The role of Praseodymium oxide-Impregnated Clinoptilolite Zeolite Catalyst to Increase Octane Number in Gasoline

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Abstract. In the present work, the role of praseodymium oxide as a promotor of active site in zeolite base as catalyst for increasing the octane number in gasoline were investigated. In this study, we used three types of catalyst, namely the activated clinoptilolite zeolite (catalyst 1), Pr₆O₁₁-impregnated clinoptilolite zeolite 0.01 (w/w%) (catalyst 2) and Pr₆O₁₁-impregnated clinoptilolite zeolite 0.1 (w/w%) (catalyst 3). Both catalyst 2 and 3 were prepared by impregnation method. The calcination temperature for all of catalysts was set at 500°C for 2 hours to remove the organic impurities and stabilize the structure of catalyst. The Si/Al ratio increased from 5.1 to 5.85 with praseodymium nitrate hexahydrate percentage in catalysts 2 and 3 were 0.14 and 0.05%, respectively. The surface area of catalysts 1 - 3 are 19.42, 18.09 and 15.22 m²/g, respectively. The activity performance of catalyst 3 with 1 and 3 % loading at 27.7°C for 2 min have increased the octane number of 0.1. Increasing octane number of 0.1 was also confirmed by GC-MS data which showed the presence of decreasing C₄-C₁₁ hydrocarbon compounds and increasing of aromatic compounds. Pr₆O₁₁-impregnated clinoptilolite zeolite catalyst is potential for application in fuel system to increase octane number at room temperature (27.7°C).

1 Introduction

Octane number is an indicator that shows the ability of gasoline to produce maximum power from machine and can hold knocking condition on the time of ignition fuel. It depends on the hydrocarbon type; some additives were used to increase the octane number gasoline such as methanol, ethanol, tetraethyl lead (TEL, Pb(C₂H₅)₄), methyl tertiary butyl ether (MTBE, (C₅H₁₂O)), tertiary butyl alcohol (TBA), tert-amyl methyl ether (TAME), and tertiary butyl formate (TBF) [1]. They were used to improve efficiency of the flame and combustion and stabilize the fuel mixture. However, the presence of additive compound induced the toxic properties and result in the carcinogenic, thus it is limited used. Therefore, it is necessary to synthesis catalyst or additive materials which were safe, economical, environmental friendly, and had a simple method.

Effective catalyst should at least have the good selectivity, activity, and durability and can produced the desired product in operating conditions that are not too extreme. To produce an effective catalyst, the role of support as the spread of the active site can increase the overall effectiveness of the catalyst. The support catalyst must have the structure which can be dispersed on the active site so that it can multiply the different number of active site on the surface catalyst.

We selected the clinoptilolite zeolite as support catalyst based on the large surface area, stable at high

temperature, high acidity properties and suitable for using in cracking process of compounds. Another advantages of natural zeolite is its existence of large quantities in nature, low price, and has a hole structure of pore size. The modification of activated clinoptilolite zeolite by praseodymium oxide was expected to minimize the nature zeolite from mineral contents as dopants, to increase the surface area, and to provide the active site of acid form [2]. The use of rare earth elements for fluid catalytic cracking [3] and the overall activity of the catalyst has been reported by Sousa-Aguiar et al. [4].

The impregnation method is well-known in the catalyst industry because its simple and relatively easy [5]. Praseodymium nitrate hexahydrate was calcined at 500°C for 2 h to obtain stable crystal of Praseodymium oxide, namely Pr₆O₁₁ [6]. The role of Pr₆O₁₁ in the catalyst was as active site on catalyst. As a catalyst, Pr₆O₁₁ exhibits good activity performance during the oxidative coupling of methane [7]. At the same period, praseodymium oxide, Pr₆O₁₁, exhibits the highest yield for the synthesis of ethane and ethylene from methane and carbon dioxide [8]. The experiment using praseodymium nitrate hexahydrate modified zeolite has also been carried out in cracking hydrocarbon process in gasoline. The results showed an increase in the octane number of gasoline of by a factor of 1.6, indicating that long chain hydrocarbon was cracked to either short chain or branched hydrocarbons. Furthermore, praseodymium

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oxide have been introduced into solid clinoptilolite zeolite to increase surface area.

In this study, synthesis of Pr₆O₁₁-impregnated clinoptilolite zeolite and its application as catalyst to increase the octane number in gasoline was investigated. To find out the effect of Pr₆O₁₁ as active sites to increase the octane number, the concentration of Pr was varied. At the first, the modification of clinoptilolite zeolite with Pr is studied. The gasoline system before and after containing Pr₆O₁₁-impregnated clinoptilolite zeolite as a catalyst are evaluated in details.

2 Experimental

2.1 Preparation of Pr₆O₁₁-impregnated clinoptilolite zeolite

Natural clinoptilolite with particle size of 200 mesh (74 µm) was obtained from Lampung (Indonesia). The modification process of natural zeolite by ion exchange process with acid treatment, calcination, and impregnation of praseodymium nitrate hexahydrate salt. Basically, the acid treatment process used to increase the Si/Al ratio. In acid treatment solutions of HCl 0.05 M, NaOH 0.05 M, NaCl and NH₄OH 0.05 M to produce activated clinoptilolite zeolite (catalyst 1) were used. Calcination was carried out by blowing air at 400°C for 4 h to obtain the catalyst 1 which is expected to be stable at high temperatures.

Praseodymium nitrate hexahydrate compounds with various concentrations; 0.01 and 0.1% (w/w), were mixed with activated clinoptilolite zeolite (catalyst 1) by using impregnation method. The mixture was stirred and heated at 60°C for 1 h. The mixture then was heated at 105°C in oven to remove water content to obtained the dehydrated Pr/zeolite. Finally, the solid was transferred to a muffle furnace and calcined at 500°C for 2 h. The powder, which is the final product of praseodymium oxide/c clinoptilolite zeolites (catalysts 2 and 3) were subjected for characterizations and catalyst experiments.

2.2. Characterization

The catalysts were characterized by Brunauer, Emmett and Teller (BET), Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS), X-ray Diffraction (XRD), dan Fourier Transform Infrared (FTIR) spectroscopy.

The performance of catalysts was evaluated at temperatures of 22.7, 40, and 60°C, and times of 2, 10, and 60 min with gasoline volume of 400 mL. The final product was characterized using FTIR, GC-MS and portable octane number. The activity test of products was calculated by conversion and selectivity the following using equations:

Hydrocarbon conversion of C₄-C₆, C₇-C₈ and C₁₁-C₁₂ ;

$$X_i = \frac{F_i^o - F_i}{F_i^o}$$

Cracking product selectivity of C₄-C₆, C₇-C₈ and C₁₁-C₁₂;

$$S_i = \frac{F_i - F_i^o}{\sum F_i - \sum F_i^o} \dots \dots \dots$$

where $\sum F_i - \sum F_i^o$ for $F_i > F_i^o$.

3 Results and Discussion

3.1. Activation of Clinoptilolite Zeolite

For natural zeolite, the presences of water molecules inside pores and free oxide on the surface, such as SiO₂, Al₂O₃, CaO, MgO, Na₂O, K₂O covered the pores of zeolite or active site were observed. Practically, they can reduce the adsorption capacities and catalytic properties of zeolite [9]. Therefore, it was the reason to activate the zeolite before it is used as catalyst. Usually chemical activation was carried out by washing the zeolite using aquadest, HCl solution, NaOH solution, NaCl saturated solution, and NH₄OH solution to remove the impurities on the pore surface. We found the impurities (Ca, Fe, and K) were reduced after activation (see Table 1). This phenomenon shows that the ability of zeolite in ion exchange depends on the number of cation exchange on zeolite. Zeolite cation could be exchanged with the other cations of alkali metal or alkaline earth, such as Si⁴⁺ and Al³⁺, because the impurities were not bound by four oxygen atoms in the framework zeolite. After the activation, calcination at 400°C for 4 h gave the acid of activated clinoptilolite zeolite.

3.2. BET Characterization

Decreasing the specific surface area of catalyst was caused by growing number of Pr₆O₁₁ metal onto the solid surface of the clinoptilolite zeolite (see Table 1). This is due to the amount of Pr₆O₁₁ metal increased, thus the probability of its diffusion into the opening of pore increased. It will be accumulated in some pores and covered them. This phenomenon was observed in catalyst 3, where surface area decreased to 15.22 m²/g. It is slightly smaller than that of clinoptilolite zeolite (18.5 to 15.7 m²/g) previously reported by Kusri et al. [11].

Table 1. BET Characterization Result

Characteristic	Catalyst 1	Catalyst 2	Catalyst 3
Surface area (m ² /g)	19.42	18.09	15.22
Pore volume (cc/g)	0.002251	0.0006907	0.001113
Pore size (Å)	17.6	17.88	17.6

3.3. SEM-EDS analysis

SEM images of activated clinoptilolite zeolite before and after modification with Pr(NO₃)₃·6H₂O are depicted in Figure 1. The catalyst have a size ranging from 1.33 to 2.59 µm. The catalyst 1 is the biggest size and catalyst 3 is the smallest because of the large number of Pr

impregnation onto surface of zeolite. Thus, the latter was able to give a good effect on performance activity test of catalyst.

Pr₆O₁₁ content in catalyst 2 was by 0.14% and the catalyst 3 was by 0.05%. It indicated that Pr was successfully impregnated into the pore of zeolite. According the Table 2, by comparing percentage of Si/Al ratio, the obtained value of Si/Al ratio catalyst 1, 2, and 3 are 5.67, 5.85, and 5.18, respectively. Based on value of acidity catalyst were expected, catalyst 1, 2, and 3 can provide the good performance to crack hydrocarbons in gasoline with better quality.

Fig 1. SEM images of (a) Catalyst 1, (b) Catalyst 2, (c) Catalyst 3

Table 2. EDS Composition

Element	mass (%)			
	Unmodified zeolite	Catalyst 1	Catalyst 2	Catalyst 3
O	46.54	41.21	43.44	47.1
Mg	1.01	0	0.84	0.87
Al	6.58	7.4	6.45	6.83
Si	33.56	42.02	37.73	35.38
K	2.88	2.95	1.85	1.93
Ca	4.38	0	1.29	1.22
Fe	5.06	1.19	1.64	1.31
Na	0	3.22	3.14	2.77
Cl	0	2.02	2.35	1.47
Zn	0	0	1.13	1.07
Pr	0	0	0.14	0.05

3.4. XRD Characterization

In general, 2θ angle of XRD pattern at 20°-30° showed as the typical for clinoptilolite zeolite. The sharp peak was interpret that clinoptilolite zeolite contained SiO₂ and Al₂O₃ [10], which are the main characteristic from zeolite. After modification with Pr₆O₁₁ similar peaks at

27 - 31° and 38 - 41° (Figure 2) were observed. This indicated that impregnation and calcination of praseodymium nitrate hexahydrate to produce the praseodymium oxide (Pr₆O₁₁) has been successfully obtained.

Fig 2. XRD patters of (a) Catalyst 1, (b) Catalyst 2, (c) Catalyst 3

3.5. FTIR studies

The main characteristic of clinoptilolite zeolite is asymmetric stretch and double ring group of O-Si-O and O-Al-O at 1040 cm⁻¹ and 599 cm⁻¹, respectively. This presence of his interpretation shows that the zeolite contains Si, O, and Al elements, as the SEM-EDX characterization. In addition, there are NH₄⁺ region at 1389 cm⁻¹, which showed that quantitatively there has been ion exchange between NH₄OH and activated clinoptilolite zeolite. According to Tanabe [12] interaction of peak absorption pyridine with Bronstead acid sites appeared at 1447-1460, 1488-1503, ~1580, and 1600-1633 cm⁻¹, whereas the interaction of pyridine with Lewis acid sites appeared at 1447-1460, 1488-1503, ~1580, dan 1600-1633 cm⁻¹, and the interaction of pyridine with hydrogen bond was appeared at 1400-1447, 1485-1490 and 1580-1600 cm⁻¹.

Changing of absorption peak was observed for catalyst 1 at 1635 cm⁻¹, to a new region, which is 1649 cm⁻¹ for catalyst 2. This changing can be estimated due to differences strength of Bronstead acid as consequently the forming praseodymium oxide, Pr₆O₁₁ on clinoptilolite zeolite surface [6]. This is in agreement with the presence of new peaks at 2θ angles of 27 - 31° and 38 - 40°. The presence of a new peak increased the acidity of the catalyst, which showed by increasing Si/Al ratio. Accordingly, SEM-EDX analysis shows a reduction of Al³⁺ ions. It indicated that impregnation of praseodymium oxide as Pr³⁺ ions has successfully replaced Al³⁺ ion, increasing its acidic ratio than catalyst 1. The absorption band at 1396 cm⁻¹ indicated the characteristic of pyridine hydrogen bond. Increasing the intensity of absorption region confirmed the increase in the Bronstead acid properties for catalyst 2.

3.6. Catalyst performance

Table 3 shows that the activity performance of catalyst 1 - 3. It indicated the presence of addition long chain hydrocarbon and less branched chain hydrocarbon. The existence of them have had low octane number and gaining of the compounds. Increasing octane number was influenced by the amount of branched or short chain hydrocarbon and the presence of alcohol or aromatic groups [13]. Thus, the research was conducted at 27.7 °C, time of 2 min, and % loading catalyst 3 is 1 and 3%, and gasoline volume is 400 mL.

Table 3. Experimental for catalyst performances to increase octance number in Gasoline

<i>Exp. 1: Temperature at 60 °C, t= 60 min, 0.1% loading catalyst</i>		
Catalyst	BO	Delta BO
Gasoline	91	0
Gasoline + Catalyst 1	90.4	-0.6
Gasoline + Catalyst 2	90.8	-0.2
Gasoline + Catalyst 3	90.4	-0.6
<i>Exp. 2: Temperature at 60 °C, t= 10 min, 0.1% loading Catalyst</i>		
Catalyst	BO	Delta BO
Gasoline	89.7	0
Gasoline + Catalyst 1	89.3	-0.4
Gasoline + Catalyst 2	89.5	-0.2
Gasoline + Catalyst 3	89.3	-0.4
<i>Exp. 3: Temperature at 40 °C, Catalyst 2, t= 2 min</i>		
% loading Catalyst	BO	Delta BO
Gasoline	89.4	0
0.5	89.4	0
1	89.4	0
1.75	89.3	-0.1
3	89.4	0
<i>Exp. 4: Temperature at 27.7 °C t= 2 min</i>		
Catalyst	BO	Delta BO
Gasoline	89.4	0
1% Catalyst 3	89.5	0.1
3% Catalyst 3	89.5	0.1

It is believed that the mechanism of cracking reaction is via the formation of carbonium ions. Each new carbonium ions induced other compounds to form new carbonium ions by the short number of hydrocarbons, so that the dominant product produced was hydrocarbon compound with a small number of carbon atoms. Addition of Pr₆O₁₁ in activated clinoptilolite zeolite improved the activity of catalyst in cracking reaction. A high conversion and selectivity product formed C₄-C₆ and C₇-C₈, while the hydrocarbon chains of C₁₁-C₁₂ was significantly decreased. It is showed by 100% conversion of C₁₁-C₁₂ was to form short hydrocarbon

chains and/or short carbonium ions and/or new hydrocarbon groups. This data was confirmed by GC-MS data.

The absorption band of hydroxyl group was observed at 3646 and 3667 cm⁻¹. The aliphatic hydrocarbon compounds was formed from combination of long-chain hydrocarbon and these were observed at 2925; 2957; 1455; 728 and 768 cm⁻¹. Frequencies was shifted about 20%. Catalyst 3 can crack the long-chain hydrocarbon compounds similar to that observed for catalytic performance of HZSM-5 zeolite for cracking of butane to light olefins [14].

Absorbance of the aromatic bond appeared on the FTIR analysis. The absorption bands that assigned for benzene groups with the C=C groups at 1580-1615 cm⁻¹ and C-H bands at 670-900 cm⁻¹ has been observed upon the addition of aromatic bonds for treatment of gasoline using catalyst 3. The presence of new peaks at 1651 and 1682 cm⁻¹ is followed by the disappearance of peak at 1614 cm⁻¹. It is indicated that the catalytic cracking reaction produced more the aromatic group after the addition of catalyst 3. This phenomenon occurred because of the acidity strength of catalyst 3 for cracking reaction. In addition, the absorption band at 1620-1680 cm⁻¹ was also indicated the presence of cluster C=C on the alkene compounds. However, in this study, we found that there is a tendency that the C=C aromatic compound are more dominant than alkenes.

Figures 3 and 4 showed the effect of performance catalyst 3 for cracking reaction. The number of branched hydrocarbon chains, aromatics, alcohols, and oxygenate compounds before and after treatment with catalyst 3 were observed clearly. The optimum operating conditions for catalyst performance using catalyst 3 was set at temperature of 27.7°C, time of 2 min, and loading catalyst of 1 and 3%. Increasing octane number of 0.1 indicated by the presence of short chain aliphatic compound, alcohol, aromatic, which has a higher octane number.

Based on the thermodynamic properties, the Gibbs energy value was presented. The Gibbs energy equation can be expressed as follows:

$$\Delta G = -RT \ln K$$

If the $\Delta G < 0$, or the value was negative, then the reaction occur spontaneously, it means that the energy conversion will large because the value of the equilibrium constant of K was large. Conversely, if $\Delta G > 0$, or the value was positive, then the reaction occur is not spontaneously, it implies that the energy conversion happens in small as well as the value of the equilibrium constant of K was relatively small.

From the results of GC-MS analysis, we assumed some reactions may occur as follows. It can be concluded that the reaction can occur spontaneously when introducing catalyst in gasoline. In this case, the Gibbs energy is negative value and value of the equilibrium constant K is large, thus the product is greater than the number of the reactants from the test results of activity of the catalyst.

The formation of n-heptane and cyclobutane as product from undecane as reactan.

$C_{11}H_{24} \rightarrow C_7H_{16} + C_4H_8$, $\Delta G_{298,15K} = -21,1\text{kJ/mol}$
 The formation of n-pentane and n-hexane as product from undecane as reactan.
 $C_{11}H_{24} \rightarrow C_5H_{12} + C_6H_{12}$, $\Delta G_{298,15} = -5,2\text{ kJ/mol}$
 The formation of ethylbenzene and n-butane as product from cyclohexane as reactan.
 $2 C_6H_{12} \rightarrow C_8H_{10} + C_4H_{10} + 2 H_2$, $\Delta G_{298,15} = -22,7\text{ kJ/mol}$

chains of C_4 - C_{11} and increasing aromatic compositions. Pr_6O_{11} -impregnated clinoptilolite zeolite catalyst is potential for application in fuel system to increase octane number at room temperature (27.7°C). The reaction can occur spontaneously when introducing Pr_6O_{11} -impregnated clinoptilolite zeolite catalyst in gasoline.

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Fig 3. Hydrocarbons Conversion and Selective of hydrocarbon in Gasoline, Before and After treatment using Catalyst 3

Fig 4. Comparison of Composition Compounds Before and After treatment using catalyst 3 in Gasoline

4 Conclusion

Praseodymium oxide modified activated clinoptilolite zeolite (Pr_6O_{11} -impregnated clinoptilolite zeolite) catalysts were synthesized and applied as catalyst to increase the octane number of gasoline. Pr_6O_{11} -impregnated clinoptilolite zeolite catalyst was synthesized by impregnation method. Based on BET characterization, the reducing of specific surface area of the catalyst was observed from 19.42 to 15.22 m^2/gr which showed by increasing number of Pr_6O_{11} on the surface of clipnotilolite zeolite. The ratio of Si/Al catalyst were in the range of 5.18 to 5.85. The use of a catalyst of 0.1% Pr_6O_{11} -impregnated clinoptilolite zeolite with mass variations of 1 and 3% catalyst loading to the 400 mL of gasoline, at temperature of 27.7°C and time for 2 minutes, the octane number of gasoline increase of 0.1. The increase in the octane number was caused by the cracking and/or reduction of hydrocarbon long

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