

## Effect of Acid Treatment on the Opening of Catalyst Pores

Donatus Setyawan Purwo Handoko

Faculty of Mathematics and Natural Sciences, University of Jember (UNEJ)

**\*Corresponding Author:** Donatus Setyawan Purwo Handoko

[kreka\\_zeolit@yahoo.com](mailto:kreka_zeolit@yahoo.com)

---

### ARTICLE INFO

*Keywords:* Zeolite,  
Calcination, Impregnation

*Received :* 09, November

*Revised :* 17, December

*Accepted:* 27, January

©2023 Handoko: This is an open-access article distributed under the terms of the [Creative Commons Atribusi 4.0 Internasional](https://creativecommons.org/licenses/by/4.0/).



### ABSTRACT

Research on the effect of acid treatment on the opening of the pore mouths on the surface of the zeolite catalyst has been carried out. The preparation of the zeolite catalyst was carried out through the processes of soaking, calcination, oxidation and reduction. Initially, the zeolite was soaked for 3 hours in distilled water, then drained and crushed until its size passed a 100 mesh sieve, followed by a calcination process with nitrogen for 5 hours. Then proceed with oxidation for 3 hours followed by a reduction process for 2 hours with hydrogen. Furthermore, the catalyst was impregnated with Ni from the salt  $\text{Ni}(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$ . After that the catalyst is stored and placed in a desiccator. Then an analysis of the catalyst obtained with AAS was carried out to determine the content of Na, Ca, Fe, Mg and K cations, and the content of Al and Si. Then continued with the analysis of acidity with gravimetric method and continued with analysis with the BET method to determine the specific surface area and pore size distribution. Furthermore, the catalyst is used in the catalytic cracking process at various temperatures.

## INTRODUCTION

In 1835, Berzelius explained the concept of the catalyst as a method of controlling the rate of a reaction. Catalyst is defined as a substance which when added to a reaction system can increase the reaction rate or accelerate the achievement of an equilibrium state of the reaction system. The role of the catalyst has no effect on the reaction stoichiometry or the reaction equilibrium constant. The catalyst is involved in a reaction but does not react to produce products and at the end of the reaction will be recovered (Satterfield, 1980).

The use of a catalyst may require only the activity or selectivity or both. Catalyst activity will usually decrease with increasing temperature, and an increase in temperature will also result in shortening the catalyst life time. If the product varies greatly thermodynamically, an increase in system temperature can cause an increase or decrease in selectivity catalyst, depending on the overall nature of the reactants and reaction products. Based on these reasons, the selectivity of the catalyst can be controlled through the temperature conditions of the reaction system.

## LITERATURE REVIEW

The acidity of the zeolite as a catalyst is an important parameter. The acidity of the zeolite as a catalyst is based on the presence of Bronsted and Lewis acid sites on the surface of the zeolite. The acid site is the active site of the zeolite as a catalyst, so that the catalytic reaction can take place due to the acidic and basic nature of the catalyst and the reactants (implementation of the Bronsted acid site) or the interaction between the electron pair donor- acceptor of the catalyst and the reactants (implementation of the Lewis acid site) or due to the presence of positive and negative charges between the catalyst and reactants (implementation of electric charges).

Acidity and acid strength of a catalyst have different meanings. According to Satterfield (1982), the acidity of a catalyst is defined as the ability of the catalyst to adsorb ammonia base due to the presence of Bronsted acid sites and Lewis acid sites on the surface of the catalyst. Acid strength is defined as the ability of the surface of the catalyst which contains Bronsted acid sites and Lewis acid sites to interact with the reactants (organic compounds). The relationship between acidity and acid strength is inverse.

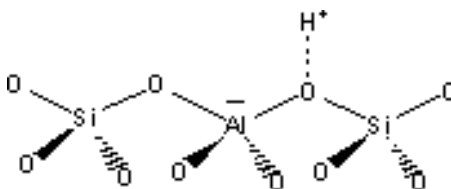


Figure 1. Bronsted Acid Site on a Zeolite Framework (Satterfield, 1982)

The increase in the Si/Al ratio due to a dealumination event is linearly related to the increase in the acidity of the zeolite. The increase in acidity due to a dealumination event is not infinitely linear, but there is a state or maximum

condition that will be achieved, and in these circumstances it is relatively difficult for Al in the zeolite framework to experience dealumination (Zhang, 1998).

Determination of the acidity of zeolite as a catalyst can be carried out gravimetrically. Gravimetric determination of acidity is based on the number of moles of  $\text{NH}_3$  adsorbed on the surface zeolite. The acidity in this case is expressed in mmol  $\text{NH}_3$ /mg zeolite. Ammonia base adsorption may occur at Bronsted acid sites and Lewis acid sites. This situation is more due to the fact that ammonia is more nucleophilic.

Quantitative determination of acidity can also be carried out by adsorption of bases from pyridine, but adsorption of pyridine bases is more likely at Lewis acid sites than at Bronsted acid sites. Weaknesses in using pyridine as an adsorbate molecule in the determination of acidity because pyridine has a larger molecular size than ammonia, and pyridine is less nucleophilic than ammonia.

The determination of the acid sites on the surface of the zeolite is better if it is carried out using the adsorption of ammonia and pyridine bases. Thus the number of Bronsted acid sites and Lewis acid sites can be predicted. The acidity from the Bronsted site tends to be stronger than the acid from the Lewis site.

## RESEARCH METHODS

### Tools and Materials

Equipment that will be used in this study include: laboratory glassware, plastic containers, plastic bottles, pH meter, 100 mesh filter, reflux tool set, vacuum desiccator, analytical balance, oven, atomic absorption spectroscopy (AAS), magnetic stirrer, vacuum pump, porcelain cup and thermometer.

The materials needed in this study include: natural zeolite, 37% HCl, distilled water, 40% HF, oxygen gas, nitrogen gas, hydrogen gas, 2M  $\text{NH}_4\text{Cl}$ , 25%  $\text{NH}_3$  p.a solution.

### Research Procedure

The zeolite was filtered through a 100 mesh sieve, then soaked in distilled water while stirring for 1 hour, then dried at 120 °C for 3 hours. The natural zeolite was soaked in 1% HF for 10 minutes. Then filtered and washed with distilled water to pH 6, then dried at 120 °C for 2 hours to obtain Active Zeolite catalyst (ZA).

The catalyst was then refluxed with 6 M HCl for 30 minutes at 90 °C. Then washed and filtered using distilled water until pH = 6 and dried at a temperature of 120 °C for 2 hours (Trisunaryanti, 1996). The zeolite sample was then refluxed with 2 M  $\text{NH}_4\text{Cl}$  at 90 °C for 2 hours with a magnetic stirrer. The sample was then filtered and washed to a pH of 6 and then dried at 120 °C for 2 hours. The sample was then followed by calcination using nitrogen gas at a

temperature of 500 °C for 2 hours and oxidation with oxygen gas at a temperature of 500 °C for 2 hours to obtain a ZAA catalyst.

The ZAA catalyst was given hydrothermal treatment by flowing water vapor for 5 hours at a temperature of 500 °C. Then it was cooled and calcined under nitrogen gas at a flow rate of 20 mL/minute for 3 hours at a temperature of 500°C and then cooled. Then it was oxidized with O<sub>2</sub> gas for 1.5 hours at a temperature of 400 °C and ZAAH catalyst was obtained. Then impregnated with Ni.NO<sub>3</sub>.6(H<sub>2</sub>O)

## RESULTS AND DISCUSSION

### Catalyst Preparation

In this study, the zeolite used was modernite zeolite in the form of granules with a diameter of ± 0.5 cm, gray-green color originating from Wonosari, Yogyakarta. The initial process carried out is washing the zeolite with distilled water so that it is free from physical impurities found in the zeolite such as dust, small stones and small leaves (coded Z). The natural zeolite was then activated by adding 1% HF concentrated acid solution. This addition aims to damage the structure of the zeolite framework so that Al can come out of the structure (Windarti et al, 2004) and remove Si outside the framework. This zeolite is coded ZA (Active Zeolite) in which its physical form becomes smoother and the color is greenish white.

The next process is zeolite activation by refluxing using 6 M HCl. This aims to clean the pore surface and is expected to increase the Si/Al ratio by dissolving Al (dealuminating). The washing process to pH 6 which is carried out after the acidification process aims to dissolve Al<sub>2</sub>O<sub>3</sub> and the remaining acid that is outside the zeolite framework. The next process is the reflux process with NH<sub>4</sub>Cl. This process aims to replace the balancing cations in zeolite such as Na<sup>+</sup> and Ca<sup>2+</sup> with H<sup>+</sup> to form H-zeolite (Rodiansono et al, 2007) which later becomes a site that is easily substituted by metals. After that proceed with the calcination process with nitrogen gas and oxidation process with oxygen gas which aims to remove impurities organic matter and water so that the zeolite pore mouths open and the specific surface area increases. This zeolite is coded ZAA (Acid Active Zeolite) in which its physical form changes to a slightly reddish color and a finer texture.

The next process is the hydrothermal process for 5 hours which aims to assist the process of rearranging the Si-OH groups in the zeolite framework after the acidity process. This zeolite is coded ZAAH (Hydrothermal Acid Active Zeolite) in which its physical form turns reddish. The final process is adding Ni and Cu metals to the zeolite through a wet imregnation process. Furthermore, calcination, oxidation and reduction processes are carried out at this stage. The purpose of the reduction process is to reduce the metal embedded in the zeolite so that it is zero charged (Ni(SO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O becomes Ni and CuSO<sub>4</sub>.5H<sub>2</sub>O becomes Cu). This zeolite was then given the code Ni-Cu/ZAAH.

### Si/Al ratio

One of the important zeolite characters to know is the Si/Al ratio, because the content of the Si/Al ratio can affect the properties of the zeolite as a catalyst. According to Suyartono (1991) natural zeolite with high Al content is less stable at high temperatures in the catalytic cracking process. According to Hamdan (1992) zeolite with a high Si/Al ratio will have high thermal stability and be effective in cracking non-polar compounds.

The graph of the increase in the Si/Al ratio can be seen in Figure 1. The data in the graph above shows that the Si/Al ratio has increased from catalyst Z to catalyst Ni-Cu/ZAAH. The increase in the Si/Al ratio of the catalyst was due to the dealumination process and hydrothermal treatment. Dealumination process is the release of Al in the framework when refluxing with 6 M HCl. Hydrothermal process for stabilizing the framework structure. The stability of the ZAAH catalyst frame structure is one of the factors for use as a catalyst as well as a metal carrier which can improve performance in catalytic cracking. In addition, the hydrothermal process can

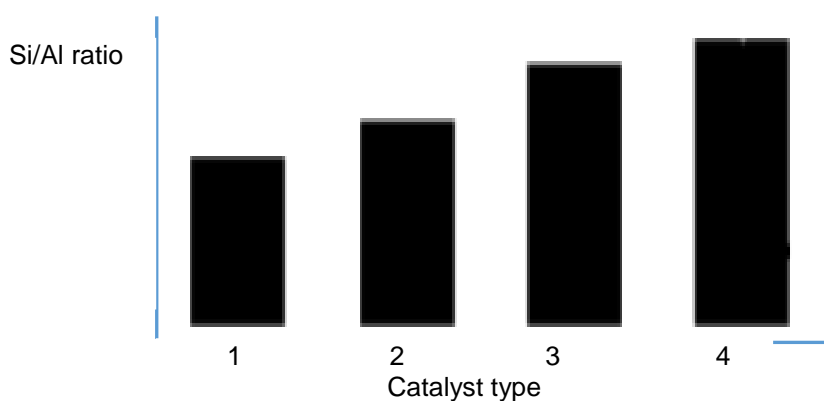


Figure 2. Types of Catalysts

### Catalyst Acidity

The acidity of the catalyst is determined using the Gravimetric method. This method is based on the difference in the weight of the catalyst before and after adsorbing the base ( $\text{NH}_3(\text{g})$ ). The acidity obtained is an accumulation of Bronsted acid sites and Lewis acid sites, both on the surface and in the pore cavity.

In the graph, catalyst Z has a low acidity value compared to other catalysts. This is because the Z catalyst still contains a lot of organic and inorganic impurities on its surface and pores so that the ability to absorb  $\text{NH}_3$  gas is very small. The ZA catalyst has undergone chemical activation, namely cleaning the surface and pores of the Z catalyst

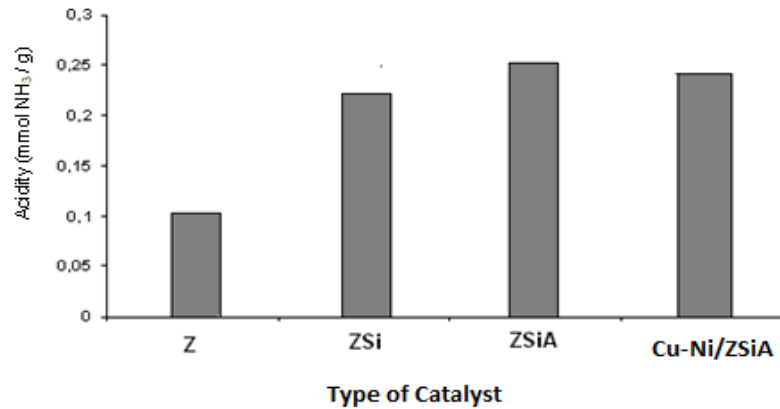


Figure 3. Catalyst Acidity of Various Types of Catalysts

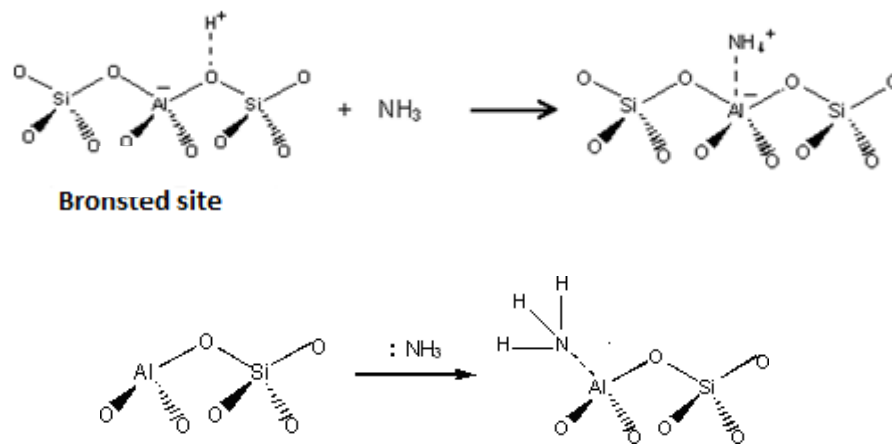


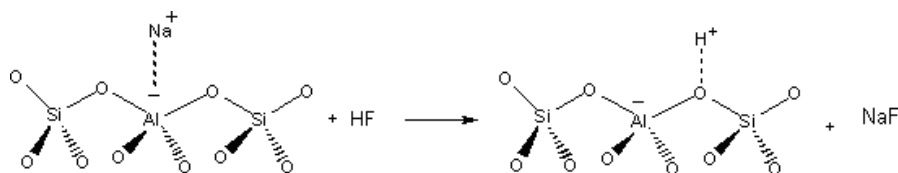
Figure 4. Chemisorption of Ammonia on the Surface of the Zeolite in Determining the Acidity of the Catalyst

The acid strength of a catalyst is explained as the ability of the catalyst surface to adsorb reactants (organic compounds), while increasing the thermal stability of zeolite when used as a catalyst at high temperatures is through deionization and dealumination. The zeolite which functioned as a carrier for Ni metal and as a catalyst was treated with acids (HF, HCl and NH<sub>4</sub>Cl). The acid treatment has an impact on deionization events, namely the release of metals such as Na, Ca, Fe, K, Mg from the zeolite surface and dealumination events, namely the release of Al from the zeolite framework (Al framework).

According to Satterfield (1982), in catalytic reactions against reactants of organic compounds, the acidity of the catalyst is directly proportional to the activity of the catalyst, namely the ability of a catalyst to convert reactant compounds into products through the formation of carbonium ions as an intermediate in cracking, polymerization and isomerization reactions. The acid

site is either a Bronsted acid site or a Lewis acid site. The acidity of the zeolite catalyst can be increased by acid treatment (HF, HCl and NH<sub>4</sub>Cl).

Treatment with 2 M HF solution on the zeolite can result in dissolving impurities that cover the pores of the zeolite, so that the pores on the surface of the zeolite become more open. Besides that, the use of HF solution will also cause the exchange of metal ions in the zeolite with H<sup>+</sup> ions from the HF solution to form Bronsted acid sites (Figure 4).



The increase in acidity is illustrated by the increasing chemisorption of ammonia on the catalyst surface quantitatively. Catalysts with increasing acidity are very advantageous, especially in the reaction of breaking long hydrocarbon chains into short hydrocarbon chains through hydrocracking reactions (Satterfield, 1982).

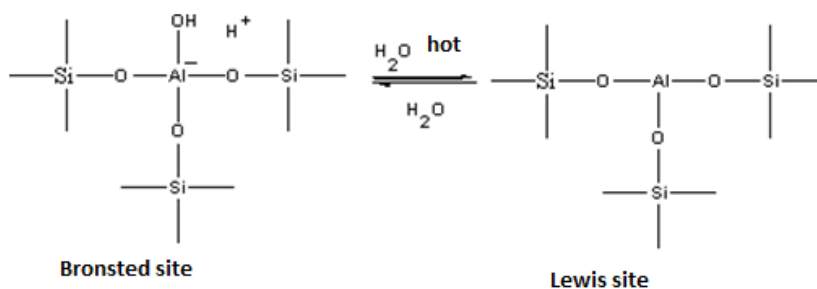


Figure 5. Exchange of Metal Ions (Na<sup>+</sup>) during Zeolite Treatment with 2 M HF

Treatment with NH<sub>4</sub>Cl also increased the acidity of the catalyst from 0.22 to 0.25 mmol NH<sub>3</sub>/g with the formation of Bronsted acid sites. This situation can be explained through the stages of the ion exchange mechanism as shown in Figure 6. Initially, NaCl was produced from the zeolite surface and in the end, ammonium hydroxide was produced from the zeolite surface.

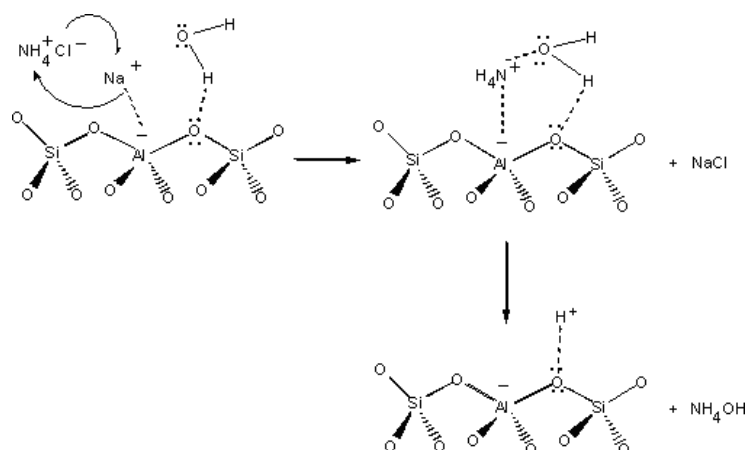


Figure 6. Formation of a Bronsted Acid Site

The acidity of the zeolite as a catalyst is determined by the presence of Bronsted acid sites and Lewis acid sites which are in equilibrium. The acid site will interact with the electron cloud on the carbon chain bond and will break the carbon chain on the adsorbed bond.

#### Si/Al Ratio and Dealumination of the Yield Catalyst

The increase in the Si/Al ratio illustrates the release of Al in the framework (Al framework) to become Al outside the framework. The presence of Al in the zeolite framework carries a negative charge which is stabilized by the presence of metal ions such as Na<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup> or H<sup>+</sup> ions, so that when the acid treatment of the zeolite either with HF or with HCl causes the Al framework to become Al outside the framework as well. has a direct impact on the reduced content of metal ions contained in the zeolite. An increase in the Si/Al ratio occurred during the zeolite treatment with HF, Na<sub>2</sub>SiO<sub>3</sub>, HCl and NH<sub>4</sub>Cl in the preparation of the Ni/ZSiA catalyst, although the increase was not very significant. The increased Si/Al ratio was the result of acid treatment with 2 M HF, 2 M HCl and 2 M NH<sub>4</sub>Cl. The increased Si/Al ratio caused the zeolite to become increasingly non-polar and the more non-polar zeolite, the easier it was to interact with other compounds. non-polar (Twaiq, 2003). The use of zeolite with relatively increased Si/Al ratio as a catalyst in the hydrogenation reaction of methyl 9-octadenoate, 1-octadecanol and 1-octadecene is relatively suitable.

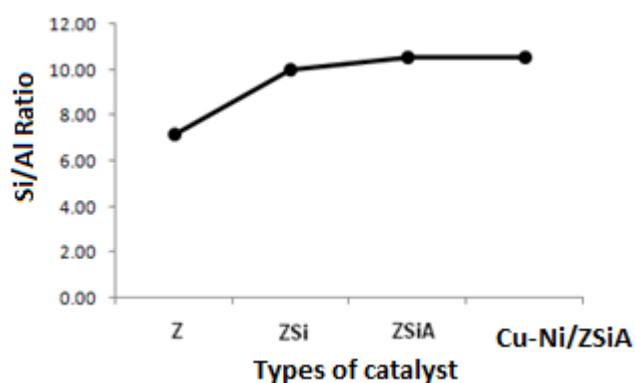


Figure 7. Si/ Al ratios of various types of catalysts, Z : zeolite catalyst, ZSi : zeolite enrichment catalyst with Si, ZSiA : acid treated ZSi catalyst, Ni/ZSiA : Ni metal impregnated ZSiA catalyst

In Figure 7 it can be seen that the Si/Al ratio of the Cu-Ni/ZSiA catalyst type decreased slightly, but not significantly (0.19%). It is possible that during the impregnation of Ni metal from  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  salt there was relatively no change in Si content and relatively no change in Al content, so the Si/Al ratio of Cu-Ni/ZSiA remained relatively constant. In the treatment of insertion of Si metal from the type of Z catalyst so that it becomes ZSi there is an increase in the Si/Al ratio of 40.17%.

Dealumination is an event where Al is released from within the zeolite framework outside the zeolite framework. The event of the release of Al from the zeolite framework causes the Si/Al ratio of the zeolite framework to increase. Dealumination events in the preparation of the catalyst were not only caused by treatment with 2% HF and treatment with 2 M HCl, but also caused during the hydrothermal process of zeolite at a relatively high temperature (500 oC). In this situation, what causes the Si/Al ratio to increase is the presence of water vapor at the calcination temperature (500 oC) in the zeolite which hydrolyzes the aluminum in the framework (Al framework) to become aluminum outside the framework. Water vapor at the calcination temperature, apart from hydrolyzing Al in the framework, also causes the oxygen framework to become unstable and as a result Si migrates to the empty place that Al left. As a consequence, the Si/Al ratio of the zeolite increases, followed by a decrease in the pore size of the zeolite as shown in Figure 9. The ratio of Si/Al in the zeolite framework increases indicating that the zeolite framework is relatively stronger or has more crystallinity.

The more dealumination occurs in the zeolite framework, the more non-polar the zeolite, the more non-polar zeolite tends to prefer non-polar feed or reactants in their interactions, such as methyl 9-octadenoate, 1-octadecanol, 1-octadecene. The treatment of zeolite as a catalyst carrier tends to be adjusted to the type of feed used, related to the polarity of the feed. According to Augustine (1995), an increase in the Si/Al ratio will have an impact on

increasing the acidity of the zeolite and thermal stability, thereby supporting the hydrogenation reaction at high temperatures.

An increase in the Si/Al ratio resulted in a decrease in the pore size of the zeolite and an increase in the capacity of the zeolite pore physisorption which is increasingly non-polar. Based on the research results, a linear relationship was obtained between increasing the ratio of Si/Al and increasing the acidity of the catalyst as shown in Figure 10. This situation can be explained that as the ratio of Si/Al increases, the pore diameter decreases so that the ability to adsorb on ammonia base as an indicator of acidity increase.

The release event of Al from the zeolite frame is depicted in Figure 8 according to Derouane (1992). The interaction of zeolite with acid solution (HCl) will release Al in the framework to become Al outside the framework, as well as the interaction of zeolite after being treated with acid followed by washing with water causes the release of Al in the framework to become Al outside the framework. Then the zeolite undergoes realignment to become a zeolite with a Si center.

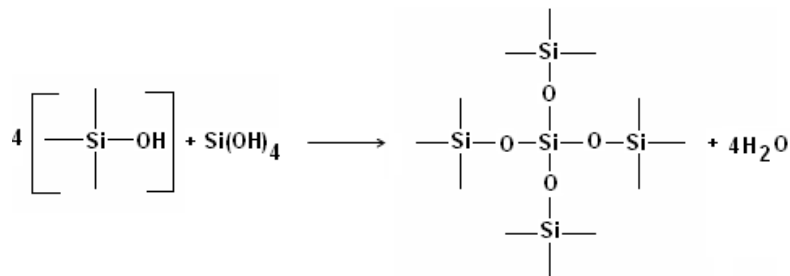
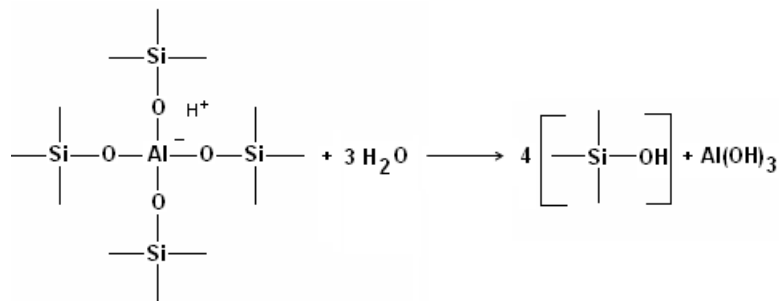
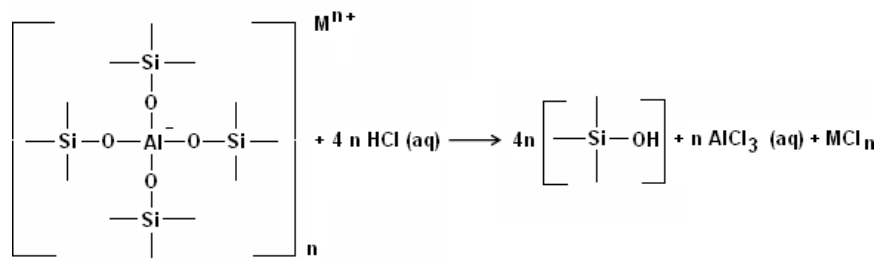


Figure 8. Release of Al Framework (Dealumination) on the Zeolite Framework

According to Twaiq (2003), the relatively high Si/Al ratio of a catalyst is very suitable for non-polar feed or reactants. Catalysts with a low Si/Al ratio tend to be more able to interact with polar reactants. Satterfield (1982), said that increasing the Si/Al ratio increased thermal stability. While Harber (1991), said that the activity of a zeolite catalyst is determined not only by the presence of the Si/Al ratio in the catalyst, but also the acidity, surface area, total pore volume and crystallinity of the catalyst.

According to Augustine (1995) and Satterfield (1980), the thermal stability of the zeolite framework can be increased by increasing the Si/Al ratio through dealumination and hydrothermal. This situation can be explained that before being treated with acids (HF, Na<sub>2</sub>SiO<sub>3</sub>, HCl and NH<sub>4</sub>Cl) the zeolite ring through -Si-O-Al- bonds forms a ring with a certain pore diameter which was initially covered by impurities to become more open due to the dissolving of impurities. The zeolite after experiencing a dealumination event as a result of the acid treatment, the zeolite ring has a more open and relatively shorter pore diameter as shown in Figure 9.

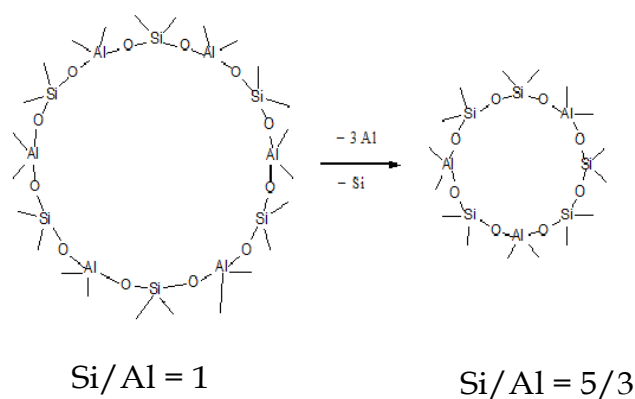


Figure 9. Illustration of Al Release Resulting in an Increase in the Si/Al Ratio, Followed by a Decrease in the Pore Diameter of the Zeolite

As a result, the pores in the 10 - 20 Å region increased significantly, followed by the pores in the 21 - 30 and 31 - 40 Å regions. The ZSiA and Ni/ZSiA catalysts still have strong crystalline properties. This situation is indicated by the presence of a fairly sharp peak of the diffractogram. This situation is very supportive in using zeolite as a catalyst .

According to Trisunaryanti (1996), acid treatment with HF, HCl and NH<sub>4</sub>Cl can result in a decrease in the metal ion content of Na<sup>+</sup>, Ca<sup>2+</sup>, Fe<sup>3+</sup> and Mg<sup>2+</sup>. During the impregnation of Ni metal from Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, the Si/Al ratio decreased, although it was relatively small. This decrease was due to the impregnation of Ni metal from Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O salt where a small portion of Si was released from the zeolite framework, thus the Si/Al ratio showed a slight decrease. Thus, from the type of catalyst Z to ZSiA and Ni/ZSiA, the ratio of Si/Al catalysts relatively increases which shows that the catalyst is increasingly

non-polar so that it is relatively compatible with the feed applied in the catalytic reaction, namely methyl 9-octadenoate, 1-octadecanol and 1-octadecene. .

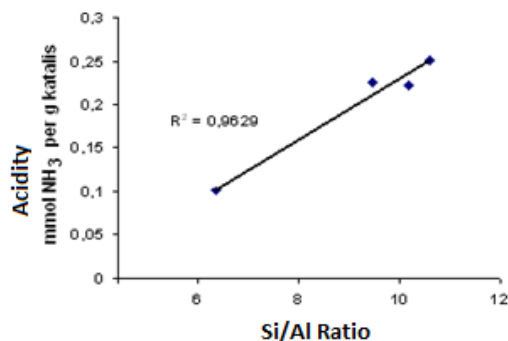


Figure 10. The Relationship Between Acidity and the Si/ Al Ratio of the Catalyst

The relationship between acidity and Si/Al ratio as shown in Figure 10. is linear. The higher the Si/Al ratio, the more acidic and non-polar the zeolite is. The more acidic the zeolite has an indicator the more H<sup>+</sup> ions are formed on the surface of the zeolite. H<sup>+</sup> ions on the surface of the zeolite, which means that the more Bronsted acid sites, the more ability to adsorb ammonia bases.

### Specific Surface Area of the Catalyst

The specific surface area of a solid gives an idea of the size of the (active) surface within a certain area per weight of the catalyst, which is expected to be able to adsorb the reactants resulting in collisions between the reactants on the surface of the catalyst and reaction products. The greater the specific surface area of a catalyst, the more active surfaces that can interact with the reactants, so that it is expected to produce a lot of products.

Based on the research results, the specific surface area of the zeolite after impregnated with Ni metal decreased slightly. This situation can be explained that the impregnation of Ni metal is relatively even but there is a small amount of accumulation at the pore mouth or part of the zeolite surface, so that the surface area of the zeolite when analyzed using the BET method shows a slight decrease. The results of the analysis with AAS the content of Ni metal in the Cu-Ni/ZSiA catalyst was 1.06% from the targeted 2.00%. So the success rate of impregnation of Ni metal into zeolite samples is 53.00%.

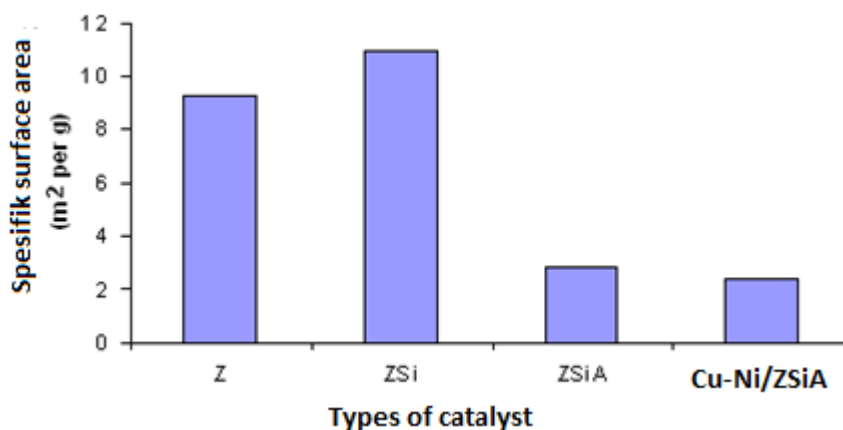


Figure 11. Specific surface area of Various Types of Catalysts, Z : Zeolite Catalyst, ZSi : Zeolite Enrichment Catalyst with Si, ZSiA : ZSi Catalyst Treated with Acid, Cu-Ni/ZSiA : ZSiA Catalyst Impregnated with Ni Metal and Cu Metal

Based on the research results shown in Figure 11 it can be explained that treatment with  $\text{Na}_2\text{SiO}_3$  increased the surface area of the catalyst. While the acid treatment causes a significant decrease in the specific surface area of the catalyst. The decrease in the surface area of the catalyst can be caused by damage to the zeolite framework when dealumination occurs and the impurities resulting from the dealumination may cover the pores of the catalyst. This situation resulted in the analysis using the BET method, the adsorbed nitrogen gas was not able to enter into the pores of the catalyst, so that what was detected was the outer surface and some of the inner surface of the catalyst.

### Frequency Distribution of Catalyst Pore Size

The frequency distribution of the pore size of a catalyst describes the number or number of pores in a certain pore size range. According to Augustine (1995), catalyst pores are divided into 3, namely micropores (less than 0.5 nm), mesoporous (1.0 - 3.0 nm) and macropores (larger than 5.0 nm). Based on Figure 12, in general the catalyst pores are in the mesoporous region. Pores in the macro pore area are relatively absent. Based on the results of analysis of the frequency distribution of pore size analysis results using the NOVA surface analyzer equipment (BET method) it can be explained that the zeolite after being treated with acid,  $\text{Na}_2\text{SiO}_3$  and Ni metal impregnation experienced a significant increase in the number of pore sizes in the 10 to 20 angstrom area.

The zeolite pores in the area of 10 to 20 angstroms show that there is a significant increase in the number of pore sizes from the Z catalyst type to the ZSi, ZSiA and Cu-Ni/ZSiA catalyst types. The increase in the number of pore sizes also occurs in the region of 21 to 50 angstroms, where the larger the pore size, the smaller the increase in the number of pore sizes.

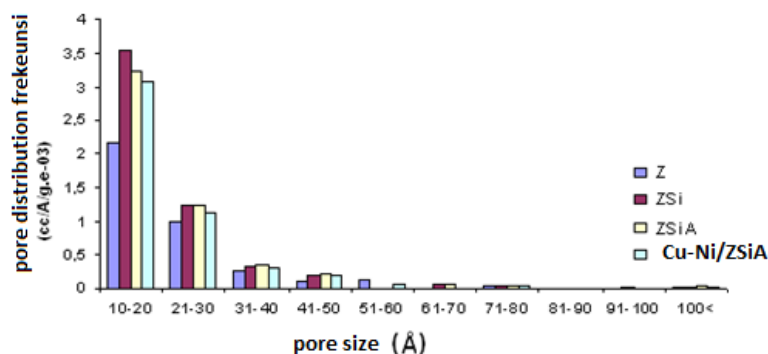


Figure 12. Frequency Pore Distribution of Various Types of Catalysts, Z : Zeolite Catalyst, ZSi : Zeolite Enrichment Catalyst with Si, ZSiA : ZSi Catalyst Treated with Acid, Cu-Ni/ZSiA : ZSiA Catalyst Impregnated with Ni Metal and Cu Metal

The majority of natural zeolites used as Ni metal carriers have pores in the 10 to 30 Å region which are very dominant. The chemical and physical treatment of zeolite has the majority impact on the pore areas, such as opening of the catalyst pores, widening of the pore mouths and closing of the pore mouths due to abrasion and closing of the inner pore channels.

The closing of the catalyst pores can be caused by the influence of the acid solvent used or the effect of the physical treatment given during the preparation of the catalyst. As a result, the pore mouth becomes wider and impurities can cover the catalyst pores (Bartholomew, 2006).

## CONCLUSION

1. There was an increase in the acidity of the catalyst on further treatment.
2. There was an increase in the ratio of Si/Al in further treatment during Cu-Ni impregnation on the surface of the zeolite.
3. There is the formation of new pores in the micro pore area.
4. There is a linear relationship between the increase in the Si/Al ratio and the acidity of the catalyst.
5. There was a decrease in the specific surface area of the catalyst treatment when impregnated Cu-Ni metal on the surface of the zeolite as a catalyst.

## REFERENCES

- Bartholomew, C. H. and Farrauto, R.J., 2006, *Fundamentals of Industrial Catalytic Processes*, 2nd edition, John Wiley and Sons Inc., New Jersey.
- Belitz, H.D., and Grosch, W., 1999, *Food Chemistry*, 2nd edition, Springer-Verlag, Berlin. Brands, D.S., Poels, E.K.,
- Costas, S. T., 2000, Dealuminated H-Y Zeolite: Influence of The Degree and The Type of Dealumination Method on Structural and Acidic Characteristics of H-Y Zeolite, *Ind. Eng. Chem.*:39, 307-319.
- Dyer, A., 1988, *An Introduction to Zeolite Molecular Sieves*, John Wiley and Sons Ltd., Chichester. Derouane, E.G., 1992, *Zeolite Microporous Solids: Synthesis, Structure, and Reactivity*, KluwerAcademic Publishers, London.
- Gasser, R.P.H., 1987, *An Introduction to Chemisorption and Catalysis by Metal*, Oxford SciencePublication, Oxford.
- Gates, B.C. 1979. *Catalytic Chemistry*, John Wiley and Sons Inc., New York.
- Hamdan, H., 1992, *Introduction to Zeolites: Synthesis, Characterization, and Modification*, Universiti Teknologi Malaysia, Penang.
- Harber, J., 1991, *Manual on Catalyst Characterization*, *Pure and Appl. Chem.*, 63, 9, 1227-1246.
- Hughes, R., 1984, *Deactivation of Catalyst*, Academic Press Inc. Ltd., London.
- Kunkeler P.J., 1998, *Zeolite Beta: The Relationship between Calcination Procedure, Aluminum Configuration, and Lewis Acidity*, *J. Catal.* 180, 234.
- Lowell, S. and. Shields, J.E, 1984, *Powder Surface Area and Porosity*, 2<sup>nd</sup> edition, Chapman and Hall, New York.
- Martinez, T.J., Diaz, C.M.J., Cambor, M.A., Fornes, V., Maesen, T.L.M. and Corma, A., 1999, *The Catalytic Performance of 14-Membered Ring Zeolites*, *J. Catal.*, 182, 463-469.
- Pachenkov, G. M., and Lebedev, V. P., 1976, *Chemical Kinetic and Catalysis*, 2<sup>nd</sup> edition., Mir Publishers, Moscow.
- Page Le, J. F., Cosyns, J. and Courty, P., 1987, *Applied Heterogenous Catalyst*, edisi 1987, Imprimerie Nouvelle, Saint Jean de Braye, Paris.

- Perry, R.H. dan Green, D.W., 1997, *Perry's Chemical Engineer's Handbook*, Mc.Graw-Hill Companies. Inc., New York.
- Pioch, D. and Vaitilingom, G., 2005, *Palm Oil and Dereovatives: Fuels or Potensial Fuels?*, *CorpsGras, Lipides*, 12, 2, 161-9.
- Rajeshwer, D., Sreenivasa Rao, G., Krishnamurthy, K., R., Padmavathi, G., Subrahmanyam, N. dan Jagdish, D. Rachh, 2006, *Kinetics of Liquid – Phase Hydrogenation of Straight Chain C<sub>10</sub> to C<sub>13</sub> Di-Olefins Over Ni/Al<sub>2</sub>O<sub>3</sub> Catalyst*, *International Journal of Chaemical Reactor Engineering*, Vol. 4, Article A17
- Ramesh, B.D., 2000, *Hydrogenation of 1-alkenes Catalysed by Anchored Montmorillonite Palladium (II) Complexes : a Kinetic Study*, *Trans. Met. Chem*, 25, 6, 639-643.
- Sang, O.Y., 2003, *Biofuel Production From Catalytic Cracking of Palm Oil*, *Energy Sources J*, 9, 25.
- Santos, L.T., 2003, *Nickel Activation for Hydrogenolysys Reaction on USY Zeolite*, *Catal. Lett.* 92, 81.
- Satterfield, C.N., 1980, *Heterogenous Catalysis in Practices*, McGraw-Hill Book Co., New York.
- Sibilia, J.P., 1996, *A Guide to Materials Characterization and Chemical Analysis*, 2<sup>nd</sup> Edition. VCHPublishers, Inc., New York.