The Effect Of SiO₂ / Al₂O₃ Ratio Over Yield And Particle Size In Zeolite from Geothermal Waste

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Abstract. Hydrogen is one of compound much used in the chemical industry. Production process of hydrogen commonly applied in the industry is steam reforming using high temperatures. Catalyst can be used in the production of hydrogen is zeolite. Zeolites are the result of mine nonmetallic, so the availability is limited. PT Geo Dipa energy unit Dieng produce industrial waste of deposition silica and it can be used as zeolite materials. The objective of this research for preparation of catalyst from solid waste of geothermal industry with varied ratio of SiO₂/Al₂O₃. The geothermal waste was calcined at a temperature of 1000 °C. The waste geothermal was mixed with 400 ml of Sodium Hydroxide 3M and added with Aluminum Hydroxide at 100 °C for two hours. Hydrothermal process was conducted at 300°C for five hours. The calcination of zeolite products for five hours at 700 °C. This research concludes that washed catalyst has a smaller yield than native. The greater ratio of SiO₂/Al₂O₃ gives smaller yield. Catalysts that are washed have smaller particle sizes than without washing. Larger ratio of SiO₂/Al₂O₃, it produces smaller particle sizes. In the analysis using the Particle Size Analyzer method, the resulting particle size is still relatively large at a micro scale.

1. Introduction
There is a continuous decline in fossil fuel usage, and, therefore, an increase in the amount of research seeking alternative fuel sources to ensure energy security and environmental protection [1]. Proportional with the increasing economic and population development in the world, the level of energy consumption has increased every year. The highest consumption is dominated by industry and transportation. However, fossil fuels used today depleted because they cannot be renewed [2]. Hydrogen is one compound much used in the chemical industry. There are several processes commonly used for biohydrogen production including: Anoxid Photosynthesis, Fermentation, Oxygenic photosynthesis, cyanobacterial hydrogen [3]. Hydrogen production process commonly applied in the industry is steam reforming and it using high temperatures [4],[5]. One catalyst can be used in the production of hydrogen is zeolite [6]. But zeolites is the result of mine nonmetallic, so the availability is limited [7].

On the other hand, PT Geo Dipa energy unit Dieng produce industrial waste of deposition silica (silica scaling). The utilization of geothermal industrial waste has been not maximized. A catalyst plays an important role in the development of the chemical industry. Today, almost all industrial
products produced through process that one stage or some use the services of the catalyst [8],[9]. For producing hydrogen, much used a catalyst of alumina as a framework of a catalyst. Geothermal waste can be used as a zeolite material by hydrothermal process [10]. Zeolites or zeolite-like materials generally have high porosity, surface area and thermal stability so zeolite has many applications including adsorbents, catalysts, photocatalyst, cation exchanger, fertilizers and various other things [11],[12].

Hydrogen gas production research is still low in glycerol conversion and selectivity. Ni/Mg-Al2O3 catalyst is used in glycerol steam reforming process that contain NiO 24,1 wt.%, MgO 26,1 wt.% dan Al2O3 of 49 wt.%. It give hydrogen selectivity 78.5% and glycerol conversion 88.0% at temperature 650 °C [13]. Ni/CeZrO2/Al2O3 catalyst give low selectivity and yield, in range 67% [14]. Various type of ZSM5 that use for hydrogen production give selectivity up to 90% [15]. So the potential process for process development is still very large. With that potential, PLTG waste can be developed to be advance material that is zeolite catalyst which has the ability to produce hydrogen. There are several things that can be observed in the characterization of catalyst, one of which is the particle size. This research was conducted with the aim to determine the effect of the ratio of SiO2/Al2O3 on yield and the particles size of the catalyst produced.

2. Methods
2.1. Materials
In this research used geothermal industry waste obtained from earth heat power plant that is PT. Geo Dipa energy unit Dieng. The waste has used as the main raw material because it is a mineral silica source. Sodium Hydroxide (NaOH) and Aluminum Hydroxide (Al(OH) 3) was used Merck Ltd. Distilled water are used produced by Integrated Laboratory of UNDIP.

2.2. Catalyst Production
2.2.1. Raw material Pretreatment
Geothermal waste was washed by using distilled water. Then drying using sun drying process. It continued by size reduction process. sieve it by 125 μm sieving size. And the last is calcination. It is done using furnace in temperature 1000 °C for five hours. And we exhale air during the calcination.

2.2.2. Synthesis Process
The second step is catalyst synthesis. There is some process: making sodium aluminate solution, stirring process, hydrothermal process, washing and calcination. On process making of sodium aluminate, 400 ml of NaOH solution 3M was boil at 100 °C and stirred at 200 rpm. During stirring process, pour Al(OH) 3 as the variable. The color of solution was change from white to be clear solution.

Then 50 gr of waste geothermal added in the solution. Stir with magnetic stirrer at room temperature at 300 rpm for 2 hours. Then hydrothermal process in temperature 300 °C for 5 hours. After cold, the hydrothermal product is removed from the tube and it washed using distilled water until neutral. The last is calcinating process using furnace in 700 °C for 3 hours and exhale with nitrogen. Weigh the catalyst product to know how much the yield and analyzed by PSA method to find out the particle size.

2.3. Variables
The controlled variables in this research are sieve size (125μm), raw material furnace for pretreatment process (1000 °C, 5 hours), mass of geothermal waste (50 gr), NaOH (3M, 400 ml), stirrer time (2 hour), hydrothermal process (300 °C, 5 hours). The response variable in this study is the yield and particle size of catalyst product. The independent variables in this study were SiO2/Al2O3 ratio (2.5; 5; 7.5; 10; 12.5; 15).
Table 1. Experiment Variables on preparation of catalyst

| Geothermal waste | NaOH | SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio | Hydrothermal process | Responses |
|------------------|------|---------------------------------|---------------------|-----------|
| 50 gr            | 3M 400 ml | 2.5               | 5 hour, 300 °C     | 1. Yield  |
| 50 gr            | 3M 400 ml | 5                 |                     | 2. Particle size |
| 50 gr            | 3M 400 ml | 7.5               |                     |           |
| 50 gr            | 3M 400 ml | 10                |                     |           |
| 50 gr            | 3M 400 ml | 12.5              |                     |           |
| 50 gr            | 3M 400 ml | 15                |                     |           |

a. Particle Size Analyzer (PSA)

One method that can be used to identify nanoparticle size is Particle Size Analyzer PSA. PSA test can identify the individual geometry properties of particles, including, the size, shape and surface profile of these particles. From the surface profile, the properties of the particles can be known, namely specific area, charge, distribution, and particle porosity. In this study the particles were analyzed based on particle volume distribution.

b. Scanning Electron Microscope (SEM)

SEM is a type of device that uses electrons. The working principle of SEM is to fire the surface of objects with high energy. When making observations, the location used by zooming in or zooming out. Based on the direction of reflection of the file at various points the profile traffic can be used using measurement programs that are on the computer [16].

3. Result and discussions

3.1. Yield

From the fig.1 can be seen that washed catalyst has a smaller yield than native. The research was conducted variation SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (2.5, 5, 7.5, 10, 12.5 and 15) the results give yield of zeolite: without washing (121.53, 106.03, 90.70, 83.11, 74.08 and 68.80 gram) and by washing (52.63, 49.89, 45.00, 39.88, 36.73 and 35.08 gr). This is due to some particle has been dissolved in distilled water. The product getting from hydrothermal process is in base condition. It shows that there are still much NaOH residue. We have to make it in neutral condition by...
washing using distilled water. In the washing process, NaOH dissolve in distilled water and it reduce the weight of product catalyst.

The data show that, if the ratio of SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} greater, it would be made smaller yield is obtained. This is because of the increasing ratio of SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}, while the addition of Al(OH)\textsubscript{3} is decreases. Ultimately, the particle is less binding mutually and it give less yield. While the catalyst without washing process, it is only subjected to calcination with the furnace at a temperature of 700 °C. At this temperature there is removal of organic materials. While the presence of NaOH cannot be eliminated, or reduced. The thing is because NaOH has a boiling point reaching 1390 °C, higher temperature is needed to eliminate it. The presence of NaOH makes the yield obtained more, but the catalyst is in alkaline condition. Particles will change at temperatures higher than 700° C. This is because at high temperatures, kinetic energy will increase and then the constituent atoms will diffuse with particles adjacent to each other and mutually binding (agglomeration) [17].

3.2. Particle Size

PSA analysis provides data in the form of particle size distribution based on cumulative volume. The particles obtained have a variety of sizes, as evidenced by the diverse distribution ranging from small to large. Based on the results of the PSA analysis, it was found that the particles have a micro size. From the difference in the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio, it is seen that there is a tendency to spread a wide size distribution. This shows that the size of the catalyst produced is not homogenic. In the PSA analysis, water is used as a media, so that the possibility of water causes small particles to join and bind together (agglomeration) and make them larger. If a calculation is made from the cumulative distribution results, particle size can be obtained. The calculation is based on the average particle size of the distribution. The calculation produces the following graph:

![Figure 2. the effect of SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} Ratio Over Particle Size in Zeolite from Geothermal](image-url)

Figure 2. the effect of SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} Ratio Over Particle Size in Zeolite from Geothermal

Figure 2 shows the effect of the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio on the catalyst particle size. The final zeolite products were analyzed using the PSA methods (particle size analyzer) and it given the result of size particles as follows: without washing (66.78, 71.04, 67.26, 61.09, 57.22 and 52.67 μm), while using washed it gives result 73.62, 73.24, 48.83, 47.12, 41.74 and 41.42 μm. From the graph it can be seen that catalysts that are washed have smaller particle sizes than those without washing. When the catalyst is washed, some particles do not adhere properly and separate from the catalyst. The catalyst without washing process, has a relatively rough surface compared to the
catalyst with washing. This condition makes it easy for the particle fusion process. In this process the nano sintering process occurs due to heating during the calcination process. On rougher surfaces, sintering is easier than on flatter surfaces. And this allows several particles to merge and form larger sizes. Illustration of the phenomena can be seen at Figure 3.

![Figure 3. Changes in Particle Structures [17]](image)

There are two mechanisms for sintering of nanoparticles: particle migration and coalescence (PMC) and Ostwald Ripening (OR). PMC involves the mobility of particles in a Brownian-like motion, with subsequent coalescence leading to nanoparticle growth. In contrast, OR involves the migration of adatoms or mobile molecular species, driven by differences in free energy. PMC and OR can occur, especially at high temperatures. The higher the temperature, the possibility of sintering of nanoparticles (PMC and OR) will be even greater. PMC and OR mechanisms are illustrated in Figure 4 and Figure 5.

![Figure 4. Mechanism of Particle Migration and Coalescence [18]](image)

![Figure 5. Mechanism of Ostwald Sintering [19]](image)

In addition, it can be seen that at a larger SiO$_2$/Al$_2$O$_3$ ratio, it produces smaller particle sizes. That is because with increasing SiO$_2$/Al$_2$O$_3$ ratio, while the addition of Al(OH)$_3$ decreases. Inversely proportional to the number of particles that bind less so that smaller particle sizes are obtained. And conversely, at a low SiO$_2$/Al$_2$O$_3$ ratio, a larger particle size is obtained because more and more bound particles. The smaller the SiO$_2$/Al$_2$O$_3$ ratio, the more Al(OH)$_3$ compounds added, and the larger catalyst particle size produced.

In the analysis using the Particle Size Analyzer method, the resulting particle size is still relatively large at a micro scale. That is because the amount of metal attached to the surface of the catalyst contained in the geothermal waste material. In addition, when testing the dispersion
medium in the form of water which allows the aglumeration process at the time of measurement is used. The possibility of small particles joining together is caused by very large water. This is one possibility of an analysis that might occur.

In addition, the particle size can also be shown according to the results of the SEM analysis at figure 6. From the figure can be seen that the ratio of SiO$_2$/Al$_2$O$_3$ 2.5 and 5, it the particle structure is denser than the others and they has a larger size than others variable. In addition, it can be seen that with the increasing SiO$_2$/Al$_2$O$_3$ ratio, the resulting particle size will be smaller. The ratio of SiO$_2$/Al$_2$O$_3$ 15 shows the smallest size of other variables. From the picture (d) it can be seen that zeolite particles have hexagonal particles shape.

4. Conclusions
This research concludes that washed catalyst has a smaller yield than native. In the washing process, NaOH dissolve in distilled water and it reduce the weight of product catalyst. The greater ratio of SiO$_2$/Al$_2$O$_3$ give smaller yield. This is because of the increasing ratio of SiO$_2$/Al$_2$O$_3$, while the addition of Al(OH)$_3$ is decreases. Catalysts that are washed have smaller particle sizes than without
washing. When the catalyst is washed, some particles do not adhere properly and separate from the catalyst. The catalyst without washing process, has a relatively rough surface compared to the catalyst with washing and makes it easy for the particle fusion process. In this process the nano sintering process occurs due to heating during the calcination process. Larger ratio of SiO$_2$/Al$_2$O$_3$, it produces smaller particle sizes. In the analysis using the Particle Size Analyzer method, the resulting particle size is still relatively large at a micro scale.

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