IOP Conf. Series: Materials Science and Engineering **214** (2017) 012028 doi:10.1088/1757-899X/214/1/012028

Effect of Calcination Temperatures on Ratio of Atomic Weight of Al/O in Sol-Gel Method for Synthesis γ Al_2O_3 as a Buffer Catalyst

Dwita Suastiyanti[1], **Sri Handayani**[2], **Maykel T.E. Manawan**[3]
[1]Mechanical Engineering Department, Institut Teknologi Indonesia (ITI)
Puspiptek Raya Street, Serpong, South Tangerang, Banten, INDONESIA
[2]Chemical Engineering Department, Institut Teknologi Indonesia (ITI)
Puspiptek Raya Street, Serpong South Tangerang, Banten, INDONESIA
[3]Politeknik Negeri Jakarta (PNJ)
Depok, West Java, INDONESIA

Email: dwita.suastiyanti@iti.ac.id

Abstract. The aim of this research was to determine the effect of calcination temperatures on the ratio of atomic weight of Al/O that could affect the formation of γ-Al_2O_3 phase. The novelty of this research is how to produce γ-Al_2O_3 in single phase and nanosize by simple method (sol-gel method).The calcination process was performed at a temperature which varied of 190°C, 275°C and 320°C for 4 hours respectively and sinter process carried out at a temperature of 420°C for 6 hours. Calcination process at temperature of 320°C for 4 hours produces powder with the ratio of atomic weight of Al/O in accordance with the ratio of atomic weight of Al/O in Al_2O_3 compound, 0.6667 (2/3). This ratio is as expected for a compound according to formula of Al_2O_3. This condition also produces alumina powder with the smallest particle size on the nanometer scale of 84.5 nm. SEM test results show that the grain is still heterogenous in size and shape. The results also show that the grain is still agglomerated.

1. Introduction

Catalyst of monometallic, Pd supported by γ Al_2O_3, are used in a variety of applications including selective hydrogenation, catalytic combustion, and vinyl acetate synthesis. Commercial catalyst of Pd/γ-Al_2O_3 typically are prepared by aqueous impregnation using inorganic salt precursors. The most common technique, incipient wetness impregnation, often results in non-uniform Pd distributions, poor Pd dispersions, and unwanted modification of the surface chemistry of the support[1]. In recent years, increasing attention has been focused on the development of nano-sized alumina powders for advanced engineering materials [2,3]. Conventional processes for synthesizing ceramic of nano powder involve mechanical synthesis, vapor phase reaction, precipitation, and combustion and sol–gel methods [4]. Catalytic dehydration of methanol over solid-acid catalysts offers a potential process for dimethyl ether synthesis. Several catalysts having activity and selectivity for the catalytic conversion of methanol to DME are known, the so called acidic dehydration catalysts [5,6,7]. Commercially γ-Al_2O_3 is used to a large extent for this reaction at a temperature range of 270 to 380°C. The sonochemical synthesis of nanophase materials has the advantage that various classes of materials can be generated simply by changing the reaction medium. So it is worthwhile to overview the different applications, where cavitations can be used efficient. Preparation of metal and metal oxide

nanoparticles immobilized on various materials is one of the key researches in nanoscience and nanotechnology, because an excellent synergy and Bifunctional effect would be expected [8]. It is well known that the alternative method for generating stabilized metal nanoparticles involves synthesizing them in or on nanoporous supports, which help define particle size and serve to immobilize the resulting particles [9]. Compound of γ-Al_2O_3 is most known transition alumina as a catalyst support compound, where the compound of γ-Al_2O_3 is stable at high temperature, physically stable, strong and malleable in the manufacturing process. However, commercially γ-Al_2O_3 is not available in single phase and still relatively expensive. The aim of this research is to produce buffer catalyst of γ-Al_2O_3 in single phase, nanoparticle size and the weight ratio of atomic Al/O = 2/3 (0.6667). It is produced by method which is easier and more economical. One way to improve the performance of the catalyst is made in size to nanoparticles of the buffer. Use of the catalyst nanoparticles have been studied by several researchers using ZSM-5 catalyst in cracking LDPE (Low Density Poly Ethilen). The results showed that the nanoparticles ZSM-5 had higher catalytic activity than the microparticles. Therefore, in this research the size of the compound of γ-Al_2O_3 was produced in the size of the nanoparticles. The method used in this research was sol-gel because this method has many advantages such as the process takes place at low temperatures, the process is relatively easy, could be applied in all circumstances (versatile), producing products with high purity and homogeneity if the parameter is varied. In addition, the most impressive of the sol-gel process is relatively cheap, and products in the form of silica xerogel produced non-toxic [10] .Alumina have had a relatively hard physical properties, relatively stable at high temperatures, low electrical conductivity, melting point high, large pore structure, and has a surface area in the range of 100-200 m^2 / g. With these characteristics, causes the alumina is often used in industries, such as absorbents, abrasives, catalysts and catalyst support. In the active form, alumina has a polar surface that is able to adsorb polar compounds. In research conducted by Rahmanpour [11], γ-Al_2O_3 synthesized from $Al(NO_3)_3.9H_2O$ (0.26M), NH_4OH (3.2%), and deionized water at pH of 7.5-8.5 with a temperature of 310 to 340 ° C for 15 hours and had crystal size of 1-2 nm.

2. Methods

Aluminum nitrate {$Al(NO_3)_3$-$9H_2O$, 99.5%}(Merck), Ammonia {NH4OH, 32%} (Merck) and deionized water were used as starting chemicals. A transparent gel-like precursor containing Al cations is precipitated at pH ~7.5–8.5 when ammonia (3.2%) and Al nitrate salt solutions (0.26 M) are mixed together in 400 ml deionized water. The solution was mixing under ultrasonic vibration and maintained at a temperature of 70ºC for 2 h. The following chemical reactions occurred during preparation:

$$Al(NO_3)_3 + 3\ NH_4OH \longrightarrow Al(OH)_3 \downarrow + 3NH_4NO_3$$

$$Al(OH)_3 \longrightarrow AlOOH \downarrow + H_2O$$

$$AlOOH \longrightarrow Al_2O_3 + H_2O$$

Sol-gel process was preceeded by the formation of a gel by heating the solution on a hot plate at a temperature of 70-80^{o}C until the gel was formed (approximately 4-5 hours). Gel was then tested by TGA / DTA to determine the temperatures of the phase transformation. The temperatures were used as references of the calcination and sintering processes. The parameters varied were the calcination temperatures of 190^{o}C, 275^{o}C and 320^{o}C respectively for 4 hours. The sintering process was done after the calcination process at a temperature of 420^{o}C for 6 hours. Characterization of the resulting powder was done by X-Ray Diffraction / XRD (Phillips type) test to confirm the formation of phases and determine the ratio of atomic weight Al/O. Observation by Scanning Electron Microscope/SEM (type JEOL/EO, JEM-1400 Version 1.0) was to determine the morphology of the grains. To determine the particle size, it was used Particle Size Analyzer/PSA type of Beckman Coulter DelsaTM Nano by using a solution of dispersing Ethyl Alcohol left for 4 days then the particle / powder was broken again by using ultrasonic. Tests using TGA / DTA (Thermal Gravimetry Analyzer / Differential Thermal Analysis) performed on gel (before the calcination process) was to determine the temperatures of the

phase transition that could be observed through the powder mass reduction and a decrease in energy when the gel was heated at temperatures of up to 1000°C. This research was conducted by the flow chart as shown in Figure 1.

Figure 1. Equipments of γ Al_2O_3 Synthesis.

3. Results and Discussion

To find out the calcination and sintering temperatures, they were tested by the TGA/DTA that the results are shown in Figure 2.

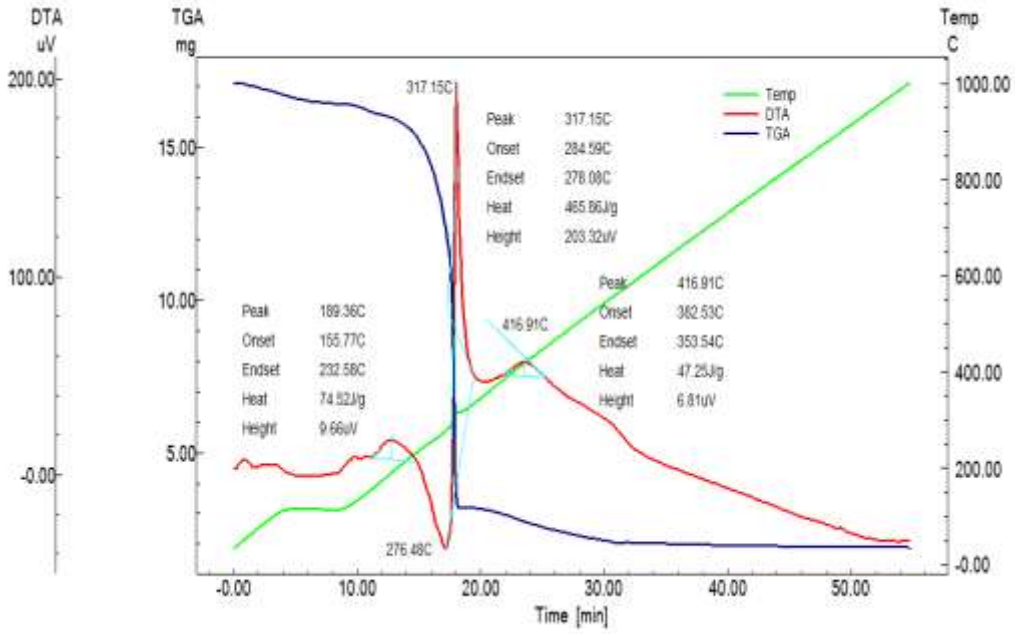
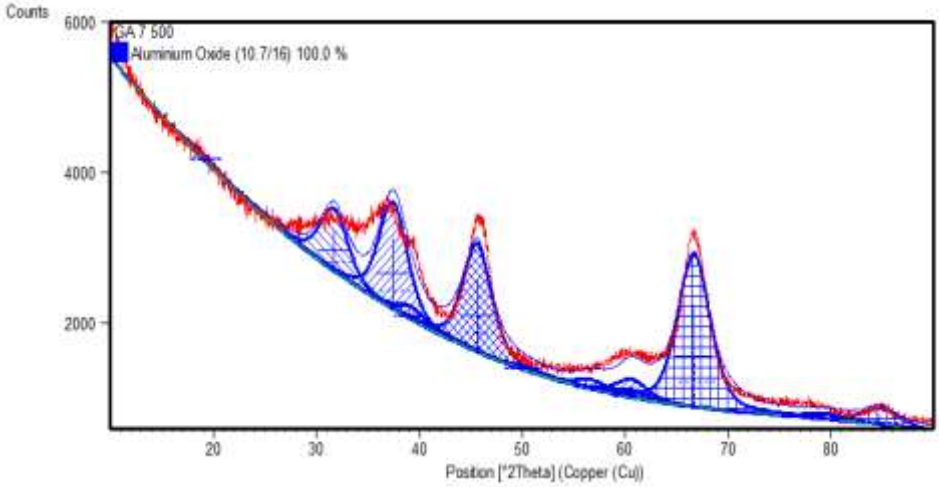


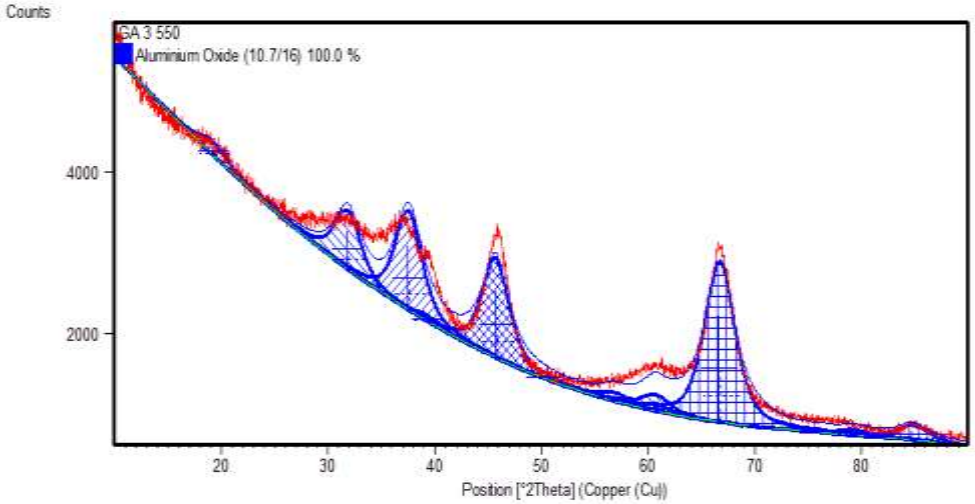
Figure 2. TGA/DTA Test of citric acid gel based on γ Al_2O_3.

Figure 2 shows that the loss of mass and energy reductions occur simultaneously in a temperatures range of 189.36°C-317.15°C. In the temperatures range, H_2O and other elements evaporated which is derived from precursor used. The calcination process is performed at temperature in the range that is at 190°C, 275°C and 320°C for 4 hours. The next energy changes on the diagram TGA / DTA occurs at temperatures of 416.91°C. At this temperature it begins to form alumina phase and it happens crystallization of alumina. So Sinter process is carried out at 420°C. The XRD results are shown in Figure 3, 4 and 5.



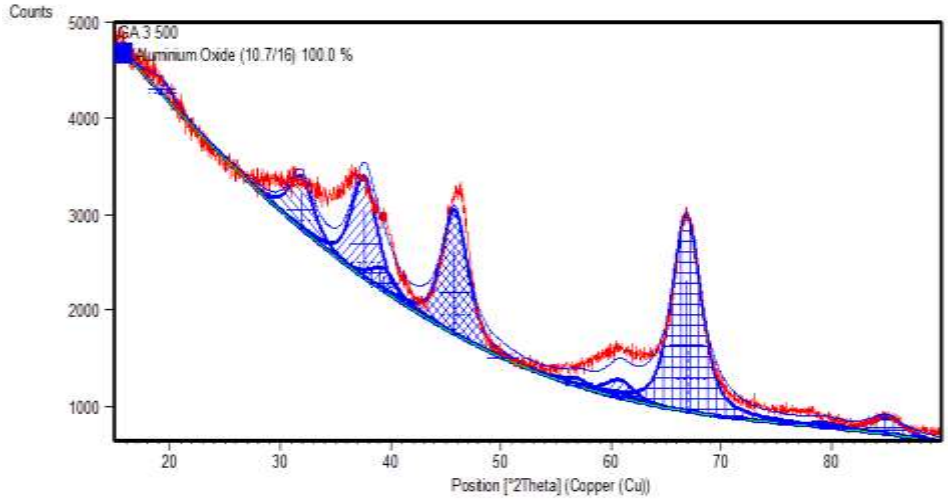
Crystallite Size	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
35 A	98-002-8260	69	Aluminium Oxide (9.6666/ 12.9999 =0.7436)	0.000	0.482	Al9.6666 O12.9999

Figure 3. XRD Result and Crystal Pattern List of Alumina Calcined at 190°C for 4 Hours.



Crystallite Size	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
31.4 A	98-002-8260	58	Aluminium Oxide (10.6666/ 16.9999= 0.6275)	0.000	0.470	Al10.6666 O16.9999

Figure 4. XRD Result and Crystal Pattern List of Alumina Calcined at 275°C for 4 Hours.



Crystallite Size	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
28.7 A	98-002-8260	69	Aluminium Oxide (10.6666/ 15.9999 =0.6667)	0.000	0.881	Al10.6666 O15.9999

Figure 5. XRD Result and Crystal Pattern List of Alumina Calcined at 320°C for 4 Hours.

Figure 3, 4 and 5 show that in fact the whole powder calcined at varied temperature having γ-phase 100% Al_2O_3. There is no impurity phase contained by powder that is calcined at temprature of 190°C, 275°C and 320°C for 4 hours respectively. It could be seen from the pattern shape in which all peak are swept by one color (blue). However ratio of atomic weight Al/O for powder calcined at 190°C and 275°C are not same with ratio of atomic weight of Al_2O_3 (2/3). Powder calcined at 320°C for 4 hours has an ratio of atomic weight of Al/O equal to the ratio of atomic weight of Al/O on Al_2O_3 powder (2/3). The lower temperature of calcined causes unexpected formation of Al_2O_3, due to insufficient of heat energy provided to achieve a balance of Al_2O_3 chemical compounds. From the results of this refinement could also be known that the γ Al_2O_3 powder calcined at 190°C, 275°C and 320°C for 4 hours has crystallite size ranged 2.87-3.50 nm. This leads to the formation of particles in nano size anyway (<100 nm). Crystal Pattern list of powder for all calcined temperatures shown in Table 1.

Table 1. Crystal Pattern List For All Samples

NO	Treatment (Sintering at 420°C for 6 Hours)	Chemical Formula	Al/O Ratio	Crystallite Size (nm)
1	Calcined at 190°C for 4 Hours	**Al**9.6666**O**12.9999	0.7436	3.50
2	Calcined at 275°C for 4 Hours	**Al**10.6666**O**16.9999	0.6275	3.14
3	Calcined at 320°C for 4 Hours	**Al**10.6666**O**15.9999	0.6667 (2/3)	2.87

To know the chemical formulas shown in Table 1, it is used the result of XRD test which has been refined by HighScorePlus (HSP) software.To determine particle size of powder, the PSA test results are shown in Figure 6. The PSA test used a solution of ethyl alcohol to dissolve the powder tested, then the crushing process is carried out by ultrasonic. Crushing process is done to break down the particles of the powder to prevent agglomeration.

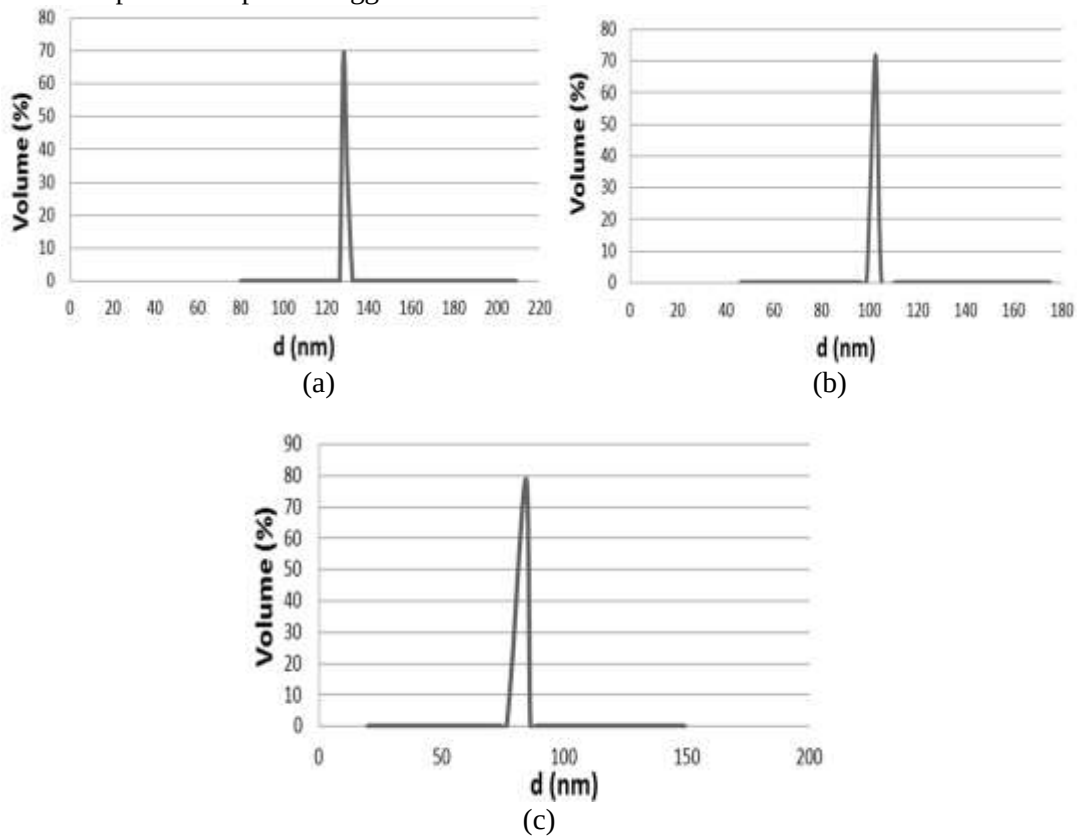


Figure 6. Particle Size Distribution (a) Calcined at 190°C (b) Calcined at 275°C (c) Calcined at 320°C.

Figure 6 shows that the powder has particle in nanosize (<100 nm) except powders calcined at 190°C for 4 hours. Powder with ratio of atomic weight of Al/O = 2/3 has the finest particle (85 nm). The results of the measurements of the particles showed that the sol-gel process has not yet reached the optimum conditions, Expected condition is a powder with a particle size of 20-30 nm when referring to crystal size of between 2.87 - 3,5 nm. To determine the morphology of the grain is observed by Scanning Electron Microscope (SEM), the result is shown in Figure 7.

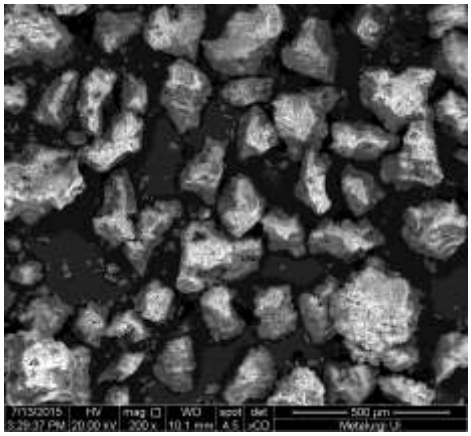


Figure 7. SEM Observation of Powder Calcined at 320^{o}C for 4 Hours.

Figure 7 shows that the powder is still in agglomeration and has not been homogenous in size and shape. Nevertheless, it could be still used as supporting material for catalyst because it would be wrapped up with other elements (for examples : Pd, Pt etc). The most important thing is purity of γ Al_2O_3 powder.

4. Conclusion

The condition of sol-gel process which is at the calcination temperatures of 190^{o}C, 275^{o}C and 320°C for 4 hours and sintering temperature of 420^{o}C for 6 hours produce γ Al_2O_3 powder in single phase without impurities phase. But this condition produces powder of γ Al_2O_3 in differences of atomic weight of Al/O. Powder having ratio of atomic weight of Al/O = 2/3 (which is expected as according to Al_2O_3) is powder which is calcined at 320^{o}C for 4 hours. The powder having nanoparticles is powder which is calcined at 275^{o}C and 320^{o}C (98 nm and 85 nm respectively). The morphology of the grain is still heterogenous in size, shape and still agglomerated. Although powder has particle in nanosize but it is not as expected particle size is about 20-30 nm when referring to the crystal size is about of 2.87-3.5 nm.

5. References

[1] Jason Kelly M, Jaehoon Kim, George W, Roberts, Henry Lamb H 2006 *North Carolina State University, Raleigh NC* 27695 (USA)
[2] Takeguchi T, Yanagisawa K, Inui T, and Inoue M 2000 *Appl. Catal. A: General* **192**
[3] Brown D.M, Bhatt B.L, and HsiungT.H 1991 *Catal*. Today **8**, 279
[4] Omid Rahmanpour, Ahmad Shariati, and Mohammad Reza Khosravi Nikou 2012 *International Journal of Chemical Engineering and Applications* **3** (2)
[5] Ohno Y, Inoue N, Ogawa T, Ono M, Shikada T, and Hayashi H, 2001, *NKK Technical Review*,
[6] Singh L. P., Agarwal, S. K., Bhattacharyya, S. K., Sharma, U., Ahalawat, S 2011 *Nanomater Nanotechnol* **1**(1) 44-51
[7] Wang A.W, Weigel S, and Muraro G, *Air Products and Chemicals Inc* 2002
[8] Kim J.H, Park M.J, Kim S.J, Joo O.S, and Jung K.D 2004 *Appl. Catal. A: General*. 26437–41.
[9] Gedanken A 2001 *Elsevier Science Ltd* 9450-9456
[10] Okitsu K, Mizukoshi Y, Yamamoto T.A, Maeda Y, and Nagata Y 2007 *Materials Letters* **61** 3429-3431
[12] Rahman O 2012 *International Journal of Chemical Engineering and Applications* **3** (2)

Acknowledgment
This research is supported financially by INSINas-RistekDikti Research Grant 2016 through letter of decree No. 266/SP2H/LT/DRPM/III/2016, Ministry for Research and Technology DIKTI, the Republic of Indonesia.