



Conversion of bioethanol over zeolites

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ABSTRACT

Tetrapropylammonium salt was replaced with different wastes from the production of caprolactam as structural units in synthesizing ZSM-5 zeolites. Ethanol conversion runs were carried out over the synthesized catalysts containing spirit fraction, X-oils and hexamethylenediammine as structural units. The catalyst with hexamethylenediammine showed better selectivity for liquid hydrocarbons and the formation of C₃–C₄ hydrocarbons was favoured by increase in the Si/Al from 30 to 50. Mechanical addition of gallium oxide increased liquid yield and catalyst life whereas impregnation of zirconium oxide resulted in a loss of selectivity for liquid hydrocarbons. Better selectivity for liquid hydrocarbons was obtained over catalysts with an average of 1 and 3 atoms of aluminum in elementary zeolite cells.

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1. Introduction

Significant attention is being given to the production of energy from renewable sources such as hydro, wind and biomass. Ethanol obtainable from biomass fermentation is a potential source of combustible hydrocarbons [1]. Apart from boosting agriculture and other economic sectors [2,3], bioethanol production provides raw materials that can be converted into combustible hydrocarbons [4] similar to those used as fuels and raw materials for petrochemical industries. Taking into consideration that using non-renewable energy sources increases carbon emissions into the atmosphere [3], enhancing the use of hydrocarbons from bioethanol will tackle one of today's major problems, i.e. environmental pollution. Adding to the aforementioned benefits, research into the application of renewable fuels helps prepare petrochemists towards finding solutions to the inevitable depletion of the world's fossil fuel reserves and also helps nations towards strategic storage of fossil fuels.

Several catalysts have been used in the conversion of cheap and readily available compounds into more valuable hydrocarbons [5,6]. Considering the fact that nature of the catalysts has a significant effect on the products' yield and distribution, certain catalyst properties and reaction conditions have to be controlled to achieve the desired hydrocarbons [7]. In the petrochemical industry, zeolites are used as catalysts for the conversion of low molecular

alcohols [5,8–11] into more valuable hydrocarbons. More often than not, catalysts have to be promoted to boost their activity and selectivity for certain hydrocarbons. To this effect much attention is given to the studies of parameters that could possibly affect the selectivity of zeolites in the production of hydrocarbons from renewable raw materials like ethanol. Zeolites are important catalysts in this area due to their high selectivity [11], which is attributed to their network structures. Many catalysts have been developed with the aim of controlling selectivity during ethanol conversion. However, no such efforts have significantly yielded a high conversion into liquid hydrocarbons that are likely to substitute those obtainable from fossil fuels.

We have studied the effect of structural units, Si/Al ratio and incorporated oxides on the activity and selectivity of HZSM-5 zeolites. ZSM-5 zeolites were synthesized and used in studying ethanol conversion. The studied parameters affected the yield and distribution of the conversion products.

2. Material and methods

2.1. Catalyst synthesis

A series of HZSM-5 catalysts were produced hydrothermally. Zeolites were synthesized using salt solution of analytical Al (NO₃)₃·9H₂O, water glass Na₂SiO₃ (29% SiO₂, 9% Na₂O, 62% H₂O) and structural units. The reagent mixture was prepared by intensive stirring of the initial reagents at a constant pH (≈10.8) by the addition of 0.1 N solution of HNO₃. Powdered high silicate zeo-

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Table 1
Promoted catalysts and their preparation.

Modified catalyst components	Preparation method	Si/Al
HZSM-5(I) and Ga ₂ O ₃	HZSM-5(I) Si/Al = 50 was mechanically mixed with gallium oxide and the mixture was mechanochemically activated in a ball mill at a temperature of 20 °C for 24 h.	50
HZSM-5(I) and Ga ₂ O ₃	HZSM-5(I) Si/Al = 30 was mechanically mixed with gallium oxide and the mixture was mechanochemically activated in a ball mill at a temperature of 20 °C for 24 h.	30
HZSM-5(I) and Fe ₂ O ₃	HZSM-5(I) Si/Al = 50 was mechanically mixed with iron oxide and the mixture was mechanochemically activated in a ball mill at a temperature of 20 °C for 24 h.	50
HZSM-5(I) and Fe(NO ₃) ₂ ·6H ₂ O	Iron oxide was impregnated into the protonized ZSM-5 before crystallization.	50
HZSM-5(I) and Zr(NO ₃) ₂ ·5H ₂ O	Zirconium oxide was impregnated into the protonized ZSM-5 before crystallization.	50

lite Si/Al = 60 was added to the mixture in order to initialize the crystallization process.

Crystallization was carried out at a constant temperature of 175 °C in a steel autoclave for a period of six days. After which, the solid phase was filtered from the mother solution, washed with distilled water until it had a pH of not more than 9. It was then dried at a temperature of 185 °C and calcined at 650 °C for a period of 6 h to get rid of organic impurities. Using the procedure, nine different zeolites with Si/Al = 30, 50 and 90 for each of the three structural units were synthesized. The obtained high silicate zeolites (NaZSM) were protonized with 25% ammonium chloride (NH₄Cl) solution at 100 g solution/10 g zeolite. The resultant solution was continuously stirred in water at 90 °C for a period of 2 h. After this, the sediment (NH₄/ZSM-5) was filtered and washed with distilled water, dried and calcined at temperature of 500–550 °C for a period of 8 h.

Mechanical mixtures were obtained by mixing oxides of the corresponding cations with the obtained catalysts and subsequent mechanochemical activation in a ball mill at a temperature of 20 °C for 24 h. The catalysts were also modified by the impregnation of analytical nitrates into their protonized zeolite forms (Table 1).

At the crystallization stage, hexamethylenediammine, X-oils (oligomers of cyclohexanone, dicyclohexanone, cyclohexanone, cyclohexanol and phenol) and spirit fractions (C₁–C₆ alcohols containing 75% amyl alcohol) were added as structural units, to obtain HZSM-5(I), HZSM-5(II) and HZSM-5(III), respectively. The catalysts degree of crystallization was calculated after their physical and chemical properties were obtained using IR spectroscopy and XRD analysis.

2.2. Experimental design and procedure

Ethanol–water azeotrope (ethanol – 96 vol.% and water – 4 vol.%) obtained from biomass was converted in a fixed bed continuous flow reactor fitted in an electrically heated stainless steel block. One gram of the catalyst was loaded in the reactor. Ethanol was charged from the top using a pump, after which it was evaporated and the vapour was passed through the catalyst layer in the reactor. Pressure was controlled using a manometer regulated with a throttle. An automatic thermo regulator was used to control temperature.

The reaction products were passed on to a condenser where they were cooled by running water and separated into liquid and gaseous phases in a separator. The liquid phase consisting of water and hydrocarbon fractions was gathered in a collector and the water was separated from the liquid hydrocarbons using a separating fun-

nel. The gas fraction passed through a scrubber and a flow meter, (soap bubble meter, with a relative accuracy of 0.5–1%) then collected in a gasometer. The gas was analyzed using a chromatograph that was directly connected to the experimental setup.

2.3. Experiment

Ethanol conversion runs were performed at a temperature of 400 °C, pressures of 1 and 3 atm, WHSV = 10 h⁻¹ for a period of 2–4 h. The gas fraction was analyzed at intervals of about 40 min and at the end of each run. The catalyst was regenerated by passing a stream of air (GHSV = 0.2 s⁻¹) at a temperature of 500 °C for a period of 60 min.

The conversion products (both gaseous and liquid) were analyzed using gas chromatography with helium (99.98%) as the carrier gas.

The composition of the gaseous product was determined chromatographically on “КристаллЛюкс-4000М” equipment: column of length 2 m and diameter 3 mm, phase – Porapak Q, gas carrier – helium 30 cm³/min, thermo programmed regime 30–150 °C. The concentration of the gases at the outlet of the column was determined using a heat conduction detector. For accurate positioning of peaks, calibration was made for individual components (methane, ethane, CO₂, propane–butane mixture and isobutene) and also experimentally using a simultaneous detector FID – Katharometer. The liquid fraction was analyzed using “КристаллЛюкс-4000М” equipment: capillary column of length 30 m and diameter 0.3 mm, phase-SE30 (non-polar dimethyl silicon elastomer), gas carrier – helium 20 cm³/min, thermo programmed regime 30–175 °C (5°/min). The components were determined at the outlet of the column using a flame ionization detector. For accuracy, the peaks were fixed using known standards. The following pure compounds were used as standards: *n*-hexane, *n*-heptane, cyclohexane, *n*-nonane, *n*-decane, benzene, toluene, *ortho*-xylene, naphthalene, diethyl ether and ethanol (96%). The retention times of the other components were determined using retention table and Kovats' index.

3. Results and discussion

The analyses conducted showed that all the synthesized zeolites belong to the ZSM-5 family. There was 100% ethanol conversion on all the catalysts. However, the catalysts showed a remarkable difference in their selectivity. From Table 2, it can be seen that HZSM-5(I) had the highest selectivity for liquid hydrocarbons. On

Table 2
Product distribution of ethanol conversion over HZSM-5 zeolites (Si/Al = 50) (*T* = 400 °C, WHSV = 10 h⁻¹, *P* = 3 atm).

Zeolite	Cumulative product composition over a period 2 h (wt.%)						Ethylene concentration (instantaneous) in the gas fraction after 2 h (vol.%)
	Liquid hydrocarbons	Methane	Ethylene	Ethane	C ₃	C ₄	
HZSM-5(I)	21	0.7	1.3	3	41	33	2
HZSM-5(II)	3	2	90	1	2	2	99.8
HZSM-5(III)	12	5	10	13	40	20	40

Table 3Product distribution of ethanol conversion over HZSM-5(I) (reaction time 4 h, WHSV 10 h⁻¹, T = 400 °C), wt.%.

Component	Si/Al = 30		Si/Al = 50		Si/Al = 90	
	Fresh catalyst, P = 3 atm	Regenerated catalyst, P = 1 atm	Fresh catalyst, P = 3 atm	Regenerated catalyst, P = 1 atm	Fresh catalyst, P = 3 atm	Regenerated catalyst, P = 1 atm
Methane	0.14	0.07	0.18	0.07	0.14	0.08
Ethane	0.89	2.43	1.37	5.42	0.82	1.47
Ethylene	1.57	2.09	1.81	2.05	1.67	1.22
Propane–propylene	25.31	21.27	29.79	24.02	25.11	20.79
C ₄ -fraction	32.07	33.98	31.47	33.17	31.30	33.69
C _{5–7} -fraction	14.53	18.54	12.43	18.55	14.07	18.23
Benzene	1.44	0.95	1.47	0.91	1.81	1.03
C ₈₊ -fraction	1.16	1.86	0.89	1.18	0.87	1.94
Toluene	7.28	5.47	6.76	5.07	8.15	6.02
Ethylenebenzene	1.27	1.36	1.13	1.03	1.22	1.35
<i>m,p</i> -Xylene	5.93	5.40	5.40	4.84	6.21	5.72
<i>o</i> -Xylene	1.69	1.33	1.46	1.14	1.87	1.64
Methylethylbenzene	3.86	2.90	3.23	2.61	3.63	4.07
Other benzenes	2.10	2.15	0.97	0.67	1.25	1.33
Naphthalene	0.78	1.23	1.65	0.27	1.90	1.07
Total liquid fraction	29.98	29.46	26.20	20.61	31.55	30.14
Aromatics from liquid fraction	89.11	81.15	90.80	86.21	91.06	82.64

the same catalyst, ethylene which was obtained from the first stage i.e., dehydration, had an initial concentration of about 0.1% in the first 20 min and increased to about 10% after 4 h of reaction time, indicating that the catalyst still retained its oligomerization activity. On the other hand, in the very first minute, HZSM-5(II) showed a high dehydration activity of ethanol to ethylene. The initial ethylene concentration was about 95% indicating a low oligomerization activity which declined towards zero after 4 h.

On HZSM-5(III), ethylene made up about 10 wt.% of the products within the first 2 h and later increased to about 40 wt.% after 2 h indicating a sharp fall in oligomerization activity. HZSM-5(III) showed a better oligomerization activity than HZSM-5(II); however, the catalyst synthesis needs to be further developed so as to increase its life. Based on the obtained results, the activity of the synthesized HZSM-5 catalysts (Si/Al = 50) is seen to be affected by the structural unit used and has the following trend:



The trend shows that the liquid yields had linear relationship to their degrees of crystallization HZSM (I) 91%, HZSM-5(III) 80% and HZSM (II) 72%.

The incorporation of hexadimethylenediamine in the synthesis of ZSM-5 zeolites greatly increased the isomerization activity of its protonized form, the product distribution on this catalyst were similar to those of HZSM-5 zeolites synthesized with the usual tetrapropylammonium salt.

The liquid yield on HZSM-5(I) Si/Al = 30 was more than 29% (Table 3). Neither reactivation nor change in pressure had any significant effect on the liquid yield, yet a change in the product distribution was observed; the concentration of aromatic hydrocarbons decreased while that of C_{5–7} fraction increased with a decrease in pressure from 3 to 1 atm. This seems to be connected with the reduced contact time of C_{5–7} intermediates with the catalyst surface at a lower pressure.

Conversion of ethanol over HZSM-5(I) Si/Al = 50 (Table 3) showed that the liquid hydrocarbon yield was affected by a change in pressure; it was 26% at a pressure of 3 atm, and 20% at 1 atm. Even though the yield was higher at 3 atm, it was less than the 29% obtained over a similar catalyst with Si/Al = 30. However, the concentration of aromatic hydrocarbons was more than that obtained on HZSM-5 Si/Al = 30. Propane–propylene concentration increased with an increase in Si/Al ratio from 30 to 50 while that of ethylene remained practically unchanged.

It can be seen in Table 3 that the yield of liquid products over the fresh HZSM-5(I) Si/Al = 90 catalyst was a little more than that over HZSM-5(I) Si/Al = 30. After the first regeneration, HZSM-5(I) Si/Al = 90 lost its activity only slightly, but the decrease in the liquid aromatic content was about 10%. (Table 3)

The aromatic hydrocarbon content over all the fresh HZSM-5 catalysts (Si/Al = 30, 50, 90) was almost the same and had a value of about 90%. It was observed that Si/Al = 50 had lower liquid yield but higher concentration of aromatic and C₃ hydrocarbons suggesting their formation from C_{5–7} fractions. Furthermore, this is also supported by the highest concentration of C₃ hydrocarbons corresponding to the lowest concentration of C_{5–7} observed.

Figs. 1 and 2 show the changes in gaseous products of ethanol conversion over HZSM-5(I) Si/Al = 30 as the reaction progressed. Initially the concentration of propane–propylene (C₃) fraction was nearly twice that of the C₄ hydrocarbons (Fig. 1). The concentration of ethylene obtained over the fresh catalyst was less than that of ethane implying the production of a considerable amount of hydrogen as a result of aromatization. At a pressure of 1 atm, ethylene concentration increased with time indicating the blockage of the oligomerization active centers. The decrease in the concentration of C_{3–4} hydrocarbons as the ethylene increased (Fig. 2) suggests that C_{3–4} hydrocarbons were not formed directly from ethylene growth but from the cracking of other oligomers containing more than four carbon atoms.

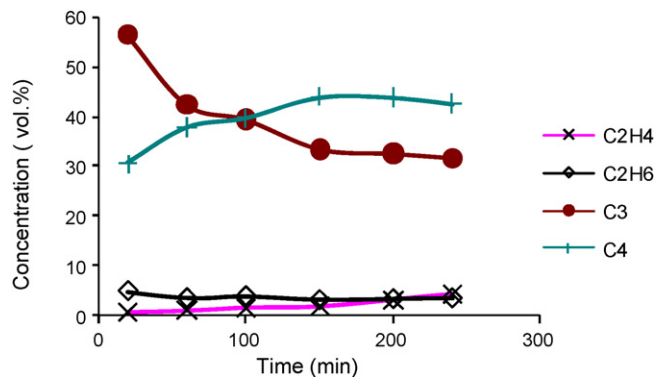


Fig. 1. Gaseous product of ethanol conversion over HZSM-5(I) Si/Al = 30 (P = 3 atm, WHSV = 10 h⁻¹, T = 400 °C).

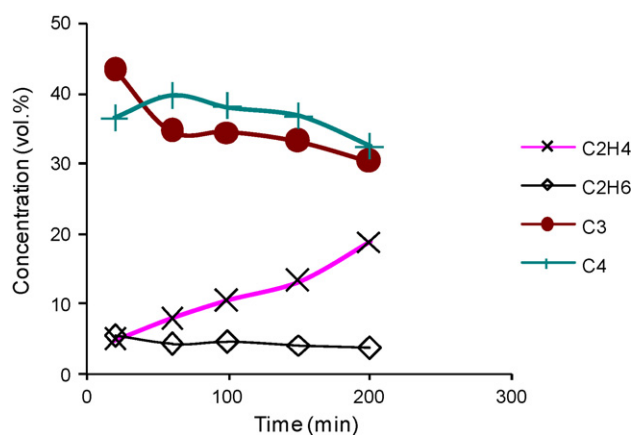


Fig. 2. Gaseous product of ethanol conversion over HZSM-5(I) Si/Al = 30 ($P = 1$ atm, $WHSV = 10 \text{ h}^{-1}$, $T = 400 \text{ }^\circ\text{C}$).

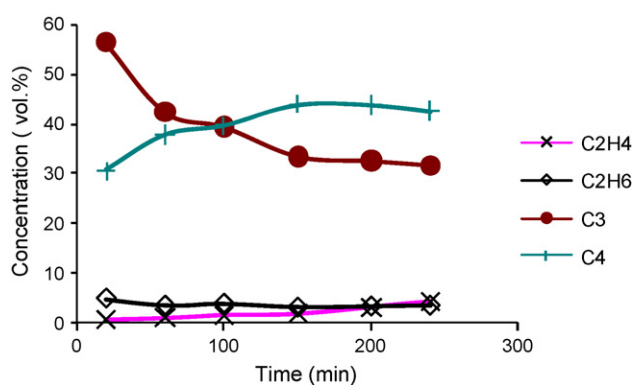


Fig. 3. Gaseous products distribution of ethanol conversion over HZSM-5(I) Si/Al = 90 ($WHSV = 10 \text{ h}^{-1}$, $T = 400 \text{ }^\circ\text{C}$, $P = 3$ atm).

HZSM-5(I) Si/Al = 90 practically maintained its selectivity for liquid hydrocarbons after 4 h. The gaseous product distribution is shown on Figs. 3 and 4. Qualitatively, gaseous product distribution agrees with that of the other runs over the HZSM-5(I) catalyst, however, the increase in concentration of ethylene with time is less pronounced. After 240 min of reaction and regeneration, the ethylene content was 3% (25% over HZSM-5(I) Si/Al = 50 and 15% over HZSM-5(I) Si/Al = 30). It is also of interest to note that after regeneration the ratio of C_3 to C_4 hydrocarbons on the HZSM-5(I) Si/Al = 90

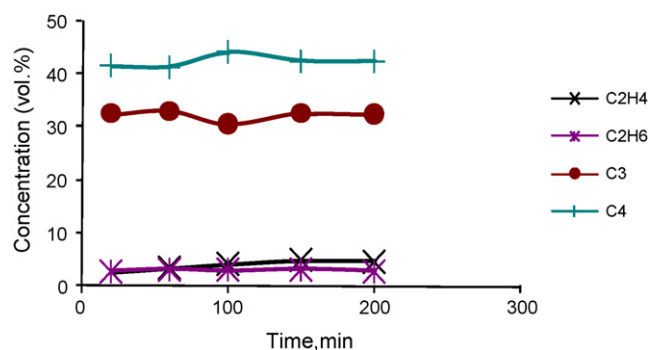


Fig. 4. Gaseous products distribution of ethanol conversion over HZSM-5(I) Si/Al = 90 ($WHSV = 10 \text{ h}^{-1}$, $T = 400 \text{ }^\circ\text{C}$, $P = 1$ atm).

was practically constant whereas volumetric concentration of C_3 was initially more than that of C_4 over HZSM-5(I) Si/Al = 30.

Promoting can have a significant effect on the properties of zeolites. In ZSM-5, cation promoters can partially occupy ion exchange sites, be located in channels and on the external surface as clusters or phases, respectively.

Mixing HZSM-5(I) Si/Al = 50 with Ga_2O_3 had a significant change on the catalyst structure, the pore volume increased from 0.11 to $0.15 \text{ cm}^3/\text{g}$. This increase in size is likely connected with the crushing of window pores that were earlier inaccessible before milling. Although there was no noticeable effect on the liquid hydrocarbon yields, after regeneration, the aromatic content decreased while that of olefins increased (Table 4). The gaseous product composition was similar to that obtained on the non-promoted catalyst, yet regeneration significantly reduced the aromatic concentration in the liquid fraction. After 4 h of reaction at atmospheric pressure there was an increase in the C_3 hydrocarbons when compared to that obtained over the non-promoted catalyst and ethylene concentration decreased by 15% when compared to that obtained over the fresh catalyst. The addition of gallium oxide thence increased the catalyst life and the yield of the propane–propylene fraction on the fresh catalyst.

Mechanical addition of iron oxide (1:1 by weight, Fe_2O_3 – desulfurization catalyst ironite sponge) to HZSM-5(I) Si/Al = 50 was observed to reduce the degree of crystallization, it was also observed that after the first regeneration there was a slight increase in the liquid product yield and a reduction in the aromatic hydrocarbons. Instantaneous concentration of ethylene in the gaseous phase after 4 h reduced to 14 vol.% as against 25% over the pure HZSM-5(I) Si/Al = 50. Metal iron is a well known catalyst of the Fis-

Table 4

Product distribution of ethanol conversion over HZSM-5(I) Si/Al = 50, promoted with 5% Ga_2O_3 (reaction time 2 h, $WHSV = 10 \text{ h}^{-1}$, $T = 400 \text{ }^\circ\text{C}$), wt.%.

Component	Fresh catalyst, $P = 3$ atm	Regenerated once, $P = 3$ atm	Regenerated twice, $P = 1$ atm
Methane	0.66	0.06	0.05
Ethane	1.01	4.42	4.28
Ethylene	3.12	1.24	0.91
Propane–propylene	35.40	21.30	21.94
C_4 -fraction	26.52	31.95	33.03
C_5 – γ -fraction	9.18	18.43	18.17
Benzene	1.66	0.75	0.71
C_8 –fraction	0.71	2.83	2.43
Toluene	7.08	4.38	4.49
Ethylbenzene	0.97	4.40	4.46
<i>m,p</i> -Xylene	5.37	1.14	1.32
<i>o</i> -Xylene	1.55	0.95	1.04
Methylethylbenzene	2.03	4.34	3.27
Other benzenes	2.24	2.33	1.77
Napthalenes	0.69	0.02	1.70
Total liquid fraction	24.16	27.15	26.81
Aromatics from the liquid fraction	93.19	75.69	78.08

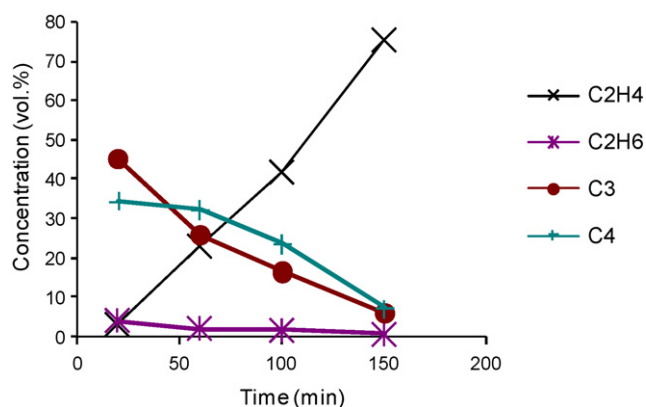


Fig. 5. Gaseous products distribution of ethanol conversion over HZSM-5(I) Si/Al=50+2% ZrO₂ (WHSV=10 h⁻¹, T=400 °C, P=1 atm).

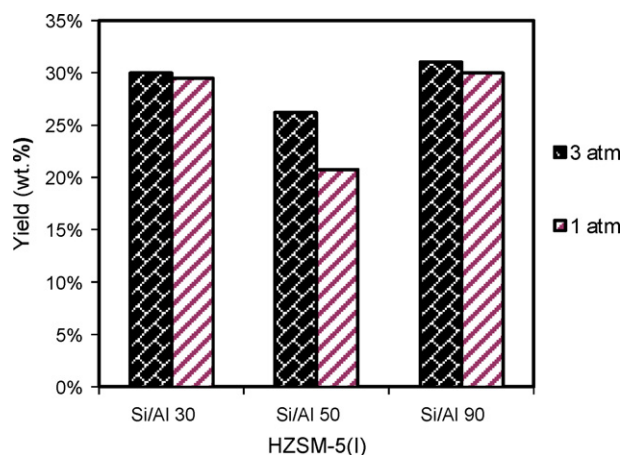


Fig. 6. Yield of liquid hydrocarbons of ethanol conversion over HZSM-5(I) (WHSV 10 h⁻¹, T=400 °C, reaction time 4 h).

cher Tropsch process, under similar reaction conditions; it should be expected to result in a significant increase in the quantity of methane produced in the gaseous phase and enhance the appearance of saturated aliphatic hydrocarbons. However, these changes were not observed, on the other hand, the concentration of methane even reduced from 0.2% to 0.1%. As a result, we suggest that iron oxide was not reduced as the reaction progressed and its mechanical addition affected catalyst regeneration positively. Similar results were obtained for the HZSM-5(I) Si/Al=30+5% Ga₂O₃.

Impregnating HZSM-5(I) Si/Al=50 with zirconium oxide resulted in a significant reduction in the liquid yield and the catalyst practically lost its activity for ethylene oligomerization after 4 h of ethanol conversion. The concentration of ethylene in the gaseous product was nearly 75% after 2 h of reaction (Fig. 5).

Ethylene (99%) was the main product obtained at 400 °C and 3 atm on HZSM-5(I) Si/Al=50 impregnated with 2% iron salt. This may be connected with the formation of iron silicate within the zeolite structure, which is inactive in the ethylene oligomerization process. The high concentration of ethylene after impregnation should be connected with the blockage of oligomerization active centers within the zeolite structure.

The yield of liquid hydrocarbons for different HZSM-5(I) is shown on Fig. 6. A clear minimum is observed in the case of the catalyst with Si/Al=50. In this case, on the average, 2 atoms of aluminum are available in each elementary zeolite cell, and as a result 2 acidic centers (for Si/Al=90–1, and for Si/Al=30–3 atoms). Heating Bronsted centers to about 400–500 °C results in dehydroxylation and formation of Lewis centers [11]. A Lewis center is formed from

two Bronsted centers [12–14]. Thus in cases of 1 and 3 atoms there are Bronsted sites which do not take part in the formation of Lewis sites. We therefore suggest that the presence of Bronsted sites that did not take part in the formation of Lewis sites favoured a better yield for liquid hydrocarbons. Despite HZSM-5 Si/Al=50 showing the lowest liquid yield, it is suggested that Lewis sites formed in this case favoured a better liquid yield at a pressure of 3 atm than 1 atm as earlier shown in Table 3.

A comparison of the initial concentration of C₃ fraction in the gaseous products of ethanol conversion over the HZSM-5(I) catalyst with different Si/Al showed that this fraction passes through a maximum. The highest concentration of propane-propylene fraction –64 vol.% was observed when the Si/Al=50 whereas for HZSM-5(I) 30 and HZSM-5(I) 90 it was 52.0 vol.% and 45 vol.%, respectively. A similar trend was noticed for ethylene after 4 h in the gaseous phase: 15 vol.%-HZSM-5(I) Si/Al=30, 25 vol.%-HZSM-5(I) Si/Al=50 3 vol.%-HZSM-5(I) Si/Al=90, implying that Si/Al=50 had the lowest oligomerization activity. It is interesting to note that the total volumetric concentration of C₃ and C₄ fractions in the reaction products remained practically unchanged with increase in the Si/Al ratio whereas an increase in pressure led to a relative increase in the concentration of propane/propylene.

4. Conclusions

From the research carried out, it was shown that HZSM-5(I) had the highest selectivity for liquid products and was active in ethylene oligomerization. Mechanical addition of gallium oxide to HZSM-5(I) Si/Al=50 affected the zeolite structure and increased the catalyst life without the formation of much ethylene. Impregnation of zirconium oxide resulted in a quick loss of catalyst selectivity for liquid hydrocarbons. It was shown that in the HZSM-5(I) catalysts with different Si/Al ratio, the better selectivity for liquid hydrocarbons was obtained over catalysts with 1 or 3 atoms of aluminum in elementary zeolite cells. Where there were 2 aluminum atoms per elementary cell, there was loss in activity.

References

- [1] V.V. Volkov, A.G. Fadeev, V.C. Kyjnimskii, O.I. Buzin, M.V. Safikov, F.A. Yandiev, I.I. Moiseev, Ecologically clean fuels from biomass, *Russ. J. Chem.* 47 (2003) 71–82.
- [2] U. Tsao, J.W. Reilly, Dehydrate ethanol to ethylene, *Hydrocarbon Process.* (February) (1978) 133–136.
- [3] V.F. Tretyakov, T.N. Burdeinaya, Motor fuels from fossil fuels, *Russ. J. Chem.* 47 (2003) 48–52.
- [4] O. Winter, M.T. Eng. Make ethylene from ethanol, *Hydrocarbon Process.* (November) (1976) 125–133.
- [5] C.B. Phillips, R. Datta, Production of ethylene from hydrous ethanol on H-ZSM-5 under mild conditions, *Ind. Eng. Chem. Res.* 36 (1997) 4466–4475.
- [6] W.R. Moser, W. Thompson, Ch. Chiang, H. Tong, Silicon-rich HZSM-5 catalyzed conversion of aqueous ethanol to ethylene, *J. Catal.* 117 (1989) 19–32.
- [7] A.T. Aguayo, A.G. Gayubo, A.M. Tarrío, A. Atutxa, J. Bilbao, Study of operating variables in the transformation of aqueous ethanol into hydrocarbons on an HZSM-5 zeolite, *J. Chem. Tech. Biotechnol.* 77 (2002) 211–216.
- [8] W.M. Meier, D.H. Olson, Atlas of Zeolite Structure Types, Structure Commission of International Zeolite Association, Pittsburgh, PA, 1978.
- [9] Y.I. Makarfi, M.S. Yakimova, L.M. Koval, V.I. Erofeev, R.M. Talishinski, A.S. Lermontov, V.F. Tretjakov, Combined conversion of ethanol and benzene on HZSM-5 industrial catalysts, in: *Alternative Sources of Chemical Feedstock and Fuel*, Ufa, Republic of Bashkiriya, May, 2008, pp. 46–47.
- [10] Y.I. Makarfi, The potentials of bio-energy in the Nigerian Energy Sector, in: *Proceedings of the 1st National Engineering Technology Conference (NETec2008)*, Zaria, April, 2008, pp. 21–24.
- [11] O. Krilov, *Heterogeneous Catalysis*, Akademkniga, Moscow, 2004.
- [12] J.D. McMillan, Bioethanol production: status and prospects, *Renewable Energy* 10 (1997) 295–302.
- [13] O.A. Anunziata, O.A. Orío, E.R. Herrero, A.F. Lopez, C.F. Perez, A.R. Suarez, Conversion of fermentation products to aromatic hydrocarbons over zeolite-type HZSM-5 in one step, *Appl. Catal.* 15 (1985) 235–245.
- [14] A.K. Talukdar, K.G. Bhattacharyya, S. Silvasanker, HZSM-5 catalysed conversion of aqueous ethanol to hydrocarbons, *Appl. Catal.* 148 (1997) 357–371.