

## Kinetic Studies of Butene Oligomerization over HZSM-5 Zeolites with Different Acidity

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### Abstract

In the present study, kinetic of butene oligomerization reaction over HZSM-5 zeolite was studied, and kinetic parameters such as rate constants and activation energy were evaluated. Initially, a number of reaction were carried out over HZSM-5 zeolite with different Si/Al ratio (20-80) at atmospheric pressure, the temperature in the range of 200-420°C and GHSV = 210-1250 h<sup>-1</sup>, and it was found that the highest quantity of C<sub>7+</sub> hydrocarbons was obtained with HZSM-5 of Si/Al molar ratio = 30. So, the zeolite with Si/Al ratio of 30 was then chosen for the kinetic study. The reaction rate was described by a power-law kinetic model based on butene consumption. The reaction followed a first-order type reaction, and the activation energy obtained suggests that butene oligomerization was limited by mass transfer.

**Keywords:** Butene oligomerization; HZSM-5; Zeolite; Kinetic study.

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## 1. Introduction

In the past years, in most commercial oligomerization processes have been used homogeneous catalysts. The use of these catalysts creates many issues, such as pollution of products by catalysts. Due to these problems, there is growing interest into heterogeneous catalysts [1].

The oligomerization of light olefins over acid type catalysts is an important process for the production of gasoline and distillate fuels [2]. The structure and strength of active sites in these catalysts determine the product selectivity. The solid phosphoric acid supported over Kieselguhr silica clay has been used commercially since the 1930s by Universal Oil Products Company (UOP) for the production of high-octane olefinic gasoline by the oligomerization of C<sub>2</sub>-C<sub>5</sub> olefins. This catalyst has several disadvantages, such as the short lifetime of catalyst, environmental concern associated with its disposal and corrosion problems [3]. So, the solid catalysts and zeolitic materials with a unique pore structure and acid sites, are extensively studied because of their easier regenerability, thermal stability, lower environmental pollution issues. Zeolites have been widely used as solid acid catalysts in petroleum processes.

The use of H-ZSM-5 zeolite (MFI topology and a well-known crystalline microporous aluminosilicate) for oligomerization of light olefins was proposed in 1970's by Mobil. The process is known as 'Mobil Olefins to Gasoline and Distillate' (MOGD) [3]. Due to shape selectivity with three-dimensional medium pores and acid properties of ZSM-5 zeolite, this catalyst then replaced the classical phosphoric acid catalyst for oligomerization [4]. Apart from its high selectivity and activity due to its structure and Si/Al ratio, which reflects the number and strength of the acid sites, the low deactivation rate of ZSM-5 zeolite is another important factor. ZSM-5 provides 95-97% olefin conversion in a commercial process called "Conversion of Olefins to Distillate" (COD) for the production of diesel fraction [5].

Butene oligomerization over ZSM-5 zeolite with different Si/Al ratio was studied at different temp. and GHSV [2-5]. The effect of Si/Al ratio of ZSM-5 in the range of 20-500 on butene oligomerization was investigated and showed that hydrocarbon products up to C<sub>12</sub> increased when the Si/Al decreased and as the temperature was reduced the product was much heavier.

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Several papers have been published on the kinetic of light olefins oligomerization reaction, covering different reaction conditions [6-11].

In this work, the catalytic activity of HZSM-5 zeolite with Si/Al molar ratios in the range of 20-80 for butene oligomerization at atmospheric pressure, the temperature in the range of 200-420°C and GHSV=210-1250 h<sup>-1</sup> was investigated. A kinetic model based on butene consumption rate using the optimum condition was then developed.

## 2. Experimental

Na-ZSM-5 zeolite with Si/Al molar ratios in the range of 20-80 was synthesized and then transformed into HZSM-5 using the ion-exchange method. Techniques such as XRD, FT-IR, SEM, EDX, TG-DTA, BET, and NH<sub>3</sub>-TPD were used to characterize the zeolite. Details of the preparation and characterization of the zeolite are previously described [12].

The set-up used to study the activity of the catalyst, and kinetic measurements for butene oligomerization consist of a tubular stainless steel reactor with 1.0 cm i.d. and 50 cm long housed in a three-zone heating jacket, a temperature controller to maintain the heating rate and the temperature of the jacket, MFC (Brooks Model 5850) and a separator. A thermocouple was placed at the center of the catalyst bed to observe the temperature change during the reaction. The gas products were analyzed using a PU 4600 Philips gas chromatograph, which connected on-line to set-up. The liquid products were collected in the separator and analyzed using a CP 3800 gas chromatograph with a flame ionization detector on a Petrocol TM DH capillary column.

## 3. Results and discussion

The liquid hydrocarbon product distribution during the butene oligomerization reaction over HZSM-5 with different Si/Al molar ratio at atmospheric pressure, different temp. (200-420°C) and GHSV (210-1250 h<sup>-1</sup>) are studied.

The results showed that the product selectivity changed with an aluminum content of the zeolite, and since the aluminum content attributes to the activity of the zeolite, therefore, for a desirable activity for oligomerization reaction, the aluminum content of zeolite plays an important role. The change in Si/Al molar ratio not only changed the activity of the zeolite but also the crystal size was affected. It can be concluded that the activity and crystal size of the zeolite simultaneously affected the hydrocarbon product distribution.

Results for hydrocarbon product distribution at different Si/Al molar ratios showed that for all Si/Al molar ratios other than 20, the C<sub>7</sub><sup>+</sup> selectivity decreased with the increase in Si/Al ratio, this can be postulated as follow; at Si/Al ratio of 20 a complex effect of acid sites and morphology of the zeolite on all reactions taking place on the zeolite, make this zeolite to behave differently which can not be correlated only by its Si/Al molar ratio and activity. These effects may be due to the fact that the oligomerization reaction is a structural sensitive reaction, where all the catalyst parameters such as crystal size, morphology, and Si/Al ratio can affect the product distribution.

Taking into account that the production of heavier olefins or oligomers (i.e., C<sub>7</sub><sup>+</sup>) is the target to reach in an oligomerization reaction, it can be seen from the results that at Si/Al =30 the C<sub>7</sub><sup>+</sup> hydrocarbons are at their most. Therefore, it can be concluded that for butene oligomerization, the optimum ratio of Si/Al is 30. This shows that the Si/Al ratio of zeolite has a pronounced effect on product distribution for the oligomerization reaction.

The increase in GHSV can always change product distribution during a catalytic reaction. This effect was also noted in this work. As can be seen from Fig. 1, the highest amount of C<sub>7</sub><sup>+</sup> hydrocarbon produced by HZSM-5 with Si/Al molar ratio of 30, at different temperatures was obtained at GHSV=210 h<sup>-1</sup>, whereas at higher GHSV, the amount of C<sub>7</sub><sup>+</sup> hydrocarbon decreased. This Fig. shows that temperature rise had two distinct effects, increase in temperature from 200 to 300°C, increased the oligomerization (i.e., production of C<sub>7</sub><sup>+</sup> hydrocarbons), while above 300°C, the lighter olefins (i.e., < C<sub>7</sub> hydrocarbons) production increased. This is an indication that the cracking of heavier olefin to lighter olefin increases with increase in temperature, this effect can be seen clearly in Fig. 1. As can be seen, parameters such as

temperature and GHSV simultaneously affected the production of different hydrocarbon products. In an oligomerization reaction, C<sub>3</sub> will oligomerize to C<sub>6</sub>, C<sub>9</sub>, C<sub>12</sub>, and etc. oligomers. These then isomerizes and re crack, forming a range of light olefins. Lastly, these then re-oligomerize to an equilibrium distribution of heavier iso-olefin. As a result of having both forward (oligomerization) and reverse (cracking) reactions, a continuous carbon number distribution occurs in the product.

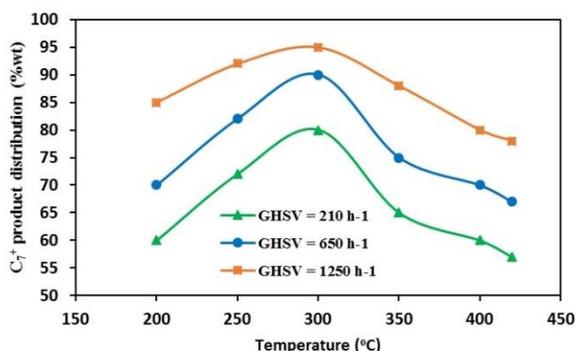


Figure 1. Effect of temp. on C<sub>7</sub><sup>+</sup> product distribution for butene oligomerization at various GHSV on HZSM-5

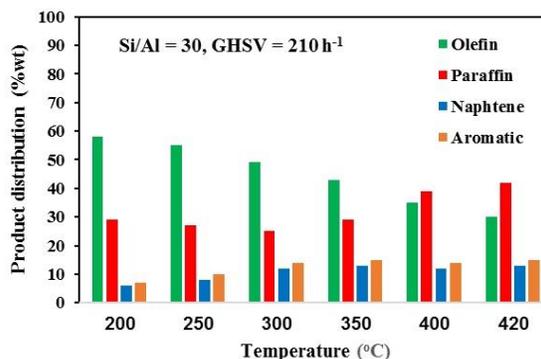


Figure 2. Liquid product distribution for butene oligomerization at different temp. and GHSV=210 h<sup>-1</sup>

The effect of temperature on hydrocarbons produced during butene oligomerization over HZSM-5 with Si/Al molar ratio of 30 and GHSV=210 h<sup>-1</sup> is shown in Fig. 2. As can be seen, at 200°C, the amount of olefin & aromatic produced is 58.1 and 7.1 wt%, respectively, whereas at 420°C, these amounts have been changed to 30.1 and 15.3 wt%.

It can then be concluded that, at lower temp., the oligomerization of olefins is the dominant reaction. A significant quantity of paraffins presumably as a result of hydrogen transfer processes are also produced. An increase in temperature increased the formation of aromatics, naphthenes, and paraffins. It can be seen from the results that the amount of C<sub>7</sub><sup>+</sup> hydrocarbons produced over zeolite with Si/Al=30 at 300°C and GHSV=210 h<sup>-1</sup> is the highest (95.2 wt %) and is the lowest (57.3 wt %) at 420°C with GHSV = 1250 h<sup>-1</sup> (Fig. 2).

#### 4. Kinetic study

During the catalyst performance evaluation, it was observed that above 300°C the cracking reaction together with oligomerization reaction take place, in order to avoid the cracking reaction, the kinetic has been studied over zeolite with Si/Al= 0 within 200-300°C and W/F=5.2-21.7 g cat./(mole C<sub>4</sub>H<sub>8</sub>/h). In this work, a kinetic model based on the butene consumption rate was considered by using a power-law reaction rate model as follows:

$$-r_{C_4H_8} = kC_{C_4H_8}^n \tag{1}$$

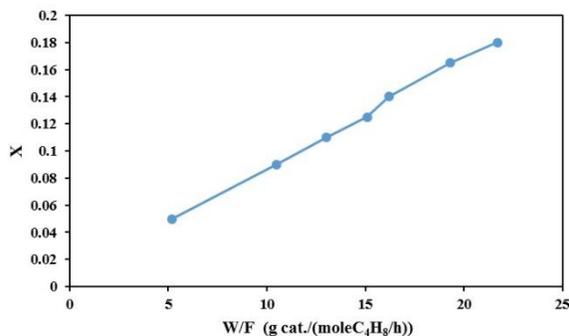
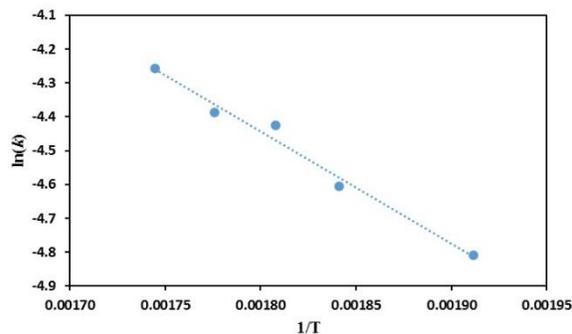
$$C_{C_4H_8} = C_{C_4H_8}^0 \times (1 - X_{C_4H_8}) \tag{2}$$

By substituting equation (2) in (1):  $-r_{C_4H_8} = k(1 - X_{C_4H_8})^n$

The reaction rate can be expressed as follow:

$$-r_{C_4H_8} = \frac{d(X_{C_4H_8})}{d(W/F_{C_4H_8}^0)} \tag{3}$$

where  $-r_{C_4H_8}$  is the C<sub>4</sub>H<sub>8</sub> reaction rate (mole C<sub>4</sub>H<sub>8</sub>/h. g cat.);  $k$  is the kinetic rate constant (mole/g cat. h);  $X_{C_4H_8}$  is the conversion of C<sub>4</sub>H<sub>8</sub>;  $F_{C_4H_8}^0$  is the feed rate (mole C<sub>4</sub>H<sub>8</sub>/h), and  $W$  is the mass of catalyst (g). Based on equation 3, results for C<sub>4</sub>H<sub>8</sub> conversion ( $X_{C_4H_8}$ ) against  $W/F_{C_4H_8}^0$  produce linear profiles (Fig. 3). The reaction rate is then calculated using these profiles (Table 1).


 Figure 3.  $X_{C_4H_8}$  vs.  $\frac{W}{F_{C_4H_8}}$  at 250°C

 Figure 4.  $\ln(k)$  vs.  $1/T$ 

The kinetic parameters for the data presented in Table 1 were estimated applying equation 3 and using non-linear least-square regression. The parameters obtained are listed in Table 2. The reaction order for butene conversion obeyed a first-order reaction showing a rate dependent- concentration. The kinetic parameters were obtained in order to estimate the activation energy by which the reaction type can be predicted (i.e., a mass transfer or a surface reaction). The activation energy can be obtained from the Arrhenius equation by plotting the kinetic rate constants at different temperatures. Logarithm form of this equation is as follows:

$$\ln(k) = \ln(A) - \frac{Ea}{R} \times \frac{1}{T} \quad (4)$$

where  $A$  is the frequency factor;  $Ea$  is the activation energy (J/mol), and  $R$  is the universal gas constant (8.314 J/mol.K). By substituting the kinetic parameters presented in Table. 2 in equation 4 and plotting the data as in Fig. 4,  $Ea$  was estimated to be 26.48 kJ/mol.

Table 1. Butene conversion and reaction rate at different temperature (200-300°C)

Temp. (°C)	(g cat./moleC <sub>4</sub> H <sub>8</sub> /h)) $\frac{W}{F_{C_4H_8}}$	%Conversion C <sub>4</sub> H <sub>8</sub>	(moleC <sub>4</sub> H <sub>8</sub> /h. g cat.) $-r_{C_4H_8}$
200	5.2	5.0	8.02E-03
	10.5	9.1	7.42E-03
	13.0	11.2	7.31E-03
	15.1	12.5	7.24E-03
	16.2	14.0	7.18E-03
	19.3	16.5	7.09E-03
	21.7	18.0	7.01E-03
230	5.2	5.6	9.68E-03
	10.5	12.0	9.08E-03
	13.0	13.2	8.88E-03
	15.1	14.5	8.71E-03
	16.2	16.2	8.68E-03
	19.3	18.4	8.56E-03
250	5.2	5.9	1.05E-02
	10.5	14.2	9.87E-03
	13.0	15.9	9.34E-03
	15.1	16.7	9.01E-03
	16.2	18.8	8.79E-03
	19.3	19.4	8.81E-03
	21.7	20.9	9.12E-03
280	5.2	6.1	1.21E-02
	10.5	15.8	1.06E-02
	13.0	17.0	9.87E-03
	15.1	18.9	9.75E-03
	16.2	20.7	9.52E-03
	19.3	21.3	9.43E-03
	21.7	22.5	9.32E-03

Temp. (°C)	$(\text{g cat.}/(\text{moleC}_4\text{H}_8/\text{h})) \frac{W}{F_{C_4H_8}^0}$	%Conversion C <sub>4</sub> H <sub>8</sub>	$(\text{moleC}_4\text{H}_8/\text{h. g cat.})^{-r_{C_4H_8}}$
300	5.2	6.5	1.33E-02
	10.5	17.7	1.16E-02
	13.0	18.5	1.08E-02
	15.1	20.9	1.01E-02
	16.2	21.8	9.85E-03
	19.3	23.1	9.66E-03
	21.7	24.7	9.56E-03

Table 2. Kinetic parameters

T (°C)	n	k (mole/g cat. h)	T (°C)	n	k (mole/g cat. h)
300	0.924	0.014179	230	0.915	0.009998
280	0.921	0.012439	200	0.913	0.008149
250	0.919	0.011960			

## 5. Conclusions

The catalytic performance of the HZSM-5 zeolites with different Si/Al molar ratios for butene oligomerization at different temperatures and GHSV was studied. The results showed that the hydrocarbon product distribution during oligomerization depends on temperature, GHSV, and molar ratios of Si/Al. For all Si/Al molar ratios other than 20, the selectivity for C<sub>7</sub><sup>+</sup> hydrocarbon decreased with the increase in Si/Al ratio. At Si/Al ratio of 20, there is a complex effect of all reactions due to their interaction with each other occur on different acid sites, make this zeolite to behave differently, which can not only be correlated by its Si/Al molar ratio and acidity. It can be concluded that the crystal size, morphology, and Si/Al ratio of the zeolite have a conjugative effect on butene oligomerization.

The results showed that the amount of C<sub>7</sub><sup>+</sup> hydrocarbons increased with increasing temperature from 200 to 300°C, and the oligomerization of olefins is the dominant reaction. At temperature above 300°C, the formation of aromatics, naphthenes, and paraffins were increased, and due to cracking, the product distribution changed to lighter hydrocarbons. The optimum condition for butene oligomerization to produce C<sub>7</sub><sup>+</sup> hydrocarbons was using a HZSM-5 zeolite with Si/Al molar ratio of 30, at 200-300°C and GHSV=210-1250 h<sup>-1</sup>. The kinetic of butene oligomerization was studied at these conditions. The reaction rate was described by a power-law kinetic model based on butene consumption. The reaction followed a first-order type reaction, and *E<sub>a</sub>* was estimated to be 26.48 kJ/mol, which suggests the reaction was limited by mass transfer.

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