EFFECTS OF SOLVENT ON TEXTURAL PROPERTIES OF $\gamma$-ALUMINA NANOPARTICLES


S.M. Siahpoosh  
Materials and Energy Research Center (MERC), Karaj-Iran  
sm.siyahpoush@merc.ac.ir

E. Salahi*  
Materials and Energy Research Center (MERC), Karaj-Iran  
e-salahi@merc.ac.ir

F. Alikhani Hessari  
Materials and Energy Research Center (MERC), Karaj-Iran  
f-a-hesari@merc.ac.ir

I. Mobasherpour  
Materials and Energy Research Center (MERC), Karaj-Iran  
i.mobasherpour@merc.ac.ir

Abstract. In the current study, $\gamma$-alumina nanoparticles with high surface area was prepared using sol–gel method in the presence of aluminum isopropoxide as an aluminum precursor and 1-butanol, tert-butanol and 2-propanol as solvent. The effects of solvent type on textural properties of the as-received and heat treated $\gamma$-alumina were investigated.

The uncalcined material was characterized by simultaneous thermal analysis method. The calcined $\gamma$-alumina nanoparticles were characterized using X-ray diffractometer, scanning electron microscope and nitrogen adsorption-desorption techniques.

Keywords: $\gamma$-alumina, nanoparticles, textural properties.
1. INTRODUCTION

Powder preparation is a great important step in ceramic processing (Masuda et al., 2006). Non-traditional methods have advantages and disadvantages according to their nature. They are divided into three main classes consist of solution, vapor phase and salt decomposition.

Traditional alumina preparation, possess relatively low surface area (less than 200 m²/g) and broad pore size distribution, which limit their catalytic applications. Despite of the presence of many researches about the synthesis of mesoporous γ-alumina, it is still a challenge to develop a facile and surfactant-free solution route for the preparation of these materials using non-traditional methods.

The usefulness of γ-alumina relies on its favorable combination of physical and textural properties, thermal properties and chemical properties (Huang et al., 2014). Pore structural properties are among the most important, since high surface area and large pore volume enable higher loading of active catalytic phases.

Properties of alumina are largely dependent on properties of boehmite, so to obtain expected alumina materials, many efforts have been done to preparation of boehmite with different morphologies and microstructures.

GAO Jian-feng et al. and Shen et al. using the precursor of aluminum nitrate and in another research D. Ma et al. using aluminum chloride precursor, produced boehmite and γ-alumina nanoparticles through hydrothermal method, the main limitation of them is the lack of high purity powder. J. Mullens et al. prepared boehmite and γ-alumina platy nanoparticles with the same method, using aluminum alkoxide precursor and achieved particles with high purity and low levels of agglomeration in the range of 30-80 nm. In another study Y. Zhai examined making the γ-alumina by ethanol precipitation, results indicated that ethanol would prevent from creation of agglomerates in the deposition.

H.Y. Zhu et al. synthesized γ-alumina nanofibres from aluminium hydrate colloids. Shen et al. developed a simple solid-phase method for the synthesis of high quality γ-alumina nanorods. M. Ma et al. and Y. Zhu et al. prepared γ-alumina powder as a bundle-like and rod-like morphology, respectively, using solvothermal method and with the precursor of aluminum chloride. Fajardo et al. and Haung et al. prepared mesoporous alumina spheres and γ-alumina membranes using sol-gel method, respectively. Vallet-Regi et al. used the spray pyrolysis method and Károly and Szépvölgyi used thermal plasma to obtain hollow alumina spheres with diameter less than 100 μm.

Chatterjee et al. illustrated crystallization of γ-Al₂O₃ at 378°C and crystallization of chain-like pure α-Al₂O₃ with low surface area at 800°C by the sol-emulsion-gel method under simultaneous mechanical agitation. Zeng et al. produced mesoporous alumina, with high specific surface area using the precursor of tri-sec-butoxide aluminum. By the similar raw material, Valente et al. produced γ-alumina and Ki-Won Jun et al. prepared the γ-alumina activated by silica and Woodfield et al. synthesized the mesoporous γ-alumina. Also, Dabbagh et al. used the alanine amino acid for the first time as a gel maker to prepare γ-alumina. Fernandes et al. and Sasani et al. to reduce the cost of raw materials, prepared mesoporous γ-alumina with sol-gel method using aluminum nitrate and aluminum chloride mineral salts, respectively, which are inexpensive precursors, but the relatively high and useful specific surface area for the adsorption process was not found. Rezaei et al. produced γ-alumina with sucrose surfactants and showed increasing of specific surface area and particle size reduction of resulted γ-alumina. However, Liu et al. did not use surfactants due to thermal instability, environmental risks and high price in the preparation of γ-alumina.

According to the researches, final product of sol-gel method has high purity and surface energy and way of process doing and achieve to small size of particles are controllable due to using solution conditions and low temperature of heat treatment (Brinker & Scherer, 1989). On the other hand, even though aluminum isopropoxide precursor is not completely soluble in ethanol (Lepot et al., 2008), but it is the most commonly used solvent to preparation of γ-alumina nanoparticles via sol-gel method and the effect of other solvents on the textural and morphological properties of prepared γ-alumina in presence of this precursor and acidic catalyst has not been studied thoroughly.

In the present study, it is focused on γ-alumina nanoparticles preparation based on sol-gel method at low temperature with specific surface area higher than 300 m²/g, high pore volume and well defined narrow pore size distribution for heavy metals adsorption. The different solvents effects were also investigated on the textural and structural properties of synthesized γ-alumina. This work was also emphasized on using
almost cheap raw materials with accepted level of purity.

2. EXPERIMENTAL PROCEDURES

2.1. STARTING MATERIALS

Preparation of the good quality γ-alumina nanoparticles was done by sol–gel method from almost cheaper raw materials without environmental pollution which has a high purity. Aluminum isopropoxide alkoxide as aluminum precursor instead of aluminum inorganic salt will produce γ-alumina powder with a higher specific surface area. On the other hand, this material is cheaper and easily available rather than many other alkoxides including tri-sec-butoxide aluminum. Aluminum isopropoxide (AIP, MERCK Art. No. 801079), 1-butanol (MERCK Art. No. 988), tert-butoxide (MERCK Art. No. 822264), 2-propanol (MERCK Art. No. 995) and acetic acid (AA, MERCK Art. No. 62) were used as starting materials. In all the preparation stages, distilled water was used. All materials were of analytical grade reagents and used as received without further purification. All glassware was cleaned with nitric acid, rinsed thoroughly and dried before use.

2.2. SYNTHESIS OF γ-ALUMINA

All experiments were conducted under air atmosphere. Aluminum isopropoxide was used as aluminum precursor, acetic acid as hydrolysis rate controller and 1-butanol, tert-butoxide and 2-propanol as solvent, during synthesis. The weight ratios of reactants AIP: Solvent, AIP: H₂O, and AIP: AA were 1:60, 1:1, and 40:1, respectively. Initially, 3g (15 mmol) of AIP was separately dissolved in 222ml (2/43 mol), 230/8ml (2/43 mol) and 229ml (2/99 mol) of 1-butanol, tert-butoxide and 2-propanol, to 0.068, 0.065 and 0.066 molar AIP solution was prepared, respectively, under continuous and vigorous magnetic stirring at room temperature for 3h until all AIP particles dissolved. Then, the mixture of 0.07ml (1 mmol) acetic acid and 3ml (166 mmol) distilled water was added to the above solution using a burette to drop-wise. The solution was magnetically stirred for 3h for completion of hydrolysis. In all time of reaction, solution was stirred at 150rpm to form a uniform product. For completion, the final solution was placed in a glass vessel at room temperature for 24h to formation of gel material. Finally, the gel was dried in an oven at 120°C for 6h and calcined in a flow of air. Obtained white dry gel, were pulverized and passed through a 70-mesh sieve.

Heat treatment for powder calcination was took place in a normal environment, using a laboratory chamber furnace which equipped with thermal string of silicon carbide and the ability to reach 1500°C maximum temperature. The samples were poured in an alumina crucible and were heated to 600°C with ramp rate of 2°C/min and were maintained in that temperature for 6h, so that γ-alumina white powder obtained after slow and gradual cooling in the furnace. In the present study, the samples were labeled as Ab, At and Ap where A represents alumina and b, t and p, represent the 1-butanol, tert-butoxide and 2-propanol solvent, respectively.

Reactivity of precursors depends on the chemical properties of them (Burgos & Langlet, 1999). Aluminum isopropoxide is sensitive to moisture and even air moisture is sufficient for the start of hydrolysis reaction. The performed final reaction at low temperature (25°C) is shown in follow:

\[
\text{Al}(\text{OR})_3 + 2\text{H}_2\text{O} \rightarrow \text{AlO(OH)} + 3\text{R(OH)}
\]

In this reaction, R is the propyl group (C₃H₇). Accordingly, the hydrolysis reaction is done completely, due to high water content and high tendency of the aluminum isopropoxide to reaction with water. In this research, using of aluminum isopropoxide precursor in solution, propylene glycol is formed as a by-product of the reaction as expected. But this compound is decomposed and came out of the system during calcination of prepared powder; without undesirable effects on the final product.

2.3. CHARACTERIZATION

2.3.1. DIFFERENTIAL THERMAL AND THERMOGRAVIMETRIC ANALYSIS (DTA/TGA)

To discover the various decomposition steps occurring in the as-dried precursor as a function of temperature and to determine the proper temperature of the calcination process of the dried sample used of the differential thermal and thermogravimetric analysis instrument (BÄHR, STA-503, Germany). It is important to determine this temperature; for the less, it is obtained lower degree of γ-alumina crystallinity so lower particle size and greater specific surface area would be achieved. As well as increasing calcination temperature allows arising the other impurity phases in the samples. For this experiment, approximately 9.93 mg of uncalcined boehmite precursor was loaded onto an alumina pan and is heated along with commercial alumina as the reference material, from room temperature to 1200°C.
under the air atmosphere with a temperature ramp of 10°C/min until no weight loss occurred.

2.3.2. X-RAY DIFFRERENTIATION (XRD)

Phase identification of the commercial and prepared samples and crystallinity of them was done by X-ray diffraction using Siemens D-500, semi-automatic, at room temperature with CuKα radiation (λ = 1.5404 Å). The samples diffraction intensity is measured in the Bragg angle (2θ) range between 20-80°, 1 second residence time per step and 0.02 degrees of step size for each point. The data are collected with sample rotation. It is noteworthy that CuKα radiation was obtained from a copper X-ray tube operated at 30 kV and 25 mA. Obtained phase were identified by comparing the diffraction angle of XRD peaks with the corresponding intensity values in the ASTM cards and PANalytical X'pert High Score Plus software, 2.2b version by 2006-11-01 release date. The full width at half maximum (FWHM) is determined accurately after correcting for instrument broadening and the particle size is then estimated by using Scherer equation in nanometer (Cullity & Stock, 2001):

\[
D_{\text{XRD}} = \frac{0.94\lambda}{\beta \cos \theta} \tag{1}
\]

Where, \( \lambda \) is the wavelength of the incident radiation, \( \beta \) is the full width of diffraction peak at half maximum intensity (FWHM) and \( \theta \) is the diffraction angle. This equation can be used when the crystalline particle size is less than 1000 Å. Calculated particle size using this method is estimated and applying the correct ratio can be improved the accuracy of this method. In order to determine the particle size, the peaks of the samples with the maximum intensity were used, due to they have the clear and appropriate separation than the others peaks. Distance values between the crystal plates have been calculated by the equation (2), known as Bragg's law.

\[
n\lambda = 2dsin\theta \tag{2}
\]

2.3.3. NITROGEN GAS ADSORPTION/DESORPTION

The specific surface area, the total pore volume, the average and distribution of pore diameter of the calcined samples were measured using a nitrogen gas adsorption/desorption isotherm from the curve data at liquid nitrogen temperature (77.4 K), using a Belsorp instrument (mini-II version). The pore volumes were determined at a relative pressure P/Po = 0.99. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation, at P/P0 range between 0.05-0.35. It should be noted that P is partial pressure in the adsorbed gas in equilibrium at 77.4 K by Pascal, and Po is the partial pressure in the absorbed gas in experimental conditions by Pascal. Pore size distributions of the samples obtained employing the Barrett-Joyner-Hatenda (BJH) model (N2 gas adsorption on silica as reference). The as-prepared samples were degassed at 150°C in a vacuum flow for 12 h to remove the water and any impurities physisorbed on the solid surface. In this test, adsorption is usually expressed by the isotherms which are equivalent to the amount of adsorbed material on the surface of the absorbent (Lowell & Shields, 1984). The contrary, desorption isotherms are obtained by measuring the amount of desorbed gas. Isotherms of I, II and III type is usually reversible, but I type could have a hysteresis loop. The hysteresis loop also can be seen in the type of IV and V. The hysteresis loop indicates on the presence of mesopores in the material and helps to achieve some information about the geometry of the pores. Assuming sphericity and same size of the particles, the measured specific surface area for samples in crystallite forms were converted to equivalent particle size according to the equation (3) (Hosseini et al., 2011):

\[
D_{\text{BET}} = \frac{6000}{\rho S_{\text{BET}}} \tag{3}
\]

Where, \( D_{\text{BET}} \) is the average particle size by nm, \( S_{\text{BET}} \) is the specific surface area expressed in m²/g and \( \rho \) is the theoretical density expressed in g/cm³.

2.3.4. SCANNING ELECTRON MICROSCOPY (SEM)

The SEM images were obtained with a CAMBRIDGE-S360 scanning microscope operated at an acceleration voltage of 20 kV and were used to study the surface of the adsorbent. To prototyping, powder samples were suspended in acetone to form a dilute suspension. One to two drops of the suspension, that its container was in the ultrasonic device, were dropped on clean glassy plates. After drying, the plates were used to produce microscopic images.

3. RESULTS AND DISCUSSION

3.1. THERMAL ANALYSIS

DTA/TGA profiles for alumina precursors provide insights into the phase transition from boehmite to γ-alumina. The DTA/TGA curves of as-dried boehmite precursor according to presence of tert-butanol as solvent and acetic acid as hydrolysis controller, during processing are shown in figure 1.
The DTA curve presents three major peaks among which two of them are endothermic and the main peak is exothermic. In light of the as-dried boehmite precursor TGA curve, it seems that there are three stages of decomposition reaction with a total weight loss of ~45%. The initial stage corresponds to an endothermic weight loss of ~20% which is attributable to the removal of physically adsorbed water and residual moisture from room temperature to 200°C. The second weight loss, between 200°C to 500°C is an exothermic process that occurred due to the decomposition of organics including adsorbed acetic acid and the removal of chemically adsorbed water molecules. It should be noted that the decomposition temperature of acetic acid is about 440°C. The third stage comes with appearance of exothermic broad peak has been happened above 500°C which is attributable to a weight loss due to the crystallization of transition alumina, oxidation of organic volatile residues, elimination of OH groups and slow continuous dehydroxylation. The total weight loss in last two stages is ~25%. A continuously falling TGA curve suggests that a slow dehydroxylation reaction proceeds as a function of temperature. TGA curve is flat at temperatures of about 600°C and it can be seen no significant loss weight at higher temperatures, meaning that the organic residues have been removed completely and the sample has reached to a stable structure. Therefore, it is suitable to perform the calcination process at temperature of about 600°C.

According to the reaction, the calculated theoretical value for the ultimate weight loss of produced γ-alumina is 15% that is much less than of actual experimental weight loss. This indicates on the presence of significant amounts of alcohol molecules that are adsorbed physically or chemically on the surface of precursor and are removed with increasing the temperature. It should be noted that about 30% difference in the total weight loss is reducing by increasing of carbon chain length of used alcohol, which can be caused by reduction of the tendency to hydrogen bonding of alcohol with larger chains.

According to the data reported by Valente et al. and Woodfield et al., the transition from boehmite to γ-alumina takes place in the range of temperature 400–700°C; their results are in agreement with those reported in the thermal analysis of the present report, since the thermal treatment of the powder at 600°C led to the formation of γ-alumina.

3.2. X-RAY DIFFRACTION

The crystalline nature of prepared samples with aluminum isopropoxide in alcoholic solvents of 1-butanol, tert-butanol and 2-propanol was studied by X-ray diffraction. All prepared samples were calcined for 6h at 600°C in air. The results in high-angle diffraction being shown in figure 2. It can be found that the resulted pattern at high diffraction angles are nearly similar and the percentages of samples crystallinity do not differ significantly. The three main reflections of γ-Al2O3 phase are clearly observed as broad peaks according with JCPDS PDF No. 001-1308 at 2θ angles around 37°, 46°, and 66° which correspond to [311], [400] and [440] planes respectively, and indicate that transformations occurred from the boehmite phase to γ-Al2O3 after calcination. The observed diffraction peaks in the XRD patterns were broad, because the crystallites were very small. Such a size indicates to their partly weak crystalline nature in the prepared γ-alumina. It should be noted that no peak of other phases of alumina is recognizable in the diffraction pattern of prepared samples and γ-alumina phase is the only detectable phase.

The calculation was done based on Scherrer equation in the [440] planes with the most intensity of diffraction and 2θ angle value of 66° for prepared γ-alumina and the average crystallite size (Dx(2θ)) for Ab, At and Ap prepares powders was respectively 5.5, 5.4 and 5.6 nm which represents nanometer structure. The results imply that the average crystallite size of the prepared powder samples with different solvents is almost in the same range of about 5 nm.
Since the d-spacing can be considered a measure of the distance between layers in a crystal structure, the values calculated by the Bragg law for the above peaks of the prepared samples XRD patterns are 0.239 nm, 0.198 nm and 0.141 nm, respectively that indicates the decrease in this distance and thus reduce the structure lattice parameter with increasing X-ray diffraction angle.

![X-ray diffraction pattern at high angles](Image)

**Fig.2. X-ray diffraction pattern at high angles diffraction for prepared samples**

### 3.3. TEXTURAL PROPERTIES

Aluminum isopropoxide has been commonly used as a precursor in ethanol, deionized water or ethanol with a small amount of deionized water as solvent for preparation of sol-gel derived γ-alumina. In the previous studies the effect of various solvents on the morphological and textural properties of γ-alumina with this method, using this precursor and in the presence of an acid catalyst has not been studied thoroughly. Even though aluminum isopropoxide is not completely soluble in ethanol (Lepot et al., 2008), it is the most commonly used solvent for sol-gel derived γ-alumina, but was slightly more soluble in the other alcohols in study.

Textural properties consist of particles specific surface area, total pore volume and average pore diameter and also average particle size of the γ-alumina prepared with sol-gel method using aluminum isopropoxide in presence of mentioned solvents and acetic acid catalyst are presented in table 1.

**Table 1. Textural properties of prepared γ-alumina**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Specific surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
<th>Average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ab</td>
<td>343</td>
<td>0.887</td>
<td>10.35</td>
<td>5.46</td>
</tr>
<tr>
<td>At</td>
<td>351</td>
<td>1.09</td>
<td>12.43</td>
<td>5.34</td>
</tr>
<tr>
<td>Ap</td>
<td>339</td>
<td>1.29</td>
<td>15.27</td>
<td>5.53</td>
</tr>
</tbody>
</table>

It is noteworthy that maximum surface area of 351 m²/g is obtained when tert-butanol is used as solvent. This proves that textural properties are influenced by the type of used solvent and this sample has the smallest particle size between all samples.

The specific surface area in the sample is relatively higher than the γ-alumina via the sol-gel method in previous researches. Taghizadeh et al. synthesized boehmite from aluminium isopropoxide, nitric acid and distilled water and aged at 70°C for 5 hours and obtained γ-alumina after calcination of boehmite, where the maximum specific surface area was 248 m²/g. Meephoka et al. synthesized γ-alumina from a mixed solution of toluene and 1-butanol in aluminium isopropoxide that aged in an autoclave system at 300°C in the presence of N₂, and calcined at 600°C, where the maximum specific surface area was 226 m²/g.

The nitrogen adsorption/desorption isotherms of sol-gel derived samples are shown in figure 3. According to IUPAC classification, the obtained isotherm for Ab sample is characterized as IV type and for other samples are V type. Prepared samples isotherms have been extended in almost flat and stretched condition until reach high relative pressures, which is the characteristic of solids with meso porosity. In addition, the significant slope change occurs in the curve at high relative pressures of about P/Pₚ=0.9, which indicates presence of some macro pores in the structure of the sol-gel derived samples. The shape of the hysteresis loops can be correlated with the change in pore structure, which in this case can be a phase transformation from boehmite to γ-alumina with different morphologies (Lowell & Shields, 1984). In this study hysteresis loops for all prepared samples occurred at a relative pressure range of P/Pₚ=0.4-0.98. They are H1 type that adsorption and desorption branches have parallel mode completely, so the most of pores are in cylindrical shape. The porosity volume in the prepared samples is relatively higher than the previous researches (Hosseini et al., 2011) (Asencios & Sun-Kou, 2012) (Meephoka et al., 2008) is confirmed with the ultimate amount of absorbed nitrogen by the samples. So that amounts are more than 600 cm³/g for prepared samples, indicating presence of large volume pores.
Pore size distributions of prepared samples obtained employing the BJH model is shown in figure 4. They indicate on relatively narrow distribution of micro and mesopores with 1-10 nanometer sizes in Ab, At and Ap samples, which the peak maximum related to each one is seen in 2.7, 2.1 and 2.1 nm, respectively. It is noteworthy, based on done research a narrow pore size distribution in the range of 1-10 nm of interest for both adsorption and catalytic applications (Lowell & Shields, 1984). The obtained results indicate that Ab sample has narrower pore size distribution and smaller average pore diameter comparing with other prepared samples.
It is evident that by varying the used solvents in the process, γ-aluminas is provided with relatively high surface area, large pore volume and suitable pore size distribution which is desirable for heavy metal adsorption. The results show that the length of alkyl chain of used alcohol as solvent plays a key role in the formation of such architectures, so the pore diameter increases with increasing chain length of the alcohol (Lowell & Shields, 1984).

As a factor to reflect the partial sintering extent of the particles, ψ can be calculated by the equation (4) (Keshavarz et al., 2011):

$$\psi = \left( \frac{D_{\text{BET}}}{D_{\text{XRD}}} \right)^3$$  (4)

Accordingly, it can be found that in the samples prepared by sol-gel method, the average particle sizes determined via XRD analysis ($D_{\text{XRD}}$) and the particle sizes determined via BET data ($D_{\text{BET}}$) showed small discrepancies, so they have ψ value close to 1, indicating that the primary crystallites sintered a little. Therefore, the obtained results showed that the partial sintering of the prepared samples particles was lower in comparison with the commercial sample. Since the sintering value of commercial sample is high, it can be said that the commercial catalyst has been synthesized by a method nearly close to the precipitation method or thermal decomposition of boehmite.

### 3.4. MORPHOLOGY

Fig. 5 shows the SEM images of the prepared γ-Al₂O₃ samples with the same magnification. As shown, the samples have spongy structure and are composed of porous and homogenous aggregates with different sizes. The results are in accordance with the particle sizes of prepared γ-alumina which were estimated by XRD and BET data. According to this, At sample particles are smaller than Ab sample. As seen from the images that for Ab sample, crystal edges are sharper than that for At. This could be attributed to more crystallinity of it.

**Fig.4. BJH model of samples: a) Ab, b) At and c) Ap**

**Fig.5. SEM images of samples (×15,000): a) Ab and b) At**

### 4. CONCLUSION

The present study was successful in synthesizing porous γ-alumina nanoparticles by using a facile sol-gel process. Varying the used solvents in the process provided γ-aluminas with relatively high surface area,
large pore volume and suitable pore size distribution which are desirable for heavy metal adsorption. The optimum was reached for the At sample with tert-butanol solvent which has a specific surface area of 351 m²/g, a pore volume of 1.09 cm³/g and particle size of 5.34 nm. This work also shows that the properties of γ-alumina are greatly influenced by the solvent type and important insights on how control textural and structural properties of aluminas, are disclosed.

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