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Characterization of NI/Zeolite Catalyst Including Specific Surface Area, Acidity, Si/Al Ratio, Cation Content in Zeolite

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A R T I C L E I N F O

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A B S T R A C T

Specific Surface Area, acidity, Si/Al ratio, and cation concentration in zeolite catalysts have all been studied in relation to Ni/zeolite catalysts. The zeolite was submerged in water for 24 hours, dried, and then calcined for 3 hours at 400 oC before being incubated for 2 hours to create the Ni/zeolite catalyst. then 24 hours of stirring soaking in 6 M HCl, followed by 3 hours of refluxing with 1 M NH4Cl and 2 hours of oxygen gas oxidation. The zeolite will subsequently be impregnated with Ni, oxidized for three hours, and reduced with hydrogen gas for two hours. Additionally, a Ni/zeolite catalyst was acquired. The catalyst's metal concentration was then determined by characterizing the Ni/zeolite mixture, Si/Al ratio, specific surface area, and acidity of the catalyst. The outcomes of the characterisation are as follows: Ca and Fe are the main metals present in the Ni/zeolite catalyst, with only trace amounts of Na, Mg, and other metals (5 mg/gram of catalyst) present. In the meantime, the catalyst's acidity was 0.24 mmol/gram catalyst acidity, its surface area was 2.18 m2/gram catalyst surface area, and its Si/Al catalyst ratio was 10.21

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INTRODUCTION

Zeolite is a natural rock whose structure is composed of Si and Al. Zeolite is widely used in its implementation as used in paint mixtures, as a catalyst. The main content of zeolite is lime or feldspar, but in its use as a catalyst the lime is removed.

The pores, channels, and cavities of a catalyst cause its inner surface area to develop. The catalyst solid particles' outer surface area equals their total surface area. According to Dyer (1988) and Derouane (1992), the information received while calculating the surface area of solids is the total surface area, which includes the inner surface area and outer surface area.

Not all reactants can result in reaction products in catalytic reactions, which always relate to an equilibrium state (Satterfield, 1980). Processes such as physisorption, chemisorption, and desorption are frequently used in catalytic reactions. Due to the localization of the reactants, molecules that are more active as intermediates and can be produced as a result of the interaction between the catalyst and the reactants accelerate, accurately, and concentrate interactions between the reactants. The reaction's activation energy decreases as a result of this circumstance.

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Zeolite has the following structure:

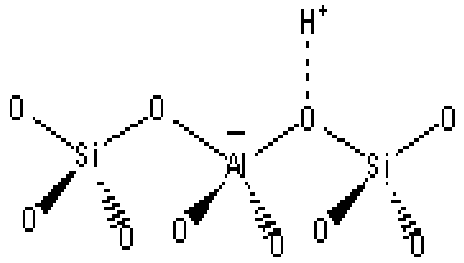

Figure 1. The Structure of the Zeolite and Bronsted Acid Sites

Indonesia is a country rich in natural zeolite deposits. The large number of zeolite minerals in Indonesia is because most of Indonesia's territory consists of volcanic rocks. The use of zeolite as a carrier or active metal support material in the manufacture of metal/carrier system catalysts requires attention to the properties of the natural zeolite itself such as: zeolite acidity, high surface area, porous structure. These properties are very important in the use of natural zeolites as active metal carriers in catalyst preparations.

METHODOLOGY

Research Materials and Methods

Tools and Materials

High-quality p.a., natural zeolite, and E.Merck materials were also utilised. Oleic acid (91.59%), 1-octadecanol (95%), 1-octadekene (90%), HCl (37%), HF (40%), NH4Cl, Na2SiO3, and Ni(NO3) 26H2O (97%), are all components of these compounds. pH paper, oxygen, nitrogen, and hydrogen gas are additional components.High-quality p.a., natural zeolite, and E.Merck materials were also utilised. Oleic acid (91.59%), 1-octadecanol (95%), 1-octadekene (90%), HCl (37%), HF (40%), NH4Cl, Na2SiO3, and Ni(NO3) 26H2O (97%), are all components of these compounds. Other components include pH paper, oxygen, nitrogen, and hydrogen gas.

Research Methods

Ni/zeolite Catalyst Preparation Procedure

The natural zeolite was washed in Erlenmeyer and dried using a vacuum drying oven and then followed by calcination by flowing nitrogen gas at 500 ^{o}C for 4 hours. Then oxidized using oxygen at a temperature of 400 ^{o}C for 3 hours (Handoko, 2001).

Natural zeolite is immersed in a 1% HF solution with a volume ratio of 1:2 in a beaker for 10 minutes at room temperature. Then filtered and washed repeatedly with distilled water until pH 6. The natural zeolite precipitate was then refluxed using 6M HCl for 30 minutes at 90 ^{o}C while stirring with a magnetic stirrer. After that it was followed by filtering and washing with distilled water up to pH 6, dried in an oven at 130 ^{o}C for 3 hours (Trisunaryanti, 1991).

Next is the addition of 1M NH4Cl into the zeolite then heated at a temperature of 90 ^{o}C for 3 hours every day for 6 days while stirring every one hour during heating. After that, it was filtered and washed with distilled water to a pH of 6, then dried in an oven at 130 ^{o}C for 3 hours. After chilling, grind it and place it in a porcelain cup. Furthermore, it was heated at 500 ^{o}C for 4 hours in the furnace and then cooled again to obtain natural zeolite with acidification (NZA) (Khairinal, 2000)

The NZA catalyst was then hydrothermalized by flowing water vapor for 5 hours at a temperature of 500 °C, cooled and followed by a calcination process using nitrogen gas, for 3 hours at a temperature of 500 ^{o}C, then cooled. The process is continued by oxidation with oxygen gas, for 1.5 hours at a temperature of 400 ^{o}C (Handoko, 2001). Then it was cooled and H5NZA catalyst was obtained.

The preparation of Ni/H5NZA (Ni/zeolite) catalyst was carried out by embedding Ni metal on the H5NZA catalyst through an impregnation process using a semi-wet method, namely by mixing the H5NZA catalyst and NiCl2.6H2O solution at a temperature of 90 oC while stirring until powder was formed and a catalyst was obtained. Ni(II)/H5NZA. Comparison of the weight of H5-NZA and the weight of NiCl2.6H2O and ZnSO4.6H2O carried, as shown in table 1.

Table 1. Weight Comparison of NiCl2.6H2O in 100 Grams of Catalyst

No	Metal Type	Impregnated Metal Weight (grams)	H5-NZA weight (grams)	Metal Crystal Weight (grams)
1	Ni	2,00	98,00	8,10

Note: BM $NiCl_2.6H_2O$ = 237,6 g/Mol

After completion, the catalyst samples were calcined with nitrogen gas at a speed of ±5 mL/sec at 500 oC for 3 hours. In the calcination process, the catalyst sample is placed in the activation reactor and heated slowly to a temperature of 500 oC while flowing nitrogen gas at a speed of ±5 mL/second. After the temperature reaches 500 oC, it is maintained for 3 hours, followed by an oxidation process by flowing oxygen gas at a speed of ±5 mL/second, a temperature of 500 oC for 3 hours then cooled (Handoko, 2001). From this process a Ni/zeolite catalyst was obtained.

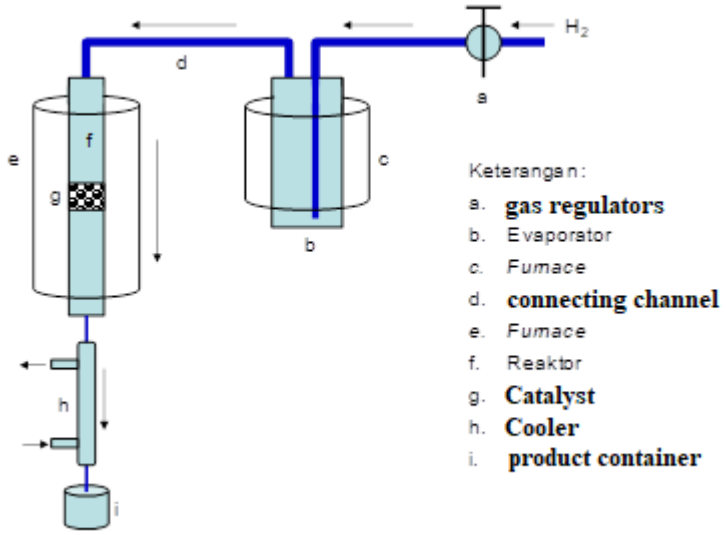

Figure 2. Fixed Bed Reactor Equipment

RESULT AND DISCUSSION

Crystallinity

When used as a catalyst or a carrier, zeolite's crystallinity is crucial. These characteristics are tightly correlated with the pore radius, pore and channel volume, and zeolite acidity. The degree of zeolite crystallinity serves as a gauge of the crystal lattice's resilience in holding onto its crystalline form. In general, the presence of an excessively high operating temperature has a negative impact on the crystal characteristics. Increasing the thermal stability of zeolite as a catalyst is by treating it with a hydrothermal process (Hamdan, 1992).

The metal catalyst theory postulates that the metals which are active in forming and breaking bonds are those having many low energy orbitals. This is possible because the valence electrons from the d orbitals mix with the electrons from the s and p orbitals, which provides a large number of low-energy electronic

states and is ideal for catalytic reactions to occur. Such conditions are the most active for breaking and forming chemical bonds (Satterfield, 1987).

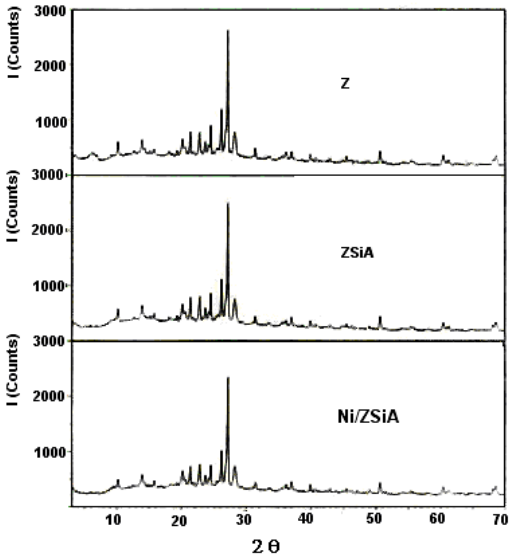

Figure 3. Diffractogram of Z, ZSiA, Ni/ZSiA Catalysts

Based on Figure 3, it can be concluded that the natural zeolite used as the carrier for the active metal Ni (ZSiA) contains mixed types, including mordenite, clinoptilolite and quartz. This situation was proven by matching the XRD diffractogram patterns of standard natural zeolite according to Treacy and Higgins (2001), with natural zeolite samples.

Table 2. Identification of the Position of the Diffraction Angle (2θ) on the XRD Diffractogram of the Catalyst Made with Standard Natural Zeolite

Zeolite type	2θ	
	Natural zeolite samples	Natural zeolite according to Treacy and Higgins (2001)
Mordenite	6,54; 13,81; 18,03; 24,42; 25,64; 25,99; 27,00; 35,58; 36,90; 39,83; 45,33; 47,91; dan 48,70	6,51; 13,83; 18,19; 24,43; 25,63; 26,04; 27,09; 35,61; 36,87; 39,82; 45,28; 47,97; dan 48,70
Clinoptilolite	19,19; 20,40; 22,38; 25,32; 25,99; 28,08; 29,81; 36,22; 45,34; dan 48,92	19,10; 20,40; 22,36; 25,35; 26,04; 28,15; 29,79; 36,19; 45,38; dan 48,92
Quartz	20,86; dan 26,70	20,86; dan 26,65

Based on Table 2, it can be seen that the resulting catalyst has increased in intensity from Z to ZSiA, this situation is due to the activation process with HCl and NH4Cl solutions, the addition of Na2SiO3 and heating at a temperature of 500 oC. This situation resulted in an increase in crystallinity, namely 300, 1429,

259 to 342, 1560 and 284 on increasing crystallinity, namely 300, 1429, 259 to 342, 1560 and 284.

Table 3. The Intensity of the Diffractogram with the Largest Peaks of the Catalyst Yields

2θ (degrees)	d (Å)	Type	Intensity (counts)		
			Z	ZSiA	Ni/ZSiA
24,39	2,26	*Mordenite*	300	342	264
25,99	2,99	*Clinoptilolite*	472	-	-
26,70	3,18	*Quartz*	270	200	164
27,00	3,30	*Mordenite*	1429	1560	1411
28,08	3,34	*Clinoptilolite*	259	284	253
29,82	3,43	*Clinoptilolite*	192	-	-
39,83	3,65	*Mordenite*	161	95	105

When the impregnation of Ni metal with Ni(NO3)2·6H2O salt caused the crystalline properties of the zeolite to decrease, namely 200, 1560 and 284 to 164, 1411 and 254. The natural zeolite used as a catalyst after being compared with standard natural zeolite according to Treacy and Higgins (2001)) has an index of similarity to the types of mordenite, clinoptilolite and quartz, so that the zeolite used has a crystal structure of the types of mordenite, clinoptilolite and quartz. Zeolite with strong crystallinity properties will be very supportive when used as a catalyst.

Metal Content in the Yield Catalyst

Figure 4 illustrates how the metal content of Ca and Fe decreased following calorimetric treatment, Si zeolite enrichment, and acid treatment. There was a little but not overly substantial rise in the Ca and Fe content of the Ni/ZSiA catalyst.

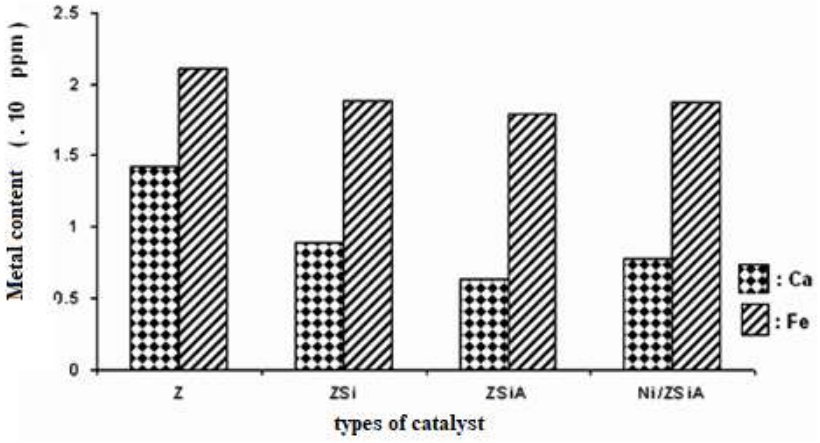

Figure 4. Ca and Fe Content of Various Types of Catalysts, Z: Zeolite Catalyst, ZSi: Zeolite Enrichment Catalyst with Si (Na2SiO3), ZSiA: ZSi Catalyst Treated with Acid, NI/ZSiA: ZSiA Catalyst Impregnated with Ni Metal

Uncontrolled catalyst yields of metals like Ca, Fe, Na, and Mg can affect how well the catalyst works (Harber, 1991). Before being used as a carrier for Ni metal, zeolite must undergo acid treatment in the production of metal/zeolite system catalysts, which aims to reduce or eliminate undesirable metals like Ca, Fe, Na, and Mg (Lestari, 2010). As a result, the impregnation time of Ni metal is anticipated to reach a quantitative maximum..

The dissolution system employed in the production of metal/zeolite system catalysts is 2 M HCl, which attempts to produce Bronsted acid sites by dissolving the metals in the zeolite using ion exchange techniques (Satterfield, 1980). Figure V.5 shows, for instance, how metal ions M+ and H+ trade places..

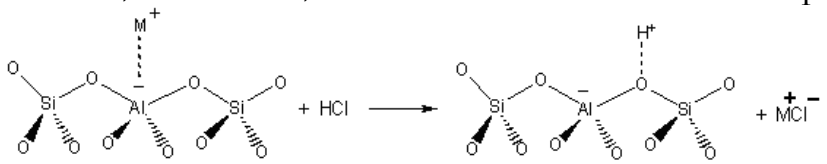

Figure 5. Exchange of M+Ions (Metal Ions) with (H+) Ions in Zeolite

The results showed that acid treatment with 2 M HCl decreased the amount of Ca and Fe in the zeolite's metal composition. through ion exchange, as shown in Figure 5. The decrease in the metal content of Ca and Fe in the zeolite in this study was used as an indicator of the reduction of other impurity metals , such as Mg, K, Na and Fe.

Yield Catalyst Acidity

Based on Figure 6. it can be explained that the acidity increases from treatment with Na2SiO3 to acid treatment. This increase in acidity indicates ion exchange results in the development of Bronsted acid sites on the zeolite's surface, as depicted in Figure 5. Ni(NO3)26H2O salt impregnation of Ni metal with this compound shows a reduction in acidity. The presence of Ni metal has likely caused a change from the Bronsted acid site to the Lewis acid site, which is the likely cause of this scenario. Bronsted acid site has a stronger acid strength than the Lewis acid site.

Measurement of zeolite acidity was carried out by the method of adsorption of ammonia base on the catalyst's exterior. The surface of the will become adsorbent with ammonia. Bronsted acid site and the Lewis acid site as shown in Figure 7. The adsorption reaches an equilibrium state, namely when a constant weight is obtained from the zeolite whose acidity is measured by the gravimetric method.

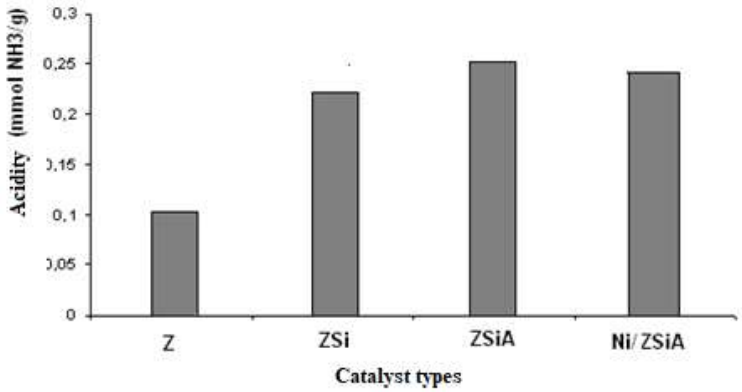

Figure 6. Acidity of Some of the Yield Catalysts
Z : Zeolite Catalyst, ZSi : Si-Enriched Zeolite Catalyst, ZSiA : Acid Treated Zsi Catalyst, Ni/ZSiA : Ni metal Impregnated ZSiA Catalyst

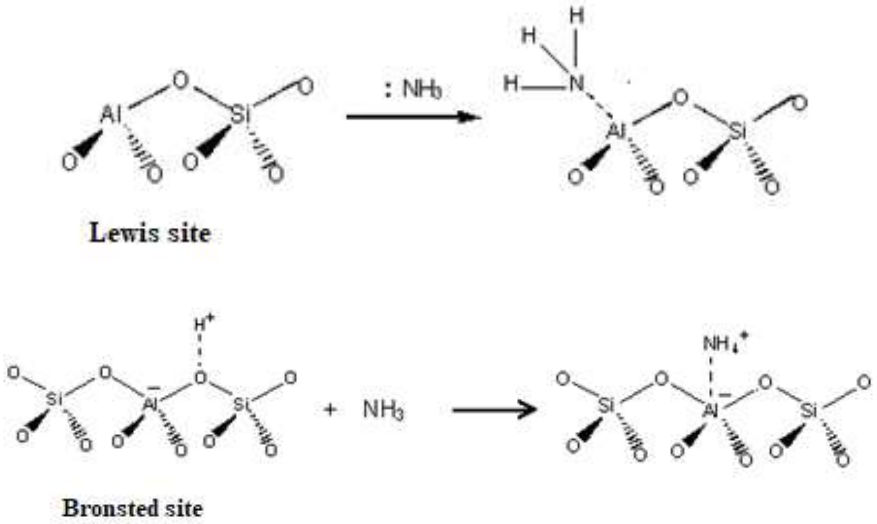

Figure 7. Chemissorption of Ammonia on the Surface of Zeolite in Determining Catalyst Acidity

The quantitative increase in the chemissorption of ammonia on the surface of the zeolite catalyst pointed to the presence of acidity. Increased acidity in catalysts has many benefits, especially when used in hydrocracking reactions, which convert long hydrocarbon chains into shorter ones (Satterfield, 1982).

The capacity of the catalyst to transform reactant compounds into products by forming carbonium ions as an intermediate is directly proportional to the acidity of the catalyst for catalytic reactions to organic compounds. in isomerization, polymerization, and cracking processes. Either a Lewis acid site or a Bronsted acid site describes the acid site. According to Satterfield (1982), acid treatment (HF, HCl, and NH4Cl) can increase the acidity of the zeolite catalyst.

Due to treatment with NH4Cl, the catalyst's acidity increased from 0.22 to 0.25 mmol NH3/g at the Bronsted acid site. Figure 8's depiction of the steps of the ion exchange mechanism can be used to describe this condition. HF was first

added to the surface zeolite solution, and then the surface zeolite was used to create NaF

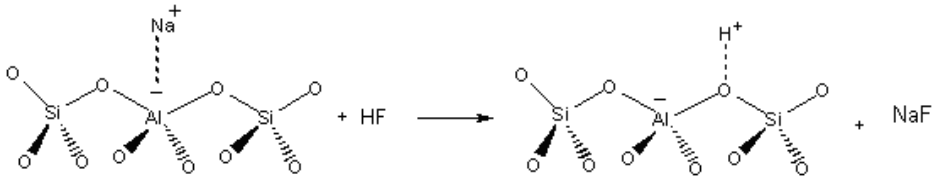

Figure 8. Exchange of Metal Ions (Na+) During Zeolite Treatment with 2 M HF

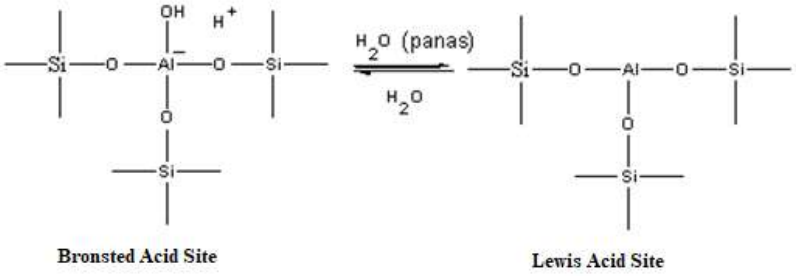

Figure 9. Equilibrium of Bronsted Acid Sites and Lewis Acid Sites (Satterfield, 1982)

By having Lewis acid sites and Bronsted acid sites that are in balance, zeolite can act as a catalyst. The carbon chain on the adsorbed bond will be broken by this acid site's interaction with the electron cloud on the carbon chain bond..

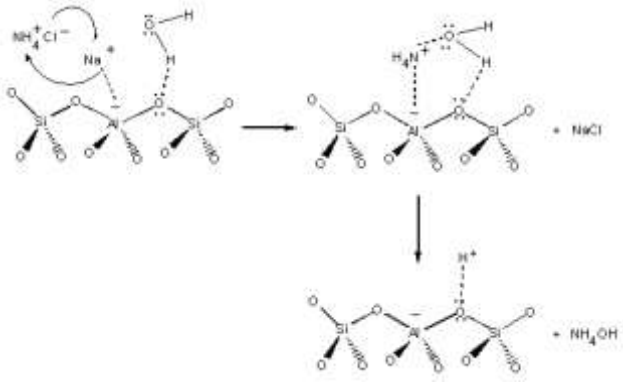

Figure 10. Formation of a Bronsted Acid Site

Through the formation of Bronsted acid sites, new chemical reactions can proceed quickly. This type of reaction is a type of SN-1 reaction, where there is an intermediate formation phase, namely the formation of Bronsted acid sites.

Si/Al Ratio and Dealumation of the Yield Catalyst

Dealumination events, which cause The release of Al from inside the zeolite framework to outside the zeolite framework is referred to as a rise in the Si/Al ratio of the zeolite framework. The zeolite hydrothermal procedure at a somewhat high temperature (500 oC), in addition to treatment with 2% HF and 2 M HCl, induces dealumination processes in the synthesis of catalysts. The

presence of water vapor at the calcination temperature (500 oC) in this case leads to the zeolite hydrolyzing the aluminum, which raises the Si/Al ratio. aluminum in the framework (Al framework) to become Outside the framework, aluminum was used (Satterfield, 1982). In addition to hydrolyzing Al in the oxygen framework at the calcination temperature, water vapor also makes the oxygen framework unstable such that Si goes into the empty space left by Al. As a result, as seen in Figure 12, the Si/Al zeolite ratio rises, which is followed by a drop in zeolite pore size. The Si/Al ratio rises in the zeolite structure, indicating that it is more durable or contains more crystallinity and has more nonpolar. thus preferring non-polar reactants

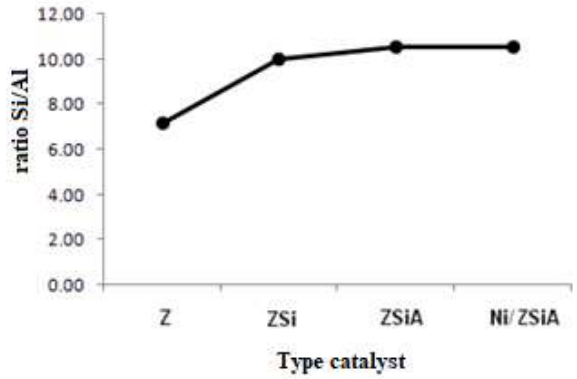

Figure 11. Si/Al Ratio of Different Types of Catalysts, Wherein Z : Zeolite Catalyst, ZSi : Zeolite Enrichment Catalyst with Si, ZSiA : Acid Treated ZSi Catalyst, Ni/ZSiA Catalyst : ZSiA Impregnated with Ni Metal

Al release events according to Derouane (1992) and shown in Figure 11 from the zeolite framework. When zeolite is exposed to acid solution (HCl), Al inside the framework will change to Al outside the framework. In a similar way, when zeolite is exposed to acid and then washed with water, Al inside the framework will change to Al outside the framework. The zeolite then undergoes restructuring and transforms back into zeolite with a Si core.

The results showed a linear relationship between increasing the Si/Al ratio and increasing the acidity of the catalyst as shown in Figure 12. This situation can be explained by increasing the Si/Al ratio, the pore diameter decreases so that the adsorption capacity of ammonia as an indicator of acidity increases. An increase in the Si/Al ratio resulted in a decrease in the zeolite pore size and an increase in the non-polar pore physisorption capacity of the zeolite. so that the zeolite prefers non-polar bait as well.

The effect of HCl (acid solution) on the zeolite will cause Al inside the framework to become Al outside the framework, likewise the interaction of the zeolite after being treated with acid followed by washing with water causes the release of Al inside the zeolite framework to become Al outside the zeolite framework. Then the zeolite undergoes realignment to become a zeolite with a Si center. Al release events from the zeolite framework are depicted in Figure 12. according to Derouane (1992).

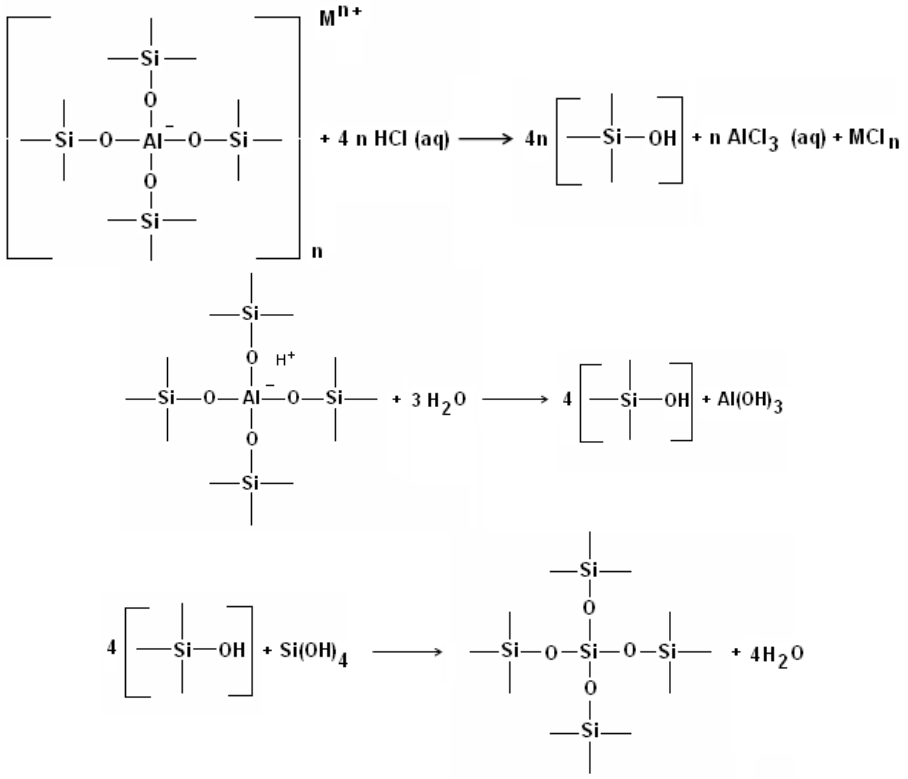

Figure 12. Release of Al Framework (Dealumination) on the Zeolite Framework

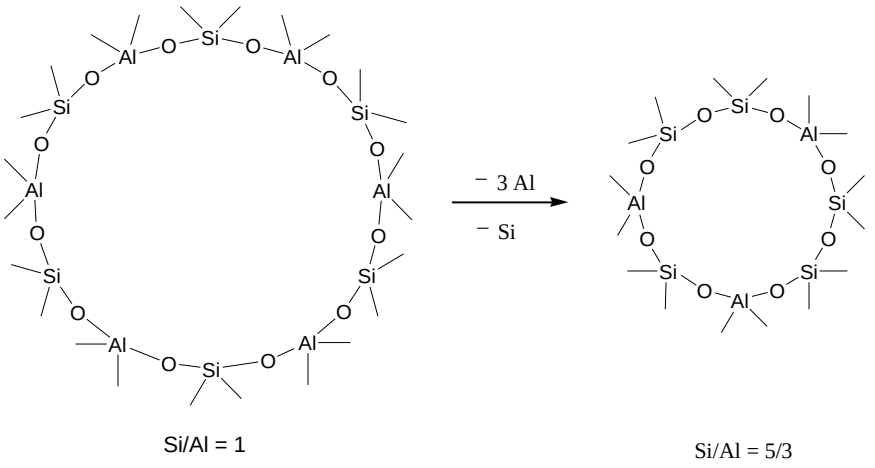

Figure 13. Ilustration of Al Release Resulting in an Increase in the Si/Al Ratio, Followed by a Decrease in the Pore Diameter of the Zeolite

As a result, the pores in the range 10 – 20 Å will increase significantly, followed by the pores in the region 21 – 30 and 31 – 40 Å, which will also increase significantly as shown in Figure 14. The ZSiA and Ni/ZSiA catalysts are still has strong crystalline properties. . This situation is indicated by the presence of a fairly sharp diffractogram peak. This situation strongly supports the use of zeolite as a catalyst.

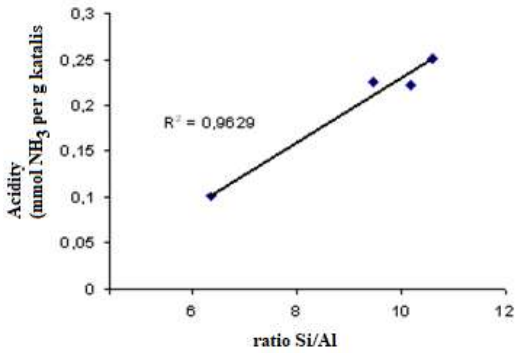

Figure 14. The Relationship Between Acidity and the Si/Al Ratio of the Catalyst

The correlation between acidity and the Si/Al ratio is linear as shown in Figure 14. The higher the Si/Al ratio, the more acidic and non-polar the nature of the zeolite is. The more acid the zeolite has as an indicator the more H+ ions are formed on the surface of the zeolite. H+ ions on the surface of the zeolite, meaning that the more Bronsted acid sites there are, the greater the ability to adsorb ammonia base.

Specific Surface Area of the Catalyst

The size of the (active) surface within a specific area per weight of the catalyst, which is expected to be able to adsorb the reactants leading to collisions between the reactants on the surface (surface area) of the catalyst and produce reaction products, is indicated by the specific surface area of a solid. The more active surfaces that can interact with the reactants there are on a catalyst's specific surface area, which increases the likelihood of collisions that result in a large number of products.

Figure 15 illustrates how treatment with Na2SiO3 improves the catalyst's surface area. While the catalyst's specific surface area is significantly reduced by The Acid Treatment. When Dealumination Takes Place, The Zeolite Framework May be harmed, and the impurities that come from the dealumination process may clog the pores of the catalyst (Figure 15). In order to prevent the adsorbed nitrogen gas from entering the catalyst's pores, an analysis utilizing the BET method was performed as a result of this condition. As a result, only the catalyst's outer surface area and a portion of its inner surface were discovered.

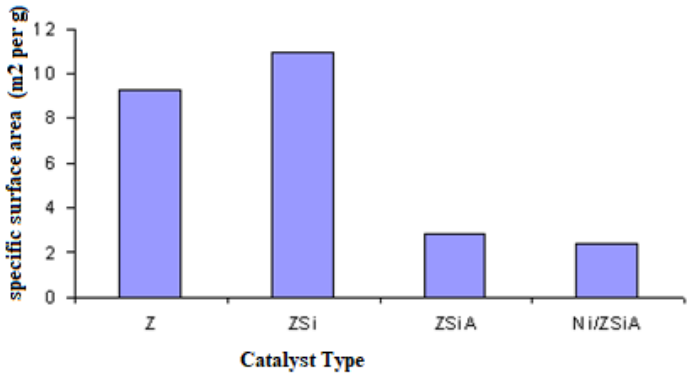

Figure 15. Specific Surface Area of Various Types of Catalysts, Z : Zeolite Catalyst, ZSi : Zeolite Enrichment Catalyst with Si, ZSiA : ZSi Catalyst Treated with Acid, Ni/ZSiA : ZSiA Catalyst Impregnated with Ni Metal

CONCLUSION

From the preparation process of the Ni/zeolite catalyst, the characterization is as follows: the metal content contained in the Ni/zeolite catalyst is Ca and Fe with very little levels of Na, Mg and other metals (< 5 mg/gram of catalyst). Meanwhile the acidity of the catalyst was 0.24 mmol/gram of catalyst and the specific surface area of the catalyst was 2.18 m2/gram of catalyst and the Si/Al ratio of the catalyst was 10.21.

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