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OLIGOMERIZATION OF LIGHT OLEFINS OVER HZSM-5 ZEOLITE CATALYST WITH DIFFERENT SI/AL RATIOS

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Abstract

Na-ZSM-5 zeolite with Si/Al molar ratios in the range of 10-50 was synthesized and then transformed into HZSM-5 using ion-exchange method. Techniques such as XRD, FT-IR, SEM, EDX, TG-DTA, BET and NH_3-TPD were used to characterize the zeolite. Light olefins oligomerization reaction was studied over HZSM-5 zeolite catalyst with Si/Al molar ratios in the range of 10-50. The reaction was carried-out at atmospheric pressure, temperature in the range of 250 - 400°C and GHSV = 195-1170 h^{-1}. The study showed that by increasing the temperature from 250 to 300°C, the C_7^+ hydrocarbons in the product increased, whereas above this temperature, they decreased. Similarly increase in GHSV caused the C_7^+ hydrocarbons in the product to decrease. The highest C_7^+ hydrocarbons were obtained with HZSM-5 of Si/Al molar ratio = 25, at temperature 300°C and GHSV = 195 h^{-1}.

Keywords: *HZSM-5; Zeolite; Light olefins oligomerization; Liquid fuels; Si/Al ratio.*

1. Introduction

Oligomerization of light olefins is an intermediate stage in the production of gasoline and distillate fuels from natural gas. It has long been known that oligomerization of light olefins to higher molecular weight hydrocarbon occur on acid-type catalyst. The products of reaction on acid-type catalyst, includes; primarily olefins from straight oligomerization or mixture of olefins, paraffins, cyclo-alkanes and aromatics from what has been termed “conjunct” polymerization [1]. Among the acid-type catalysts, phosphoric acid on Kieselguhr and ZSM-5 zeolite are able to catalyze such a reaction [2]. The technology via phosphoric acid on Kieselguhr, goes back to 1935 to convert propene and butene to C_6-C_{10} isoolefins. The use of ZSM-5 zeolite 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 and acid catalyzed properties of ZSM-5 zeolite, this catalyst then replaced the 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, its low deactivation rate compared with other type of zeolites, is also another important factor for its catalytic behavior [5-6]. Light olefins oligomerization over ZSM-5 zeolite with different Si/Al ratio was investigated at different temperature and GHSV [7-12]. The hydrocarbon produced at 277°C and above, was predominantly gasoline rather than distillate and as temperature was reduced, the product was much heavier hydrocarbons (C_{11}-C_{20}) [13]. 1-butene oligomerization over H-ZSM-5 zeolite has been investigated in a differential reactor operating at ambient pressure. Optimum conditions for selectivity for C_8^+ hydrocarbons (86 wt.%) was obtained with H-ZSM-5, at 200°C and 0.5 bar [14].

The effect of Si/Al ratio of ZSM-5 in the range of 20-500 on propene oligomerization at 220-300°C was investigated and showed that as Si/Al ratio decreased, hydrocarbon products of up to C_{12} were increased. This is in agreement with the work done by Gnep *et al.* [15], where it was found that in propene oligomerization over ZSM-5 with Si/Al ratio of 30 at 300°C, hydrocarbon products of up to C_{13} were produced.

In this work HZSM-5 zeolite with Si/Al molar ratio in the range of 10-50 with different crystal size and morphology was synthesized. Their performance as catalyst for light olefins oligomerization at atmospheric pressure, temperature in the range of 250 - 400°C and GHSV = 195-1170 h^{-1} was investigated.

2. Experimental

2.1. Reagents

The reagents used in the present study were aluminum sulfate ($Al_2(SO_4)_3.18H_2O$, laboratory grade, Merck), sulphuric acid solution (H_2SO_4, 98%, Aldrich), silicagel powder (grade 923, 100-200 mesh, Aldrich), sodium hydroxide (NaOH, flake, Merck), Tetrapropylammonium bromide (TPA-Br, $C_{12}H_{28}BrN$, Merck), ammonium nitrate (NH_4NO_3, laboratory grade, BDH) and propene and butene (99.5 % purity, Linde)

2.2. HZSM-5 preparation

ZSM-5 zeolite was first synthesized from a hydrogel mixture prepared by combining two solutions as follows:

Specified amount of aluminum sulfate was dissolved in de-ionized water and after complete digestion, the required amount of sulphuric acid solution was added to the solution and it was named as solution A. Sodium silicate solution with the composition of 29.50 wt% SiO_2 and 10.50 wt% Na_2O was prepared by dissolving silica gel powder in an alkaline solution and it was named as solution B. Solutions A and B were mixed together under vigorous agitation until a homogenous gel mixture was obtained. Tetrapropylammonium bromide solution was then added to the gel mixture and stirring was continued for about 2 h. The final gel mixture had a pH = 10.5.

The gel mixture was put into a 500 cc high-pressure stainless steel autoclave reactor (manufactured by Autoclave Engineers INC. (BURTON CORBLIN, 60101 NOGENT OISE), France) and synthesis was carried out under agitation speed of 700 rpm at 180 °C for 24 h. At the end of the synthesis, the solid product was filtered and washed several times with warm de-ionized water. The solid product was dried at 120°C and then calcined at 550°C for 3 h under airflow in order to remove the organic template trapped inside the zeolite pores and the final product was Na-ZSM-5. The zeolite was then ion-exchanged with 2 M solution of ammonium nitrate with the ratio of 1 g zeolite/10 cc solution for 24 h under stirring at 80°C to transform Na-ZSM-5 to NH_4^+-ZSM-5. Afterwards, the NH_4^+-ZSM-5 was filtered and washed with de-ionized water. The sample was calcined at 550°C for 3 h under airflow to decompose the ammonium ions to produce HZSM-5.

The gel molar compositions and synthesis conditions used in this work to synthesis ZSM-5 with different Si/Al molar ratios are given in Table 1.

Table 1. Gel molar compositions and synthesis conditions* for ZSM-5 with different Si/Al molar ratios

TPA-Br	Na_2O	Al_2O_3	SiO_2	H_2O
9.15	8.0	1.0	60	2 137.5
9.95	8.0	1.0	100	3 562.5
10.6	8.0	1.0	115	4 096.9
10.5	8.0	1.0	125	4 453.1

** Temperature and synthesis time were 180°C and 24 h*

2.3. Characterization

The synthesized samples were analyzed by X-ray diffraction (XRD) for phase identification using a Philips PW 1840 equipped with a Cu Kα radiation, $\lambda = 1.54060$ Å at 40 kV and 25 mA with a nickel filter in the range of $2\theta = 5 - 90^o$.

The FT-IR spectra of the zeolite were recorded using BRUKER Model IFS 88 in the range 1300-400 cm^{-1} on thin wafers of KBr in which 1 wt. % of zeolite was dispersed.

The morphology and crystal size of the zeolite were examined using a Philips scanning electron microscope (SEM) model XL30. The samples were coated with gold. Coating was performed by physical vapor deposition (P.V.D.) method for 400 s at 10-3 Torr in a BAL-TEC sputter coater model SCDOOS. The aluminum and silicon content of the zeolite were analyzed using Energy Dispersive X-ray (EDX) microanalysis coupled with SEM. The sodium content of the sample was analyzed using a Perkin-Elmer Atomic Absorption Spectrometer Model AAnalyst 200.

Thermal analyses to determine the removal rate of water and template trapped insides the zeolite pore, were carried out using a Simultaneous Thermal Analyzer Model STA 1640. The temperature of the sample was raised at a rate of 10ºC min^{-1} from ambient to 700°C in an air flow of 50 cm^3 min^{-1}. In the thermograms, the weight loss, the differential temperature and the temperature of the sample were plotted simultaneously.

The surface area of the zeolites was determined using a BET method on QUANTA CHROME physical adsorption series using nitrogen as adsorbate at –196°C. The samples were preheated at 200°C for 2 h to remove moisture and degassed at 300°C under vacuum. The sample was allowed to cool, nitrogen was fed into the system and adsorption of the gas took place and surface area of the zeolite was then evaluated.

The acidity of the zeolite was measured by NH_3-TPD using a chemical adsorption instrument of AMERICAN Micrometrics 2900. The samples were first heated up to 500°C with a helium flow of 20 cm^3 min^{-1} for 1 h in order to desorb all traces of adsorbed water and then cooled to 100°C. The adsorption of NH_3 was then started and continued until saturation. Desorption was achieved by increasing the temperature from 100 to 700°C at a rate of 10ºC min^{-1}.

2.4. Light olefins oligomerization

2.4.1. Set-up

The set-up used to study light olefins oligomerization is shown in Figure 1. The set up was consisted of a tubular stainless steel reactor with 0.9 cm i.d. and 40 cm long housed in a three-zone heating jacket, a temperature controller to maintain the heating rate and the temperature of the jacket, mass flow controller (Brooks Model 5850), a separator and a GC to analyze the product.

2.4.2. Procedure

The prepared zeolite powder was made into disk-shaped pellet with 2 mm thickness and 10 mm diameter. The pellet was then grounded and sieved to particles with approximately 1 mm in size needed for the reaction and 2 g of the particles were placed in the reactor (Figure 1).

Prior to each experiment the reactor was heated up to 550°C under a flow of N_2 at atmospheric pressure and kept at this temperature for 2 h. The reactor was then allowed to cool down to the reaction temperature under the flow of N_2. After reaching the desired temperature, it was maintained for 1 h at that temperature, and after that the flow of nitrogen was stopped and light olefins was fed to the reactor through mass flow-controller (MFC). A thermocouple was placed at the center of the catalyst bed to observe the temperature change during the reaction. The liquid products were collected in the separator and analyzed using a CP 3800 gas chromatograph equipped with a flame ionization detector on a Petrocol TM DH capillary column. For each experiment, fresh catalyst was used. Reaction conditions used in this work for light olefins oligomerization are given in Table 2.

Table 2. Reaction conditions for propene oligomerization*

Propene flow rate (cc min^{-1})	10, 37 and 60
GHSV (h^{-1})	195, 731 and 1170
Reaction temperature (°C)	250, 300, 350 and 400

* *All reactions were carried out at atmospheric pressure*

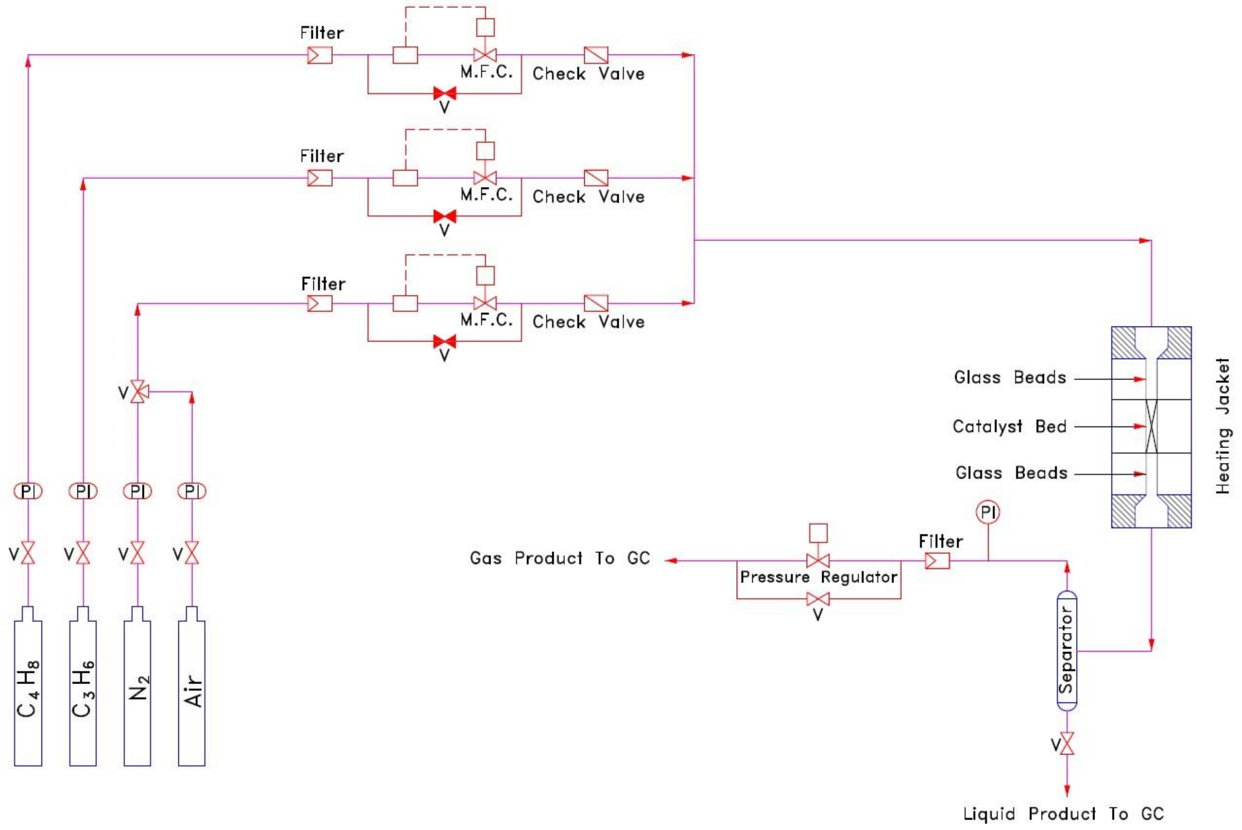

Figure 1. Set-up used for propene oligomerization

3. Results and discussion

The gel compositions in Table 1 produced ZSM-5 zeolite with different Si/Al molar ratios, morphology and crystal size. In this work they are referred to as ZSM-5 (X), where X refers to 10, 25, 40 and 50 molar ratio of Si/Al.

The X-ray diffraction (XRD) patterns of the as-synthesized ZSM-5 zeolite with different Si/Al molar ratios are shown in Figure 2. All samples gave similar XRD patterns, and agreed well for ZSM-5 reported in the reference [16].

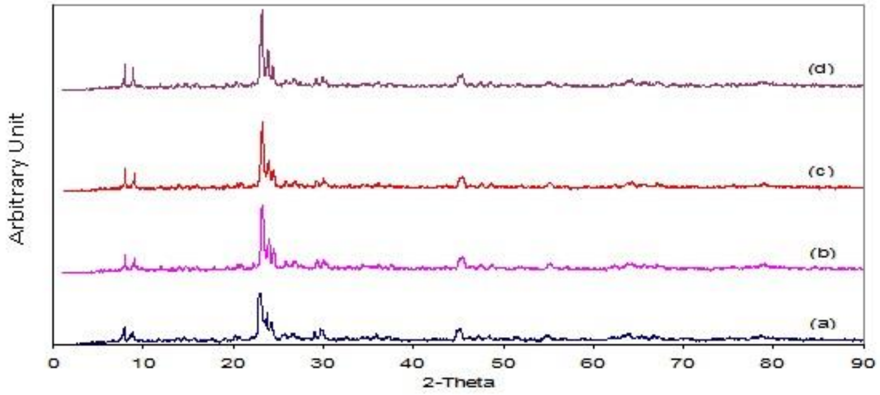

Figure 2. XRD patterns of the synthesized ZSM-5 zeolite with different molar ratios of Si/Al: (a) 10, (b) 25, (c) 40 and (d) 50

To further examine the purity of the as-synthesized ZSM-5 zeolite, the infrared absorption spectra of the sample were also taken. Figure 3 shows the infrared absorption spectra of the as-synthesized zeolite with different molar ratios of Si/Al in the region of 1300-400 cm^{-1}. The absorption bands near 788, 1084 and 1218 cm^{-1} are characteristic of SiO4 tetrahedron units. The strong absorption band in the region 1000-1200 cm^{-1} has been assigned to the internal vibration of SiO_4, AlO_4 tetrahedral for ZSM-5, and also for silica and quartz. The graph shows that the asymmetric stretching vibration frequencies at 1218 and 1084 cm^{-1} generally shift to higher wavenumbers with an increase in the Si/Al ratio. The bands near 1218 and 543 cm^{-1} provide information on the differences between these zeolites (ZSM-5) and other zeolite types. The external asymmetric stretching vibration near 1218 cm^{-1} was assigned to the presence of structures containing four chains of 5-membered rings arranged around a two-fold screw axis, as in the case ZSM-5 structure [17]. The band around 1084 cm^{-1} is attributed to the internal asymmetric stretching vibration of Si-O-T linkage and is observed to shift towards higher wavenumbers with increasing Si/Al ratio of the zeolite. This shift is due to the slightly lower mass of aluminum as compared to that of silicon [18]. The band near 788 cm-1 is assigned to the symmetric stretching of the external linkages, and the strong band near 543 cm^{-1} is attributed to the double five-ring lattice vibration of the external linkages [19]. The absorbance at around 450 cm^{-1} is due to the T-O bending vibrations of the SiO_4 and AlO_4 internal tetrahedral. The absorption bands around 543 and 450 cm^{-1} are characteristic of the ZSM-5 crystalline structure and the ratio of the intensities of these two peaks provides an approximate estimate of the degree of crystallinity of a given zeolite sample [20]. The ratio of the absorbance of these two bands falls between 0.74-0.85 for as-synthesized forms of zeolites. These value compare to a literature value of 0.8, suggested for pure ZSM-5 zeolites. The FT-IR spectra confirmed that, the synthesized zeolites exhibit good crystallinity. This is in agreement with the results of XRD.

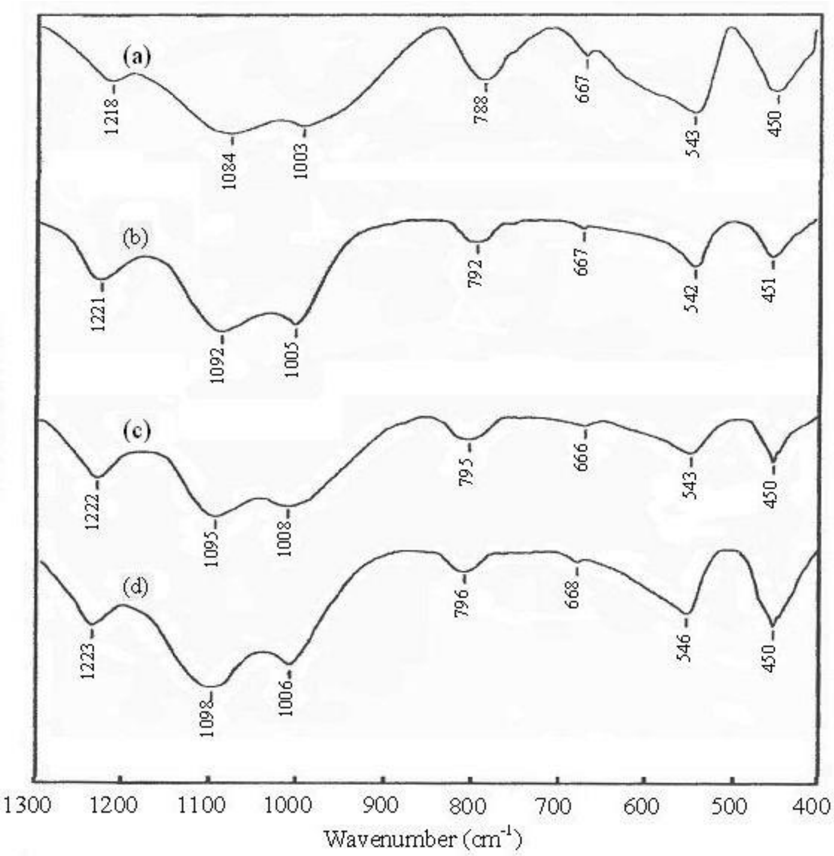

Figure 3. FT-IR spectra of the synthesized ZSM-5 zeolite with different molar ratios of Si/Al: (a) 10, (b) 25, (c) 40 and (d) 50

The morphology and crystal size of the synthesized ZSM-5 zeolite examined using SEM are shown in Figure 4. The samples had different crystal morphologies, from ellipsoidal to cuboidal and also aggregate of highly intergrowth crystals with uniform size distribution. The results show that increase in the aluminium content of the zeolite, decrease its crystal size and change its morphology.

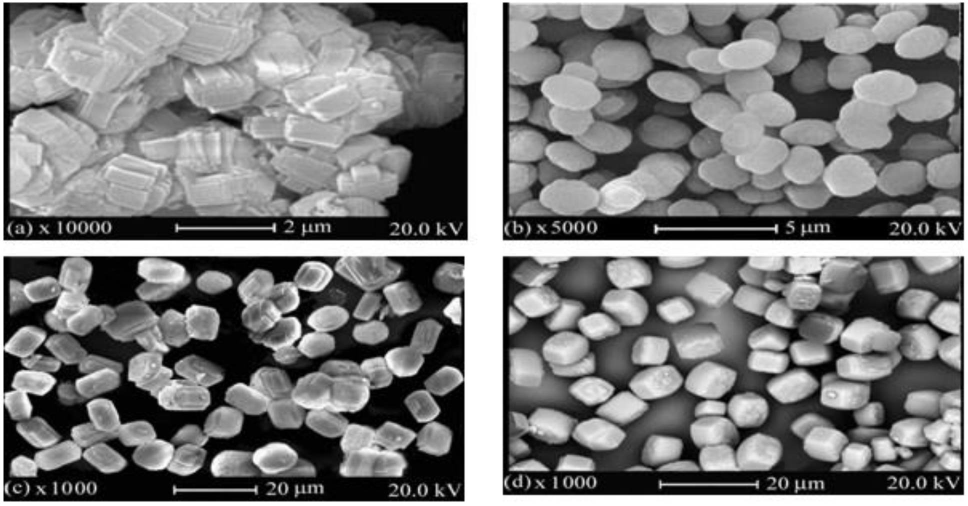

Figure 4. Scanning electron micrographs of the synthesized ZSM-5 zeolites with different molar ratios of Si/Al: (a) 10, (b) 25, (c) 40 and (d) 50

Surface area of the samples determined by BET method showed that, the surface area of the samples increased with increase in molar ratios of Si/Al (Table 3).

Table 3. Properties of HZSM-5 zeolite with different Si/Al molar ratios

Sample	BET surface area ($m^2\ g^{-1}$)	Crystal size µm	Total acidity mmole NH_3/g catalyst
HZSM-5(10)	355	aggregates	27.02
HZSM-5(25)	371	2	21.38
HZSM-5(40)	386	7	19.93
HZSM-5(50)	392	9	19.93

Thermogravimetric analysis of the synthesized ZSM-5 zeolite was carried out to determine the removal rate of water and template from zeolite. TGA and DTA curves of the samples are shown in Figure 5. The total percent weight losses in the temperature range 20-600°C represent water loss as well as loss of template. These two losses are overlapped in the thermogram and thus provide an approximate estimation. Dehydration occurred below 300°C. The weight loss in the temperature up to 300°C represented by a broad region in the thermogram is believed to be due to water loss. The water loss decreased with increasing Si/Al ratio of the zeolites (Figure 6). This is because the acidity of the zeolite decreases with increasing Si/Al ratio in zeolite; thus increases its hydrophobic nature. Therefore, less water is present in the zeolites with low aluminum content. The weight loss in temperature range of 300-600 °C can be attributed to template removal increases with increasing Si/Al molar ratio of the zeolites.

The acidity of the HZSM-5 zeolite with different Si/Al molar ratios determined by NH_3-TPD, are shown in Figure 7. All samples exhibit two well resolved desorption peaks: the low-temperature peak (LTP) at 210-255°C and the high-temperature peak (HTP) at 420-465°C. LTP and HTP generally correspond to weak and strong acid sites, respectively. As shown in Figure 7, the peak intensity at 420-465°C increased as the Si/Al ratio decreased. This is primarily due to the increase in extra-framework aluminum content as well as the in the framework. Figure 7 also shows that the desorption temperature of ammonia from the strong acid sites shifted to higher temperature as the Si/Al ratio decreased, strongly suggesting the existence of aluminum in extra-framework positions.

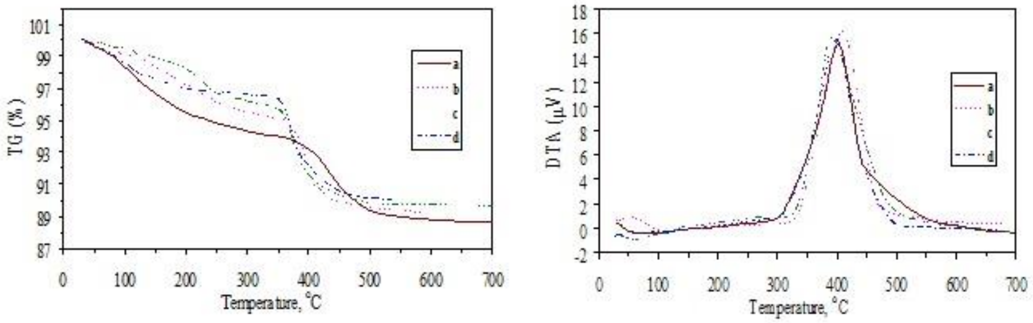

Figure 5. TGA and DTA curve of the synthesized ZSM-5 zeolites with different molar ratios of Si/Al: (a) 10, (b) 25, (c) 40 and (d) 50

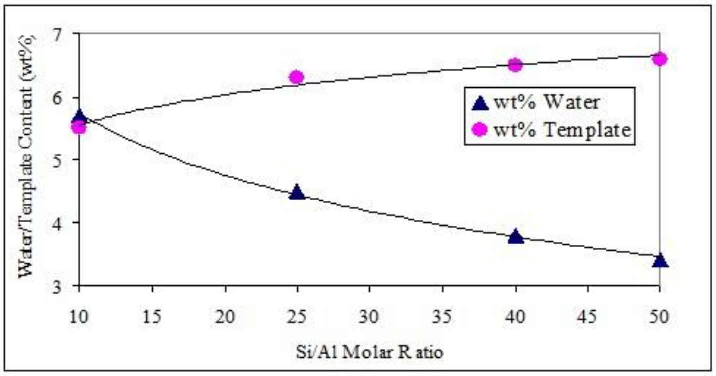

Figure 6. Water and template contents as a function of Si/Al molar ratio of the as-synthesized zeolites

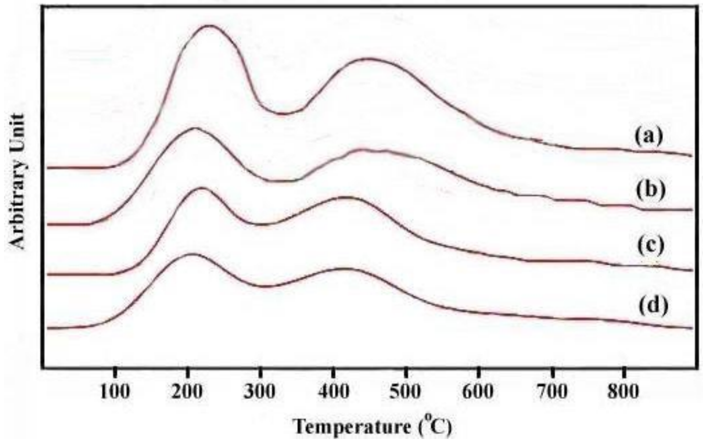

Figure 7. NH_3-TPD profile of HZSM-5 with different molar ratios of Si/Al: (a) 10, (b) 25, (c) 40 and (d) 50

The total acidity for HZSM-5 with different molar ratio of Si/Al is shown in Table 3. This table shows that the total acidity of HZSM-5 decrease with increasing of Si/Al molar ratio, which agrees well with those, reported in the literature [21-22]. Other properties of HZSM-5 zeolite with different Si/Al molar ratios are also listed in this table.

3.1. Oligomerization of light olefins over HZSM-5 zeolite

The hydrocarbon product distribution during light olefins oligomerization reaction over HZSM-5 with different Si/Al molar ratio at different temperatures and GHSV are shown in Figure 8.

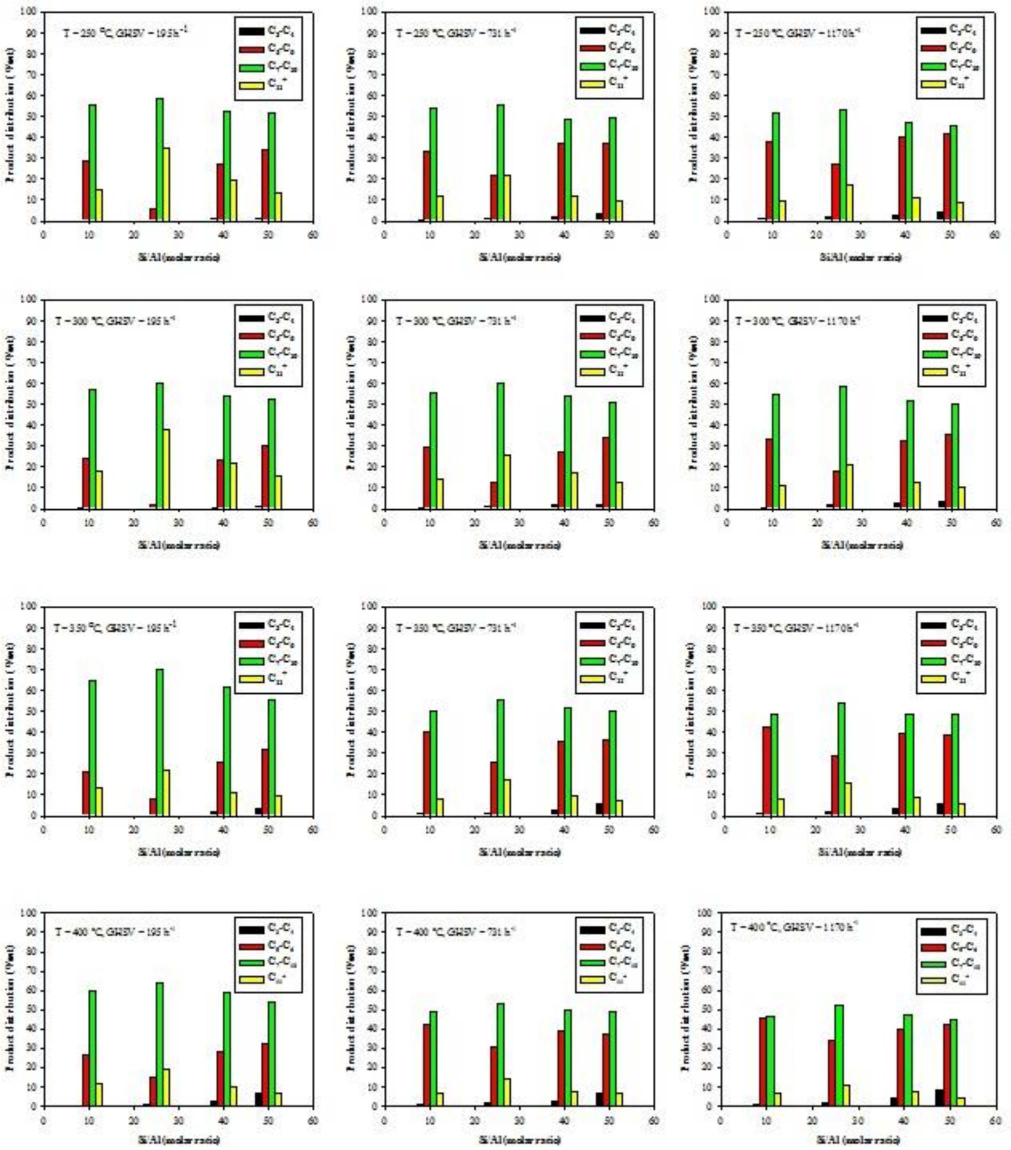

Figure 8. Product distribution obtained for light olefins oligomerization at atm. pressure, various temperatures and GHSV on HZSM-5 with different Si/Al molar ratios

The results showed that the product selectivity changed with aluminum content of the zeolite and since the aluminum content attributes to the acidity of the zeolite, therefore for a desirable acidity for oligomerization reaction, the aluminum content of zeolite plays an important role. As it is shown in Table 3, the change in Si/Al molar ratio not only changed the acidity of the zeolite but also the crystal size was affected. It can be concluded that, the acidity and crystal size of zeolite simultaneously affect the hydrocarbon product distribution.

Results for hydrocarbon product distribution at different Si/Al molar ratio showed that for all Si/Al molar ratios other than 10, the selectivity for C_7^+ hydrocarbon decreased with the increase in Si/Al ratio. At Si/Al ratio of 10, 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. These effects may be due to that in which 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_7^+) is the target to reach in oligomerization reaction. It can be seen from the results that at Si/Al =25 the C_7^+ hydrocarbons is at its most and therefore it can be concluded that for light olefins oligomerization the optimum ratio of Si/Al is 25. This shows that Si/Al ratio of zeolite has a pronounced effect on product distribution for oligomerization reaction.

The increase in GHSV can always change the product distribution during a catalytic reaction. This effect was also noted in this work. As it can be seen from Figure 8, the highest amount of C_7^+ hydrocarbon produced at different temperatures was obtained at GHSV = 195 h^{-1}, whereas at higher GHSV, the amount of C_7^+ hydrocarbon decreased.

Figure 8 shows that temperature rise had two distinct effect, increase in temperature from 250 to 300°C, increased the oligomerization (i.e., production of C_7^+ hydrocarbons) but above 300°C, the lighter olefins (i.e., < C_7 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 Figure 9. As it can be seen, parameters such as temperature and GHSV affected simultaneously the production of different hydrocarbon product.

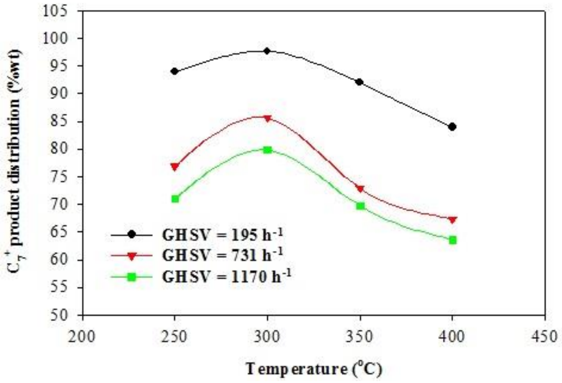

Figure 9. Liquid product distribution obtained for light olefins oligomerization at atm. pressure, different temperatures and GHSV on HZSM-5 with Si/Al molar ratio of 25

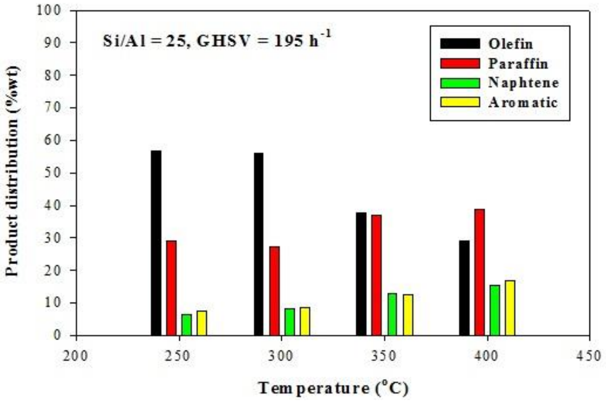

Figure 10. Effect of temperature on C_7^+ product distribution for light olefins oligomerization at various GHSV on HZSM-5 with Si/Al molar ratio of 25

It is postulated [23], that in oligomerization reaction, propene will oligomerize to C_6, C_9, C_{12}, etc., oligomers. These then isomerizes and recrack, forming a range of light olefins. Lastly, these then reoligomerize 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.

The effect of temperature on hydrocarbons produced during light olefins oligomerization reaction over HZSM-5 with Si/Al molar ratio of 25 and GHSV = 195 h^{-1} at different temperatures is shown in Figure 10. As it can be seen, at 250°C, the amount of olefin & aromatic produced is 56.85 and 7.58 wt%, respectively, whereas at 400°C, these amounts have been changed to 28.99 and 16.74 wt%. It can then be concluded that, at lower temperature, oligomerization of olefins is the dominant reaction. A significant quantity of paraffins presumably as a result of hydrogen transfer processes is also produced. Increase in temperature, increased the formation of aromatics, naphtenes (cycloalkanes) and paraffins.

It can be seen from the results that the amount of C_7^+ hydrocarbons produced over zeolite with Si/Al=25 at 300°C and GHSV = 195 h^{-1} is the highest (97.68 wt %) and is the lowest (63.6 wt %) at 400°C with GHSV = 1170 h^{-1} (Figure 9).

4. Conclusions

NaZSM-5 zeolites with different molar ratios of Si/Al in the range of 10-50 were first synthesized. They were then calcined under the airflow at 550 °C to remove the template. Afterwards, the zeolites were ion-exchanged with a 2.0 M aqueous solution of ammonium nitrate at 80°C for 24 h and transformed into HZSM-5. All synthesized samples as confirmed by their X-ray diffraction and IR patterns, were pure ZSM-5.

SEM images showed that the morphology of the synthesized zeolites was cubical, hexagonal and ellipsoidal in shape. In zeolite with Si/Al molar ratio of 10, intergrowth and twinning of crystal with high aggregation were observed, whereas for other Si/Al ratio, crystals with well-defined morphology were observed. The BET surface areas of the prepared HZSM-5 zeolites increased with increasing Si/Al molar ratio. The crystal size of the zeolite also increased with the increase in Si/Al molar ratios. Analysis by TGA showed that water content of the synthesized zeolite decreased, while the template content increased with increasing Si/Al molar ratios. NH_3-TPD profiles showed that zeolite with different Si/Al molar ratios had different acidity and total acidity decreased with increasing the Si/Al molar ratio.

The catalytic performance of the prepared zeolites with different Si/Al molar ratios for light olefins oligomerization at different temperatures and GHSV was studied in a fixed-bed reactor. The results showed that the hydrocarbon product distribution during oligomerization reaction highly depends on molar ratios of Si/Al, temperature and GHSV. A simultaneous effect of the acidity and crystal size of zeolite is also thought to change the product distribution. For all Si/Al molar ratios other than 10, the C_7^+ selectivity decreased with the increase in Si/Al ratio, this can be postulated as follow; at Si/Al ratio of 10 a complex effect of acid sites and morphology of the zeolite on all reaction taking place on the zeolite, make this zeolite to behave differently which cannot be correlated only 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 light olefins oligomerization.

The results showed that the amount of C_7^+ increased with increasing temperature from 250 to 300°C. Above 300°C, due to cracking, the product distribution changed to lighter hydrocarbons. The results also showed that at low temperature (i.e., 250°C), oligomerization of olefins is the dominant reaction while at higher temperature, the formation of aromatics, naphtenes (cycloalkanes) and paraffins increased.

The results showed that the optimum condition for light olefins oligomerization reaction to produce C_7^+ hydrocarbons, was using a HZSM-5 zeolite with Si/Al molar ratio of 25, at 300°C and GHSV = 195 h^{-1}.

Acknowledgements

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References

[1] Knifton JF, Saderson JR. Olefin oligomerization via zeolite catalysis, Catalysis Letters, 1994; 28: 223-230.

[2] Peratello S, Molinari M, Bellussi G, Perego C. Olefins oligomerization: thermodynamics and kinetics over a mesoporous silica–alumina, Catalysis Today, 1999; 52: 271-277.

[3] van Grieken R, Escola JM, Moreno J, Rodriguez R. Liquid phase oligomerization of 1-hexene over different mesoporous aluminosilicates (Al-MTS, Al-MCM-41 and Al-SBA-15) and micrometer/nanometer HZSM-5 zeolites,Applied Catalysis A: General, 2006; 305: 176-188.

[4] Sanati M, Hornell Ch, Jaras SG. Oligomerization of alkene by heterogen. Catalyst, Catalysis, 1999; 14: 236-287.

[5] Schonlinner J, Kohler E, Burgfels G, Schmidt F, Wernicke HJ, de Pontes M, Roberts HL. Conversion of olefins to diesel, Conf. Industrial Applications of Zeolites, Brugge-Belgium, October 2000.

[6] Benito PL, Gayubo AG, Aguayo AT, Olazar M, Bilbao J. J. Chem. Tech. Biotechnol., 1996; 66: 183-191.

[7] Olefin oligomerization process, US patent 9580525, 2017.

[8] Dzikh IP, Lopes JM, Lemos F, Ribeiro FR. Transformation of light alkenes over templated and non-templated ZSM-5 zeolites,Applied Catalysis A: General, 1999; 177: 245-255.

[9] Popov AG, Fedosov DA, Ivanova II, Vedernikov OS, Kleimenov AV, Kondrashev DO, Miroshkina VD, Abrashenkov PA, Kuznetsov SE. A ZSM-5 zeolite-based catalyst for oligomerization of the butane–butylene fraction, Petroleum Chemistry,March 2016; 56(3): 237–243.

[10] Verrelst WH, Martens LRM. WIPO Patent 9,522,516 A1, 1995.

[11] Borges P, Ramos Pinto R, Lemos MANDA, Lemos F, Védrine JC, Derouane EG, Ramôa Ribeiro F, Light olefin transformation over ZSM-5 zeolites: A kinetic model for olefin consumption, Applied Catalysis A: General, 2007; 324(1): 20-29

[12] Borges P, Pinto RR, Lemos MANDA, Lemos F, Vedrine JC, Derouane EG, Ribeiro FR. Light olefin transformation over ZSM-5 zeolites: A kinetic model for olefin consumption, Applied Catalysis A: General, 2007; 324: 20-29.

[13] Oliveira P, Borges P, Ramos Pinto R, Lemos MANDA, Lemos F, Védrine JC, Ramôa Ribeiro F. Light olefin transformation over ZSM-5 zeolites with different acid strengths – A kinetic model, Applied Catalysis A: General, 2010; 384(1–2): 177-185.

[14] Coelho A, Caeiro G, Lemos MANDA, Lemos F, Ramôa Ribeiro F. 1-Butene oligomerization over ZSM-5 zeolite: Part 1 – Effect of reaction conditions, Fuel, 2013; 111: 449-460.

[15] Gnep NS, Bouchet F, Guisnet MR. Comparative study of the oligomerization of C_2-C_5, olefins on HZSM-5, Symposium on alkylation, aromatization, oligomerization and isomerization of short chain hydrocarbons over heterogeneous catalysts, New York City Meeting, August 1991; 620-626.

[16] Treacy MMJ, Higgins JB, Von Ballmoos R. Collection of simulated XRD powder patterns for zeolites, Elsevier, New York 1996; 523.

[17] Wang F, Fang K, Hu J, Ren J, Sun Y. Propene oligomerization over ZSM-5 zeolites with varying crystal size, State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, 2010; Taiyuan, 030001, P. R. China.

[18] Li X-B, Hu J-X, Wang F, Ren J. Propene oligomerization over zirconium containing ZSM-5 zeolites, Journal of Fuel Chemistry and Technology, 2004; 32(4): 498-503.

[19] Fan W, Li R, Ma J, Fan B, Cao J. Synthesis, characterization and catalytic properties of MFI-type zeolites prepared in the system Na_2O SiO_2 Al_2O_3 $H_2N(CH_2)6NH_2$ NH_4F, Microporous Materials, 1995; 4: 301-307.

[20] Saidina Amin NA, Anggoro DD. Dealuminated ZSM-5 zeolite catalyst for ethylene oligomerization to liquid fuels, J. Natural Gas Chemistry, 2002; 11: 79-86.

[21] Ali MA, Brisdon B, Thomas WJ. Synthesis, characterization and catalytic activity of ZSM-5 zeolites having variable silicon-to-aluminum ratios, Applied Catalysis A: General, 2003; 252: 149-162.

[22] Costa C, Dzikh IP, Lopes JM, Lemos F, Ribeiro FR. Activity–acidity relationship in zeolite ZSM-5. Application of Brönsted-type equations, J. Mol. Catal. A: Chem., 2000; 154: 193-201.

[23] Kriván E, Tomasek S, Hancsók J. Application Possibilities of Zeolite Catalysts in Oligomerization of Light Olefins, Periodica Polytechnica Chemical Engineering, 2014; 58(2): 149-156.

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