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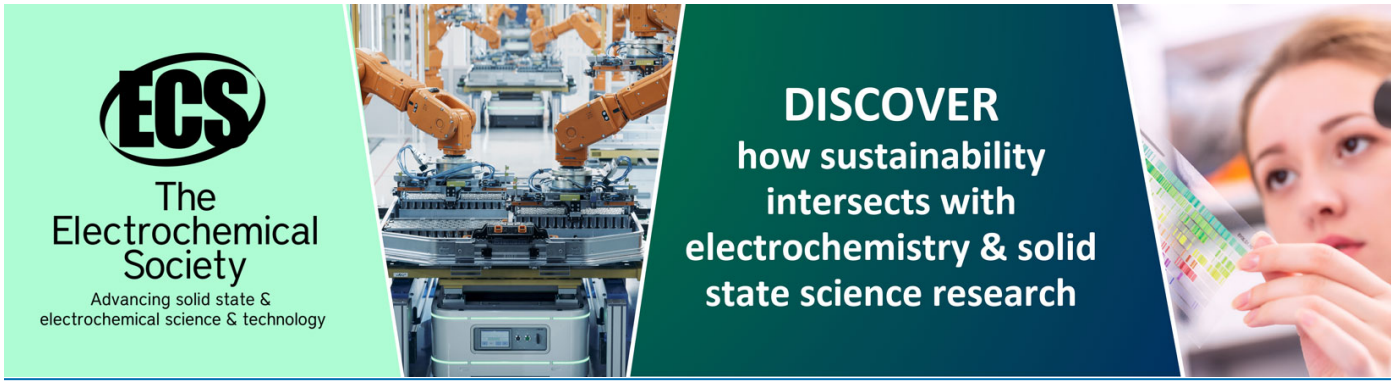

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Synthesis and Characterization of ZSM-5 Catalyst at Different Temperatures

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Abstract. ZSM-5 is a synthetic zeolite which contains silica (Si) and alumina (Al) with the ratio of silica greater than the alumina. The catalyst is known as ZSM-5 because it has a pore diameter of 5 Å (angstroms) and it has more than five Si/Al ratios. The catalyst has a high production cost and a complex production process which is highly influenced by time and temperature. Based on that fact, the focus of this research is studying the production process of ZSM-5 and investigating the effect of time and temperature on the crystallinity and the morphology of ZSM-5. In this research, Latourette *et al.* method was used, followed by the calcination at different temperatures (500 °C, 600 °C, 700 °C, 800 °C) in 5 and 7 hours. Subsequently, ZSM-5 was characterized using XRD (X-ray Diffraction) and SEM (Scanning Electron Microscope). The XRD analysis shows that the peak of standard ZSM-5 synthesis is at 2 theta degree 23. Prior to the calcination, ZSM-5 has an average crystallinity of 37.7337%. However, after the calcination, the crystallinity of the catalyst increased as the temperature rises. At 500 °C, 600 °C, 700 °C , and 800 °C the crystallinity increases to 39.1959%, 44.0927%, 42.9425%, and 44.8806%, respectively. Meanwhile, calcination time affects the XRD peak intensities by increasing the ZSM-5 crystal cores. The longer the calcination time, the higher the peak intensity is.

1. Introduction

Cracking is a process that is widely used in research and industry, especially in hydrocarbon-related ones. However, the hydrocracking process traditionally requires high operating temperatures and can cause environmental problems. Therefore, the use of transition metals, silica, zeolite-modified zeolite, mesoporous mixed oxide catalyst, and metal organic frameworks, was developed in the catalytic cracking process [2]. The catalytic cracking process can break down complex hydrocarbons to simpler ones at low temperature and pressure [1]. Catalytic cracking is widely used to produce biofuel from vegetable oils [3].

A catalyst that is widely used in the catalytic cracking process is zeolite [1]. Zeolite is the best catalyst for oil cracking process because it has a high thermal stability, has microcrystalline structure, and able to concentrate the reactants that are contained in the pores [2]. In addition, the aluminosilicate framework of zeolite provides high cation-exchange capacity, high adsorption, and has hydration-dehydration property. However, the use of zeolite as catalysts is limited because it has narrow pores. Due to this fact, the reactant components which have a large molecular size will have difficulty in

mass transfer process[4-5]. Furthermore, the zeolite is a non-metal mining product that has limited availability. These drawbacks encourage researchers to study about the synthesis of zeolite or ZSM-5.

Synthesis of ZSM-5 catalyst (Zeolites Socony Mobil-5) was first performed by Argauer and Landolt which is patented by Mobil Oil Corporation in 1972 [8]. ZSM-5 is a synthetic zeolite which contains silica (Si) and alumina (Al) with the ratio of silica greater than the alumina. The existence of aluminum and Si/Al ratio of ZSM-5 catalyst causes ZSM-5 to have acidic property [9]. This property makes the catalyst has the function as a catalyst support, adsorbent, etc. [10]. It has pore diameter range of 5 Å (angstroms) and it has more than five Si/Al ratio. ZSM-5 has a medium pore size (0.54 nm × 0:56 nm) and has two intersecting three-dimensional channels with one straight parallel channel and the other running parallel defined by sinusoidal 10-membered ring openings of 5.3 Å × 5.6 Å and 5.1 Å × 5.5 Å [2, 6-7].

ZSM-5 catalyst can be used to manufacture a variety of products through a catalytic cracking process. Types of products that can be produced by ZSM-5 catalyst are influenced by physical properties of the catalytic material and constituent of ZSM-5 catalyst. There are several parameters that can affect the properties of ZSM-5 catalysts. These parameters are the silica source, the alumina source, template, and crystallization conditions [6]. To understand these parameters, the characterization of the catalyst by means of morphology, crystallinity, and catalyst framework structure analysis is needed. Analysis of the catalyst morphology can be done by using a Scanning Electron Microscope (SEM), while the crystallinity analysis and the structure of the catalyst can be analyzed by using XRD.

In this research, synthesis of ZSM-5 catalyst with Latourette *et al.* method [11] at the various temperatures, calcination time, and catalyst supports was conducted. After that, the produced catalysts were analyzed by using SEM and XRD to understand their characteristics.

2. Methods

2.1. Materials

Materials that are used in this research are: Aluminum Sulfate ($Al_2(SO_4)_3.18H_2O$), Cobalt Nitrate ($Co(NO_3)_2.6H_2O$), Nickel Nitrate ($Ni(NO_3)_2.6H_2O$), Sulfuric Acid 98% (H_2SO_4), Sodium Silicate and Sodium Hydroxide (both were supplied by Merck Ltd.), distilled water (obtained from Laboratory of Membrane Research Centre Diponegoro University), Methanol, and Glycerol (both were supplied by Indrasari Chemical Store).

2.2. Catalyst synthesis

Catalyst was synthesized according to Latourette *et al*. [11] method. Firstly, Solution A as the source of alumina was prepared. The solution contains 26.7 grams of Aluminum Sulfate ($Al_2(SO_4)_3.18H_2O$), 56 grams of 98% Sulfuric Acid (H_2SO_4), and 15 grams of distilled water. After that, Solution B as the source of silica was prepared. The solution contains 56 grams of Sodium Silicate and the same amount of 40% Sodium Hydroxide (NaOH). Subsequently, Solution A and Solution B were mixed. After that, the mixture was homogenized by a homogenizer at a speed of 12000 rpm. After obtaining a homogeneous mixture, crystallization is done by using an autoclave reactor at 200 °C in 6 and 8 hours. After the crystallization, ZSM-5 catalysts as products were washed with distilled water and then dried overnight.

The ZSM-5 products crystals were analyzed by using XRD to determine their degree of crystallinity. After that, ZSM-5 undergone calcination process at various temperatures of 500 °C, 600 °C, 700 °C and 800 °C in 5 and 7 hours. After this process, the product was analyzed using XRD to determine their crystallinity and their catalysts structure. SEM analysis was also conducted to find out the morphology of the catalysts.

2.3. Catalyst impregnation

ZSM-5 Catalyst was impregnated using a Nickel and Cobalt metal ions. 0.5 grams of Nitrate Cobalt ($Co(NO_3)_2.6H_2O$) and Nickel Nitrate ($Ni(NO_3)_2.6H_2O$) was dissolved in 25 ml of distilled water. Then, the solution was mixed with 5 grams of ZSM-5 catalyst, heated to 60 °C, and stirred with

a magnetic stirrer at a speed of 600 rpm for 4 hours. After that, the mixture was left to stand for 24 hours, and then filtered and dried by using an oven at 110 °C for 1 hour. Finally, the mixture was undergone calcination process at 600 °C for 6 hours.

2.4. Catalyst characteristic

The ZSM-5 catalyst products were characterized with morphology and crystallinity analysis. The analysis of crystallography conducted by using XRD-7000S Shimadzu with Copper X-ray tube target, 30 kV voltage, 30 mA current, and Kα radiation. XRD data was analyzed with PCXRD software. Morphology of catalyst data was analyzed with JEOL PC Scanning Electron Microscope (PCSEM) model JSM-6510LA with x5000 magnification. These analysis processes were conducted in Center of Research and Service Diponegoro University (CORES DU).

3. Results and discussions

3.1. The effect of crystallization time

In the production of the ZSM-5 catalyst variations of crystallization time of 6 and 8 hours was performed. Crystallization time is one parameter that plays an important role on the properties of the catalyst since the catalyst products were harvested at different times [12]. During the variation of crystallization time, the crystallization takes place at temperatures of 200 °C.

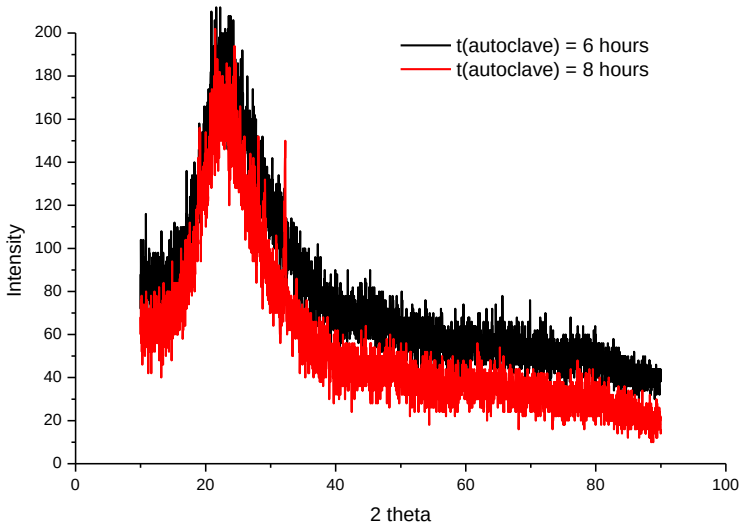


Figure 1.XRD pattern of ZSM-5 Synthesis on difference crystallization times.

Figure 1 shows the results of the XRD analysis of the ZSM-5 catalyst in the autoclave for 6 and 8 hours. The graph shows that the longer the crystallization time, the more compact the catalyst structure is. This fact can be seen from the intensity at 2 theta degree 21 and 23. Furthermore, the long crystallization time also affects the degree of crystallinity.

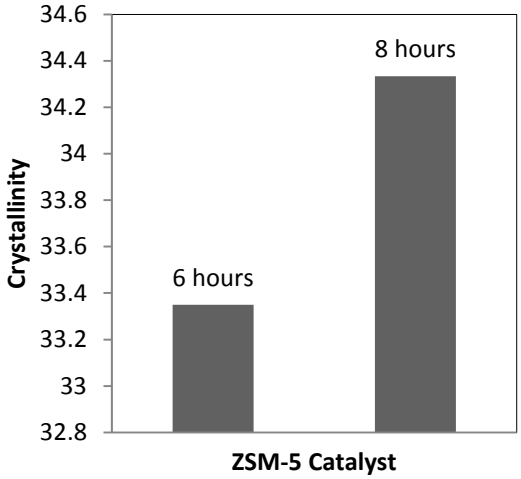


Figure 2.ZSM-5 crystallinity on difference crystallization time.

Figure 2 shows that the longer time of crystallization, the higher the catalyst crystallinity is. At 6 hours crystallization time, the ZSM-5 catalyst has a crystallinity of 33.35% whilst at 8 hours it has a crystallinity of 34.33%. Nevertheless, their degree of crystallinity is still low, consequently after the crystallization process is done the calcination process is conducted.

3.2. The effect of calcination temperature

To improve their crystallinity, the ZSM-5 catalysts were undergone calcination process. Calcination process was carried out at various temperatures of 500 °C, 600 °C, 700 °C and 800 °C for 5 hours. After calcination process, ZSM-5 catalysts were analyzed by using XRD to determine their degree of crystallinity. Then, the structure was being compared with the commercial one (standard).

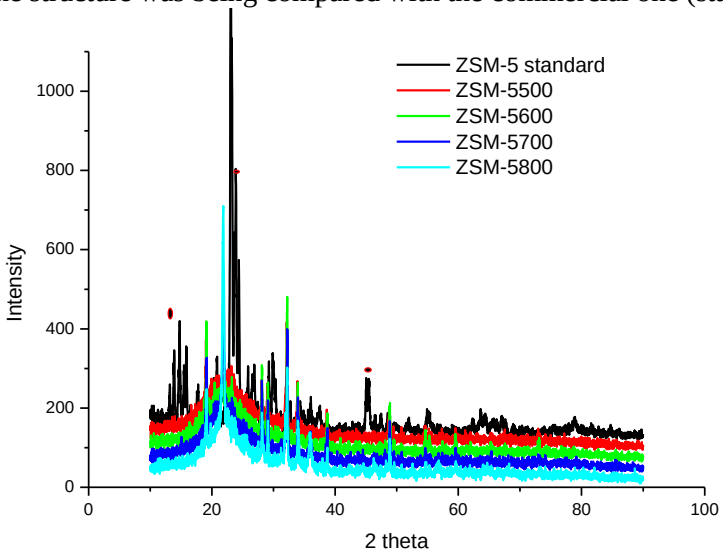
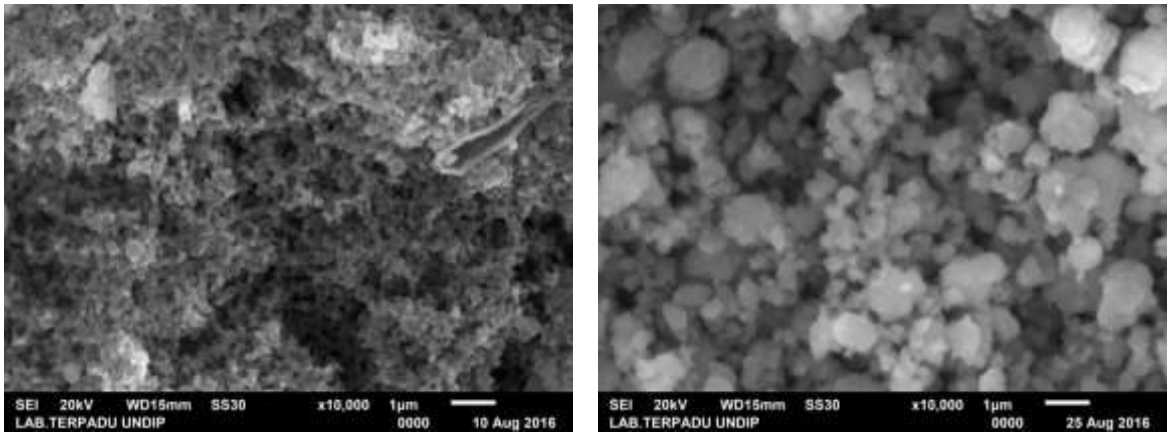


Figure 3.XRD pattern of synthesized ZSM-5 at different temperatures and the comparison to standard ZSM-5.

Figure 3 shows synthesized and standard ZSM-5 diffractograms which were undergone calcination at various temperatures. In general, all of the diffractograms shows a similar result. The presence of aluminum and silica in a commercial ZSM-5 is shown in 2 theta degrees 13°, 23° and 45° [10, 13]. However, synthesized ZSM-5 that has the peak at 2 theta degrees 13°, 23° and 45°, has a lower intensity compared to commercial ZSM-5. Furthermore, synthesized ZSM-5 also has other peaks. This is because the degree of crystallinity of synthesized ZSM-5 is quite low which made the catalyst has

an amorphous structure [14]. The SEM analysis results in Figure 4 reveals that the morphology of synthesized ZSM-5 is still fairly amorphous. This is shown by the surface structure of the catalyst which clumped each other, whereas on commercial ZSM-5 has a separated structure due to its fairly high crystallinity [15].



(a) **(b)**

Figure 4. Photographs of ZSM-5 catalyst (a. Synthesized; b. Standard ZSM-5).

Compared to the crystallinity of commercial ZSM-5, synthesized ZSM-5 has a fairly low crystallinity. Figure 5 shows the crystallinity of synthesized ZSM-5 calcination are 39.2% at 500 °C, 44.1% at 600 °C, 42.9% at 700 °C and 44.9% at 800 °C. In the other hand, commercial ZSM-5 has a crystallinity of 76.1%.

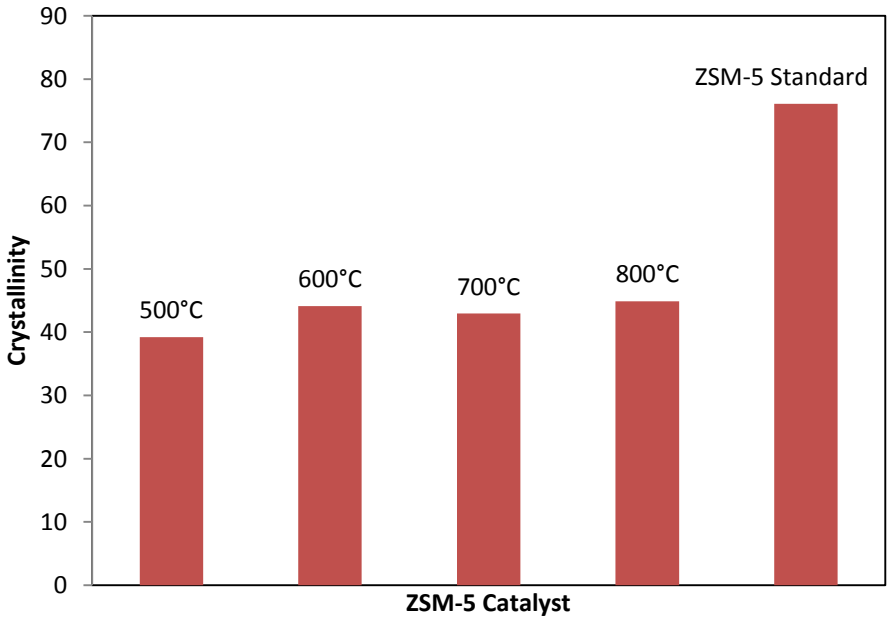


Figure 5.ZSM-5 Crystallinity on difference calcination temperature.

3.3. The effect of calcination time

ZSM-5 catalyst products were not only undergone calcination at various temperatures but also in various calcination times. The variations of calcination times were 5 and 7 hours with calcination temperature of 700 °C. Then, the synthesized ZSM-5 was analyzed by using XRD to determine the degree of crystallinity and its suitability to the standard ZSM-5. Figure 6 shows that the synthesized ZSM-5 with calcination time of 5 hours has a better intensity than the 7 hours. This also can be seen from the degree of crystallinity provided in Figure 7. The synthesized ZSM-5 with calcination time of

5 hours has a crystallinity of 42.9%, while synthesized ZSM-5 with calcination time of 7 hours has a crystallinity of 40.2%. It can be concluded that the optimal calcination time is 5 hours. In conclusions, the variables that affect the properties of the catalyst are the crystallization time and temperature of calcination.

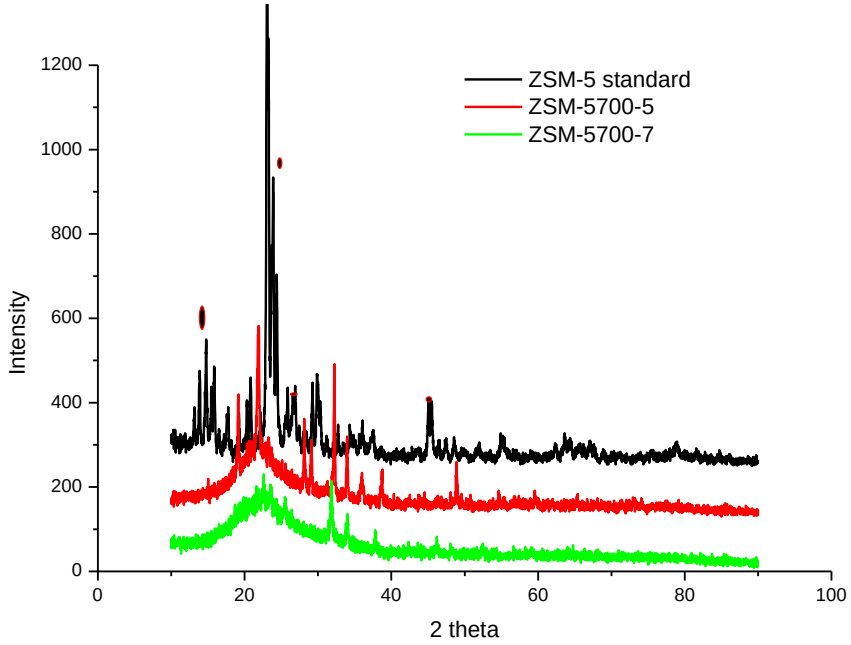


Figure 6.XRD pattern of synthesized ZSM-5 in various calcination times and standard ZSM-5.

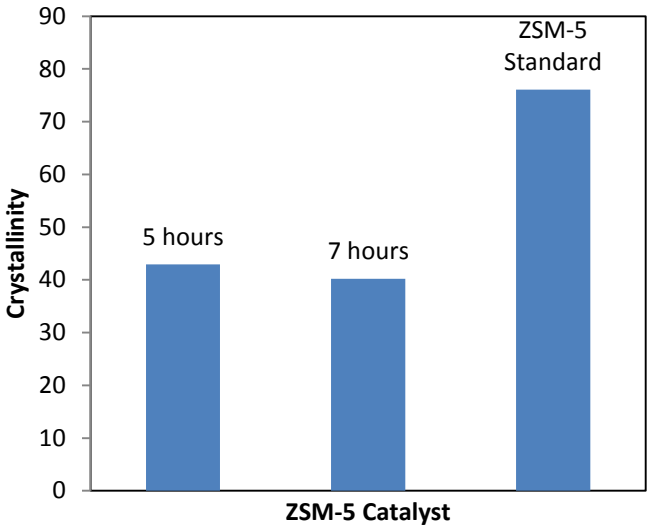


Figure 7.ZSM-5 crystallinity in difference calcination times.

4. Conclusions

It can be concluded that crystallization time affects the physical properties of ZSM-5 catalyst. The longer the time of crystallization, the more compact the physical properties are. This is because they have better crystallinity. In addition, the calcination temperature on ZSM-5 catalyst production also affects the crystallinity of the catalyst. The higher the temperature is, the better the catalyst's

crystallinity. Besides, the morphological structure of the catalyst is also improved by the high calcination temperature.

5. Acknowledgements

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