QO‘QON DAVLAT
PEDAGOGIKA INSTITUTI
ILMIY XABARLARI
(2025-yil 2-son)

TABIIY FANLAR

NATURAL SCIENCES

CATALYTIC AROMAMENTATION OF HEXANE IN HIGH-SILICA ZEOLITES OF DIFFERENT COMPOSITIONS

Khudoyor Rahmatov
ORCID ID 0000-0003-4976-5541
Associate Professor, Candidate of Chemical Sciences, Karshi Engineering-Economics Institute, 180100, Republic of Uzbekistan, city of Karshi, Mustakillik Street, 225., E-mail: zavod.lab@mail.ru

Shokhista Djuraeva
ORCID ID 0009-0004-1302-1326
Associate Professor, Doctor of Philosophy in Chemistry (PhD), Karshi Engineering-Economics Institute, 180100, Republic of Uzbekistan,City of Karshi, Mustakillik Street, 225.

Eshdavlatova Hosila
ORCID ID 0009-0000-0293-3478
A student Karshi Engineering-Economics Institute, 180100, Republic of Uzbekistan, city of Karshi, Mustakillik Street, 225.

Abstract. In this article, the catalytic properties of zeolites used for the catalytic conversion of hexane with a linear structure to aromatic hydrocarbons are studied, and the methods of preparation of catalysts of some metallic elements high silica zeolite analogues of mesoporous high-silicon aluminosilicates with high selectivity for the conversion of saturated hydrocarbons are presented, H-High silica zeolite -40 type containing acid and high zinc. comparison of the initial rate of hexane conversion in silica mesoporous zeolites and it was found that the introduction of zinc causes a decrease in the catalyst activity. The contribution of metal-containing centers has been reported to decrease the yield of low molecular weight saturated hydrocarbons and to increase the yield of hydrogen and aromatic hydrocarbons. It was found that aromatic hydrocarbons generate 4 hydrogen molecules per molecule on bifunctional catalysts, while only 2 molecules are generated on acidic high-silica mesoporous zeolites.

Purpose of work: It consists in studying the principles of obtaining high-octane motor fuel by catalytic aromatization of hexane in silicon zeolites of different compositions and the kinetics of gas condensate conversion in high silicon mesoporous zeolites.

Keywords: zinc, catalyst, heterogeneous catalysis, n-hexane, conversion, saturated hydrocarbons, naphthene, unsaturated, aromatization, aromatic hydrocarbons, toluene, acid, trimethylbenzene, mesoporous, aluminosilicate, branching, aromatic hydrocarbons, toluene, acid, trimethylbenzene, hydrodealkylation.

INTRODUCTION

Catalytic reforming is one of the main processes of petroleum refining, which allows obtaining the high-octane component of motor fuel and individual aromatic hydrocarbons, and is a source of cheap hydrogen [1-12].

The international market offers the latest catalytic technologies to meet the recently established stringent requirements of a number of countries: ultra-deep hydrotreatment [13-17], catalytic isomerization and dehydrogenation process [18], isoselectoform [19], and reforming without hydrogen circulation [20].

High catalytic activity, regular structure, and ion exchange capacity make zeolites used for the catalytic conversion of linear hexane to aromatic hydrocarbons and zeolite-containing catalysts used for the catalytic conversion of linear hexane to aromatic hydrocarbons unique objects for the study of heterogeneous catalysis. The pores of zeolites used for the catalytic conversion of linearly structured hexane to aromatic hydrocarbons are highly crystalline materials, so their internal surface is defined by a system of regularly repeating pores in three-dimensional space. The variety of catalytic properties of zeolites used for the catalytic conversion of hexane with a linear structure into aromatic hydrocarbons is primarily explained by the presence of several different types of crystal frameworks and the possibility of modifying the specific structural properties of the frameworks by controlled ion exchange methods.

Zeolites, which are used for the catalytic conversion of linear hexane into aromatic hydrocarbons in the industrial processes of petrochemical and oil refining, are widely used as catalysts mainly in hydrocarbon conversion reactions.

The aromatization reaction of low molecular weight alkanes has been intensively studied, especially in the last 15-20 years, using mesoporous high-silica aluminosilicate-type hydrogen forms of zeolites (НЦВК, НЦВМ, HZSM-11) used for the catalytic conversion of linear hexane to aromatic hydrocarbons [24-26]. The selectivity of the conversion of saturated hydrocarbons increases significantly when mesoporous high-silicon aluminosilicates are modified with certain elements, their cations or oxides: Cu, Zn, Cd, РЗЭ, Al, Ga, In, Sn, V, Cr, Mo, Mn, Co, Ni, Pd, Pt [27]. The most effective are Zn, Cd, Ga and Pt. Function of modifiers [28-31] consists of a sharp increase in the Lewis acidity of the catalyst, and functionally [32-34] consists in the ability to suppress the cracking reaction, as well as to activate initially saturated hydrocarbon molecules.

Today, the most promising work is related to the study of the activity of selected catalysts for the catalytic aromatization of hexane with a linear structure based on mesoporous high-silicon zeolites and obtaining aromatic hydrocarbons in the upgrading of petroleum raw materials. [34-54].

EXPERIMENTAL

The strength of the acidic centers of the catalyst was evaluated by the maximum temperature in the thermal desorption curve, and their concentration was expressed in μmol per 1 g of catalyst desorbed at the moment of fixation of the desorption peaks and was determined by the amount of ammonia. The quality of the obtained samples was controlled by IK spectroscopy and X-ray phase analysis. The IK spectra of the studied high-silica zeolites were recorded in the 2000-400 cm^{-1} range on tablets containing KBr (1.2 mg high silica zeolite for 300 mg KBr) in air on a Nicolet 5700 IR-Fourier spectrometer. The specific surface area of the catalyst and the parameters of its porous structure were determined by the method of low-temperature nitrogen adsorption using an automatic gas adsorption analyzer Sorbtometer M (Russia).

The acidity properties of the obtained samples were studied by the temperature programmed desorption method of ammonia. Ammonia was adsorbed on the high purity sample at 100 °C.

Ammonia was desorbed from the surface of high-silica zeolites in a linear heating mode at a rate of 10 degrees/min. The strength of the acid centers of the catalysts was evaluated by the maximum temperature in the thermal desorption curves, and their concentration was determined by the amount of desorbed ammonia when the desorption peaks were fixed and expressed in μ/mol per 1 g of catalyst. X-ray phase analysis was performed on a DISCO-VER D8 diffractometer (Bruker) using monochrome Cu Ka radiation and a Lynx-Eye detector. Scanning in the angular range 2υ = 5-80 degrees, each angle is 0.02 degrees, accumulation at one point - 3 s. The specific surface area of the catalyst sample was calculated using the Brunauer, Emmett, Teller multipoint method. Catalyst volume and pore size were determined from adsorption and desorption isotherms at a relative pressure of $P/P_0 = 0.99$ using the Barett-Joyner-Halenda model. Qualitative and quantitative analysis of gaseous and liquid products was carried out using Chromatek-Crystal 5000.2 chromatograph. BP-1 PONA capillary column (100 m x 0.25 mm x 0.5 μm) for liquid phase composition and GS-Gas-Pro capillary column (60 × 0.32 mm) for gas phase composition and corrosive S- II (4 m × 2 mm, 60/80) was carried out. The calculation of the conversion of raw materials and the selectivity of the formation of reaction products was carried out using the data of chromatographic analysis of the composition of raw materials of gas and liquid reaction products, as well as data on their quantitative yield.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Conversion of normal structure hexane. The efficiency and conversion dependence for different groups of products in the aromatization of normal structure-hexane with H-High silica zeolite-40, 2%Cu*8%Zn/H-High silica zeolite-40 and 8 % Zn/silicate catalysts are shown in Figures 1-3.

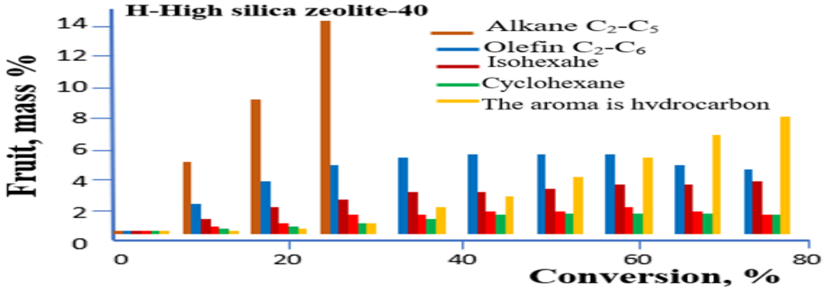


Figure 1. Dependence of the productivity of individual product groups on the degree of conversion of normal structured hexane in the synthesis of aromatic hydrocarbons in high-silica mesoporous zeolite with H-High silica zeolite-40 content.

As can be seen from Figure 1, in the synthesis of aromatic hydrocarbons in the high-silicon mesoporous zeolite with H-High silica zeolite -40, the conversion rate is 20-25% to alkanes, 25-60% to olefins, and finally to 60-80%, the main part of the finished product is olefin, isohexane and aromatic hydrocarbons.

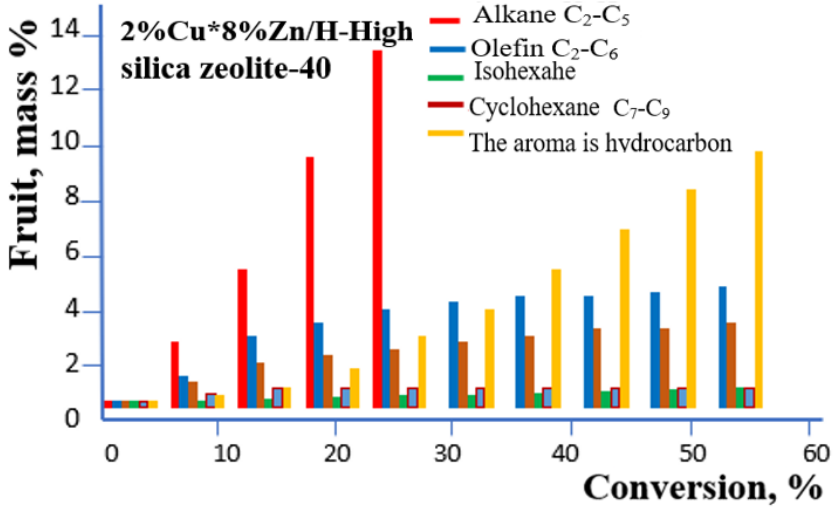


Figure 2. Dependence of the yield of individual product groups on the degree of conversion in the aromatization of hexane with a normal structure on a catalyst containing 2%Cu*8%Zn/H-High silica zeolite-40

As can be seen from Figure 2, in the synthesis of aromatic hydrocarbons in high-silicon mesoporous zeolite with 2%Cu*8%Zn/H-High silica zeolite-40, the conversion rate is 20-25% to alkanes, 25-30% to olefins, and finally to 30% of the finished product. the main part is olefin and aromatic hydrocarbons.

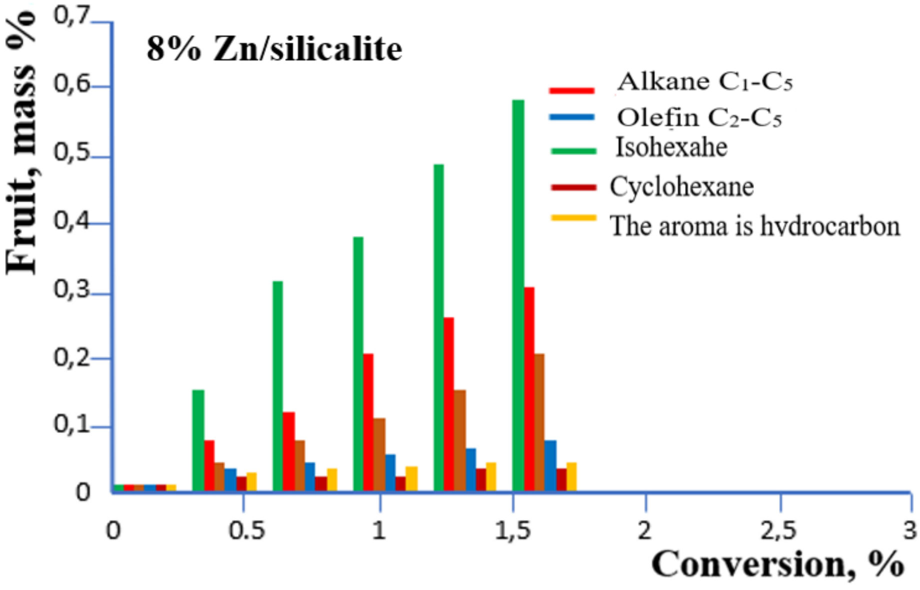


Figure 3. Dependence of the yield of individual product groups on the degree of conversion in the aromatization of hexane with a normal structure on a catalyst containing 8% Zn/silicalite

It can be seen from Figure 3 that in the aromatization of hexane with a normal structure on the 8%Zn/silicalite catalyst, regardless of the conversion level, the main part of the finished product is hexane and alkanes, and partly cyclohexanes.

As can be seen from the figures 1-3 above, the catalytic aromatization of hexane to obtain high-octane motor fuel in the catalyst containing 2%Cu*8%Zn/H-High silica zeolite-40 has a high efficiency of formation of aromatic hydrocarbons.

Similar relationships are observed for H-High silica zeolite-40 and 2%Cu*8%Zn/H- High silica zeolite-40 catalysts. In both catalysts, the final process products are C_2-C_5 saturated hydrocarbons and aromatic hydrocarbons. The yield/conversion curves for isoparaffins during normal structure-hexane conversion in H-High silica zeolite-40 and 2%Cu*8%Zn/H-High silica zeolite-40 are almost identical (Figure 4).

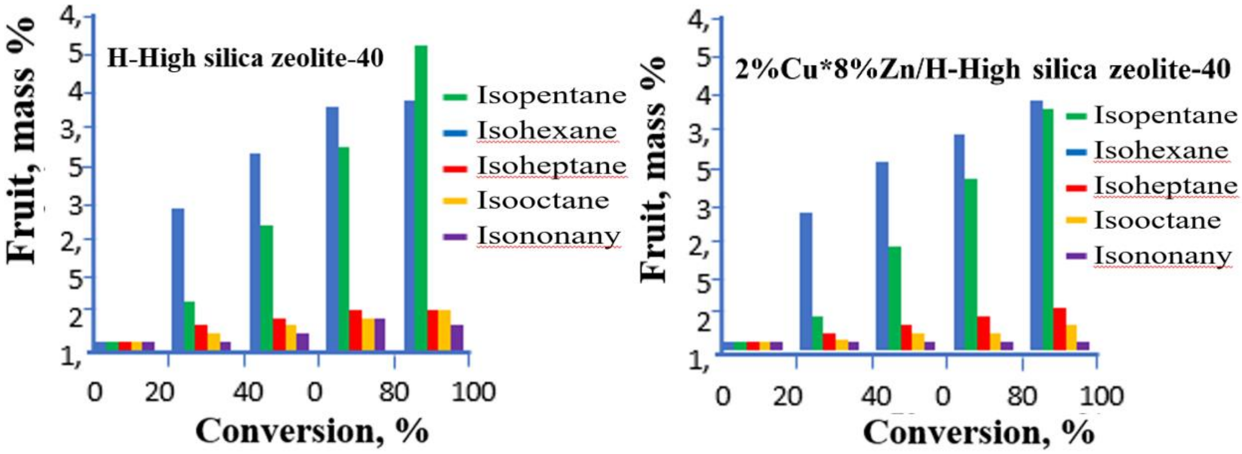


Figure 4. Dependence of conversion of normal structured hexane to isoparaffins on H-High silica zeolite-40 and 2%Cu*8%Zn/H-High silica zeolite-40 high silica mesoporous zeolite catalyst

As can be seen from Figure 4, the yield/conversion curves for isoparaffins during the conversion of normal structured hexane on the high-silica mesoporous zeolite catalyst with H-High silica zeolite-40 and 2%Cu*8%Zn/ H-High silica zeolite -40 are almost the same.

Effect of modification with zinc. As mentioned above, the performance/conversion dependence for H-High silica zeolite-40 and 2%Cu*8%Zn/ H-High silica zeolite -40 has the same characteristics. However, some differences can be detected in the performance/conversion curves for H-High silica zeolite-40 and 2%Cu*8%Zn/ H-High silica zeolite-40 on placement. For saturated hydrocarbons with C_2-C_5 content, the graphs match exactly. Since the latter is a product of the process of breaking hexane carbon-carbon bonds with a normal structure, it can be concluded that this process is carried out in both catalysts. This is also indicated by the matching of the initial part of the curves for hydrocarbons of the unsaturated ethylenic series with a composition of C_2-C_5. However, as the conversion increases, the yield of unsaturated ethylene series hydrocarbons in 2%Cu*8%Zn/H-High silica zeolite-40 is lower than that of H-High silica zeolite-40.

Analysis of the initial selectivity of conversion of normal structure hexane H-High silica zeolite-40, 2%Cu*8%Zn/H-High silica zeolite-40 and 8%Zn/silicate showed that the modification of high-silica mesoporous zeolite H-High silica zeolite-40 with zinc The contribution of process products and the increase in the percentage of products with the breaking of carbon-carbon bonds leads to a slight decrease in dehydrogenation and isomerization in the early stages of the process (Fig. 5). In 8%Zn/silicate, the main primary process is dehydrogenation.

As can be seen in Figure 5, the analysis of the initial selectivity of the normal structure hexane H-High silica zeolite-40, 2%Cu*8%Zn/ H-High silica zeolite-40 and 8%Zn/silicate conversion showed that H-High silica zeolite-40 is higher modification of silica mesoporous zeolite with zinc leads to a slight decrease in the contribution of process products and the percentage of products that go with the breaking of carbon-carbon bonds in the initial stages of the process.

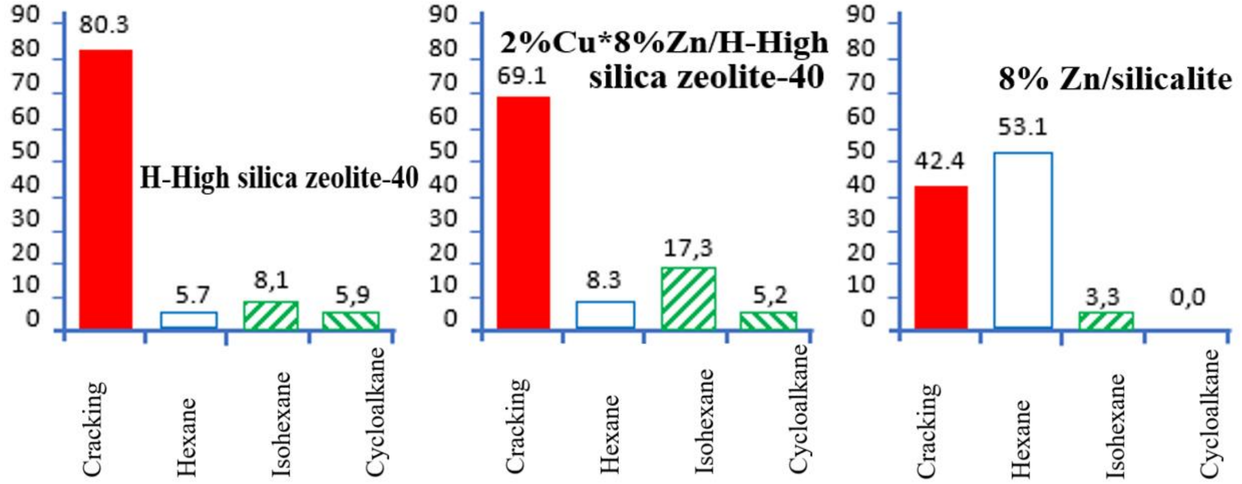


Figure 5. Initial selectivity (%) of normal structure hexane conversion in H-High silica zeolite-40 2%*8%Zn/H-High silica zeolite-40 and 8%Zn/silicates

Correlation between acidic and catalytic properties. Comparison of the initial rate of conversion of hexane with normal structure in H-High silica zeolite-40 acid and zinc-containing high-silica mesoporous zeolites (Fig. 6) showed that the introduction of zinc leads to a decrease in catalyst activity. This is related to the decrease in the acidity of high-silica mesoporous zeolite when modified with zinc.

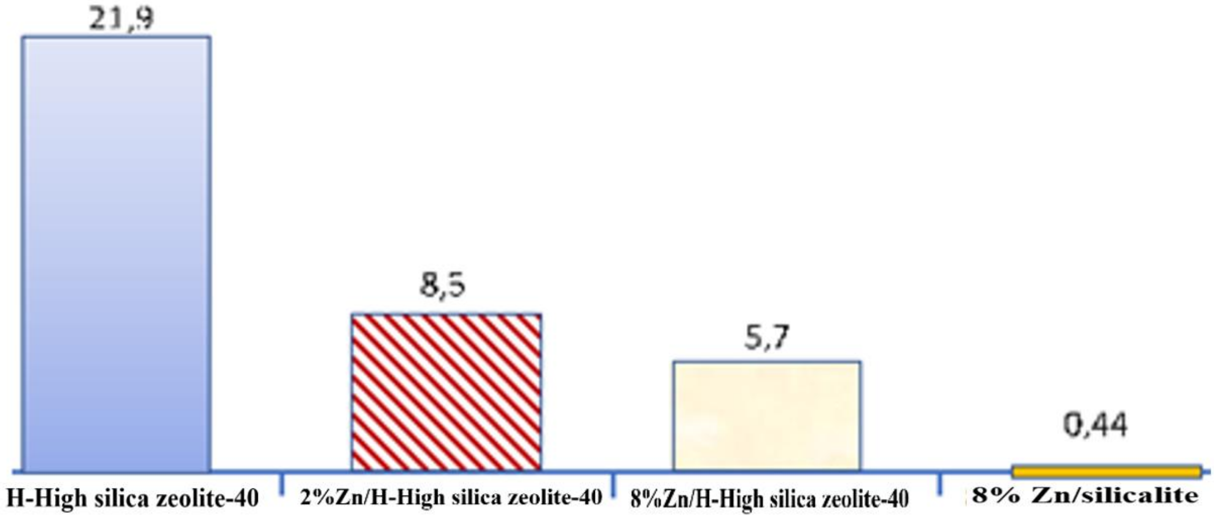
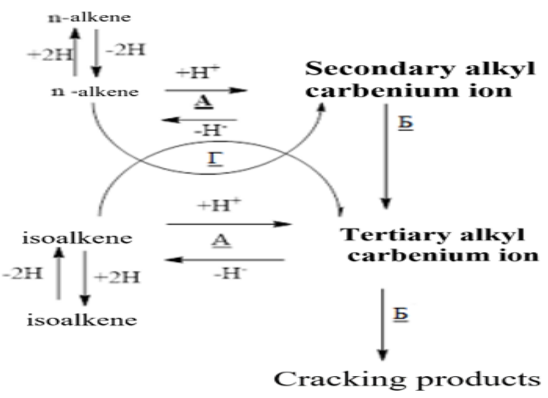
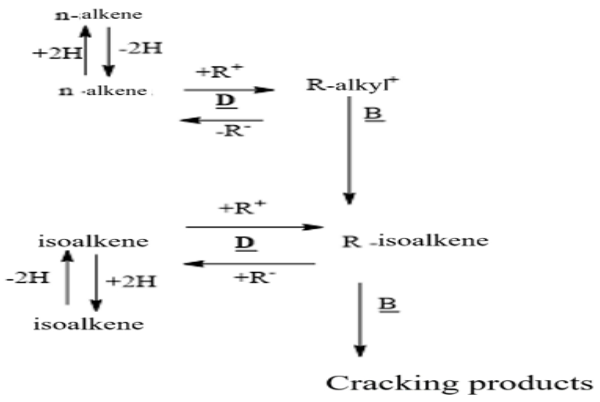


Figure 6. Propane initial conversion rates (g/g-s) in high silica zeolite-type acidic and Zn-containing high-silica mesoporous zeolites.

Figure 6 compares the initial rate of conversion of hexane with normal structure in high-silicon mesoporous zeolites containing H-High silica zeolite-40 acid and zinc, and it can be seen that the introduction of zinc leads to a decrease in catalyst activity. Therefore, it is not advisable to add zinc to high-silicon mesoporous zeolites.The mechanisms of the transformation of saturated hydrocarbons in acidic and metal-containing high-silica mesoporous zeolite catalysts have been repeatedly discussed in recent years, and the main attention has been focused on the initial stage of their transformation - that is, the activation of saturated hydrocarbons in high-silica mesoporous zeolites. This phase is still a controversial issue. In this regard, in this work, the activation mechanisms of saturated hydrocarbons are considered in more detail, and further details of their transformation are only briefly described.

Mechanism of aromatization in acidic high-silica mesoporous zeolites. In contrast to changes in acid catalysts, protonation of the primary carbynium ion in the acidic centers of metal-containing high-silica mesoporous zeolites occurs by protonation of the unsaturated ethylene series from hydrocarbons and dehydrogenation of saturated hydrocarbons. The main processes for the transformation of saturated hydrocarbons in metal-retaining high-silica mesoporous zeolites are shown in the scheme below.





A-Is the process of protonation and deprotonation in the acid centers of high silica mesoporous zeolite.

B-Is the rearrangement of the structure of the carbynium ion.

V-The process of carbene ion with breaking of carbon-carbon bonds.

G-Silicon or monohydrate sealifting acidified marmaladed learning adsorption and desorption.

D - alkylation-dealkylation process with adsorbed tertiary carbocations.

Acidic centers catalyze processes of oligomerization, carbon-carbon bond breaking, and cyclization. The contribution of metal-containing centers leads to a decrease in the yield of undesired lower molecular weight saturated hydrocarbons and an increase in the yield of hydrogen and aromatic hydrocarbons. An aromatic hydrocarbon generates 4 molecules of hydrogen per molecule on bifunctional catalysts, while only two molecules are generated on acidic high-silica mesoporous zeolites.

CONCLUSION

1.In contrast to propane, it was shown that the conversion of normal structured hexane in high-silica mesoporous zeolites containing Zn occurs via the chain carbenium ion mechanism.

2.Kinetic analysis of gas-condensate conversion in H-High silica zeolite-40 and 2%Cu*8%Zn/H-High silica zeolite-40 high-silica mesoporous zeolites showed that the intermediate formation of simple saturated hydrocarbons, isosaturated hydrocarbons and naphthenes through unsaturated ethylene series aromatic hydrocarbons hydrocarbons and lower molecular weight saturated hydrocarbons, in the following order: n-saturated hydrocarbons→naphthenes→isosaturated hydrocarbons; modification of high-silica mesoporous zeolite catalyst with zinc changes the initial conversion rate components and helps to increase the efficiency of aromatization processes.

REFERENCES

1. Кузьмина Р.И. Каталитический риформинг углеводородов / Кузьмина Р.И., Севостьянов В.П., Сидоров Г.М., Корякин В.А. – С.: Саратовский юридический институт МВД России, 2010. – 252 с.

2. Шехматова А.Д., Шайхутдинова Р.Р., Хаматшин А.Д., Валеева Г.М., Гатин Т.Р., Аксёнов К.Г., Столяров Д.П. Установка каталитического риформинга // Мировая наука: журнал. - 2020. - №8. – 41 с.

3. Технология переработки нефти. Первичная переработка нефти : учебники и учеб. пособия для студентов высших учебных заведений. В 2 ч. Ч. 1. / Под ред. Глаголевой О.Ф., Капустина В.М. – 1-е изд., перераб. и доп. – М.: Химия, 2006. – 400 с.

4. Хатмуллина, Д. Д. Катализаторы риформинга // Молодой ученый: журнал. — 2014. — № 1. — С. 136-138.

5. Пат. 59053 Российская Федерация. Установка для каталитического риформинга бензиновых фракций. / Фалькевич Г.С., Барильчук М.В., Ростанин Н.Н., Иняева Г.В.,

Беляев А.Ю., Виленский Л.М., Ростанина Е.Д. - Заявка № 2009127405/22 от 31.07.2006; опубл. 10.12.2006, Бюл № 16.

6. Михайло М.Н. Металл-цеолитные катализаторы с мезопористой системой для процесса селективного превращения метана в ароматические углеводороды : автореф. дис. ... канд. хим. наук / Михайло М.Н. – Москва, 2017. – 132 с.

7. Кузьмина, Р. И. Превращение углеводородов на никелевом катализаторе Ni/ЦВМ / Р. И. Кузьмина, М. Ю. Степанов // Современное общество: глобальные и региональные процессы : Материалы I международной научной конференции, Санкт-Петербург, 2017. – С. 22-23.

8. Ромаденкина С.Б. Превращение стабильного гидрогенизата на каталитических системах Pt/ЦВМ, Pr/ЦВМ / Ромаденкина С.Б. [и др.] // Известия Саратовского университета: журнал. – 2022. – № 4. – С. 398-404.

9. Иванов В. А., Ромаденкина С. Б. Превращение н-гексана в условиях каталитического риформинга // Modern Science. 2021. № 11-3. С. 30–36. ID: 47275556

10. Аниськова Т. В., Ромаденкина С. Б., Кузьмина Р. И. Превращение стабильного катализата установки каталитического риформинга на катализаторе R-98 // Известия Саратовского университета. Новая серия. Серия: Химия. Биология. Экология. 2017. Т. 17, вып. 4. С. 394–396. https://doi.org/10.18500/1816- 9775-2017-17-4-394-396

11. Белый А. С. Современное состояние, перспективы развития процесса и катализаторов риформинга бензиновых фракций нефти // Катализ в промышленности. 2014. № 5. С. 23. ID: 21997499

12. Пат. 2727887 РФ. Установка каталитического риформинга с непрерывной регенерацией катализатора / Лебедской-Тамбиев М. А., Калабин Д. А., Ермоленко А. Д., Шишкин С. Н., Яблоков А. С., Александров Д. С., Дьяченко К. В., Воронина Ю. В., Чулков К. С., Черненко А. А., Завьялова Н. Н., Ханова Н. Г. Опубл. 24.07.2020. Бюл. № 21.

13. Пат. 2677283 РФ. Способ получения биметаллических катализаторов с градиентной структурой на основе платины/ Алексенко А. А., Гутерман В. Е., Беленов С. В., Новомлинский И. Н., Меньщиков В. С. Опубл. 16.01.2019. Бюл. № 2.

14. Трегубенко В. Ю., Веретельников К. В., Белый А. С. Триметаллические катализаторы риформинга Pt-SnZr/γ-Al2O3 // Кинетика и катализ. 2019. Т. 60, № 5. С. 618–623. https://doi.org/10.1134/S0453881119040233 7. Романовский Б. В. Основы катализа : учебное пособие. М : БИНОМ. Лаборатория знаний, 2015. 172 с.

15. Георгиева Э. Ю., Михайлова М. Д., Мартынова А. В. Анализ эксплуатационных характеристик катализаторов риформинга // Инновационные научные исследования: теория, методология, практика : сборник статей XVII Международной научнопрактической конференции. Пенза : Наука и Просвещение, 2019. С. 189–191. ID: 37629159