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Hydrothermal synthesis and characterization of nano-particles γ -Al₂O₃

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Abstract. The study of hydrothermal treatment on the phase formation and the crystallites of gamma-alumina (γ -Al₂O₃) was performed. Different reaction time and temperature of hydrothermal treatment were investigated. The preparation of γ -Al₂O₃ includes precipitation of aluminum nitrate nonahydrate by ammonia, aging, washing, transferred the gel into the hydrothermal reactor, drying, and calcination at 600 °C. The precipitation was stopped at pH equals 7.5. The reaction times of hydrothermal treatment were 1 – 2 hours, and the temperatures were 140 – 200 °C. X-Ray Diffraction analysis was used to investigate the phase formation and the particle size. The results show all the samples represented pure nano γ -Al₂O₃. The examination of hydrothermal treatment of γ -Al₂O₃ reveals as the reaction time longer, the crystallite grows bigger, as well as the higher temperature applied. The smallest γ -Al₂O₃ obtained based on the Scherrer equation is 4 nm and the biggest is 6.5 nm. Interestingly, the peaks of the γ -Al₂O₃ prepared by hydrothermal treatment at the longest time and the highest temperature have shifted into a higher diffraction angle. In the case of this sample, the peaks shifted into a higher diffraction angle. That is means there is a change in the lattice structure of γ -Al₂O₃ probably was affected by the lattice of hydroxyl content.

1. Introduction

Alumina, Al₂O₃, is a ceramic material used in across-the-board applications for adsorbents, abrasives, catalysts, and catalyst supports [1–7]. The extensive use of Al₂O₃ in heterogeneous catalysis has ascended since its high chemical and thermal stability as well as its desirable textural properties such as porosity, surface area, and acidity/basicity [3,4,8]. Alumina has many phases depend on the condition. The phase transformation of alumina is closely related to temperature [9–11]. The most stable phase is alpha-alumina (α -Al₂O₃) present at a temperature higher than 1100 °C. The highest specific surface area is gamma-alumina (γ -Al₂O₃) present at 400 – 600 °C. So that γ -Al₂O₃ is a metastable phase among alumina phases. Gamma-alumina is also frequently used as a support of heterogenous catalysts due to its high specific surface area, high thermal stability, and desirable acidity/basicity. It is also used widely as catalysts and adsorbents for chemical processes [2,12–19]. Commercially γ -Al₂O₃ has been prepared through precipitation and sol-gel route [1,2,8,9].

Nowadays the attention has shifted towards nanostructured materials since changing the morphology at the nanoscale can probably lead to materials with different physical and chemical properties, regardless of the widespread use of bulk γ -Al₂O₃ [2,9]. By controlling the morphology, it can lead to selective contact of support and metal so that different metal support interactions are observed [20–24].



These specific interactions can offer stability to metal nanoparticles. The surface properties of the nanoparticles also play an important role in their catalytic properties [19,25,26]. For instance, the surface area of TiO was closely related to a hydrothermal parameter such as filling factor, temperature, stirring, raw materials specific surface area, and reaction time [27]. The hydrothermal treatment also affected the total acidity, acidity distribution on γ -Al₂O₃. However the textural properties of the γ -Al₂O₃ like specific surface area prepared by hydrothermal treatment almost the same to those samples prepared by precipitation, as well as the pore volume of samples [28]. The hydrothermal treatment also affected the binding energy of Pt on γ -Al₂O₃ so that it increases the selectivity of propane dehydrogenation and its turn over frequency (TOF) [25].

To prepare nanoparticle different structure-direct-agent alike surfactant and others were used in the synthesis using either room temperature such as precipitation or hydrothermal treatment method under high temperature over 100 °C and high pressure by autoclave reactors [1,15,29]. In this present work, we prepared nanoparticle of γ -alumina by hydrothermal treatment compared with precipitation method. The samples crystallized well and the growth of diameter crystallize size was observed at hydrothermal treatment. Then we investigated the effect of crystallization temperature and reaction time under hydrothermal treatment. The prepared γ -alumina was characterized by X-Ray Diffraction (XRD) analysis.

2. Experimental

2.1. Preparation

Gamma-alumina (γ -Al₂O₃) was prepared from aluminum nitrate nano hydrate (Merck, 98.5% in wt.). All the chemicals were used as received without any further purification. Initially, aluminum nitrate nano hydrate was dissolved in water under vigorous stirring. The molar ratio of water to aluminum nitrate nano hydrate was equal to 1. An aqueous ammonia solution (Merck, 25% in wt.) was added dropwise until the pH of the supernatant was 7.5. After aging for 1 hour, the slurry was transferred into a hydrothermal reactor and it was treated at 140 – 200 °C for 1 – 2 hours. The white gel thus obtained was recovered by filtration and washed with deionized water. After drying overnight at 110 °C, the solid thus obtained was calcined in air at 600 °C for 6 h. As a reference, another γ -Al₂O₃ was prepared by precipitation method in the same way as the above without hydrothermal treatment.

2.2. Characterization

Powder X-Ray Diffraction (XRD) analysis was performed using monochromatic Cu K α radiation (PanAnalytical). The diameter crystallite sizes were calculated by the Scherrer equation.

3. Results and discussion

3.1. Peak intensity

Figure 1 shows the XRD pattern of γ -Al₂O₃ synthesized by precipitation (1a) and hydrothermal treatment (1b-d) after calcination at 600 °C, for 6 h. Three intense peaks were identified. According to US Patent US Patent No. US 2009/0104.108 1A, three peaks of typical γ -Al₂O₃ appeared at 38°, 45°, and 67° after calcined at 600 °C for 6 h [30]. According to Rahmanpour, the peaks of calcined γ -alumina at 550 °C for 4 h appeared at 37.8°, 45.7°, and 66.9° [2]. Moreover, the pattern was compared with Joint Committee on Powder Diffraction Standards (JCPDS) 29-0063 as supplied in the supporting information (see Figure S1) and it also showed three intense peaks at 38°, 45°, and 67° assigned to (3 1 1), (4 0 0), and (4 4 0) consecutively with the lattice is face-centered cubic (fcc). Therefore, the prepared material represents the single phase of γ -Al₂O₃ so that it was synthesized successfully via both precipitation and hydrothermal treatment.

Figure 1 also shows the effect of hydrothermal treatment on the diffraction peaks intensity. All γ -Al₂O₃ prepared by hydrothermal treatment (Figure 1 b-d) shows the diffraction peaks intensity higher than that prepared by precipitation. It also shows under hydrothermal treatment that as the temperature

increase, the diffraction peaks intensity increases as well as the reaction time. That figure shows that under hydrothermal treatment, the particles were recrystallized and it grew into bigger particles. It is also clear that the γ - Al_2O_3 under hydrothermal treatment has good crystallinity compared with that prepared by precipitation.

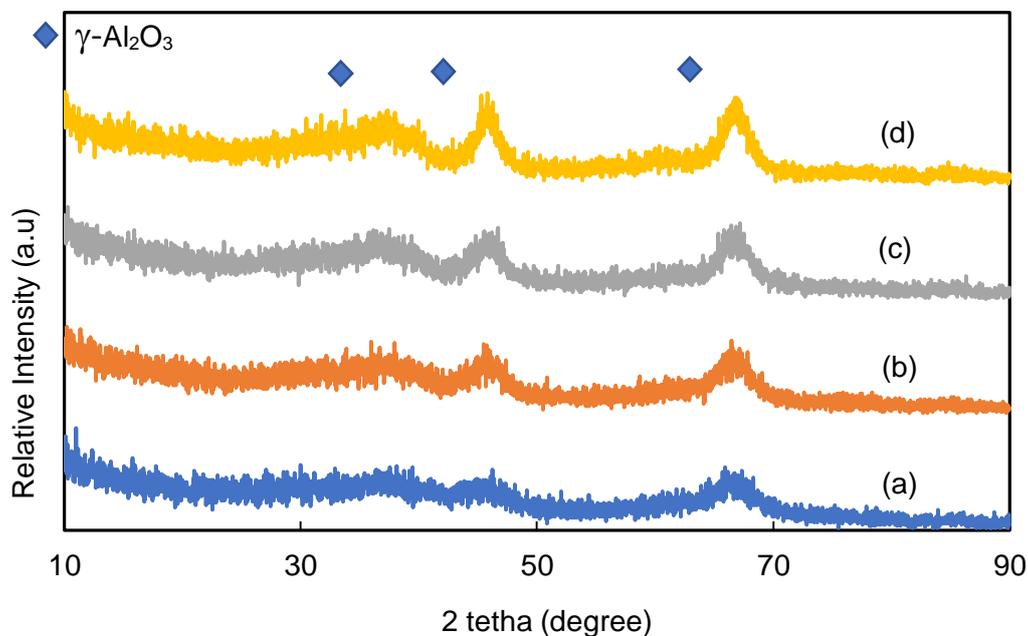


Figure 1. X-Ray Diffraction of γ - Al_2O_3 after calcination at 600 °C for 6 h for precipitation (a) and hydrothermal (b-d) at different conditions b) 140 °C for 1 h, c) 140 °C for 2 h, and d) 200 °C for 2 h.

3.2. Average crystallite size

The broadening of the peaks occurs in the γ -alumina prepared by precipitation as shown in Figure 1 (a). The hydrothermal treatment at 140 °C – 200 °C for 1 – 2 h leads to more matching of the (d) spacing and increase the intensity. That is means the crystallites grow bigger than that prepared by the precipitation method. To confirm the size of the diameter crystallite, Scherrer calculation was performed. The Scherrer equation was shown in equation 1 where D is the diameter crystallite, k is a dimensionless shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM), and θ is the Bragg angle.

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

Table 1. Diameter crystallite sizes of γ - Al_2O_3 after calcination at 600 °C for 6 h for precipitation (a) and hydrothermal (b-d) at different conditions b) 140 °C for 1 h, c) 140 °C for 2 h, and d) 200 °C for 2 h.

Identity	Sample	D (nm)
a	γ - Al_2O_3 - Precipitation	3.73
b	γ - Al_2O_3 - HT 140 °C, 1h	4.08
c	γ - Al_2O_3 - HT 140 °C, 2h	4.59
d	γ - Al_2O_3 - HT 200 °C, 2h	6.53

Table 1 shows the diameter of the crystallite size. It shows the crystallite sizes of samples prepared by hydrothermal treatment growth bigger than that prepared by precipitation. During hydrothermal treatment, the crystallite restructure. Jun-Cheng et. al showed the hydrothermal treatment of γ -Al₂O₃ for prolongation of the reaction time led to a decrease in the specific surface area which closely related to the overgrowth of the surface crystallites [28]. Based on the crystallite size, it could be inferred that the bigger crystallite size, the surface area probably also decreased. The specific surface area of samples at moderate hydrothermal conditions (140 °C, 1 – 2 h) is quite the same. However, the specific surface area at a high temperature (200 °C), even for moderate reaction time, is decreased.

3.3. Shifted peaks at a higher diffraction angle

Figure 2 shows the XRD of samples at 55 – 75 degrees. It clearly shows that at the moderate hydrothermal condition (140 °C, 1-2 h) the peaks quite the same with the sample prepared by precipitation. However, at the high temperature (200 °C) the peaks shifted into a higher diffraction angle. Compared with samples prepared by precipitation, the shifted peaks at hydrothermal treatment were observed for ZnS, ZnAl₂O₄, and BaTiO₃ [31–33]. Hayashi and Ebina showed that as the hydrothermal temperature increase, the peaks intensity of diffraction pattern increase and shifted, and the lattice hydroxyl content decreased thus, tetragonality might be closely related to the lattice hydroxyl content along with to the particle size [33]. A similar state probably applied to this sample that at the high-temperature hydrothermal treatment the peaks intensity increased and shifted so that the structure was affected by the lattice of hydroxyl content.

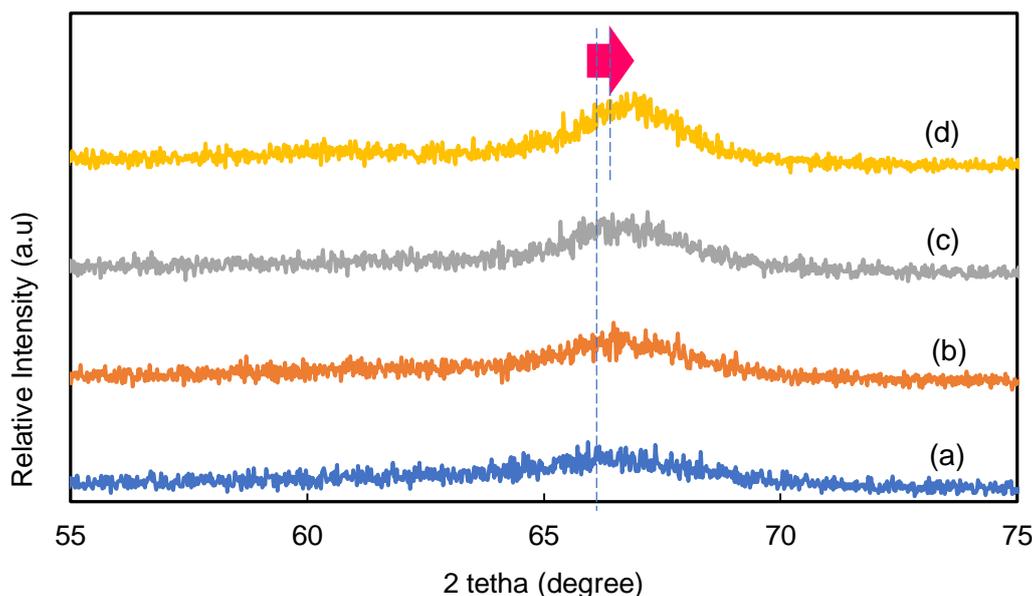


Figure 2. X-Ray Diffraction of γ -Al₂O₃ after calcination at 600 °C for 6 h for precipitation (a) and hydrothermal (b-d) at different conditions b) 140 °C for 1 h, c) 140 °C for 2 h, and d) 200 °C for 2 h.

4. Conclusion

Nanoparticles of γ -Al₂O₃ were successfully synthesized through hydrothermal treatment. The crystallites size diameter of γ -Al₂O₃ prepared by a hydrothermal treatment was bigger than those prepared by precipitation. They are 4 – 6.5 nm, in contrast to those prepared by precipitation (3.7 nm). The prolonged hydrothermal treatment time, as well as the higher temperature, the crystallites grow bigger. The shifted peaks into higher diffraction angle of γ -Al₂O₃ were observed on the 200 °C and 2 h of hydrothermal treatment indicating the crystal lattices were affected by the lattice of hydroxyl content.

5. Supporting information

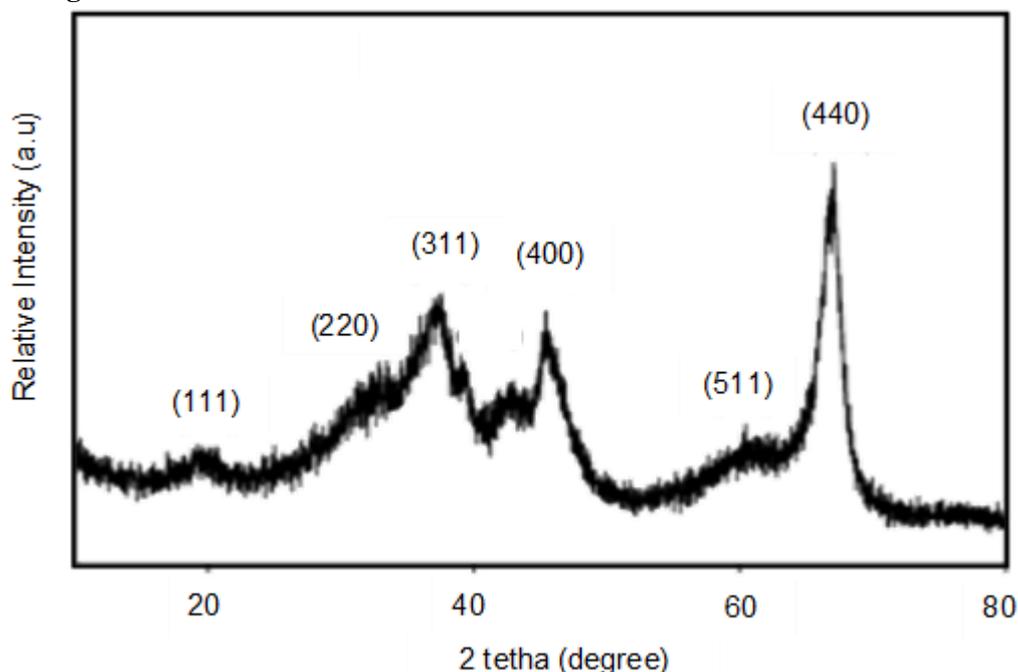


Figure 3. X-Ray Diffraction (XRD) patterns of gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$) of Joint Committee on Powder Diffraction Standards (JCPDS) 29-0063.

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