

The role of bronsted acid sites in cleavage of 1-Octadecene compounds(long carbon chain) Being a compound with short carbon chain bonds

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Abstract

Research has been carried out on acid zeolite to break long carbon chain bonds into shorter ones using acid zeolite. The catalyst used is made from zeolite which is treated with calcination with nitrogen at a temperature of 400 oC for 2 hours then followed by hydrothermal treatment at a temperature of 500 oC for 2 hours and then impregnation with Ni metal, then oxidation with oxygen for 3 hours. at a temperature of 500 oC. Then the cracking process was carried out on the methyl oleate compound with a zeolite catalyst impregnated with Ni metal using a Fluid Bed reactor operated at a temperature of 500 oC for 30 minutes while hydrogen gas was flowing at a speed of 10 mL/minute. The results obtained are that based on analysis using GCMS are as follows: the process of breaking down alkane compounds obtained from the interaction between the catalyst surface in the upper layer can interact again with the catalyst surface in the lower layer, in line with the feed flow. This interaction may result in shorter alkane compounds and other forms of compounds such as cyclic, aromatic or isomeric forms.

Key words: impregnation, zeolite, fluid bed, cracking

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I. INTRODUCTION

The use of zeolite as an active metal carrier in the manufacture of metal/carrier system catalysts requires paying 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 preparation.

According to Twaiq (2003), catalytic cracking of palm oil to produce liquid hydrocarbon fuel has been studied in a fixed bed microreactor operated at atmospheric pressure, temperature 723 K and WHSV 2.5 h⁻¹ using mesoporous molecular sieve MCM-41. Mesoporous aluminosilicate with an S/Al ratio of up to 50 was synthesized using the hydrothermal method. Catalyst material with a crystal structure of MCM-41 with a mesoporous pore size with a surface area of between 550 to 1200 m²/g and has an average pore size of 1.8 to 2.8 nm. MCM-41 catalyst shows high activity for palm oil cracking. The MCM-41 material is selective for the formation of linear hydrocarbons, especially C₁₃. The liquid product yield decreases with increasing catalyst surface area. Selectivity for gasoline increases while diesel selectivity decreases with conversion from palm oil.

II. METHODOLOGY

1. Research Materials and Tools

The research materials used were: Wonosari natural zeolite from PT Prima Zeolita, materials from E.Merck and quality p.a. consisting of: oleic acid (91.59 %), 1-octadecanol 95 %, 1-octadecene 90 %, HCl 37 % (v/v), HF 40 % (v/v), NH₄Cl, Na₂SiO₃, Ni(NO₃)₂·6H₂O 97 %. Other materials such as: oxygen, nitrogen and hydrogen gas (P.T. Samator Gas), pH paper.

The equipment required for the research is: a set of fixed bed reactors, thermocouples, thermometers, ovens, hot-plates, laboratory glassware, analytical balance (Mettler RE 200), atomic absorption spectroscopy (AAS, Varian FS 220), GC-MS (Shimadzu QP-2010S), surface area analyzer NOVA 1000 (Quantachrome Nova Win2 version 2.2), X-ray diffractometer (XRD, Shimadzu-6000).

2. Research Procedures

This research procedure is divided into several stages such as catalyst preparation, making methyl 9-octadecenoate, hydrogenation of methyl 9-octadecenoate with a ZSiA catalyst, catalytic hydrogenation of 1-

octadecanol with a ZSiA catalyst, hydrocracking of 1-octadecene with a Ni/ZsiA catalyst.

2.1. Ni/ZSiA Catalyst Preparation

Zeolite with a passing size of 100 mesh is soaked in distilled water and washed while stirring. Then soaked in 2% HF for 30 minutes, then washed with distilled water, repeated 3 times, then dried in the oven at a temperature of 120 oC for 3 hours. Next, it was oxidized with oxygen at a temperature of 500 oC for 2 hours and calcined with nitrogen at a temperature of 500 oC for 2 hours with a gas flow rate of 20 mL/minute to obtain a Z catalyst (Handoko, 2001).

Next, the Z catalyst was washed using a 2 M HCl solution with a ratio of zeolite: HCl solution = 1: 2 (v/v) while stirring for 20 to 30 minutes (Zhang, 1999). Next, the zeolite samples were washed using distilled water until pH = 6 and dried in an oven at a temperature of 120 oC for 3 hours and continued with oxidation using oxygen gas at a flow rate of 20 mL/minute at a temperature of 500 °C for 2 hours and calcination with nitrogen gas at a rate of flow 20 mL/minute at a temperature of 500 °C for 2 hours. Then to the Z catalyst in a beaker, 5% (w/w) of Na-Silicate (Na₂SiO₃) was added which was dissolved in distilled water and then heated at a temperature between 80 oC to 90 oC for 24 hours while stirring using a magnetic stirrer. Then the sample was cooled and continued with oxidation with oxygen gas at a temperature of 500 °C for 2 hours with a gas flow rate of 20 mL/minute and continued with calcination with nitrogen gas at a temperature of 500 °C for 2 hours with a gas flow rate of 20 mL/minute to obtain a ZSi catalyst.

The ZSi catalyst was cooled and a 2 M NH₄Cl solution was added to the 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 continued with the oxidation process using oxygen gas at a temperature of 500 °C for 2 hours with a gas flow rate of 20 mL/minute and continued with calcination with nitrogen gas at a temperature of 500 °C for 2 hours with a gasflow rate of 20 mL/minute to obtain the ZSiA catalyst. .

Impregnation of Ni metal (Ni 2% (w/w)) on the surface of the ZSiA catalyst was carried out using the wet impregnation method. 9.91 g of Ni(NO₃)₂·6H₂O salt was dissolved in 100 mL of distilled water while stirring until homogeneous, then 100 g of sample (ZSiA catalyst) was added. Then it is heated and evaporated at a temperature of 80 oC to 90 oC (at 1 atm) while stirring so that the water component will slowly evaporate. After the water component has evaporated, the sample is placed in an oven at a temperature of 120oC for 2 hours and continued with the oxidation process with oxygen gas at a temperature of 500oC for 2 hours with a gas flow rate of 20 mL/minute and reduction at a temperature of 500oC with hydrogen gas flowing at 20 mL/minute to obtain a Ni/ZSiA catalyst (Handoko, 2001).

Each stage of treatment is analyzed for metal content using AAS, acidity using the gravimetric method, crystallinity using XRD and surface area using the BET method.

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Tools used in research

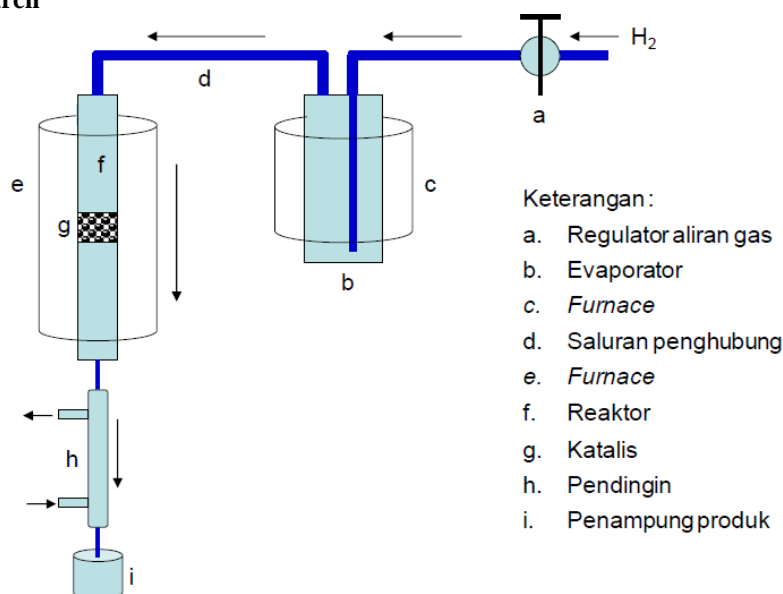


Figure 1. Cracking equipment

III. Results and discussion

Catalytic hydrogenation of 1-octadecanol with a ZSiA catalyst in a fixed bed reactor at a temperature of 400 oC produced 49.60% alkane and alkene products with a chain length < C18. The catalytic hydrogenation mechanism of 1-octadecanol is thought to follow two main stages, namely reduction of the alcohol group to alkene and breaking of the alkene bond to form shorter chain alkanes and alkenes. The mechanism is as follows,

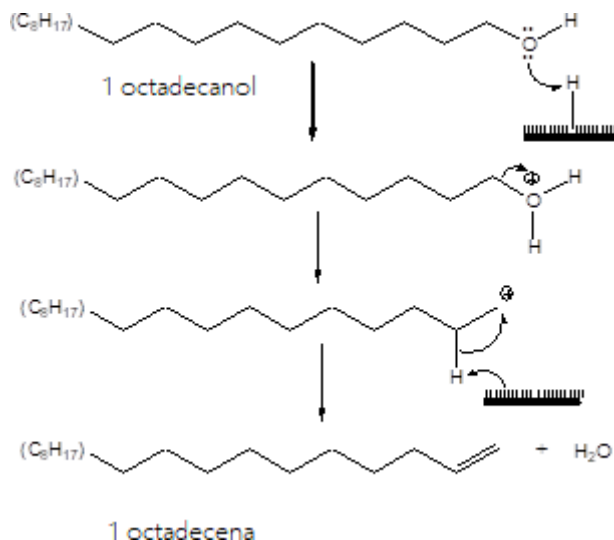


Figure 2. Conversion of 1-Octadecanol to 1-Octadecene

According to Campbell (1988), the 1-octadecene compound then forms its isomers, namely 5-octadecene and 9-octadecene with relative concentrations of 14.37 and 10.40%. The conversion mechanism of 1-Octadecene is as follows,

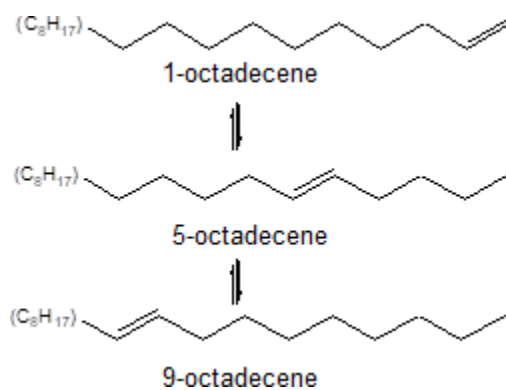


Figure 3. Isomerization of 1-Octadecene

Furthermore, the compounds 1-octadecene, 5-octadecene and 9-octadecene undergo further cracking to form shorter alkane and alkene compounds.

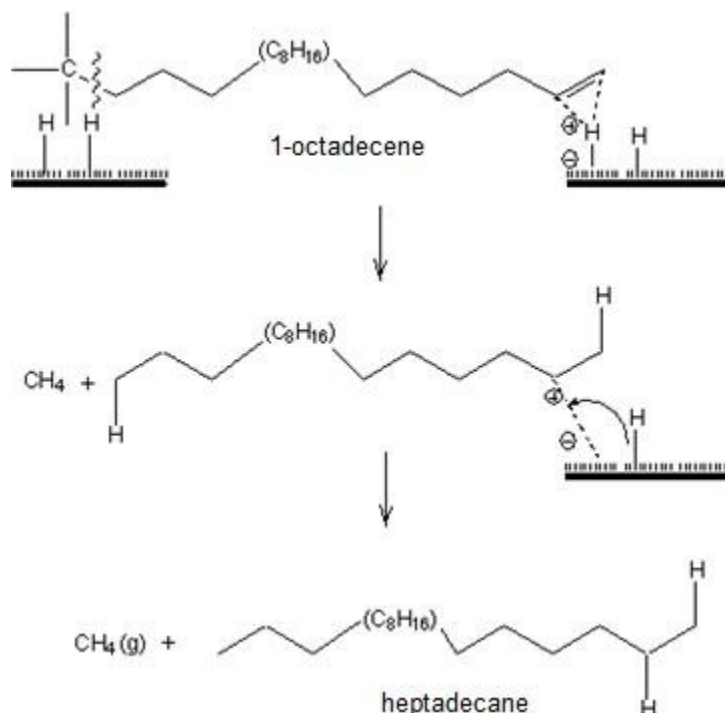


Figure 3. Conversion of 1-Octadecene to heptadecane and methane

Reactants that have been adsorbed on the surface of a solid can experience a "migration" event, namely the movement of molecules in one dimensional plane. Molecules that migrate (in a fixed adsorbed position) are very likely to collide with other molecules.

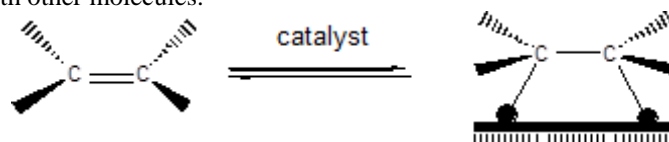


Figure 4. Illustration of ethane adsorbed on the catalyst surface

Thus, the more reactant molecules are adsorbed on the surface of the catalyst solid, the greater the probability of collisions occurring and producing reaction products. Collisions (encounters) between reactant molecules have less energy but occur between active reactant molecules so a lower activation energy is required.

According to Campbell (1988), the long chain bond breaking products can be alkanes or short chain alkenes as shown in the mechanism in the picture below. In the hydrogenation process on the catalyst surface, at a hydrogen flow rate of 10 mL/minute, both conditions show maximum results. At a hydrogen flow rate of 10 mL/minute, hydrogen adsorption onto the catalyst surface was very good. At a hydrogen flow rate of 10 mL/minute, relatively more hydrogen is adsorbed on the catalyst surface quantitatively compared to a faster hydrogen flow rate, so it is possible for the hydrogen to be in a condensed state and undergo dissociation and migration. The relatively fast migration of hydrogen allows the possibility of collisions with 1- octadecene molecules and the production of reaction products <C12 which is greater.

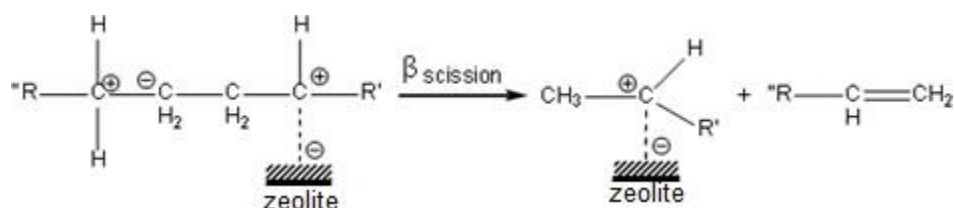


Figure 5. A beta shift occurs and a short compound is formed

The process of breaking down alkane compounds obtained from the interaction between the catalyst surface in the upper layer can interact again with the catalyst surface in the layer below. In line with the feed flow. This interaction may result in shorter alkane compounds and other forms of compounds such as cyclic, aromatic or isomeric forms. The following is an illustration of breaking a long chain into a short chain.

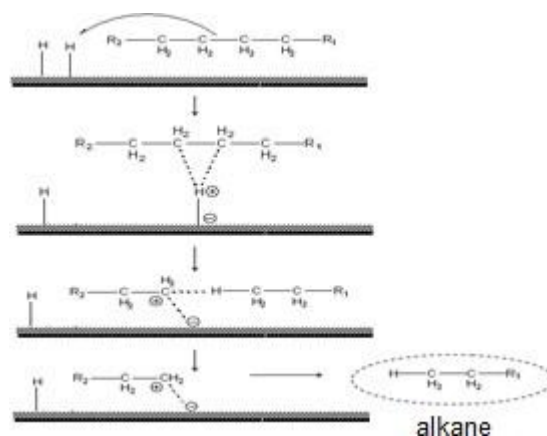


Figure 6. Event of breaking a long chain into a short chain

IV. CONCLUSION

In breaking long chain bonds into short chains, it will be easier to interact with the presence of Bronsted acid sites to form short chain bonds. The acidity and strength of acid 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 catalyst surface. Acid strength is defined as the ability of the catalyst surface containing Bronsted acid sites and Lewis acid sites to interact with reactants(organic compounds). The relationship between acidity and acid strength is inverse.

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