surface area [1-4]. Common methods to prepare γ-alumina nanopowders are mechanical synthesis [5], vapor phase reaction [6], precipitation [7], combustion [8], and sol-gel [9] methods. Precipitation is a simple and fast chemical route which is used for synthesis of γ-alumina nanopowders. Aluminum oxide–hydroxide, γ-AlOOH, (Boehmite) is considered as the starting material for the preparation of γ-alumina. Dehydration of γ-boehmite to form γ-alumina involves short-range rearrangements of atoms only in the crystal structure. The temperatures at which they are formed are variable and depend on the crystallinity of the γ-boehmite precursor as well as on the thermal treatment conditions. It has been known that morphology and crystalline size of the γ-alumina are very much sensitive to characteristics of boehmite and boehmite crystallinity that later is known to be related to preparation conditions [10]. The most

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common raw materials for synthesis of boehmite are aluminum alkoxide, aluminum nitrate and aluminum chloride [11, 12]. The last precursor has some advantages such as low cost, non-flammability, and non-toxicity [13]. In preparation of the γ-alumina nanopowders by precipitation method using $AlCl_3.6H_2O$ as precursor, the most important preparation parameters are $AlCl_3/H_2O$ ratio, pH of the solution after adding precipitating agent (ammonia or NaOH), HNO_3 to solution volume ratio, peptizing temperature, and aging time. Many studies have been made on preparation of γ-alumina nanopowders by precipitation method [14]. However, most of these studies have not investigated the effects of some parameters such as pH, peptizing temperature and aging time simultaneously on the crystalline size and mean size of the prepared γ-alumina nanopowders.

In this work, the precipitation method was used to prepare γ-alumina nanopowder using $AlCl_3.6H_2O$ in water with possibility to obtain precipitate [15]. The main objectives of this research were to investigate the effect of pH after adding precipitating agent, peptizing temperature, and aging time on the crystallite size of the prepared γ-alumina. Furthermore, the ultrasonic vibration of boehmite sol was employed in the preparation procedure, and the effects of ultrasonic vibration time on the crystallite size of the prepared γ-alumina were investigated. To study the effects of these parameters on the crystallite size of the obtained γ-alumina, experiments were set based on the statistical design of experiments (DOE). The data obtained from the experiments were then statistically analyzed. X-ray diffractometry (XRD) technique with CuKα radiation was used to determine formations of γ-boehmite, γ-alumina and crystalline size. The desired calcination temperature was selected according to simultaneous thermal analysis (STA). Finally, the nanostructure of the obtained nanopowder was studied by transmission electron microscopy (TEM). To the best of authors' knowledge the effects of aforementioned parameters have not been studied systematically and precisely on the crystallite size by the other researchers. This study deals with the application of experimental design method to investigate the effect of process parameters on the crystallite size distribution in a narrow range.

2. Materials and methods

2.1. Nanopowder synthesis

Aluminum chloride hexa-hydrate (Merck) was used as starting material. Ammonia solution (25% wt) as a precipitating agent and nitric acid (65% wt) as a peptizing agent were used from Merck Chemical Co.

Table 1
Controlling factors and their levels including L_9 (3^4)

Factors				
Level	pH	Aging time (hr)	Peptizing temp.(°C)	Ultrasound time (min)
1	9.0	24	30	0
2	8.5	48	45	5
3	8.0	72	60	10
Exp. No	pH	Aging time (hr)	Peptizing temp.(°C)	Ultrasound time (min)
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

standard octagonal array

The precipitate was filtered and washed with distilled water to remove the chloride ions. The obtained precipitate was dispersed in distilled water. To study the effects of aging time, the suspension was kept at room temperature for given time in Table 1. Then it was heated at 80°C for 3 h. After reaching the temperature of suspension to the ambient temperature; the precipitate was peptized at mentioned temperature in Table 1 and pH of about 3.0 by addition of diluted nitric acid solution (0.3% wt) to obtain a boehmite stable sol in the end of peptizing. To study the effect of ultrasonic vibration on the crystallite size of the prepared nanopowder, the boehmite sol was placed in ultrasonic bath (Power Sonic 405, Korea) for the given time in Table 1. After aging, solution was dried at 100°C for 24 h. The prepared powder was calcined at 550 °C for 2 h.

2.2 Experiment design

Influence of different process parameters on the crystallite size were investigated using design of experiment method. As the time and financial constraints play important role in experimental work, before conducting the experiments, appropriate levels for the input factors are needed. In this study, the input factors and corresponded levels are shown in Table 1. According to previous studies [16, 17] the appropriate levels were chosen. According to full factorial design, for a set of four factors with three levels, normally, 3^4=81 experiments needed to be conducted. A robust experimental design (here Taguchi method) was applied due to the large number of experiments resulting from many parameters which needed to be optimized. According to the Taguchi method an orthogonal array of L9 (Table 1) was used. Resulting only nine experiments can be replaced with 81 experiments. The Taguchi method is a combination of statistical and mathematical techniques that can be used to determine the conditions of experiment and obtain an optimum condition. In addition, the variability of conditions can be introduced using the signal to noise (S/N) ratio. In this way, the experimental condition having the minimum S/N ratio is considered as the optimal condition. Moreover, in order to decide whether the effect of the input factors is significant the statistical analysis of variance (ANOVA) was used.

2.3. Sample characterization

X-ray diffractometry technique with CuKα radiation (Siemens, D-500, Germany) was performed for structure analysis. Line broadening of XRD peaks is also used for crystalline size determination. Differential thermal analysis (DTA) and thermogravimetry analysis (TGA) were used with a rate of 10°C/min with the STA PL-1640 equipment. The experiments were conducted under air atmosphere up to 1200 °C for both DTA and TGA. The mean particle size and size distribution of the boehmite sols were determined by particle size analyzer, using a nanosizer (SYMPATEC, NANOPHOX, Germany). The morphology of prepared γ-alumina nanopowder was observed using TEM (Philips, CM-120). In this regard, the prepared nanopowders were dispersed in about 3mL ethanol. One droplet of the dispersed nanopowder solution was then dripped onto copper grid where the sample was dried at room temperature before TEM analysis.

3. Results and discussion

Alumina has been attributed to the following phenomena: (a) precipitation reaction in which $AlCl_3$ reacts with ammonia and produces aluminum hydroxide, (b) aging step in which $Al(OH)_3$ converts to γ-boehmite, (c) calcination in which γ-boehmite transformed to γ-alumina [13].

3.1. TGA and DTA analysis

Figure 1 presents TG and DTA curves of the dried γ-boehmite powder. TG curve illustrates three main areas within the measured temperature range.

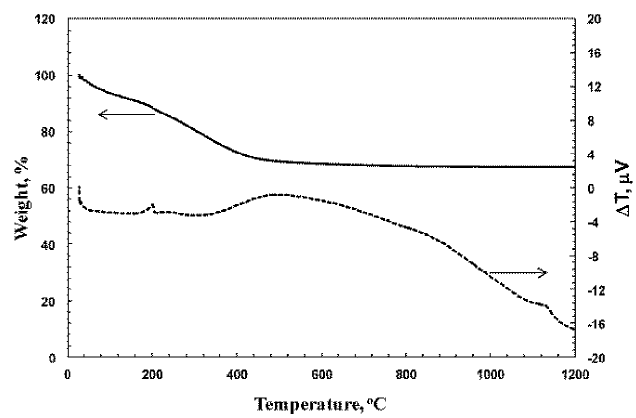

Fig. 1. DTA and TG curves of the γ-boehmite

In the first area from 25 to 180°C about 9% weight loss is observed that has been attributed to desorption of adsorbed water. The second area is from 180 to 550°C where the weight loss is 24% is due to transition the boehmite to γ- alumina. There is no significant weight loss in the third area from 550 to 1200°C. The total weight loss of 33% in the precipitant after calcinations is in agreement with the reported data by hassanzadeh-Tabrizi and Taheri-Nassaj [13]. DTA curve in Figure 1 shows small endothermic peak at about 301°C that corresponds to endothermic heat transition γ- boehmite to γ-alumina. It can be also seen from DTA curve that transformation begins at about 252°C.

3.2. XRD analysis

The XRD pattern of the precipitate sample (Boehmite) and calcinated precipitate samples of Table 1 are shown in Figure 2.
Comparison of XRD pattern of the precipitate and calcinated samples to JCPDS Card 21-1307 and JCPDS Card 10-0425 revealed that precipitate was boehmite which after calcinations transformed to γ-alumina. The average crystallite size was estimated from the corresponded peak (020) (by Debye-Scherrer equation) [18] and presented in Table 2.

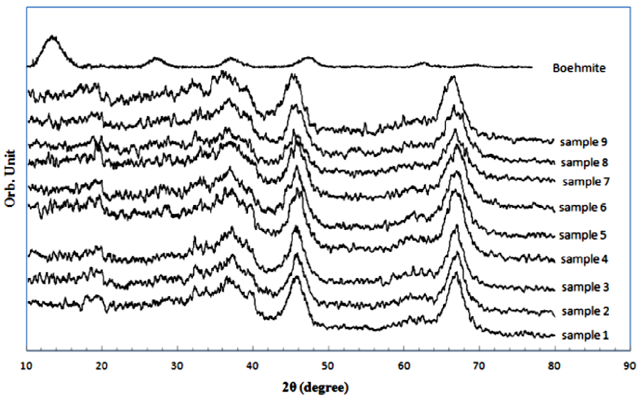

Fig. 2. The XRD patterns of boehmite and γ -alumina samples

As it is seen, the average crystallite size of boehmite and γ-alumina samples are less than 3 nm and 4 nm, respectively. Furtheremore, The (440) peak of γ-alumina has a stronger intensity than the (400) peak, indicating that the (440) planes may be the preferential growth direction. On the other hand, boehmite has provided more intense peaks compared to γ-alumina samples. In the following, the results of statistical analysis of the given experimental data in Table 2 are presented.

3.3 Effect of process parameters on the crystallite size

Table 2 presents the mean measured crystallite size of samples. In this section, the S/N ratio type S (the smaller, the better) was chosen for minimizing the crystallite size of samples:

$$\frac{S}{N_s} = -10\, Log1/n(\sum y_i^2) \qquad (1)$$

Where, S/N is defined as the signal/noise ratio, y_i is the characteristic property, and n is the number of repetition in each experiment.

Exp. No.	Reading 1	Reading 2	Mean ± SD	S/N_s
1	2.89	2.73	2.810 ± 0.113	-8.978
2	2.34	2.45	2.395 ± 0.078	-7.589
3	2.97	2.77	2.870 ± 0.141	-9.163
4	2.73	2.63	2.680 ± 0.071	-8.565
5	2.03	2.23	2.130 ± 0.141	-6.576
6	2.51	2.75	2.630 ± 0.170	-8.409
7	2.72	2.80	2.760 ± 0.057	-8.820
8	3.46	3.49	3.475 ± 0.021	-10.82
9	2.98	2.90	2.940 ± 0.057	-9.368

Table 2
Experimental data (responses) and sample statistics for the crystallite size

Effects of different process parameters on the crystallite size of samples are also illustrated in Figure 3 which is explained in detail as following.

3.3.1. Effect of pH after adding the precipitating agent

The behavior of crystallite size of samples is complex in different levels of pH. The data reported in Table 2 was statically analyzed leading to the minimum size correspond to the largest surface area of γ-alumina nanopowders. Figure 3 shows mean of S/N ratios for the crystallite size of γ-alumina nanopowders versus levels of input parameters using Taguchi method. As it is seen, increasing pH from 8 to 8.5 leads to the decrease of the crystallite size of γ-alumina, while increasing pH from 8.5 to 9 increases the crystallite size. Okado *et al* [19] have reported that the crystallite size of the boehmite increased almost linearly with increasing pH.

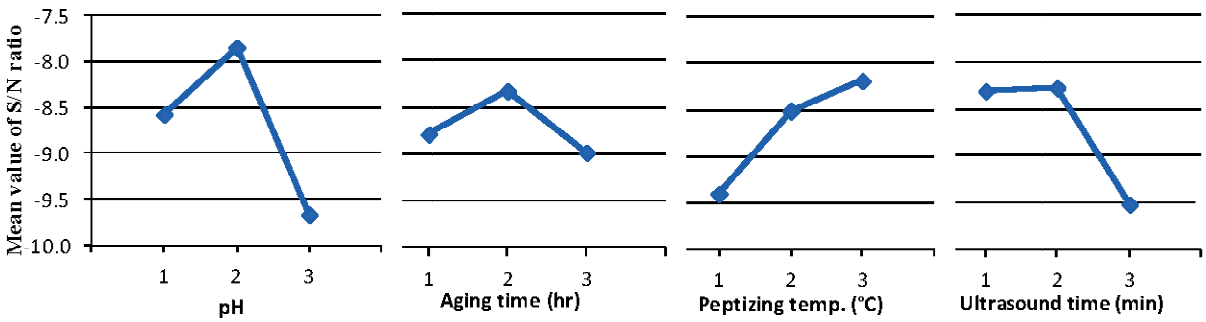

Fig. 3. Mean of S/N ratios for the crystallite size of samples versus levels of input parameters using Taguchi method.

This permanent increase is caused by enhancement of grain growth by a dissolution–reprecipitation mechanism during aging due to the increased solubility of boehmite with increasing solution pH. However, with increasing pH from 8 to 9, specific surface area decreases due to the agglomeration of boehmite particles. The results of ANOVA for the crystallite size of samples (Table 3) show that the crystallite size of samples is highly affected by pH after adding precipitating agent (43.367%).

Table 3
Analysis of ANOVA for the crystallite size

Factors	DOF	Sum of Sqrs.	Variance	F-Ratio	P (%)
pH	2	1.027	0.513	46.385	43.367
Aging time (hr)	2	0.065	0.032	2.937	1.85
Peptizing temp.(°C)	2	0.491	0.245	22.164	20.223
Ultrasound time (min)	2	0.635	0.317	28.665	26.435
Error	9	0.099	0.011	--	8.125
Total	17	2.319	--	--	100

3.3.2. Effect of aging time

The effect of aging time of the precipitate on the crystallite size of γ-alumina is shown in Figure 3. These results were obtained according to statistical analysis performed on the presented data in Table 2. The results show that increasing aging time from 24 to 48 h leads to the decrease of the crystallite size of γ-alumina, while further increasing in the aging time from 48 to 72 h increases of the crystallite size. The results of ANOVA for the crystallite size of samples (Table 3) show that aging time has least influence on the crystallite size of samples (1.85%). According to Table 4, the optimal condition on the crystallite size is obtained at aging time = 48h. Some researchers [19, 20] have reported that the crystallite size of the boehmite always increases with increasing aging time.

3.3.3 Effect of peptizing temperature

Figure 3 demonstrates the effect of peptizing temperature on the crystallite size of γ-alumina. As it is seen, the crystallite size decreases with increasing peptizing temperature. No results about this parameter have been observed in open literatures. It seems that peptizing temperature increases causes partly dissolution of bohemite precipitant. The results of ANOVA for the crystallite size of samples (Table 3) show that peptizing temperature (20.223%) is other important factor affecting on the crystallite size.

3.3.4. Effect of ultrasonic vibration time

The effect of ultrasonic vibration time of boehmite sol on the crystallite size of γ-alumina is shown in Figure 3. The results represent that the crystallite size of γ-alumina overlay increases with increasing time of ultrasonic time. The similar results were not found in this issue but it has been confirmed for synthesized ZnO nanoparticles by [21].

Analyzing the experimental results illustrated in Table 3 reveals the most effective parameters on the crystallite size of γ-alumina. The results show that pH affects the crystallite size more than any other studied parameters.

According to analysis of ANOVA it is expected that optimum conditions of the four aforementioned factors with corresponding levels presented in Table 4 cause to decrease the crystallite size to 2.096 nm. In addition, one confirmation experiment is conducted and the crystallite size of samples of 2.064 nm is obtained for this sample (Table 4).

Table 4
Optimal setting and corresponding verification experiment for the crystallite size

Optimal setting		Prediction of Taguchi	Confidence interval (95%)	Verification Exp. (mean)
Factors	Level			
pH	8.5			
Aging time (hr)	48	2.096	± 0.139	2.064
Peptizing temp.(°C)	60			
Ultrasound time (min)	5			

Owing to the confidence interval (95%) achieved, the verification experiment is in good agreement with Taguchi predictions (2.096±0.139). Figure 4 shows the average size and size distribution of a Boehmite sol, obtained by nanosizer. The average size of the particles in sol was found 80 nm with a narrow size distribution.

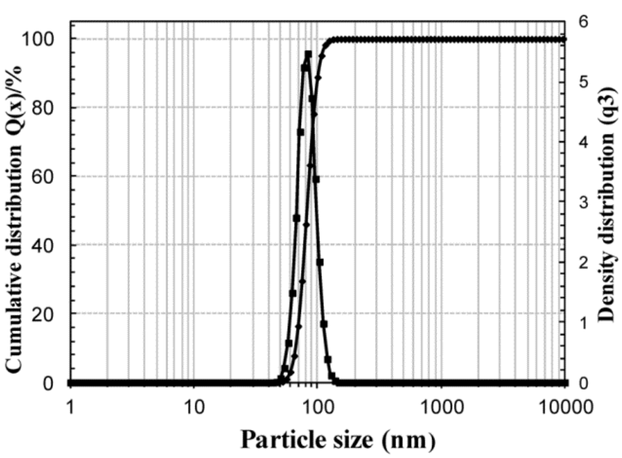

Fig. 4. The particle size distribution of prepared boehmite sol

This represents that boehmite nanoparticles in sol aggregate while the average crystallite size of boehmite at 100 ^{o}C (as crystalline phase in the dried precipitate) was estimated about 2.74 nm based on Figure 2.

TEM micrograph of calcined sample 1 at 550^{o}C (γ-alumina) has been presented in Figure 5.

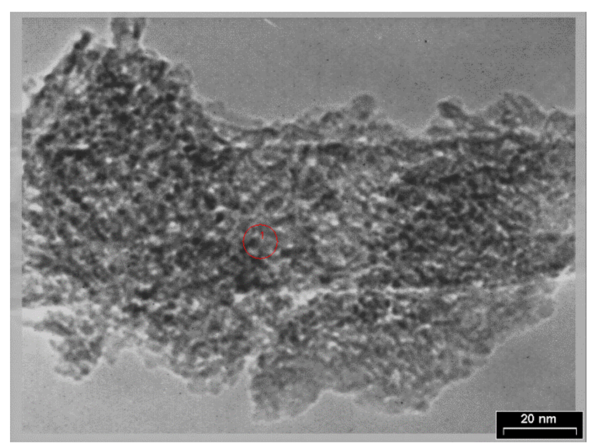

Fig. 5. TEM images of the γ- Alumina nanoparticles

The Figure clearly shows that the shape of nanopowder does not look precisely spherical. The size of nanopowder based on TEM analysis was smaller than 5 nm. Furthermore, uncontrolled aggregation of nanoparticles during precipitation and calcinations caused the formation of agglomerates.

4. Conclusions

Aluminum hydrate was synthesized by the precipitation method from inexpensive materials such as an inorganic aluminum salts. The absorbed water was evaporated at 100°C and powder was dehydrated (conversion of boehmite into gamma alumina) at 550°C. The calculated Boehmite and gamma alumina crystallite sizes were found to be less than 4 nm. The Nano-sized Al_2O_3 particles were prepared with an average size of 2.74 nm from low cost $AlCl_3.6H_2O$ via an economical precipitation method. In addition, the total weight loss of 33% was obtained in the precipitate after heat treatment due to removal of water. To evaluate the results, the obtained data were statistically analyzed. Considering the statistical analysis of experiments, the pH after adding precipitating agent is the major parameter affecting crystallite size. In contrast, aging time has the smallest effect on the crystallite size. In preparing boehmite, pH after adding precipitating agent and ultrasonic vibration time contribute to compose of smaller γ- alumina nanoparticles.

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