JOURNAL OF ENERGY, MATERIALS, AND INSTRUMENTATION TECHNOLOGY

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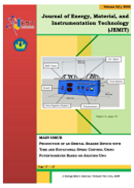

Analysis of the Effect of Variations of Silica Concentration on Synthesis γ-Al_2O_3

Nadhifatul Fuadiyah[1*], Roniyus Marjunus[1], Wawan Rustyawan[2], and Syafriadi[1]

1. Departement of Physics, Universitas Lampung, Bandar Lampung, 35141
2. Pertamina Research Technology and Innovation, Jalan Raya Bekasi KM 20, East Jakarta, 13920

Article Information

Article history:
Received June 13, 2022
Received in revised form November 2, 2023
Accepted November 28, 2023

Keywords: *buffer γ-Al_2O_3, Carboxyl, Siral, ZSM, and Green fuel*

Abstract

Research has been carried out to analyze the effect of variations in silica concentration on the synthesis of γ-Al_2O_3. This research was conducted to determine the variation of Silica against the support γ-Al_2O_3which is the best as a hydrotreating catalyst in the green fuel industry by using several physical characteristics and analyzing the effect of silica variations on the surface area, pore volume, and pore size of the support. This study uses materials such as Boehmite (AlOOH), equates, 25% NH4OH solution, 6% HNO3, and several variations of Silica such as (Carboxyl, SIRAL, and ZSM). In the process of making supports γ-$Al_2O_3$with the sol-gel method in order to homogenize the solutions and silica powders as a buffer variant, it becomes AlOH powder, which is then printed with a press and calcined at a temperature of 550^{o}C gradually to become powder.buffer γ-Al_2O_3. From the study results, the best variation of γ-Al_2O_3 silica buffer was carboxyl with a concentration of 6% because several characterization studies showed superior results to γ-Al_2O_3 support without silica variation. The results of the Surface Area Analyzer characterization greatly affect the hydrotreating catalyst process in the green fuel industry, namely the γ-Al_2O_3 buffer with the addition of 6% silica carboxyl concentration. This is because a large surface area, pore size, and large pore volume can contain more impregnant solution, and the amount of active phase dispersed will also be greater.

Informasi Artikel

Proses artikel:
Diterima 13 Juni 2022
Diterima dan direvisi dari 2 November 2023
Accepted 28 November 2023

Kata kunci: *Penyangga γ-Al_2O_3, Karboksil, Siral, ZSM, dan Green fuel*

Abstrak

Telah dilakukan penelitian tentang analisis pengaruh variasi konsentrasi silika pada sintesis γ-Al_2O_3. Penelitian ini dilakukan untuk mengetahui variasi silika terhadap penyangga γ-Al_2O_3 yang paling baik sebagai katalis hydrotreating pada industri green fuel dengan menggunakan beberapa karakterisasi fisik serta menganalisis pengaruh variasi silika terhadap luas permukaan, volume pori, dan ukuran pori penyangga. Pada penelitian ini menggunakan bahan-bahan seperti boehmit (AlOOH), aquades, larutan NH_4OH 25%, HNO_3 6%, serta beberapa variasi silika seperti (karboksil, SIRAL, ZSM). Dalam proses pembuatan penyangga γ-Al_2O_3 dengan metode sol-gel guna menghomogenkan larutan-larutan serta serbuk-serbuk silika sebagai varisi penyangga tersebut setelah itu, menjadi serbuk AlOH yang kemudian di cetak dengan alat press dan di kalsinasi dengan suhu 550^{o}C secara bertahap agar menjadi serbuk penyangga γ-Al_2O_3. Dari hasil penelitian variasi silika penyangga γ-Al_2O_3 terbaik adalah karboksil dengan konsentrasi 6%, sebab dari hasil penelitian di beberapa hasil karakterisasi menunjukkan hasil lebih unggul dari penyangga γ-Al_2O_3 tanpa variasi silika. Hasil karakterisasi Surface Area Analyzer yang diperoleh sangat mempengaruhi proses katalis hydrotreting pada industri green fuel yaitu pada penyangga γ-Al_2O_3 dengan penambahan silika karboksil konsentrasi 6%. Hal ini dikarenakan memiliki luas permukaan yang besar, ukuran pori, dan volume pori yang besar dapat memuat larutan impregnan yang lebih banyak dan jumlah fasa aktif yang didispersi akan lebih banyak pula.

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* Corresponding author.
E-mail address: nadhifatulfuadiyah30@gmail.com

1. Introduction

Oil production in Indonesia continues to decline every year while its consumption increases. In the future, the oil demand will increase. As The National Energy Council (2016) indicated, the projected escalation in Indonesia's oil demand is envisaged to precipitate a potential fuel crisis in response to this impending challenge, PT. Pertamina has strategically outlined plans to develop alternative fuels sourced from plants, focusing on green fuel. Green fuel is a bio-hydrocarbon compound. The characteristics are generally the same as fossil-based hydrocarbon compounds, so they can be mixed at a percentage level of any amount without needing to adjust the vehicle engine. Green fuel is an excellent choice to meet domestic liquid fuel needs and substitute crude oil or fuel from domestic production (EBTKE Public Relations, 2018). In order to identify, develop, and extract alternative energy sources, careful consideration of the primary factors, namely energy, economy, and ecology, is imperative. Therefore, the system developed must be able to produce energy in large quantities at low costs and have a good impact on the environment.

In green fuel production, a buffer is needed to provide a large surface to spread the active components, broaden the contact surface, and be more efficient. Physical properties that must be considered in choosing support are surface area, porosity, stability, in the range of reaction and regeneration conditions, mechanical strength (hard and robust against pressure), and low price (Topsoe, 1996). In this research, the synthesis and characterization of the buffer will be carried out by Al_2O_3, which will later be applied to making green fuel. However, the researchers only looked for some Si and Al content in variations of silica addition. Silica is a chemical compound with the molecular formula SiO_2 (silicon dioxide), which can be obtained from mineral, vegetable, and crystalline silica synthesis. Therefore, in this study, a buffer was used AL_2O_3, which is relatively cheap and easy and is based on a high Si or Al ratio, which can increase the acid strength and the conversion of hydrocarbons that affect the catalytic cracking reaction process. Based on this background, this research was conducted by varying the Al_2O_3 with other types of Silica to modify the structure, pores, and surface area to make it easier to use in the catalyst process and improve the support's physical characterization. Al_2O_3 is to be applied in the process of making green fuel. The results that have been varied are then analyzed for the content of Si and Al in it to determine the optimum conditions.

2. Research Methods

This research was carried out in February 2019 and completed at the Catalyst and Materials Laboratory of PT. Pertamina (PERSERO) Directorate of Processing Research and Technology Center, Pulo Gadung, East Jakarta. The equipment used in this research includes X-ray diffraction (XRD) Empyrean PANalytical, X-ray fluorescence (XRF) Axios PANalytical, Surface Area Analyzer (SAA) AUTOSORB-6B, Furnace, hydraulic machine, analytical balance, desiccator, bowl and stirrer molds, porcelain dishes, spatulas, measuring flasks, and glassware. The materials used in this study include Boehmit (AlOOH), distilled water, NH_4OH 25% (Pro-Analysis E-Merck Germany), HNO_3 6% (Pro-Analysis E-Merck Germany), SIRAL (Silica Alumina), CARBOXI (-COOH) and, ZSM (Zeolite Socony Mobil).

2.1 Buffer Synthesis

This experimental method was carried out in two stages, namely, the stage of making supports with variations of Silica and the stage of characterization testing. The manufacturing step is carried out by weighing 25 g of Boehmite and putting it in a mixing bowl. Then, Boehmite was added with 3 ml of distilled water and homogenized with a stirrer for 1 minute. Then, add 17 ml of 6% HNO_3 and stir it again for 15 minutes to form a sol-gel.

Then 2.5 mL of 25% NH_4OH was added and stirred with a stirrer for 1-2 minutes to obtain aluminum hydroxide powder. Every time we mix the solution, ensure it is evenly mixed/smooth by looking at the results of the boehmite material that does not clump. Then, the material is printed using a hydraulic press. Then, it is calcined at a temperature of 550°C for 5 hours but gradually, as shown in **Figure 1** (Rustyawan, 2019).

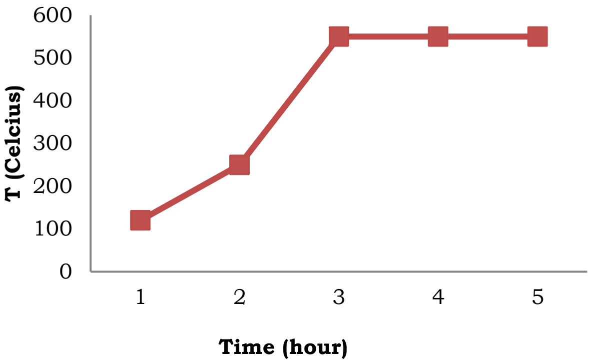

Figure 1. Temperature calcination graph

2.2 Variations of Silica to the support

With the total amount of material that is 25 g, the silica mass concentration variations are carried out as in **Table 1**.

Table 1. Silica Variations.

No	Silica names	Concentration Silica Mass (%)	Weight of Silica (gram)	Weight of Boehmite (grams)
1.	SIRAL (Alumina Silica)	1	0.25	24.75
		3	0.75	24.25
		6	1.5	23.5
2.	Carboxyl	1	0.25	24.75
		3	0.75	24.25
		6	1.5	23.5
3.	ZSM-5	1	0.25	24.75
		3	0.75	24.25
		6	1.5	23.5

Then Boehmit and each variation of Silica based on concentration were put into a mixing bowl before the sol-gel formation.

2.3 Sample Analysis

Analysis of catalyst support was carried out using X-ray diffraction (XRD), X-ray fluorescence (XRF), and Surface Area Analyzer (SAA).

1. X-ray diffraction (XRD). The sample was ground and then placed and flattened on the sample plate. This diffraction test was carried out using XRD Empyrean PANalytical using Cu radiation at a voltage of 40 kV and a current of 25 mA with an angle range of 5-90^o.The XRD instrument is allowed to analyze with the start position (2ɵ) at 6.0300°, end position (2ɵ) at 89.9700°, step size (2ɵ) at 0.0600°, and scan step time at 2.5000 s. The selected program is a slow scan 5-90^0. Then, a peak will appear on the computer, and an analysis of the spectrum of the emerging peak will be carried out.

2. X-Ray Fluorescence (XRF). The sample was weighed 12 grams and then mashed. The powder is put in an aluminum cup. The aluminum crucible containing the sample was pressed using a hydraulic presser. The sample was placed in the sample holder in the XRF device, and then quantitative measurements were made of the components with a voltage of 40kV and a current of 45 mA. The analysis results were obtained by the percentage of compounds in the buffer γ-Al_2O_3 prepared and the buffer γ-Al_2O_3 support with its silica variation.

3. Surface Area Analyzer (SAA). The surface area, pore diameter, and pore volume were analyzed using ASAP 2400. Sample preparation and degassing were carried out by weighing the empty cell samples that had been cleaned previously, and their weight was recorded. The sample is inserted into the sample cell and weighed close to a tolerance of 0.1 mg (the estimated weight depends on its surface area value). It successfully installed furnace cover, fastening screws, and cell samples used without the use of a filter rod. Mounted on one of the ports of the degassing station and tightened the screws to avoid leakage during degassing. The degassing process lasts for ± 3 hours.

The degassing results are checked by observing the set point number on the monitor layer. If the set point number on the computer monitor screen already shows 0, the sample cell is transferred to the nearest cooling station to speed up the cooling process. After cooling, the samples were transferred to ASAP 2400 to analyze surface area (m^2/g), pore volume (cc/g), and pore size (A). The flow chart of this research follows **Figure 2**.

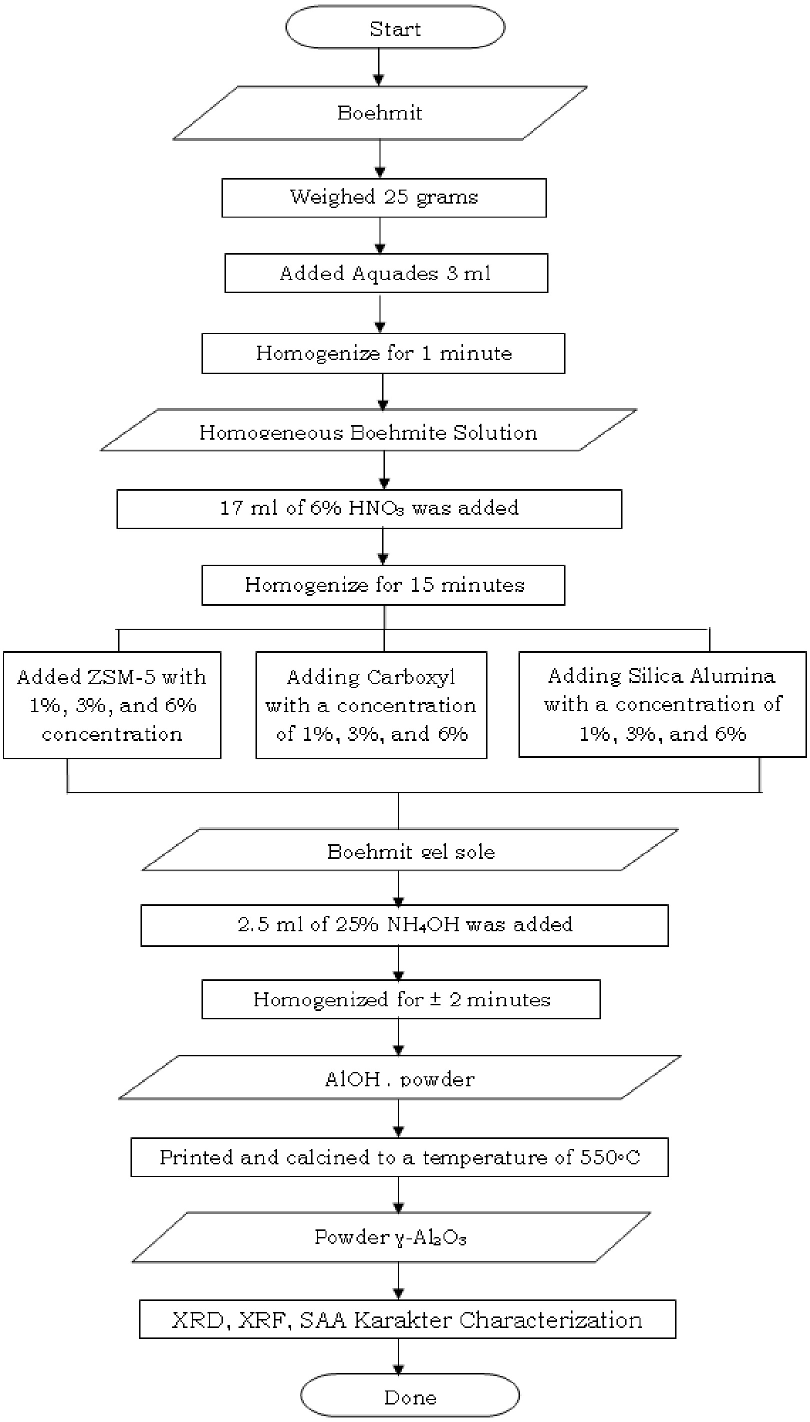

Figure 2. Research flow chart.

3. Results and Discussions

3.1 Buffer Characterization Using XRD

The diffraction angle values between the diffractograms obtained with the standard crystal diffractograms from the database were compared to determine the similarity of the synthesized crystal structures. The diffraction pattern of the γ-Al_2O_3 buffer used in this study, based on ICDD no. 98-009-9836, has three typical peaks at 2θ angles: 36.97°, 46.11° and 66.70°. These three peaks are similar to the three typical peaks γ-Al_2O_3 in the research of Zhang et al. (2016), namely at angles of 2θ: 37.59°, 45.84° and 67.00°. The following **Table 2** is the result of 2θ in this study.

Table 2. The peak yield of XRD is 2θ.

Variation	Concentration (%)	2θ (o)	I (au)
γ-Al_2O_3	-	45.86	1026
		60.02	350
		67.03	1169
Carboxyl	1	45.87	1093
		60.03	388
		67.05	1177
	3	45.87	1112
		60.03	349
		67.05	1127
	6	45.87	1189
		60.03	404
		67.05	1143
Siral	1	45.87	1216
		60.03	390
		67.05	1304
	3	45.87	1234
		60.03	372
		67.05	1221
	6	45.87	1187
		60.03	399
		67.05	1344
ZSM	1	45.87	1155
		60.03	412
		67.05	1208
	3	45.87	1156
		60.03	400
		67.05	1240
	6	45.87	1195
		60.03	402
		67.05	1203

The γ-Al_2O_3 buffer diffractogram was seen in the study with 2θ = ±37.06˚, ±45.84˚, and ±66.74˚ with clear peak separation and high peak intensity.

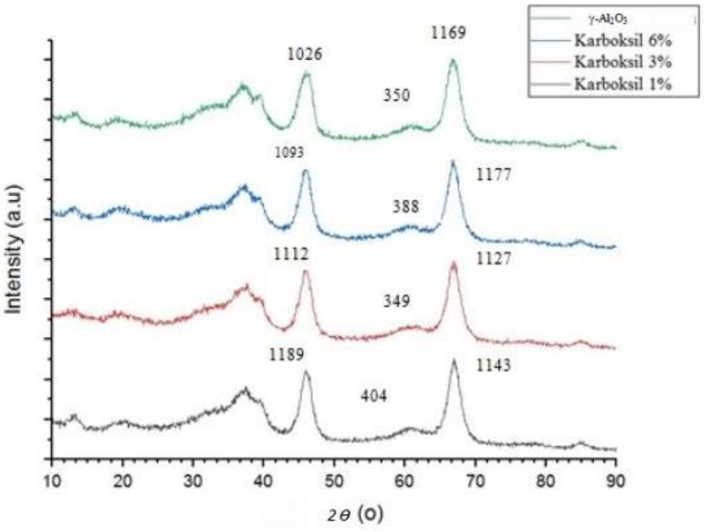

Figure 2. Buffer γ-$A_{l2}O_3$ Difactogram with Carboxyl Variation.

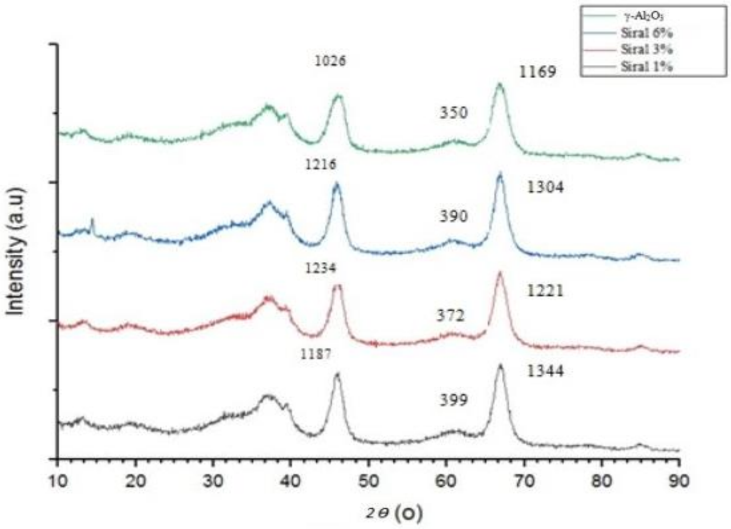

Figure 3. Buffer γ-$A_{l2}O_3$ Difactogram with Siral Variation.

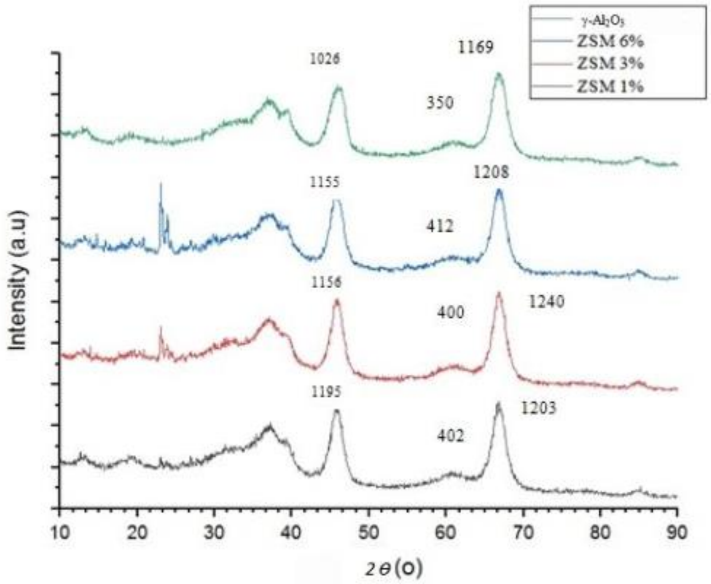

Figure 4. Buffer γ-$A_{l2}O_3$ Difactogram with ZSM Variation.

The diffractograms shown in **Figures 2**, **3**, and **4** show that the trend of the intensity of the γ-Al_2O_3 buffer with carboxyl variations is as high as that of spiral and ZSM variations. However, the results of the intensity values are not the same. Silica in the form of amorphous causes the appearance of insignificant peaks in the diffraction pattern. The relative intensity is a parameter that indicates the number or number of crystal planes being measured. So, the γ-Al_2O_3 support has the same diffractogram pattern as the Silica variation of γ-Al_2O_3 support. Meanwhile, from the intensity value listed based on XRD results, the best is the γ-Al_2O_3 buffer with a ZSM variation of 6% with the highest peak value.

3.2 Buffer Characterization Using XRF

Before being analyzed using XRF, the catalyst was pulverized first. The goal is to minimize the stress on the energy on the surface so that it can compensate for the peak position on the diffractogram. The Axios Panalytical XRF (X-Ray Fluorescence) instrument analyzed the support components. This instrument can detect several elements, including Silica and alumina, which are the most significant components of the catalyst support.

Table 3. XRF Analysis Results.

No	Sample	Concentration Variation (%)	Composition Si (%)	Composition Al (%)
1	γ-Al_2O_3	-	0.004	0.996
2	Carboxyl	1	0.023	0.977
		3	0.053	0.947
		6	1.004	0.899
3	Siral	1	0.008	0.992
		3	0.003	0.997
		6	0.009	0.990
4	ZSM	1	0.170	0.982
		3	0.042	0.958
		6	0.085	0.914

Based on the analysis of the levels of Silica and Alumina in the buffer sample, it can be seen that the sample supports γ-Al_2O_3 and has a Silica content of 1.004% and an Alumina content of 0.899%. Meanwhile, the levels of Silica and Alumina from each buffer with varying concentrations can be seen in **Table 3**. Based on these data, the silica content of the buffer sample with a carboxyl variation of 6% is greater than the silica content of the γ-Al_2O_3 buffer sample and other variations. According to Okamoto et al. (1998), Silica can form a silanol group (Si-OH), which acts as a Bronsted acid, and Silica can also act as a Lewis acid (Si+). The uniqueness of Silica is that it has four free electrons in the outer shell, which tends to lose or accept electrons so that the acidity level will affect the activity of the hydrotreating catalyst.

3.3 Buffer Characterization Using SAA

The surface area of the support is a parameter that significantly influences the number of active sites in the catalyst that will interact with the feed molecules to determine a catalyst's activity level (Topsoe, 1996). **Figure 5** shows the results of the surface area of the γ-Al_2O_3 support with several variations of Silica.

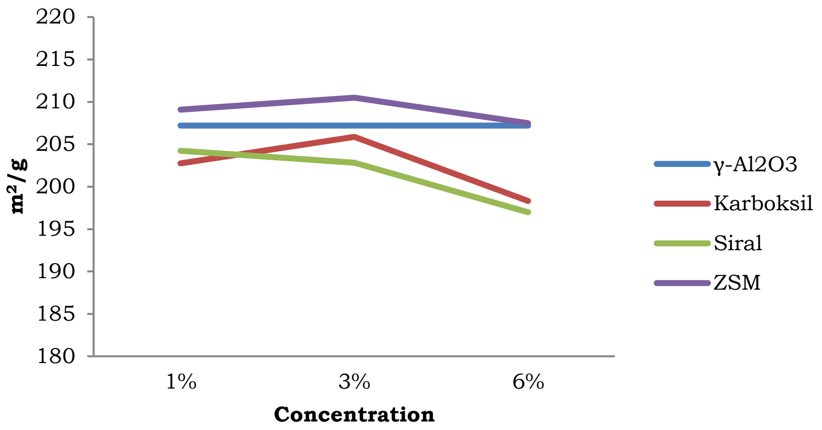

Figure 5. Graph of Buffer Surface Area against Silica Variation.

In the green fuel industry using hydrotreating catalysts, γ-Al_2O_3 is a desirable type of alumina because it has a large surface area, especially around 250-350 m^2/g, and can regenerate catalytic activity after intensive use under extreme operating conditions (Satterfield, 1997). By looking at the results in the picture above, it can be seen that the surface area of the γ-Al_2O_3 support with variations in Silica has a standard surface area that does not follow the standard to be the base material for hydrotreating catalysts, where the results obtained for the γ-Al_2O_3 support are 207 m^2/g. In comparison, the range of the γ-Al_2O_3 support with variations in Silica is 198 – 210 m^2/g. The pore volume of the catalyst, which has macro-sized pores, is less covered by metal impurities than micro-sized pores. Alumina with a dominant macro-sized pore distribution has a relatively large pore volume (Rana et al., 2005). Buffers with large pore volumes can contain more impregnants, and the amount of active phase dispersed will also be more significant. **Figure 5** shows the results of the pore volume of the γ-Al_2O_3 buffer with several variations of Silica.

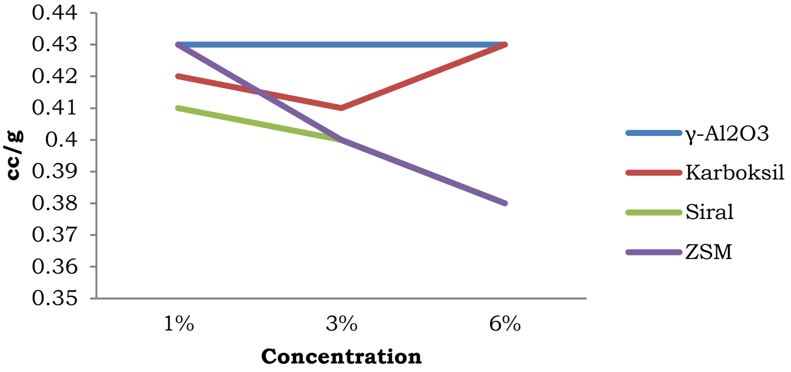

Figure 6. Graph of Buffer Pore Volume against Silica Variation.

The pore volume in each sample did not show relevant results with increasing silica concentration, as shown in **Figure 6**. The figure above shows the optimum pore volume in the γ-Al_2O_3 support sample without being varied and the γ-Al_2O_3 support with a 6% carboxyl concentration variation, 0.43 cc/g. Based on the data shown in Figure 13, the pore volume of the γ-Al_2O_3 support with various carboxyl concentrations of 1%, 3%, and 6% is relevant to the commercial alumina standard, which is 0.400 cc/g (Chemical, 2017). Meanwhile, as the concentration increases, the γ-Al_2O_3 buffer with siral and ZSM variations shows a lower value.

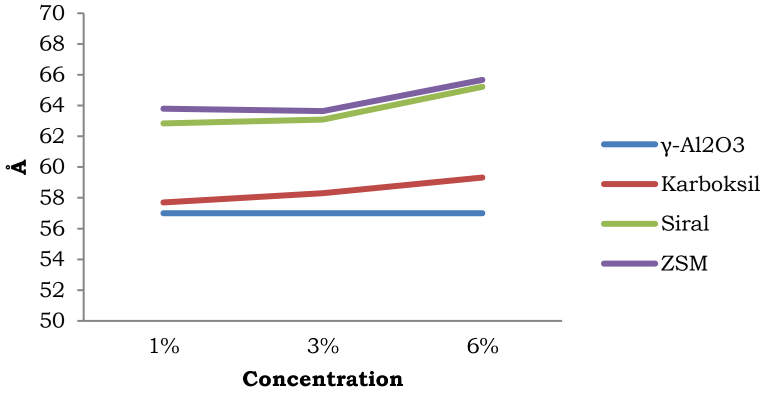

Figure 6. Graph of Buffer Pore Size against Silica Variation.

At a smaller pore size, the activity will be limited by diffusion, whereas at a larger pore size, the active surface area will be smaller. The gamma alumina buffered catalyst with a predominantly macro-sized pore distribution resulted in a high hydrodematalization catalytic reaction (HDM) and a low hydrodesulfurization catalytic reaction (HDS) (Rana et al., 2005). Alumina with a dominant macro-sized pore distribution has a relatively large pore volume (Lussier & Wallace, 2002). The larger the pore volume, the more impregnants can be loaded, and the active phase is dispersed. This study's analysis resulted in a larger pore size than the γ-Al_2O_3 support without variations in Silica, namely at each addition of silica concentration to the γ-Al_2O_3 support. However, the results relevant to the pore volume were found in the γ-Al_2O_3 support with a carboxyl concentration variation of 6%.

4. Conclusions

The research that has been done, several conclusions can be drawn as follows: The best variation of γ-Al_2O_3 silica buffer is carboxyl with a concentration of 6% because the results of several characterization studies show that the results are superior to γ-Al_2O_3 support without silica variation. The research results significantly affect the hydrotreating catalyst process in the green fuel industry, which is the γ-Al_2O_3 buffer with the addition of 6% silica carboxyl concentration. This is because a large surface area, pore size, and large pore volume can contain more impregnant solution, and the amount of active phase dispersed will also be more significant.

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