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THE CONVERSION OF ETHANOL ON THE HZSM-5 ZEOLITE MODIFIED WITH LANTHANUM

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The conversion of ethanol to hydrocarbons in the presence of lanthanum-modified ZSM-5 zeolite in the temperature range 300⁰ – 450⁰C at flow-type atmospheric pressure was studied and it was shown that the modification of ZSM-5 zeolite and imposed temperature affect the distribution of ethanol conversion products. Modification of HZSM-5 zeolite with lanthanum plays an important role in increasing the yield of isoparaffin hydrocarbons, as well as has a substantial impact on the quality and octane number of the catalyst. The catalyst obtained from the conversion of ethanol at 300⁰ – 350⁰C complies with the Euro-5 standard for the content of benzene (<1.0%), aromatic (<30%) and olefin (<2.0%) hydrocarbons.

Keywords: *ethanol, isomerization, cracking, aromatization, hydrocarbons, zeolite, ZSM-5, conversion.*

doi:

Introduction

Due to the growing consumption of motor fuels and the severe environmental requirements, an intensive search is conducted for alternatives of traditional hydrocarbon raw materials. One of the available alternative sources of raw materials is bioethanol. Bioethanol is one of the raw materials obtained by biomass fermentation [1, 2]. The implementation of direct conversion of fermentative mixtures and ethanol hydrocarbons is possible on catalysts based on ZSM-5 [3–5]. The ZSM-5 zeolite is a three-dimensional structure and has two different channels with ten-rings. In its structure, an alternating zigzag channel 0.53×0.56 nanometer is connected with straight channels 0.51×0.55 nanometer [6], which prevents the formation of hydrocarbons with the number of carbon atoms in a molecule larger than 12, thereby providing a high selectivity of the process of converting methanol and ethanol into hydrocarbons in the gasoline series [7, 8]. When ethanol is converted to zeolite with structure ZSM-5, aliphatic and aromatic hydrocarbons of various structures are formed. In the reaction of ethanol conversion, strong acid centers are responsible for the process of formation of aromatic hydrocarbons, and the main intermediate of the reaction is ethylene [5, 9, 10].

Studies of the influence of pressure, temperature and volumetric velocity of ethanol

flow [11] showed that in the flow reactor at a volumetric speed of 2.4 h⁻¹ the largest outputs of the liquid hydrocarbon fraction (70%) are reached by the temperature of 350⁰C. The ratio of aromatic products is 45–50%.

Modification of zeolite ZSM-5 Mn or Zn results in the production of selective dehydration of ethanol into ethylene [12].

The authors [13] proposed modification of zeolite by gallium oxide. Modification of ZSM-5 by gallium oxide, without reducing the number of Lewis acid centers, significantly reduces the number of Bronsted centers of catalyst, as a result of which the selectivity of liquid-hydrogen increases.

Introduction to the Na- ZSM-5 catalyst of copper and cobalt [14] leads to the production of diethyl ether, acetaldehyde, ethylene and carbon oxides. These catalysts, obtained by ion exchange method, are not suitable for the liquid hydrocarbon fraction from ethanol.

Additives of some metals are able to change the ratio of aromatic aliphatic hydrocarbons. The addition of Cr or Ni leads to an increase in the output aromatic hydrocarbons, the introduction of Zr increases the output of isoparaffin hydrocarbons [14–16]. It was shown in [17–19] that the modification of zeolite of the ZSM-5 type with rare earth metals is accompanied by the formation of acid centers of

various strengths, as well as their fixation in the form of cations and oxides of inside zeolite cavities, and on the outer surface, which are involved in the isomerization, alkylation and flavoring.

In this regard, the purpose of this work was the influence of modifying the HZSM zeolite with lanthanum on selectivity in cracking reactions, isomerization and aromatization in the process of converting ethanol.

Experimental part

The protonic parent H-ZSM-5 zeolite was obtained by ion-exchange of the commercially available ZSM-5 (Nizhergorskiesorbenty, Russia, Si/Al=33) with NH_4Cl and following by calcinations² 5.0 g H-ZSM-5 was refluxed twice in 100 ml of 1.0M NH_4Cl solution for 6h and then calcined (in air) at 550°C for 4 h. Modification La/HZSM-5 zeolites were prepared in the aqueous lanthanum nitrate benzene solution. The impregnated powder was dried at 110°C for 4 h and then calcined at 500°C for 4h in air to obtain Ni/H-ZSM-5, and reduced with hydrogen at 380°C to obtain La/H-ZSM-5 for 2 hours, to obtain a catalyst of 1% Ni/H-ZSM-5. Prior to the use as catalysts zeolites were granulated by pressing without any filler or binder under maximum pressure of $2.5 \cdot 10^7$ Pa, and sieved to obtain particles with a diameter of 0.2–0.3 mm.

XRD pattern of the catalyst was collected by powder X-Ray diffractometer with Cu K_α radiation ($\lambda=0.15406$ nm) operated at 40 kV and 30. Scanning 2θ range from 10 to 80° with a scanning step length of 0.0167°.

The catalytic experiments were carried out in a fixed bed: continuous down flow tubular quartz micro-reactor (1.0 cm ID and 5m long) was placed inside a microprocessor controlled furnace. In a typical run, about 2.0 g of catalyst was charge into the reactor and the reaction was carried out at atmospheric pressure in the temperature range 300–450°C with feeding of 1 h⁻¹ volumerate.

The products were analyzed in a gas chromatograph Agilent HP with 100m·250 μm capillary column using a flame ionization detector (FID). The analysis was performed in

the temperature programming mode from 50°C to 250°C with a heating rate of 10°C per minute. The results of gas chromatographic analysis were calculated selectivity and product yield.

Results and discussion

Figure 1 shows XRD patterns of La/HZSM-5 and HZSM-5 as reference. Characteristic diffraction peaks of HZSM-5 ($2\theta=7.8, 8.7, 23.0, 23.8, 24.2^\circ$) were found from these La/HZSM-5 catalysts. On the other hand, the new peaks presented at $2\theta=23.2^\circ$ and 23.6° , were detected from La/HZSM-5 comparing with the parent HZSM-5. On the other hand, no diffraction peaks belonging to La and La oxides were detected from these catalysts, indicating that La species might highly disperse on HZSM-5 surface.

Fig. 1. X-ray diffraction patterns of HZSM-5 and La-HZSM-5 zeolite samples.

From the data of Table 1, it is clear that the distribution of products when converting ethanol to HZSM-5 is significantly dependent on the reaction temperature. As the temperature increases, the output of alkenes decreases, and as a result, the output of propane of aromatic hydrocarbons increases. At a temperature of 300°C, the main part of the product reaction is propane-11.3 wt.%, isoalkanes- $\text{C}_4\text{--C}_6$ -12.4 wt.% and aromatic hydrocarbons $\text{C}_6\text{--C}_8$ -10.2 wt.%. With an increase in temperature from 300°C to 450°C, the output of ethylene decreased from 5.8 wt% to 0.6 wt% and the content of the aromatic fraction $\text{C}_6\text{--C}_8$ from 10.2 wt.% to 18.2 wt.% and the heavy aromatic fraction $\text{C}_9\text{--C}_{14}$ from 2.1 wt% to 8.7 wt %.

Table 1. Composition of ethanol conversion products on HZSM-5

Products	Product content, wt%			
	300 ⁰ C	350 ⁰ C	400 ⁰ C	450 ⁰ C
H ₂	–	–	0.1	0.1
C ₁ –C ₂	0.1	0.4	1.6	2.7
C ₂ H ₅ OH	1.9	1.4	–	–
C ₂ H ₄	4.7	5.8	1.3	0.6
C ₃ H ₈	11.3	12.6	15.4	17.0
<i>n</i> -C ₄ –C ₅	0.6	0.8	0.7	0.6
<i>n</i> -C ₆ H ₁₄	0.7	0.2	0.1	–
<i>iso</i> -C ₄ –C ₆	12.4	10.7	9.3	5.3
<i>iso</i> -C ₇ –C ₁₄	1.4	1.2	1.0	0.4
<i>n</i> -C ₇ –C ₁₄	0.5	0.3	0.2	0.1
EthylenesC ₄ –C ₆	2.6	1.2	0.9	0.3
EthylenesC ₇ –C ₁₄	1.1	0.4	0.3	0.3
ARU-C ₆ –C ₈	10.2	13.8	15.4	18.2
ARU-C ₉ –C ₁₄	2.1	3.6	5.5	8.7
Naphthens C ₅ –C ₆	0.1	0.2	0.3	0.1
Naphthens C ₇ –C ₁₄	0.2	0.3	0.3	0.4
H ₂ O	50.1	47.1	47.6	45.2

Fig. 2. The dependence of the selectivity for the reactions of Sk, Si, Sa on temperature on the HZSM-5 catalyst.

Figure 2 shows the selectivity dependence on reactions of isomerization, cracking and aromatization at various temperatures. It can be seen that in the temperature range of 350⁰–450⁰C in the presence of H-ZSM-5 selectivity in the cracking and aromatization is higher than selectivity in the reaction of isomerization. At a lower temperature (300⁰C), the selectivity in isomerization (27.6%) is slightly higher than aromatization selectivity (24.6%). The increase in reaction temperature to 450⁰C leads to a sharp increase in selectivity in aromatization (49.1%).

Thus, in the temperature range of 350⁰–450⁰C, the HZSM-5 has a high cracking and aromatizing ability.

Table 2 shows that the introduction of 1.0 wt. % La in HZSM-5 changes the ratio of isoparaffin and aromatic hydrocarbons. The ad-

dition of lanthanum to zeolite leads to a significant increase in the output of isoparaffin products and a decrease in the output of cracking products and aromatic hydrocarbons. At the modified catalyst in temperature range 300⁰C – 330⁰C there is an increase in the output of ethylene. The maximum output of isoparaffin hydrocarbons C₄–C₆ and C₇–C₁₄ is reached at 350C and is 17.4 wt.% and 3.7 wt.% respectively. Significant growth in the output of aromatic hydrocarbons is observed in the temperature range of 400–450⁰C.

The figure shows the dependence of selectivity on reactions of isomerization, cracking and aromatization when converting ethanol on a modified catalyst. It can be seen that the increase in temperature from 300⁰C to 350⁰C results in an increase in selectivity in the reaction of isomerization from 35.2% to 41.3%.

Table 2. Composition of ethanol conversion products on LaHZSM-5

Products	Product content, wt %				
	300 ⁰ C	330 ⁰ C	350 ⁰ C	400 ⁰ C	450 ⁰ C
C ₁ -C ₂	–	0.7	1.2	2.1	3.8
C ₂ H ₅ OH	1.9	0.9	0.2	–	–
C ₂ H ₄	2.5	1.6	1.0	0.6	0.8
C ₃ H ₈	8.3	9.8	11.4	13.8	15.9
n-C ₄ -C ₅	1.9	2.4	0.6	0.7	0.9
n-C ₆ H ₁₄	0.8	0.1	0.1	0.1	0.1
iso-C ₄ -C ₆	14.8	15.9	17.4	14.1	10.4
iso-C ₇ -C ₁₄	2.7	3.4	3.7	2.3	1.0
n-C ₇ -C ₁₄	0.8	0.3	0.2	0.1	0.1
Alkenes C ₄ -C ₆	3.8	1.9	0.9	0.3	–
Alkenes C ₇ -C ₁₄	1.9	0.9	0.4	0.2	–
ARU-C ₆ -C ₈	4.1	6.8	9.6	12.8	16.4
ARU-C ₉ -C ₁₄	3.6	3.8	3.3	2.1	1.1
Naphthens C ₅ -C ₆	0.8	1.1	0.9	0.1	0.1
Naphthens C ₇ -C ₁₄	1.9	1.7	1.2	0.4	0.3
H ₂ O	50.4	48.8	48.9	49.7	49.1

Fig. 3. The dependence of the selectivity for S_k, S_i, S_a reactions on the temperature on the catalyst. **Fig. 4.** Temperature dependence of the octane number of catalysts obtained on a modified zeolite. **Fig. 5.** Temperature dependence of aromatic hydrocarbons.

Further increase in temperature to 450°C results in a decrease in selectivity of isomerization up to 22.4%. A comparison of the data obtained with the results of [18, 20] shows that increase alkyl radical length in alcohols leads to concomitant increase in the yield of isoparaffinic and aromatic hydrocarbons.

In the whole temperature range under study, with the temperature increase, selectivity in cracking reactions (from 16.7% to 38.7%) and aromatization (from 15.5% to 34.4%) increases.

Thus, modification of the HZSM-5 zeolite and temperature substantially affects the distribution of ethanol products. Modification of HZSM-5 with lanthanum plays a decisive role in the increase of the output of isoparaffin hydrocarbons, which favorably affects the quality of catalysis.

From Figure 4, it is clear that with the increase in temperature, the octane number of the received catalyst increases due to the increase in the content of isoparaffin and aromatic hydrocarbons.

The best hydrocarbon composition on the modified sample is achieved at 350°C: isoparaffin – 21.1 wt. %, aromatic – 12.9 wt. %.

From the data Figure 5 it is visible that in the temperature range 300–350°C the aromatic fraction C₆–C₈ practically does not contain benzene. At temperatures above 350°C, the output of benzene rises to 1.1 wt. %.

Thus, the catalyzate obtained during the conversion of ethanol at 350°C corresponds to the Euro-5 standard for the content of benzene (no more than 0.1 wt. %), isoparaffin and aromatic hydrocarbons.

Conclusion

The regularities of ethanol conversion on HZSM-5 zeolite modified with lanthanum have been established. The main processes occurring during the reactions are oligomerization, isomerization, cracking and aromatization.

Modification of HZSM-5 with lanthanum plays a decisive role in increasing the yield of isoparaffin hydrocarbons during ethanol conversion. The maximum yield of isoparaffin hy-

drocarbons C₄–C₆ and C₇–C₁₄ is achieved at 350°C and amounts to 17.4 wt%, respectively.

The aromatic fraction C₆–C₈ contains practically no benzene, and the resulting catalysis complies with the Euro-5 standard.

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КОНВЕРСИЯ ЭТАНОЛА НА ЦЕОЛИТЕ HZSM-5, МОДИФИЦИРОВАННОМ ЛАНТАНОМ

Б.А.Бабаева, С.Э.Мамедов

В интервале температур 300–450⁰C на проточной установке при атмосферном давлении проведено исследование превращения этанола в углеводороды на цеолите типа ZSM-5, модифицированном лантаном. Модифицирование цеолита ZSM-5 и температура процесса влияет на распределение продуктов превращения этанола. Модифицирование HZSM-5 лантаном, играет решающую роль в возрастании выход изопарафиновых углеводородов, что благоприятно влияет на качественный состав и октановое число катализата. Катализат, полученный при превращении этанола при 350⁰C соответствует стандарту Евро-5 по содержанию бензола (не более 1,09мас.%), ароматическим (не более 30%) и олефинам (не более 2.0%) углеводородом.

Ключевые слова: этанол, изомеризация, крекинг, ароматизация, ZSM-5, углеводороды, конверсия.

LANTANLA MODİFİKASIYA OLUNMUŞ HZSM-5 SEOLİT KATALİZATORUNDA ETANOLUN ÇEVİRİLMƏSİ

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Axın tipli atmosfer təzyiqə 300–450⁰C temperatur intervalında lantanla modifikasiya olunmuş ZSM-5 seolitinin iştirakında etanolun karbohidrogenlərə çevrilməsi öyrənmiş və göstərilmişdir ki, ZSM-5 seolitinin modifikasiya olunması və prosesin temperaturu etanolun çevrilmə məhsullarının paylanmasına təsir edir. Lantanla HZSM-5 seolitinin modifikasiyası isoparafin karbohidrogenlərin çıxımının artmasında mühüm rol oynamaqla yanaşı katalizatın keyfiyyət tərkibinə və oktan ədədinə əlverişli təsir edir. Etanolun 350⁰C-də çevrilməsindən alınmış katalizat benzolun (<1.0%), aromatik (<30%) və olefin (<2.0%) karbohidrogenlərin miqdarına görə "Avro-5" standartına uyğun gəlir.

Açar sözlər: etanol, izomerləşmə, krekinq, aromatikləşmə, ZSM-5, karbohidrogenlər, çevrilmə.