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Synthesis and Characterization of γ -Al₂O₃/SiO₂ Composite Materials

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Abstract. This article reports the synthesis process of γ -alumina/SiO₂ composite from aluminium powders and amorphous nanosilica through the means of tetra-methyl-ammonium hydroxide (TMAH) as the mixing medium which produced aluminium hydroxide Al(OH)₃ in the form of white powders. The crystal structures, microstructures, and mapping of the atomic constituent of γ -Al₂O₃ and γ -Al₂O₃/SiO₂ samples were respectively analyzed via X-ray diffraction (XRD), and scanning electron microscopy-energy dispersive X-ray SEM-EDX. At the calcination temperature to 300 °C, the samples still had boehmite phase, and the boehmite phase transformation to γ -alumina phase occurred at temperature of 700-900 °C. The γ -alumina phase began to form at the calcination temperature of 500-700 °C with the crystal structure of (440), (511), (400), (222), (311), and (111). The similar diffraction pattern was also shown by the γ -Al₂O₃/SiO₂ composite for the calcination temperature of 700 °C and 900 °C. The microstructure analysis of the γ -Al₂O₃/SiO₂ showed that SiO₂ particles were smaller and round while the γ -Al₂O₃ particles were bigger and elongated. Additionally, the mapping results showed SiO₂ and γ -Al₂O₃ particles were homogenously distributed.

Keywords: Composite, γ -Al₂O₃, SiO₂, composite, calcination.

1. Introduction

Nowadays, knowledge and technology have rapidly developed. This case is inseparable from the dominant role of research on materials which supports the production process in the industrial field. Almost 75% of chemical manufacturing processes require the catalyst assistance. Such fact has encouraged a high number of researchers to synthesize both inorganic and organic catalysts for further development. The purpose of such synthesis is to create a wide utilization of catalysts with minimum side effects on the environment [1]. One of the frequently used catalysts in industrial fields is γ -Al₂O₃. The use of γ -Al₂O₃ as a catalyst and catalyst support [2-4] is based on several advantages. The first



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advantage is that γ - Al_2O_3 has a broad surface area and ability to capture undesirable dirt. The second advantage is that γ - Al_2O_3 possesses a relatively high thermal stability it has a high melting point (2318°C). Third, the structure of γ - Al_2O_3 simplifies the combination process of its molecules with active phase molecules, so that a compact catalytic structure can be formed [5]. Mesoporous γ - Al_2O_3 is one of the widely-used supporting catalysts for commercial application. The catalytic performance highly depends on the supporting combination of texture, chemical, and physical characteristics [4].

Tetragonal γ - Al_2O_3 can be formed from boehmite at calcination temperature between 450 and 750°C [2, 11]. The γ - Al_2O_3 is a solid nanoporous material with low bulk density, low thermal conductivity, and has a tendency to have an amorphous structure, high porosity, and high specific surface area [12]. Nano-sized SiO_2 , as a porous, non-conductive, and multi-compatible solid material, tends to have an amorphous structure [13]. SiO_2 nanoporous material has an extremely broad application, e.g. as absorbent [9], packaging [15], separator and electrode in Li-ion battery system [16, 17], drug delivery agent [18], and so on. There are numerous researchers conducting research on alumina- SiO_2 composite material with the focus on its low bulk density characteristic, and SiO_2 doping effect on high heat resistance and the surface area at temperature changing [7]. This study focused on the γ - Al_2O_3 synthesis and the formation of nano SiO_2 composite (amorphous) as the filler.

2. Materials and Methods

Aluminum powder (Merck product) is a matrix with a high purity (98.1%), 2.70 gram/cm^3 density, and a melting point at 600°C . The second material was a nanometer-sized SiO_2 powder with a high amorphous phase and high purity ($>95\%$) which was prepared from natural quartz through a hydrothermal-coprecipitation process [8]. Lastly, a Merck pro-analysis TMAH (*tetramethylammonium hydroxide*) solution was utilized as the mixing medium. The sample preparation consisted of two stages. The first step was preparing the γ - Al_2O_3 sample by adding aluminum powder (Al) into the TMAH solution to produce a white colored solid. The second step was a combustion process in a furnace at 300°C for 2 hours until it produced boehmite $\text{Al}(\text{OH})_3$. The next step was creating the γ - $\text{Al}_2\text{O}_3/\text{SiO}_2$ sample by adding the prepared SiO_2 into the TMAH solution and then stirred until it became homogeneous (~ 1 -2 hours). The γ -alumina/ SiO_2 was formed through a calcination process at 700°C temperature in the oven. Characterization was done through XRD to identify the phase and structure, FTIR to analyze the functional radical-group, and SEM-EDX to analyze the microstructure profile of γ - $\text{Al}_2\text{O}_3/\text{SiO}_2$.

3. Results and Discussion

Figure 1 presents the diffraction pattern of $\text{Al}(\text{OH})_3/\text{SiO}_2$ (aluminum hydroxide) pattern with the nanosilica particle as the filler. There were ten diffraction peaks, which include the $\text{Al}(\text{OH})_3$ and SiO_2 peaks. The existence of the $\text{Al}(\text{OH})_3$ peak showed that the material produced at this stage had a boehmite phase [5,6,14–20]. It was due to the Al as a matrix reaction to an oxidation of TMAH as well as the role of Al as a dispersion medium of SiO_2 in the first process, as shown in Figure 2. TMAH is a quaternary ammonium salt, with the chemical formula of $\text{N}(\text{CH}_3)_4^+ \text{OH}^-$, which relatively oxidized the Al. Such process would initiate an exothermic process, namely a process of releasing C, N, and H_2 gasses, characterized by a production of steam. The Al and SiO_2 powder in TMAH formed a new compound of $\text{Al}(\text{OH})_3$, SiO_2 , and $\text{C}_3\text{H}_{12}\text{N}$ group released during the process.

However, such peak of aluminum hydroxide $\text{Al}(\text{OH})_3$ could not be identified anymore after the calcination process had reached 700°C , yet, there is a new emerging peak which is identified as alumina phase. There was a transformation from the boehmite phase into γ -alumina phase [20]. The tetra-methyl-ammonium cation $[\text{C}_4\text{H}_{12}\text{N}]^+$ which was bound to an oxygen atom would be released after the calcination process had reached 300°C . Based on the diffraction patterns after the calcination process had reached 300°C in 2 hours, the synthesized white powdered material is dominated by Boehmite phase (Figure 1) [20]. The diffraction patterns identify many less sharp peaks originated from impurities (not alumina), such as nitrate, carbonate, and other impurities which can be found in

Boehmite/SiO₂ composite, refer to the chemical equation in Figure 2 (there are C, N, and H elements) [21].

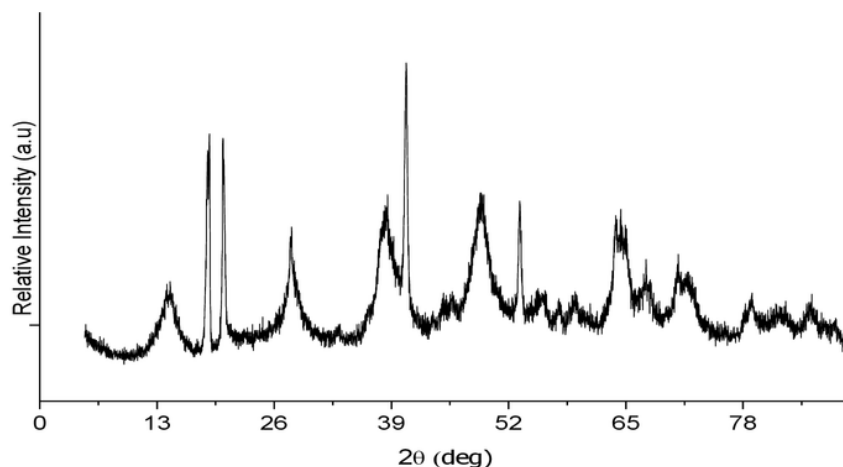


Figure 1. Diffraction patterns of Al[OH]₃/SiO₂ (amorphous) sample

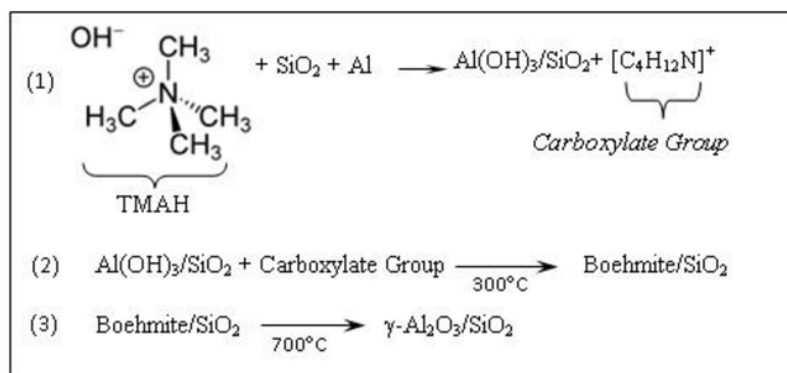


Figure 2. Reaction of amorphous Al and SiO₂ via TMAH: (1-2) Boehmite/SiO₂ and (3) gamma-alumina/SiO₂

Figure 3 identifies the X-ray diffraction patterns of γ -Al₂O₃ and γ -Al₂O₃/SiO₂. There was a significant match [18, 19] in the comparison between the data of the X-ray diffraction test and the data of standard XRD on *gamma* alumina (reference). The relatively similar peaks also have fairly similar intensity values (see Table 1). From the intensity values between gamma alumina/SiO₂ which exceeded 50%, it can be seen that the synthesized gamma alumina and the standard gamma alumina were relatively similar (39.40°). However, there were several peaks, which were visible in the γ -Al₂O₃/SiO₂. The peaks could not be identified in the conventional gamma alumina, but they could be identified in the synthesized γ -Al₂O₃ sample, namely at 2θ 34.83 angle with 21% relative intensity value, 37.38 angle with 64.09% intensity value, and at 2θ 41.26 angle with 4.55% relative intensity value. It is interesting since, at the angles of 2θ 19.58°, 37.79°, and 60.85°, the relative intensity values of 6.96%, 59.19%, and 10.31% shifted on the standard γ -Al₂O₃ (namely 2θ = 19.45°, 37.60°, and 60.90°). The different diffraction patterns between γ -Al₂O₃ and γ -Al₂O₃/SiO₂ and the standard data (standard γ -Al₂O₃) are likely to be influenced by the process and the core material of the γ -Al₂O₃ phase

formation [7, 22]. One important factor in the preparation method is aluminum hydroxide decomposition temperature. The phase formation from boehmite into γ - Al_2O_3 requires a temperature higher than 300 °C. It is in accordance with the boehmite phase at the temperature of 300 °C in this study (Fig.1). The γ - Al_2O_3 phase requires the temperature of 500-700 °C [23] which is also in line with the γ - Al_2O_3 phase formed in this research at 700 °C and a new phase of δ - Al_2O_3 formation would emerge at the temperature of 900°C (Fig. 3(a-b)) [19,20].

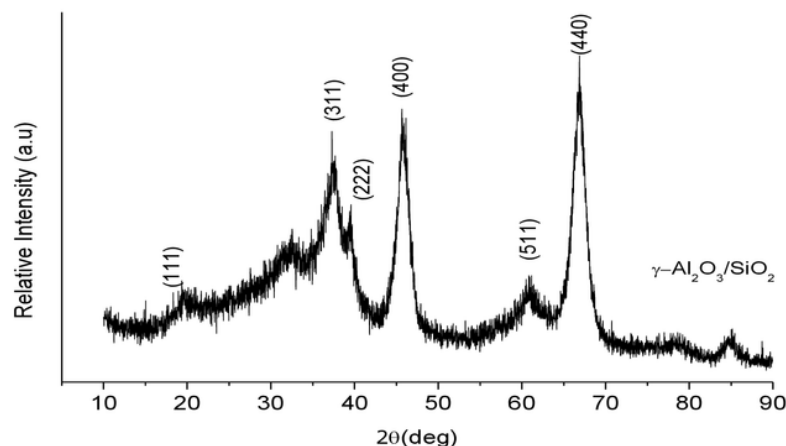


Figure 3. Diffraction patterns of $\gamma\text{Al}_2\text{O}_3/\text{SiO}_2$ sample

Table 1. XRD data of γ - Al_2O_3 and γ - $\text{Al}_2\text{O}_3/\text{SiO}_2$

2θ (deg)	γ - $\text{Al}_2\text{O}_3/\text{SiO}_2$ ^{bl}		hkl, ICDD: 29-1486, 29-0063 10-0425
	d-spacing (Å°)	I/Io (%)	
19.58	4.529	6.96	[111]
34.83	2.573	21.00	[220]
37.38	2.403	64.09	[311]
39.40	2.284	36.76	[222]
41.26	2.186	4.55	
45.73	1.980	77.00	[400]
60.85	1.521	10.31	[511]
66.85	1.398	100	[440]
84.87	1.142	6.97	[444]

Figure 3 (a-b) shows the XRD diffraction patterns of synthesized γ - Al_2O_3 and γ - $\text{Al}_2\text{O}_3/\text{SiO}_2$ samples for 20% SiO_2 with a calcination treatment at the temperatures of 700 °C. It can be seen that the gamma alumina phase was dominantly formed in the crystal structures of (440), (511), (400), (222), (311) and (111) (6, 18, 20, 24, 25). The SiO_2 content in γ - $\text{Al}_2\text{O}_3/\text{SiO}_2$ sample was not identified in the diffraction pattern due to the small relative intensity possessed by the SiO_2 particle. The SiO_2 diffraction pattern (nanometer order) is usually cannot be seen since it has an amorphous phase. In this case, the calcination still has the amorphous phase up to the temperature of 700°C, such as at the temperature of 300 °C in which the boehmite $\text{Al}(\text{OH})_3$ phase was still dominant [15,21,26].

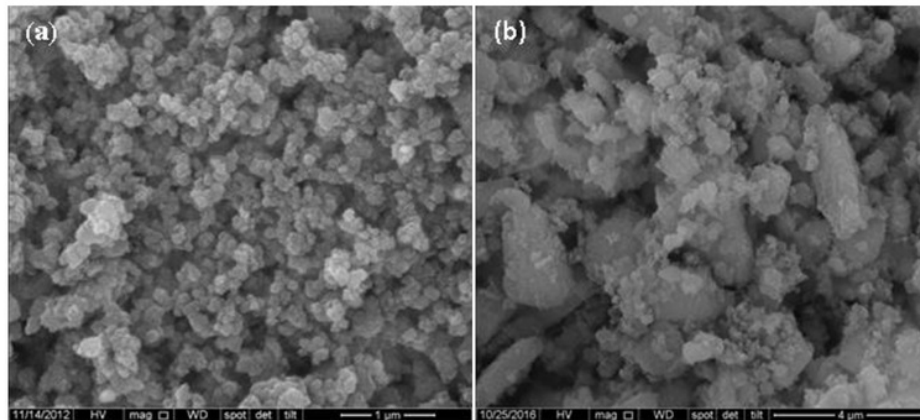


Figure 4. SEM image of (a) SiO_2 and (b) $\gamma\text{-Al}_2\text{O}_3/\text{SiO}_2$ samples

The morphology and microstructures of SiO_2 and $\gamma\text{-Al}_2\text{O}_3/\text{SiO}_2$ particles are shown in Figure 4. (a) The SiO_2 nanoparticle profile was smaller than the nanoparticle profile of $\gamma\text{-Al}_2\text{O}_3$ and had the tendency to be in round shape, while (b) the profiles of $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 particles substituted inside them forming $\gamma\text{-Al}_2\text{O}_3/\text{SiO}_2$. It can be seen that the $\gamma\text{-Al}_2\text{O}_3$ form elongated and is bigger than the form of SiO_2 , while the SiO_2 particle was filling the gaps among the Al_2O_3 . The distribution of SiO_2 and $\gamma\text{-Al}_2\text{O}_3$ particles can be seen in Figure 5. Meanwhile, the SEM-EDX test results of the $\gamma\text{-Al}_2\text{O}_3/\text{SiO}_2$ sample (20%) were characterized with their respective *At%* (atomic percent) of Al, Si and O of 38.81; 3.83 and 57.36%; the mapping results identified the homogeneity of SiO_2 and $\gamma\text{-Al}_2\text{O}_3$ distributions [5, 14, 19].

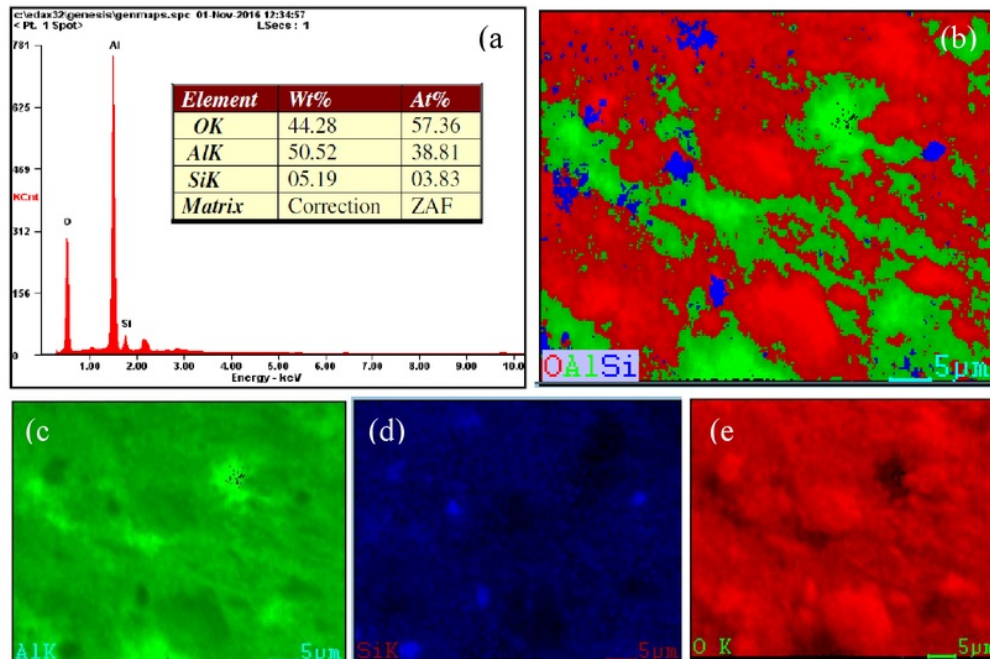


Figure 5. (a) EDX-elemental content and SEM-EDX mapping area of (b) Al-Si-O, (c) Al, (d) Si, and (e) O for $\gamma\text{-Al}_2\text{O}_3/\text{SiO}_2$

4. Conclusion

The γ - $\text{Al}_2\text{O}_3/\text{SiO}_2$ composite material has been synthesized from the aluminum base material using TMAH as a medium. The mixing of SiO_2 nanoparticles (amorphous) and γ -alumina particles was by a wet-mixing method, assisting in the formation of a homogeneous γ - $\text{Al}_2\text{O}_3/\text{SiO}_2$. The γ - Al_2O_3 particle shape in γ - $\text{Al}_2\text{O}_3/\text{SiO}_2$ appeared larger and elongated; the composite structure appeared to be more dominant γ -alumina, amorphous SiO_2 particles. The active medium of TMAH can be as a solvent for dispersing SiO_2 nanoparticles and in the mixing process of Al and SiO_2 are oxidizing, activating Al powder and transforming into γ -alumina.

Acknowledgments

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