# **Conversion of 1-octadecanol to 1-octadecene**

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# Abstract

1-Octadecene can be produced from 1-octadecanol through the reduction process using ZSiA catalyst in a fixed bed reactor operated at 400 °C. The reduction process was performed using hydrogen as a reduction agent gas. Five grams of 1-octadecanol was poured into evaporator and 5 g of catalyst was put into the reactor fixed bed system. Furthermore, the reactor was heated up to 400 °C and the evaporator was heated to the boiling point of 1-octadecanol. Then the product was flowing through the cooler and was collected in the bottle. The product was analyzed using GCMS.

The reduction process of 1-octadecanol produced 20,21 % of 1-octadecene, 14,37 % of 5-octadecene and 10,40 % of 9-octadecene. The product had physical properties, of yellow and flammable. Keyword: 1-octadecanol, 1-octadecene, fixed bed reactor, ZSiA catalyst

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#### **INTRODUCTION** I.

Methyl oleate conversion into gasoline fraction compound (biogasoline) can be made in stages. The reduction reaction of methyl oleate (methyl 9-octadecenoate) into alcohol (1-octadecanol), the reaction of 1octadecanol to alkenes (1-octadecene) through the reduction reaction, subsequent hydrocracking alkenes into alkanes and shorter chain alkenes (<C12). Theoretically, a series of reactions are very likely to be done at the lab via catalytic hydrogenation using ZSiA catalyst and catalytic hydrocracking catalyst using Ni / ZSiA. In this study, the conversion of 1-octadecanol to 1-octadecene via catalytic hydrogenation was carried out.

Alcohol dehidration reaction at 170 °C with the help of homogeneous catalysts (H<sub>2</sub>SO<sub>4</sub>) will produce alkenes, such as in Figure 1.

$$\begin{array}{cccc} & & & \\ & & H_2 SO_4 \\ & & Heat \\ \hline 2 & CH_3 CH_2 CH_2 CHCH_3 & & \\ \hline & & elimination \\ \hline 2 & -pentanol \\ \hline & & & \\ \hline \hline & & & \\ \hline \hline & & & \\ \hline & & & \\ \hline \hline & & & \\ \hline \hline \\ \hline & & & \\ \hline \hline & & & \\ \hline \hline \\ \hline \hline & & & \\ \hline \hline & & & \\ \hline \hline \\ \hline \hline \\ \hline \hline \\ \hline \hline \\ \hline$$

Figure 1. Alcohol elimination reaction (Fessenden dan Fessenden, 1986)

When an alcohol is reacted with sulfuric acid, it will take a series of reactions as in Figure 2. In general, primary alcohols to produce sulfate ester at low temperatures.



Figure 2. Reversible reaction of alcohols at several temperatures (Fessenden dan Fessenden, 1986)

Primary alcohol will produce ether at moderate temperatures and will produce alkene at high temperatures, although it is inevitable that the products obtained will be in the form of a mixture. Tertiary alcohols and most of the secondary alcohol will produce alkenes (Fessenden and Fessenden, 1986).

Fatty alcohol is an alcohol that is produced by the hydrogenation of fatty acid esters. In general, fatty alcohol derived from saturated fatty acids. Boiling point and melting point of alcohol (Table 1) is likely increase regularly with increasing chain length (number of carbon atoms). The longer the carbon chain, it will have an impact on the polarity of the hydroxyl group. Hexanol and octanol is slightly soluble in water, decanol and fatty alcohols with longer chains are not soluble in water, octadecanol and longer chain can absorb moisture from the air during storage.

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1 aD	le 1. The physica	r properties of	some com	pounds fatty are	01101	
IUPAC name	common name	molecular formula	Mr (g/mol)	Hydroxyl number (mg KOH/g)	Mp (°C)	Bp (°C) (p.kPa)
1-Dodecanol	Lauryl alcohol	$C_{12}H_{26}O$	186,3	300	23	260
1-Tetradecanol	Miristyl alcohol	$C_{14}H_{30}O$	214,4	261	38	172 (2.67)
1-Hexadecanol	cetyl alcohol	$C_{16}H_{34}O$	242,5	230	49	194 (2.67)
1-Heptadecanol	Margaryl alcohol	$C_{17}H_{36}O$	256,5	218	54	-
1-Octadecanol	Stearyl alcohol	C <sub>18</sub> H <sub>38</sub> O	270,5	207	58	214 (2.67)

(1 atm = 101,325 kPa), (Perry's, 1997)

Based on Table 1, because the boiling point of 1-octadecanol relatively very high, then through a process of catalytic hydrogenation using a ZSiA catalyst in a fixed bed reactor at high temperature (400 ° C) it will produce 1-octadecene, 3-octadecene, 5-octadecene and 9-octadecene.

According to Gasser (1987), reactions using catalysts involve physisorption, chemisorption and desorption events. The physisorption event is a state where reactant molecules in the gas phase are adsorbed on the catalyst surface and involves van der Waals forces. The physisorption event is exothermic and the amount of energy released is - 40 kJ/mol. Chemisorption is the event of electron exchange and the formation of chemical bonds between reactant gas molecules and the catalyst surface and is exothermic. The amount of energy released in the chemisorption event is - 400 kJ/mol.

Reactants that are adsorbed on the catalyst surface can migrate, allowing collisions between one reactant and another until a reaction occurs and produces an intermediate product on the catalyst surface (activated complex adsorbed, ACA). Next, the product will experience a spontaneous desorption event, where the energy required for the desorption event ( $\lambda$ des) is fulfilled from the energy value released from the chemisorption event. The desorption event in a catalytic reaction is endothermic.



Path of reaction

Figure 3. Energy changes in the catalytic reaction stage compared to reactions without a catalyst (Satterfield, 1980 and Gasser, 1987)

Information :

λads <i>Eads</i> ACH ACA <i>Ecat</i>	::	Heat of adsorption of reactants (exothermic) Activation energy in the physisorption process of reactants on the catalyst surface The state of the activated complex without a catalyst (activated complex homogenous) Adsorbate activated complex state with catalyst (activated complex adsorbed) Activation energy in the process of chemisorption of reactants with a catalyst to form the
Edes $\Delta E_{hom}$ $\Delta H_R$ $\lambda des$	::	ACA state (exothermic) Activation energy for the desorption process Activation energy of a reaction without a catalyst Enthalpy of reaction without catalyst (exothermic process) Enthalpy of the desorption process (endothermic)

Based on the phases involved in the reaction, catalysts are divided into three, namely homogeneous catalysts, heterogeneous catalysts, homo-heterogeneous catalysts. This distinction is based on the differences in the reactant and catalyst phases in their interactions. In heterogeneous catalysts, the catalyst generally has a solid phase, and the reactants are in the liquid or gas phase. The choice of catalyst type is adjusted to the type of reaction (Atkins, 1997),

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No.	Type of Catalyst	Function	Example
1	Metal	Hidrogenasi, Dehidrogenasi	Fe, Ni, Pt, Ag
2	Semiconductive Oxides and Sulfides	Oxidation, Desulfurization	NiO, ZnO, MgO Bi <sub>2</sub> O <sub>3</sub> , MoO <sub>3</sub>
3	insulator oxide	Dehydrated	Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , MgO
4	Acid	Polymerization, Isomerization, Alkylation	H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>

(Satterfield, 1980)

The stages in a catalytic reaction with a heterogeneous catalyst according to Wu (2005) and Augustine (1996), are as follows:

1. Diffusion (mass transfer) of reactants from the fluid phase to the outer surface of the catalyst.

2. Diffusion of reactants from the pore mouth through the catalyst pores to the area around the inner surface of the catalyst.

3. Adsorption of reactants on the catalyst surface.

4. Reaction on the catalyst surface.

5. Desorption of reaction products from the catalyst surface.

6. Product diffusion from the inner surface through the catalyst pores to the pore mouths on the outer surface.

7. Diffusion (mass transfer) of the product from the catalyst surface to the fluid phase

The process of reactant adsorption on a heterogeneous catalyst surface is based on collisions or encounters between reactant molecules in the fluid phase and the catalyst surface. According to Gasser (1987), there are several types of collisions that may occur on the surface of a solid (catalyst), namely :

1. Reactant molecules that hit the catalyst are reflected from the surface of a solid that is completely or partially elastic. In this process, no energy exchange occurs (dE = 0) or partial energy exchange occurs. Collisions of reactant molecules on the surface of a solid will be reflected back with the same energy as the molecules collided or reflected with almost the same energy.

2. Reactant molecules are adsorbed on the surface and energy transfer or exchange occurs ( $dE \neq 0$ ). In this phenomenon, collisions between reactant molecules and the catalyst surface will be partially reflected and based on the amount of energy released, this adsorption phenomenon is divided into two types, namely:

3.

a. Physisorption

Physisorption is the process of physical absorption of gas molecules on the surface of a solid which is associated with weak attractive forces (Van der Waals) of the reactant molecules and the catalyst surface. The basic idea of the physisorption process is the electrostatic force of attraction between molecules and if this force occurs

between atoms or molecules and the surface then what occurs is only a physical force of attraction without any chemical changes. Physisorption has a relatively small heat of adsorption, namely around 40 kJ/mol (exothermic). In physisorption, the adsorbed gas molecules will be easily released again by increasing the system temperature.

b. Chemisorption

Chemisorption is chemical adsorption which is associated or described with the exchange of electrons and the formation of chemical bonds between the adsorbed reactant molecules and the surface of a solid (interaction between electron orbitals). Chemisorption is generally preceded by a physisorption process, and in chemisorption the energy released is quite large, namely around 400 kJ/mol (exothermic).

### Material

### II. METHODS

Materials used in the study are: natural zeolite from Wonosari produced by PT Prima Zeolita, materials and quality of E.Merck pa of: oleic acid (91.59%), 1-octadecanol 95%, 37% HCl (v / v), HF 40% (v / v), NH4Cl, Na<sub>2</sub>SiO<sub>3</sub>. Other materials such as gaseous oxygen, nitrogen and hydrogen (PT Samator Gas), pH paper.

### Equipment

Equipment required in the study are: a set of fixed bed reactor, thermocouples, thermometers, oven, hot-plate, glassware laboratory equipment, analytical balance (Mettler RE 200), GC-MS (Shimadzu QP-2010S).

# III. PROCEDURE

A number of catalysts ZSiA (5, 10 and 15 g) was placed in a fixed bed reactor system and heated to temperature of 400  $^{\circ}$  C. A total of 5 grams of 1-octadecanol placed into the column evaporator and evaporated at 400  $^{\circ}$ C while hydrogen stream is introduced to flow in passing the catalyst. Catalytic reaction products flow through tube of silicone and placed in a glass bottle.





## Preparation ZSiA catalyst

Zeolites with size of 100 mesh pass soaked and washed in distilled water while stirring. Then soaked with 2% HF for 30 minutes, washed with distilled water and repeated up to 3 times, then dried in an oven at a temperature of 120  $^{\circ}$  C for 3 hours. Subsequently oxidized with oxygen at a temperature of 500  $^{\circ}$  C for 2 hours and calcined in nitrogen at a temperature of 500  $^{\circ}$  C for 2 hours with a gas flow rate of 20 mL / min to obtain a catalyst Z.

Catalyst then washed using 2 M HCl solution with a ratio between zeolite : HCl = 1 : 2 (v / v) while stirring for 20 to 30 minutes (Zhang , 1999). Furthermore zeolite sample was washed using distilled water until pH = 6 and dried in an oven at a temperature of 120 ° C for 3 hours , followed by oxidation using oxygen gas with a flow rate of 20 mL / min at a temperature of 500 ° C for 2 hours and calcined in nitrogen gas at a rate of flow of 20 mL / min at a temperature of 500 ° C for 2 hours . Then into the catalyst results in a glass beaker Z added Na - Silicate (Na<sub>2</sub>SiO<sub>3</sub>) by 5 % (w / w) were dissolved in distilled water and then heated at a temperature between 80 °C to 90 °C for 24 hours while stirring using a magnetic stirrer . Then the sample was cooled and continued oxidation with oxygen gas at a temperature of 500 ° C for 2 hours with a gas flow rate of 20 mL / min and continued calcination with nitrogen gas at a temperature of 500 ° C for 2 hours with a gas flow rate of 20 mL / min and continued calcination with nitrogen gas at a temperature of 500 ° C for 2 hours with a gas flow rate of 20 mL / min and continued calcination with nitrogen gas at a temperature of 500 ° C for 2 hours with a gas flow rate of 20 mL / min to obtain the catalyst ZSi .

ZSi catalyst was cooled and added into a solution of 2 M NH<sub>4</sub>Cl in a glass beaker with a ratio of 1: 2 (v / v) and the mixture was heated again at a temperature of 90 ° C for 4 hours with a magnetic stirrer (Zhang, 1999). Then cooled and followed by oxidation using oxygen gas at a temperature of 500 ° C for 2 hours with a gas flow rate of 20 mL / min and continued calcination with nitrogen gas at a temperature of 500 ° C for 2 hours with a gas flow rate of 20 mL / min to obtain a catalyst ZSiA .

# IV. RESULTS AND DISCUSSION

#### Crystallinity of ZSiA Catalysts

According to Harber (1991), material requirements zeolite as the catalyst are surface area, the ratio of Si / Al, acidity, cation content and crystallinity. The properties are very related to the pore radius, pore volume and acidity contained in the zeolite. Crystallinity of the zeolite force crystal lattice in maintaining the shape of the crystal. The requirements of a material as a catalyst are that the material must have a crystalline properties and stable as the material currently used as a catalyst.

Properties of zeolite crystals can also affect the ability in the adsorption process. If a zeolite crystals has low crystal lattice, zeolite will be easily damaged and will cause blockage of the pore mouth, reduction in pore volume and decrease the amount of acid. Furthermore, zeolite will decrease its activity as a catalyst.

The method used to analyze the crystal structure of the catalyst is the result of X-ray diffraction (XRD). Basic principles of chemical analysis used in XRD is the distance between the characteristics planes (d). The position of the diffraction angle (2  $\theta$ ) and the distance between planes describe the type of crystal, while the intensity indicates the crystallinity of a solid (West, 1984; Sibilia, 1996). Through quantitative analysis is performed by comparing the diffractogram of natural zeolite samples with standard diffractogram natural zeolite.

Z catalyst shows the crystalline nature of the catalyst, as well as treated with sodium silicate (Si enrichment) and acid treatment (HF, HCl,  $NH_4Cl$ ) which is expected to be an exchange of ions and the formation of Bronsted acid sites (ZSiA catalyst). Treatment with Ni metal impregnation catalyst surface to ZSiA still shows the nature of the crystal as shown in Figure 5.



Figure 5. Diffractogram of Z and ZSiA catalyst

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

Table 3 Identification of the diffraction angle position (20) in the XRD diffractogram of catalysts made with standard natural zeolites

Types of	2	20
zeolites	Natural zeolite samples	Natural zeolite according to Treacy and Higgins (2001)
Mordenite	6,54; 13,81; 18,03; 24,42; 25,64; 25,99;	6,51; 13,83; 18,19; 24,43; 25,63; 26,04;

	27,00; 35,58; 36,90; 39,83; 45,33;	27,09; 35,61; 36,87; 39,82; 45,28;
	47,91; dan 48,70	47,97; dan 48,70
Clinoptilolite	19,19; 20,40; 22,38; 25,32; 25,99;	19,10; 20,40; 22,36; 25,35; 26,04;
_	28,08; 29,81; 36,22; 45,34; dan 48,92	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 4, 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 had an impact on increasing the crystallinity, namely 300, 1429, 259 to 342, 1560 and 284.

Ta	Table 4 Intensity diffractogram with the largest peak from the resulting catalyst				
20				Intensity (count	s)
(degrees)	d	Types of zeolite			
	(Å)		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 impregnating Ni metal with  $Ni(NO_3)_2 \cdot TH_2O$  salt causes the crystal 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 a similarity index to the types of mordenite, clinoptilolite and quartz, so the zeolite used has a crystal structure of mordenite, clinoptilolite and quartz types. Zeolite with strong crystallinity will be very supportive when used as a catalyst.

#### Si/Al Ratio and Results Catalyst Dealumination

An increase in the Si/Al ratio illustrates the release of Al within the framework (Al framework) to Al outside the framework as shown in Figure 6. The presence of Al in the zeolite framework carries a negative charge which is stabilized by the presence of metal ions such as Na(+), Ca(2+), K(+), Mg(2+), Fe(3+) or H(+) ions, so that when acid is treated with the zeolite either with HF or HCl, apart from causing the Al framework to become Al outside the framework, it also has a direct impact on reducing the metal ion content in the zeolite. Figure 6 shows an increase in the Si/Al ratio at the treatment stage with HF, Na<sub>2</sub>SiO<sub>3</sub>, HCl and NH<sub>4</sub>Cl in making the Ni/ZSiA catalyst, although this increase is not very significant. The increase in the Si/Al ratio is the result of acid treatment with HF 2 M, HCl 2 M and NH<sub>4</sub>Cl 2 M. The increase in the Si/Al ratio causes the zeolite to become more non-polar and the more non-polar the zeolite will interact more easily with non-polar compounds (Twaiq, 2003). The use of zeolite with a relatively increased Si/Al ratio as a catalyst in the hydrogenation reaction of methyl 9-octadecenoate, 1-octadecanol and 1-octadecene is relatively suitable.



Figure 5. Si/Al ratio of various types of catalysts, Z: zeolite catalyst, ZSi: zeolite catalyst enriched with Si, ZSiA: ZSi catalyst treated with acid, Ni/ZSiA: ZSiA catalyst impregnated with Ni metal

In Figure 6, it can be seen that the Si/Al ratio on the Ni/ZSiA catalyst type decreased slightly, but not significantly (0.19%). What is possible is that during the impregnation of Ni metal from the Ni(NO<sub>3</sub>)<sub>2</sub>·<sup>3</sup>H<sub>2</sub>O salt there is relatively no change in the Si content and there is relatively no change in the Al content, so that the Si/Al ratio of Ni/ZSiA remains relatively constant. In the treatment of inserting Si metal from the Z catalyst type so that it becomes ZSi, the Si/Al ratio increases by 40.17%.

Dealumination is the event that Al from within the zeolite framework comes out of the zeolite framework. This Al release from the zeolite framework causes the Si/Al ratio of the zeolite framework to increase. Dealumination events in catalyst preparation were not only caused by treatment with 2% HF and 2 M HCl, but were also caused by the hydrothermal process of the zeolite at a relatively high temperature (500 °C). In this situation, what causes the Si/Al ratio to increase is the presence of water vapor at the calcination temperature (500 °C) in the zeolite which hydrolyzes the aluminum in the framework (Al framework) into aluminum outside the framework. Water vapor at calcination temperature, apart from hydrolyzing Al in the framework, also causes the oxygen framework to become unstable and as a result Si moves to the empty space left by Al. As a consequence, the Si/Al zeolite ratio increases and is followed by a decrease in the zeolite pore size as shown in Figure 7. The Si/Al ratio 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 is, the more non-polar zeolite has a tendency to prefer feeds or reactants that are non-polar in their interactions, such as methyl 9-octadecenoate, 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), increasing the Si/Al ratio will have an impact on increasing zeolite acidity and thermal stability, thereby supporting hydrogenation reactions at high temperatures.

Increasing the Si/Al ratio results in a decrease in the zeolite pore size and increases the physisorption ability of the zeolite pores which are increasingly non-polar. Based on the research results, a linear relationship was obtained between increasing the Si/Al ratio and increasing catalyst acidity as shown in Figure 9. This situation can be explained that as the Si/Al ratio increases, the pore diameter decreases so that the adsorption ability of the ammonia base as an indicator of acidity increases.

The Al release event from the zeolite framework is depicted according to Derouane (1992). The interaction of zeolite with an acid solution (HCl) will release the Al in 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 Al in the framework to become Al outside the framework. Then the zeolite undergoes rearrangement to become a zeolite with a Si center.





Figure 7. Al Framework release (dealumination) in the zeolite framework

According to Twaiq (2003), the relatively high Si/Al ratio of a catalyst is very suitable for non-polar feeds or reactants. Catalysts with a low Si/Al ratio have a tendency to be more able to interact with polar reactants. Satterfield (1982), said that increasing the Si/Al ratio increases thermal stability. Meanwhile, Harber (1991), said that determining the activity of a zeolite catalyst is not only determined by the presence of the Si/Al ratio in the catalyst, but it is also necessary to pay attention to 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 by the fact that before being treated with acid (HF, Na<sub>2</sub>SiO<sub>3</sub>, HCl and NH<sub>4</sub>Cl), the zeolite ring through the –Si–O–Al– bond forms a ring with a certain pore diameter which was initially covered by impurities and becomes more open due to the dissolution of the impurities. After experiencing a dealumination event as a result of acid treatment, the zeolite ring has a pore diameter that is more open and relatively shorter as shown in Figure 8.





As a result, the pores in the 10 - 20 Å region increase quite significantly, followed by the pores in the 21 - 30 and 31 - 40 Å regions as shown in Figure V.14. ZSiA and Ni/ZSiA catalysts still have quite strong crystalline properties. This situation is indicated by the presence of a quite sharp peak in 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 content of Na (+), Ca(2+), Fe(3+) and Mg(2+) metal ions. During the impregnation of Ni metal from Ni(NO<sub>3</sub>)<sub>2</sub>•<sup>\*</sup>H<sub>2</sub>O salt, the Si/Al ratio decreased, although relatively slightly. This decrease was caused by impregnation of Ni metal from the Ni(NO<sub>3</sub>)<sub>2</sub>•<sup>\*</sup>H<sub>2</sub>O salt, a small portion of Si was released from the zeolite framework, thus the Si/Al ratio showed a decrease, although slightly. Thus, from Z to ZSiA and Ni/ZSiA catalyst types the Si/Al catalyst ratio relatively increases which shows that the catalyst is increasingly non-polar so that it is relatively suitable for the feed used in the catalytic reaction, namely methyl 9-octadecenoate, 1-octadecanol and 1-octadecene.



Figure 9. Relationship between acidity and Si/Al catalyst ratio

The relationship between acidity and the Si/Al ratio as in Figure 9. is linear. The higher the Si/Al ratio, the more acidic the zeolite is and the more non-polar it is. The more acidic the zeolite is, the more H+ ions are formed on the surface of the zeolite. H+ ions on the surface of the zeolite, which means that the more Bronsted acid sites there are, the greater the ability to adsorb ammonia bases.

#### Catalytic hydrogenation of 1-octadecanol to 1-octadecene

Hydrocracking compound 1-octadecanol done in a fixed bed reactor system at 400 ° C with a catalyst ZSiA and weighing as much as 10 g of 1-octadecanol reactants pure compounds as much as 10 g. Pure compound 1-octadecanol have physical properties as follows: in the form of solids have a molecular formula  $C_{18}H_{38}O$ , the purities 95%, the boiling point of 336 ° C, density of 0.81 g / mL and the melting point of 58 oC. Prior to catalytic hydrocracking process using a catalyst ZSiA, compound 1-octadecanol was analyzed using GC-MS first. The results showed that compound 1-octadecanol detected at a retention time of 23.33 minutes and is shown in Figure 10.



Figure 10. Chromatogram GCMS of compound 1-octadecanol

GC-MS chromatograms showed that 1-octadecanol detected 70.65%. These results are due to solvent percentage of 1.75% (1) of diethyl ether and 23.11% (3) of chloroform participate counte. If the solvent does not counted, then 1-octadecanol percentage can reach 95%.





GC-MS chromatogram results in thermal cracking of 1-octadecanol compounds is shown in Figure 11. Product of the thermal cracking of 1-octadecanol compounds are presented in Table 5 is the dominant product 9-octadecene compound (12.60%).

Name of Compound	SI	t <sub>R</sub> (min)		Number of (%)
4-dodecene	96		3,28	1,50
5-tetradecene	95		4,18	0,83
Pentadecane	96		7,72	0,62
Hexadecane	95		12,23	0,51
7-hexadecene	95		14,01	3,88
9-octadecene	97		14,14	12,60
3-octadecene	96		14,34	9,45
5-octadecene	97		14,67	8,68
Octadecane	96		22,65	1,13
Number of				39,20

Table 5. Product of alkanes and alkenes with chain length <C18 of the thermally cracking reaction 1octadecanol at 400 oC (expected data library Shimadzu GCMS QP2010)

GC-MS chromatograms of the analysis of catalytic hydrocracking reaction products with 1-octadecanol ZSiA catalyst showed a number of product compounds as shown in Figure 8. Products from catalytic hydrocracking reaction with 1-octadecanol ZSiA catalyst at a temperature of 400  $^{\circ}$  C to produce compounds alkanes and alkenes in the range of chain lengths up to C18 bonds reached 49.60% as shown in Table 5 and the resulting dominant compound is 1-octadecene the relative concentration which reached 20.21%

Based on Table 5, it can be shown that the catalytic hydrocracking 1-octadecanol produce quite a lot compounds 1-alkenes and some types of alkane compounds. Acquisition of alkane compounds relatively fewer than alkenes through hydrocracking process is far from perfect, such as the small amount of hydrogen that flowed quantitatively to increase the pressure or the possibility of hydrogen so that the amount of hydrogen is quite abundant and physisorption processes between hydrogen with 1-octadecanol functional groups expected quite effective.

The hydrogen adsorption on the catalyst surface are less optimal because less pressure will also cause the amount of hydrogen on the surface of the catalyst is quantitatively be reduced, so that the probability of collision between the adsorbed hydrogen with 1-octadecanol functional groups will also be reduced, thus the products produced alkanes and alkenes are 49.60%.



Figure 12. Potential energy diagram (Campbell, 1988)

The occurrence of collisions can take place more easily when the process begins with physisorption, followed by chemisorption process. Based on the potential energy diagram, the chemisorption always begins with physisorption events. When feed adsorbed on the catalyst surface, the spontaneous chemisorption or reaction on the catalyst surface.





According to Morrison (1979), the catalytic reaction of alcohols at relatively high temperatures generally produce alkenes. According to Campbell (1988), by catalytic hydrogenation of alkenes mechanism "Horiuti-Polanyi" alkane compounds will be generated. Thus the catalytic hydrocracking reaction with 1-octadecanol ZSiA catalyst at a temperature of 400  $^{\circ}$  C produced a lot of alkenes and alkanes.

Table 6. Catalytic hydrocracking reaction product 1-octadecanol compounds into alkanes and alkenes
compounds with chain length <c18 (expected="" 400="" a="" at="" c="" data="" gc-ms<="" library="" of="" shimadzu="" td="" temperature="" °=""></c18>
<b>OD2</b> (10)

Name of compound	t <sub>R</sub> (menit)	number of
		(%)
5-dodecene	3,28	0,23
Heptadecane	7,73	0,80
Pentadekana	12,23	0,30
7-hexadecene	14,01	3,29
9-octadecene	14,15	10,40
1-octadecene	14,38	20,21
5-octadecene	14,63	14,37
		49.60

Catalytic hydrogenation of 1-octadecanol with ZSiA catalyst in a fixed bed reactor at a temperature of 400  $^{\circ}$ C produced alkanes and alkenes with chain length <C18 as much as 49.60%. Mechanism of catalytic hydrogenation 1-octadecanol expected to follow two main phases, namely the reduction of the alcohol groups into alkenes and alkene bond breaking a chain alkanes and alkenes shorter. The mechanism is as follows,



According to Campbell (1988), compound 1-octadecene then form the isomer is such as 9-octadecene and 5-octadecene with relative concentrations 14.37 and 10.40%.



Hexane was unraveled to gas compounds or volatile compounds as follows,



#### V. CONCLUSION

Catalytic hydrogenation of 1-octadecanol to N-octadecane (where N = 1, 3, 5 and 9) can be done with ZSiA catalyst in a fixed bed reactor. Product of catalytic hydrogenation process of 1-octadecanol is compounds flammable and its main product is N-octadecene where N = 1, 3, 5 and 9. The products of catalytic hydrogenation with ZSiA and fixed bed reactor system has a tendency to increase with increasing hydrogen flow rate of 20, 40 to 60 mL / min and increasing the temperature of the reaction system 400, 450 and 500 °C. The main products of catalytic hydrogenation of 1- octadecanol to 1-octadecene be reached 20,21%, a 5octadecene reached 14.37% and a 9-octadecene reaches 10.40%

#### REFERENCES

- [1]. [2]. Anderson, J.R. and Boudart, M., 1981, Catalysis Science and Technology, First Edition, Springer Verlag, Berlin.
- Augustine, R.L., 1996, Heterogeneous Catalysis for Chemist, Marcel Dekker Inc., New York.
- Bartholomew, C. H. and Farrauto, R.J., 2006, Fundamentals of Industrial Catalytic Processes, 2nd edition, John Wiley and Sons Inc., [3]. New Jersey.
- Belitz, H.D., and Grosch, W., 1999, Food Chemistry, 2<sup>nd</sup> edition, Springer-Verlag, Berlin. [4]
- [5]. Bell, A.T., 1987, Support and Metal Support Interaction in Catalyst Design, John Wiley & Sons, New York.
- Boudart, M. and Bell A.T., 1987, Catalyst Design, 1st edition, A Wiley-Interscience Publication, New York. [6].
- [7]. Brands, D.S., Poels, E.K., Dimian, A.C. and Bliek, A., 2002, Solvent-Based Fatty Alcohol Synthesis Using Supercritical Butane : Flowsheet Analysis and Proses Design, J. Am. Chem, Vol 79 (1).
- [8]. Boudreaux A., Kevin, 2013, General Chemistry, Departement of Chemistry, Angelo University, San Angelo, Texas.
- [9]. Claus, J.H.J., Claus M., Jindrich H., Iver S. and Anna C., 2000, Mesoporous Zeolite Single Crystals, J. Am. Chem. Soc.: 122, 7116-7117
- [10]. 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.
- [11]. Campbell, I. M., 1988, Catalysts at Surfaces, Chapman and Hall Ltd., New York.
- Gasser, R.P.H., 1987, An Introduction to Chemisorption and Catalysis by Metal, Oxford Science Publication, Oxford. [12].
- [13]. Harber, J., 1991, Manual on Catalyst Characterization, Pure and Appl. Chem., 63, 9, 1227-1246.
- Rajeshwer, D., Sreenivasa Rao, G., Krishnamurthy, K., R., Padmavathi, G., Subrahmanyam, N. dan Jagdish, D. Rachh, 2006, [14]. 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
- [15]. Yoon, C., 1997, Hydrogenation of 1,3-butadiena on Platinum Surfaces of Different Structures, Catal. Lett, 46, 37.
- [16]. Zhang, W. and Smirniotis, P.G., 1999, Effect of Zeolite Structure and Acidity on the Product Selectivity and Reaction Mechanism for n-Octane Hydroisomerization and Hydrocracking, J. Catal., 182, 400-416.