



## **The Effect of Acid Strength of Bronsted Acid Site on The Ability of Catalyst to Break The Carbon Chain Bonds of 1-Octadecenes Into Alkanes and Short Chain Alkenes as a Substitute for Fossil Fuel**

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**ABSTRACT** - Research has been carried out on the strength of acids on their ability to break carbon chain bonds. The preparation of the zeolite catalyst includes soaking the zeolite in distilled water for 24 hours, followed by calcination and oxidation, then followed by reduction. Further acid treatment with 6 M HCl. Then followed by washing with H<sub>2</sub>O until neutral pH (pH = 7), then dried in an oven with a temperature of 105 °C, then after becoming a zeolite catalyst used in the cracking reaction of 1-octadecenes into alkanes and short chain alkenes. The results obtained are as follows for the type of zeolite catalyst with code Z having a very low acidity level of 3.15 mmol NH<sub>3</sub>/mg Zeolite, then the zeolite has been modified by a calcination process for 24 hours given the code ZCA which shows a moderate acidity level of 5,76 mmol NH<sub>3</sub>/mg Zeolite, then the catalyst with the code ZCAO is zeolite which has been calcified and oxidized and shows a yield of 9.54 mmol NH<sub>3</sub>/mg Zeolite. Catalytic hydrocracking of 1-octadecene with ZCAO catalyst at a variation of the hydrogen flow rate of 20 mL/minute and a temperature of 450 °C resulted in alkanes and alkenes < C<sub>12</sub> which was 15.29% maximum, followed by a hydrogen flow rate of 10 mL/minute at temperatures of 500 and 400 °C.

**Keywords:** zeolite, calcination, oxidation

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### **INTRODUCTION**

The catalytic conversion of palm oil using a zeolite composite catalyst with micro-meso pores in a fixed bed system reactor operated at 450°C resulted in a gasoline product of up to 48% (w/w) of 99% by weight of converted palm oil (Sang, 2003). Meanwhile Twaiq (2003), explained that

the catalytic cracking process of palm oil using a catalyst type MCM-41 and a fixed bed system reactor operated at a temperature of 450 °C produced linear liquid hydrocarbon compounds (straight chain). Gasoline products will increase with a decrease in diesel (biodiesel) products in the conversion of palm oil (Santos, 2003). Yoon (1997), the use of vegetable

oils as a source of engine fuel in motorized vehicles is based on several reasons, such as (1) renewable, (2) environmentally friendly, (3) biologically degradable. In general, chemical reactions in the chemical industry (such as petroleum processing) use a catalyst in the process. The process of using a catalyst is very advantageous, because the rate of chemical processes can be faster. Catalysts used in the petroleum processing industry are generally heterogeneous catalysts that have a high surface area and acid sites. Many studies have explained that certain types of zeolite (especially acid Y zeolite, synthetic faujasite, clinoptilolite) are able to work well as petroleum crackers (Sutarti and Rachmawati, 1994: 37).

Augustine (1996) states that 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.

### Catalyst acidity

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 catalytic reactions can take place due to the acidic and basic nature of the catalyst and the reactants (Bronsted acid site implementation) or the interaction between electron pair donors and acceptors of the catalyst and reactants (Lewis acid site implementation) or due to the presence of positive and negative charges between the catalyst and reactants (implementation of electric charge).

Acidity and acid strength of a catalyst have different meanings. According to Satterfield (1982),

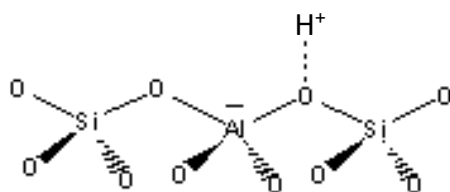


Figure 1  
Bronsted acid site on a zeolite framework (Satterfield, 1982)

the acidity of a catalyst is defined as the ability of 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.

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 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 of the zeolite. The acidity in this case is expressed in  $\text{mmol NH}_3/\text{mg zeolite}$ . 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.

Anderson (1981), suggests that 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.

## METHODOLOGY

The tools needed in this research are reactor, thermocouple, furnace, glassware, automatic voltage regulator, Erlenmeyer. The materials needed are 1-octadecane, zeolite, oxygen gas cylinders and nitrogen gas.

### Z catalyst preparation

Natural zeolite from Wonosari, Yogyakarta in the form of granules with a diameter of  $\pm 0.5$  cm is

immersed in distilled water while stirring with an iron stirrer for one hour at room temperature. Then it was filtered, the clean precipitate was dried in an oven at 100 °C for 3 hours. Then mashed by grinding and then filtered through a 100 mesh sieve.

Sample Z which had been cleaned and crushed to pass 100 mesh, as in process number one above, was calcined by means of flowing nitrogen gas at 500 °C for 4 hours, then oxidized with oxygen at 400 °C for 2 hours, so that catalyst Z was obtained. Preparation of ZCAO catalyst Sample Z which has been cleaned, then crushed to pass 100 mesh, as in process number one above. The zeolite was immersed in a 1% HF solution with a volume ratio of 1:2 in a plastic container, for 10 minutes at room temperature. Then filtered and washed repeatedly with distilled water until pH = 6. Then followed by 6M HCl treatment. Z catalyst was then refluxed using 6M HCl for 30 minutes at 90 °C while stirring with a magnetic stirrer. After that it was continued by filtering and washing with distilled water until the pH was equal to 6. Then it was dried and ground to obtain ZCA catalyst. The ZCA catalyst was then dried in a Vacuum Drying Oven at a pressure of 20 cmHg for 3 hours at 130 °C. The next process was the 1M NH<sub>4</sub>Cl treatment, in which the ZCA catalyst and 1M NH<sub>4</sub>Cl were heated at 90 °C for 3 hours every day and repeated every day for one week and shaken every one hour during heating. After finishing, the zeolite was filtered and washed with distilled water until pH = 6, dried in an oven at a temperature of 120 °C to 130 °C. After chilling the ZCA was mashed and placed in a porcelain cup and calcined for 4 hours, at a temperature of 500 °C in a Muffle Furnace (calcination without nitrogen gas) and followed by an oxidation process for 3 hours with an oxygen flow rate of 20 mL/minute, then the catalyst was coded with ZCAO. After cooling, the ZCAO catalyst is used in the 1-octadecene cracking reaction.

## RESULTS AND DISCUSSION

Hydrocracking Reaction of 1-Octadecene with ZCAO Catalyst 10 g of pure 1-octadecene sample (90 %) was placed in the evaporator column and 10 g of ZCAO catalyst was placed in the fluidized-bed reactor column. Furthermore, the reactor column is preheated, so as to reach the desired catalytic reaction temperature (400, 450 or 500 °C). After the reactor temperature is reached, the evaporator column is immediately heated until evaporation occurs, hydrogen is flowed at a certain speed (10, 20, 30 and 40 mL/

minute).

The 1-octadecene vapor with hydrogen will flow so that it passes through the catalyst surface. The resulting reaction product (organic liquid product, OLP) was collected in a sample bottle for up to 30 minutes and the reaction product was analyzed using GC-MS.

### Catalyst Crystallinity

According to Harber (1991), the requirements for zeolite materials as catalysts are surface area, Si/Al ratio, acidity, cation content and crystallinity. These properties are closely related to the pore radius, pore volume and acidity contained in the zeolite. Zeolite crystallinity is a measure of the strength of the crystal lattice in maintaining its crystalline shape. One of the requirements for a material as a catalyst is that the material must have crystalline properties and be stable when the material is used as a catalyst.

Bartholomew (2006) the nature of the zeolite crystal can also affect its ability to adsorption. If a zeolite has low crystalline properties, the zeolite crystal lattice will be easily damaged and will cause clogging of the pore mouths, reduction in pore volume, and a decrease in the amount of acid. As a further consequence, the zeolite will experience a decrease in its activity as a catalyst. The method used to analyze the crystal structure of the prepared catalyst is X-ray diffraction (XRD). The basic principle of

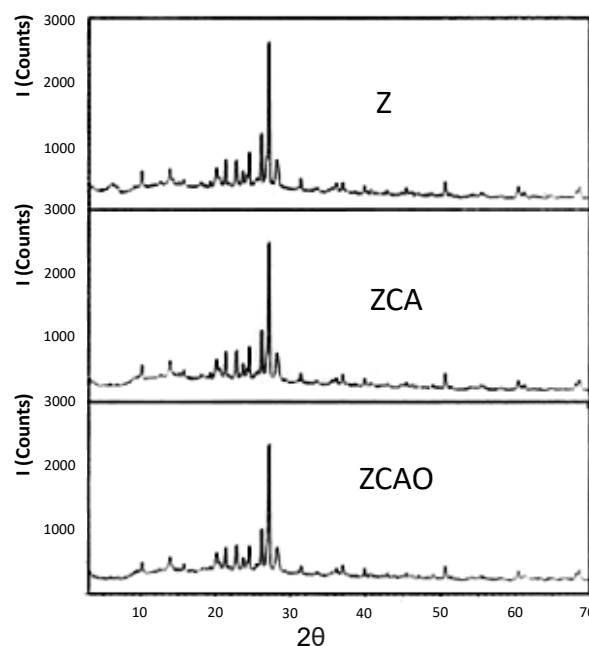


Figure 2  
Z, ZCA, ZCAO catalyst diffractogram

Table 1  
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)
<i>Mordenite</i>	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
<i>Clinoptilolite</i>	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
<i>Quartz</i>	20,86; dan 26,70	20,86; dan 26,65

chemical analysis used in XRD is the characteristic distance between planes (d). The position of the diffraction angle (2θ) and the distance between the planes describe the type of crystal, while the intensity indicates the crystallinity of a solid (West, 1984; Sibilia, 1996). Quantitative analysis was carried out by comparing the diffractogram of natural zeolite samples with standard natural zeolite diffractograms. The characterization results with XRD are presented on Figure 2. From the XRD results it can be said that the catalyst still has crystalline properties as a catalyst. One of the requirements for a material to be used as a catalyst is that it has properties, one of which is crystalline properties. Based on Table 1. it can be concluded that the natural zeolite used has a mixed content 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.

Based on Table 2. it can be seen that the resulting

Table 2  
The intensity diffractogram with the largest peak of the yield catalyst

2θ (level)	d (Å)	Type	Intensity (counts)		
			Z	ZCA	ZCAO
24,39	2,26	<i>Mordenite</i>	300	342	264
25,99	2,99	<i>Clinoptilolite</i>	472	-	-
26,70	3,18	<i>Quartz</i>	270	200	164
27,00	3,30	<i>Mordenite</i>	142	1560	1411
28,08	3,34	<i>Clinoptilolite</i>	259	284	253
29,82	3,43	<i>Clinoptilolite</i>	192	-	-
39,83	3,65	<i>Mordenite</i>	161	95	105

catalyst has increased in intensity from Z to ZCAO, this situation is due to the activation process with HCl and NH<sub>4</sub>Cl solutions, the addition of Na<sub>2</sub>SiO<sub>3</sub> 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.

The natural zeolite used as a catalyst after comparison with standard natural zeolite according to

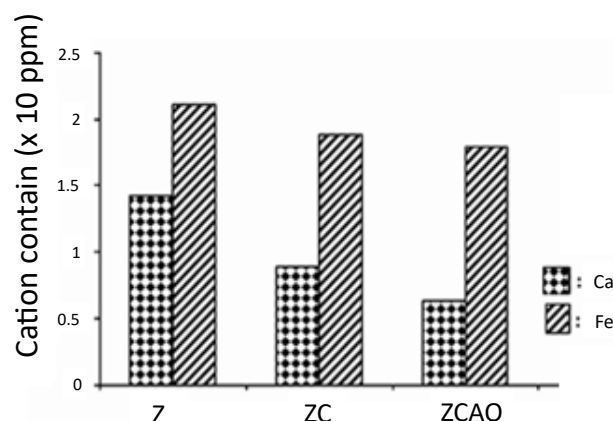


Figure 3a

The content of Ca and Fe metals from various types of catalysts, Z: zeolite catalyst, ZC: zeolite enrichment catalyst with Si (Na<sub>2</sub>SiO<sub>3</sub>), ZCA: ZCAO catalyst treated with acid and oxidized with oxygen, Ni/ZCA: ZCA catalyst impregnated with Ni metal.

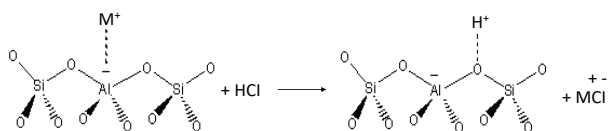
Treacy and Higgins (2001) has an index of similarity with the types of mordenite, clinoptilolite and quartz, so that the zeolite used has a crystal structure of the types of mordenite, clinoptilolite and quartz. Zeolite with strong crystallinity properties will be very supportive when used as a catalyst.

The content of metals such as Ca and Fe in uncontrolled yield catalysts can interfere with the performance of the catalyst (Harber, 1991). In the preparation of metal/carrier system catalysts, zeolite

before being used as a Ni metal carrier is subjected to acid treatment which aims to reduce or eliminate the presence of unwanted metals as catalysts such as Ca, Fe, Na and Mg (Lestari, 2010). The acid used in

will be adsorbed on the surface of Bronsted acid sites and Lewis acid sites. The adsorption reaches its equilibrium state, when a constant weight of zeolite is obtained, the acidity of which is measured by the gravimetric method.

Figure 3b  
 Exchange of M+ ions (metal ions) with H+ ions in zeolite



the preparation of the metal/carrier system catalyst is 2 M HCl which aims to dissolve the metals in the zeolite through ion exchange techniques to form Bronsted acid sites (Satterfield, 1980). As an example of the exchange of metal ions, M+ with H+ which is depicted in Figure 3a.

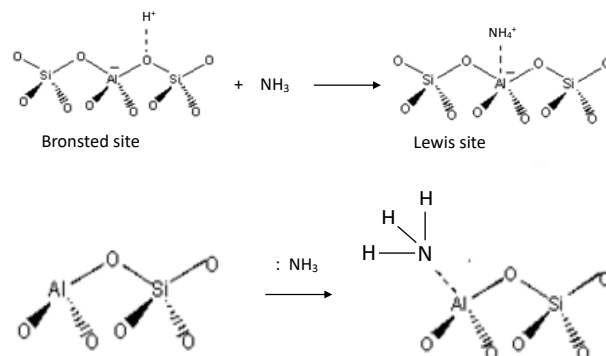
The results showed that acid treatment with 2 M HCl resulted in a decrease in the metal content of Ca and Fe in the zeolite through ion exchange, as shown on Figure 3b. The decrease in the metal content of Ca and Fe in the zeolite in this study was used as an indicator of the reduction of other impurity metals, such as Mg, K, Na and Fe.

### Yield Catalyst Acidity

Based on Figure 4 it can be explained that the acidity increases starting from the calcination treatment to the acid treatment. This increase in acidity indicates the formation of Bronsted acid sites on the surface of the zeolite through ion exchange, as shown in Figure 3b. Measurement of zeolite acidity was carried out by the method of adsorption of ammonia base on the surface of the catalyst. Ammonia

According to Satterfield (1980) and Van Santen (1995), the acidity (acid amount) of a catalyst is

Figure 5  
 Chemisorption of ammonia on the surface of zeolite in determining catalyst acidity

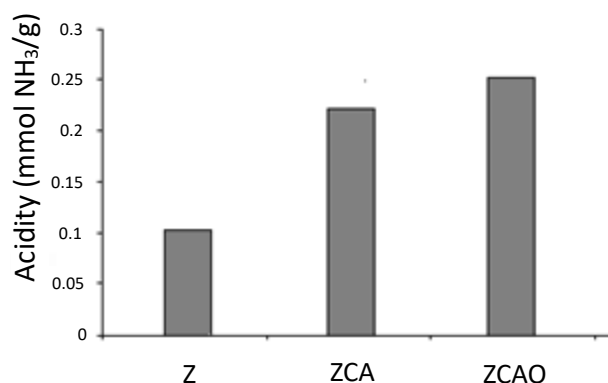


defined as the amount of mmol of base (ammonia) adsorbed by Bronsted acid sites and Lewis acid sites per gram on the surface of the catalyst. The more ammonia base that can be adsorbed on the surface of the catalyst, the higher the acidity of the catalyst, according to Satterfield (1980).

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 NH4Cl). 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 NH4Cl).

Figure 4  
 Acidity of some of the resulting catalysts Z : zeolite catalyst, ZCA : the zeolite has been modified by a calcination process for 24 hours given and acid treatment, ZCAO : zeolite (ZCA) which has been calcified, acidity and oxidized treatment.



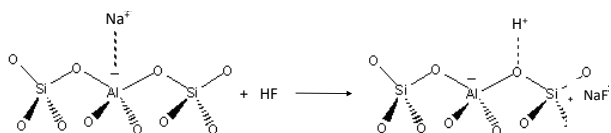


Figure 6  
Exchange of metal ions (Na<sup>+</sup>) during zeolite treatment with 2 M HF

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 6).

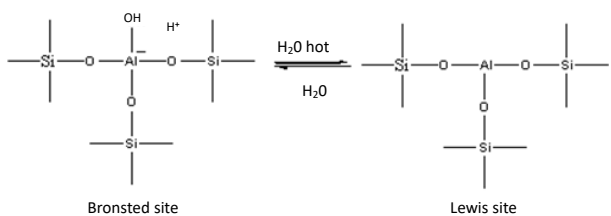


Figure 7  
Equilibrium of Bronsted acid sites and Lewis acid sites (Satterfield, 1982)

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).

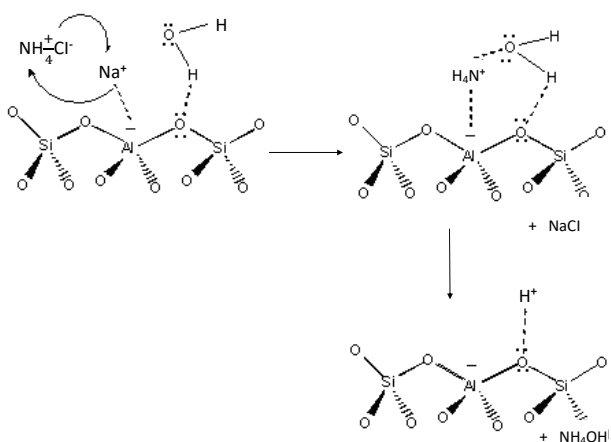
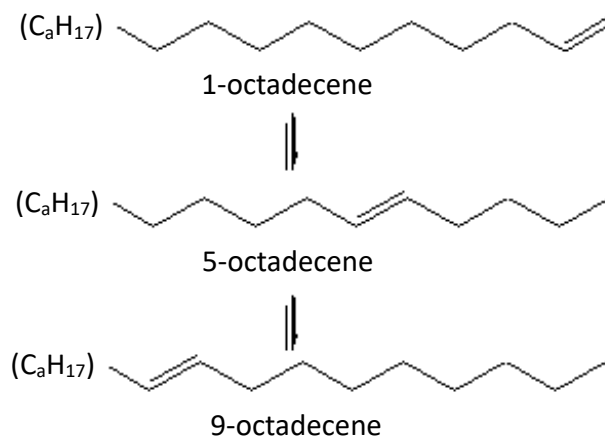


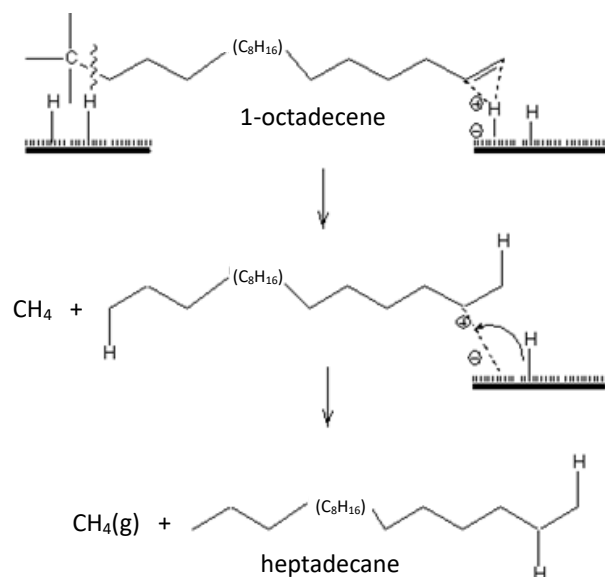
Figure 8  
Formation of a Bronsted acid site

Treatment with NH<sub>4</sub>Cl also causes an increase in the acidity of the catalyst, with the formation of Bronsted acid sites. This situation can be explained through the stages of the ion exchange mechanism as shown in Figure V.8. Initially, NaCl was produced from the zeolite surface and in the end, ammonium hydroxide was produced from the zeolite surface.

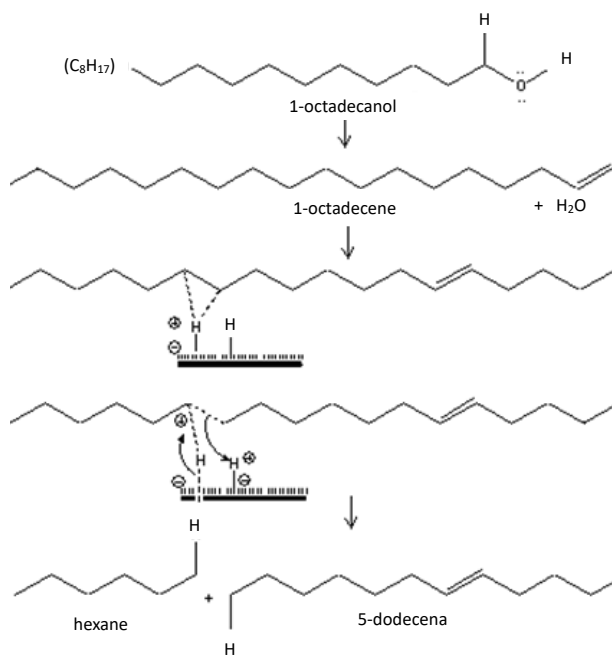
The acidity of the zeolite as a catalyst is determined by the presence of Bronsted acid sites and



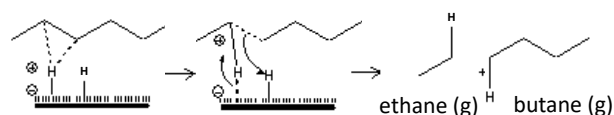
Lewis acid sites which are in equilibrium. The acid site will interact with the electron cloud on the carbon chain bond and will break the carbon chain on the



adsorbed bond. According to Campbell (1988), the 1-octadecene compound then formed its isomers, namely 5-octadecene and 9-octadecene with relative concentrations of 14.37 and 10.40%. Furthermore, the 1-octadecenes, 5-octadecenes and 9-octadecenes undergo further cracking into shorter alkanes and alkenes.



The mechanism of the 1-octadecanol compound to 5-dodecene is thought to follow the following steps: alcohol dehydration, double bond shift, bond breaking to 5-dodecene and hexane, hexane hydrogenation to smaller compounds (ethane and butane) in the gas.



Then hexane decomposes into gaseous compounds or volatile compounds as follows,

## CONCLUSION

The mechanism of the catalytic reaction mechanism consists of several stages, namely the first is the initiation stage, and the second is the propagation stage and the third is the termination stage.

Catalytic hydrocracking of 1-octadecene with ZCAO catalyst at a variation of the hydrogen flow rate of 20 mL/minute and a temperature of 450 °C resulted in alkanes and alkenes < C<sub>12</sub> which was 15.29% maximum, followed by a hydrogen flow rate of 10 mL/minute at temperatures of 500 and 400 °C.

## GLOSSARY OF TERM

Symbol	Difinition	Unit
Z	Zeolite	
ZC	Zeolite Calcination	
ZCA	Zeolite Calcination Acidity	
ZCAO	Zeolite Calcination Acidity Oxydation	
XRD	X-Ray Difraction	

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