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SELECTIVE HYDROGENATION OF BENZENE OVER RH-PROMOTED ZEOLITE CATALYSTS

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Abstract

Studied selective hydrogenation process of benzene over Rh- promoted zeolite catalysts. Developed methods of application modifying by active ingredients. Determine the effect of the rhodium content in the hydrogenation of benzene. By gas-liquid chromatography, the reaction products of various catalysts. The structure and morphology of synthesized modified carbon materials by electron microscopy.

Keywords: benzene, catalysts, hydrogenation, promotion, zeolite.

Introduction

Aromatic hydrocarbons have good performance characteristics (increase the octane number). However, due to environmental constraints aromatics content in today's regulated products. Technical Regulations of the Customs Union (Russia, Belarus and Kazakhstan), set requirements for different types of fuels in these countries. From 1 January 2013 all diesel fuel into circulation in the territory of the Customs Union, the indicators must be no lower than for Class 3 (analogous to Euro-3). Contain no more than 350 ppm of sulfur and less than 11 wt.% of polycyclic aromatic compounds, and have a cetane number of not less than 51 (for summer grades). An elevated level of aromatic hydrocarbons worsens environmental and technological properties of fuels: increases the tendency to carbon deposition, increased particulate emissions from the engine. In order to reduce the content of sulfur and aromatic compounds in the oil fractions are used, mainly, various hydrogenation processes: hydrotreating; hydroforming; hydrodearomatization [1].

At the heart of the process is hydrodearomatization hydrogenation reaction of aromatic hydrocarbons. In this work selected dearomatization optimal conditions based on the hydrogenation reaction of benzene to cyclohexane. Cycloalkanes attached to motor fuel high performance level and are of higher quality raw materials in the catalytic cracking process. They have a high degree of saturation, low filterability limit temperature, high strength and density. In the lubricating oil composition, they ensure a high viscosity index [2-4].

The hydrogenation reaction takes place at a bifunctional catalyst. The use of catalysts with a strong dehydrating ability, such as chromium oxide or platinum on non-acidic alumina, the cyclization mechanism is favored by a stepwise unsaturated compound. The catalyst based on zeolite, promoted by Rh operates under milder conditions and has greater selectivity for compounds with a terminal double bond than conventional systems based on cobalt and platinum [5-7].

It was found that the promoters have a strong influence on the yield of cyclohexane. On the Ru-Co-B / γ -Al₂O₃ catalyst and the yield is 34.8% of cyclohexane in the presence of ethylenediamine and ZnSO₄. Also used as promoter of La and Ce. Cyclohexane to yield Ru-La-B / ZrO₂ catalyst was 53%. Thus, the addition of La as a promoter, increased selectivity to cyclohexane [8-10].

The aim of this work is to develop catalysts for the hydrogenation of benzene and study the effect of the phase composition of the active phase of their catalytic properties.

Materials And Methods

The work investigated the hydroisomerization reaction of benzene comprising a stage of hydrogenation to cyclohexane (CH), followed by isomerization to methylcyclopentane (MCP), rhodium over carbon catalyst. As a carrier used as a pure zeolite, and mixtures thereof with Tonkerisskaya clay while their ratio was varied within wide limits. Rhodium deposited by impregnation of solutions of rhodium nitrate salts.

The qualitative compositions of the products obtained in the studied catalysts were analyzed by chromatography. The activity of the catalysts and determining their path ipso investigated on the original flow-type laboratory plant with a fixed bed of catalyst at conditions of temperature 250 - 500 °C and atmospheric pressure for rhodium catalysts, feed space velocity 1-4 h⁻¹.

Results And Discussion

Determined the elemental composition of the catalysts modified rhodium (Figure 1). Maximum catalytic activity and selectivity in the hydrogenation reaction of benzene at temperatures of 300-350 °C and 25 atm. exhibits a zeolite catalyst modified with rhodium. Very low catalytic activity of the catalyst manifested on the basis of aluminum oxide.

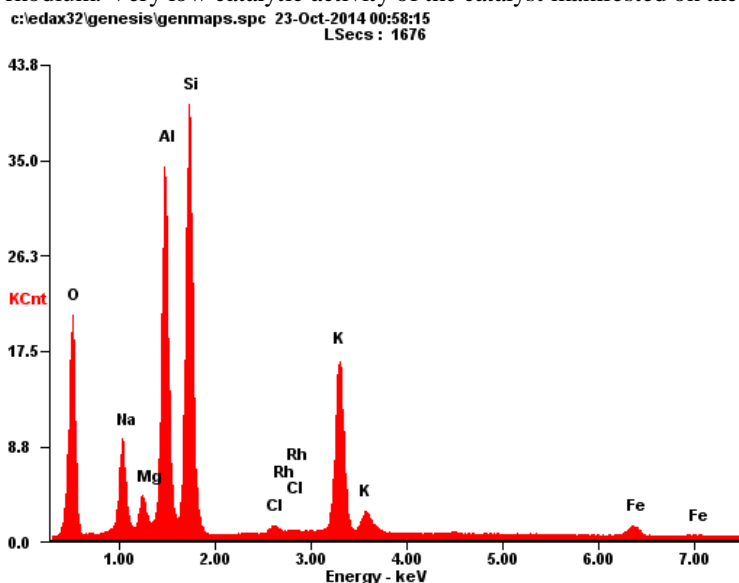
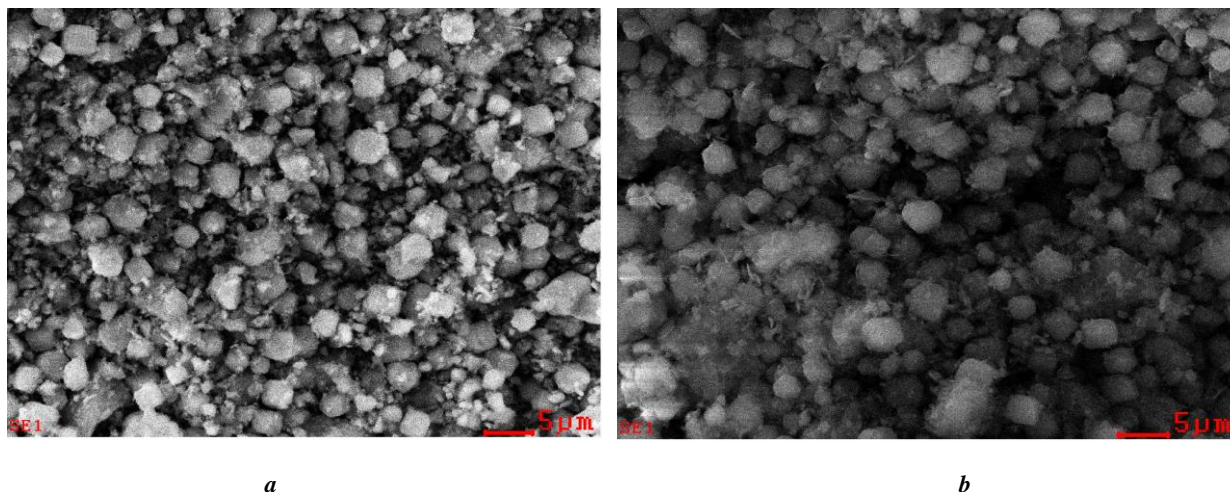
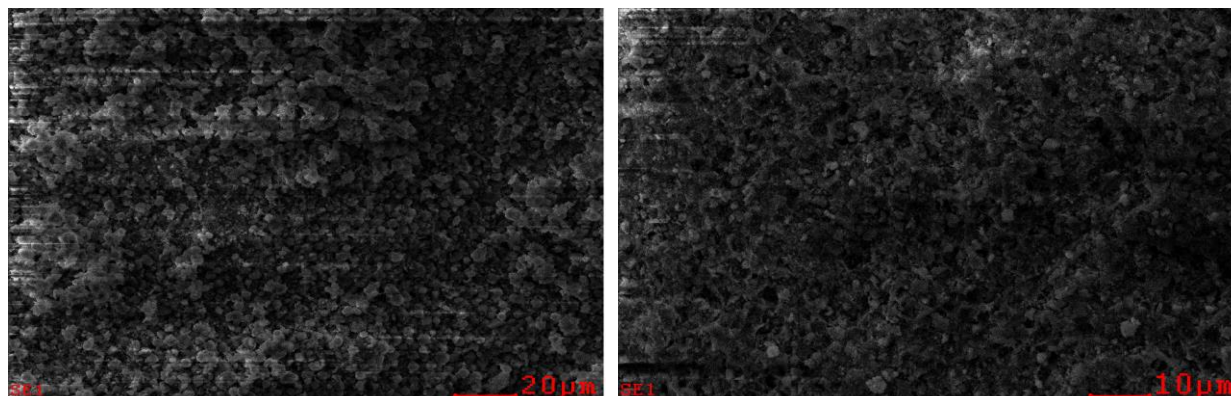


Figure 1 - The elemental composition of the Rh- promoted catalyst

The synthesized rhodium catalysts were studied by electron microscopy. We investigated the morphology of both the original and modified matrix. Figure 2 shows the results of SEM. As can be seen from the figure on the modified matrix looser surface. Over zeolite modified with rhodium and clay (10%) carbonized during 5 hours shows the formation of carbon nanofibers.





a) zeolite A3; b) Rh-promoted zeolite; c) Rh-promoted zeolite and clay (10%) carbonized 3 hours; d) Rh-promoted zeolite and clay (10%) carbonized 5 hours

Figure 2 – SEM image of the promoted catalysts

Determined by electron microscopy, the elemental composition of the starting zeolite and the zeolite is modified by various noble metals. The data presented in Table 1

Table 1 - The elemental composition of the catalyst modified with various metals

Element	Wt. %		
	Zeolite + Co ²⁺ (5 %)+ clay	Zeolite + Rh (1 %)+ clay	Zeolite + Rh (0,5 %)
ClK		0.39	1.24
OK	44.12	39.75	30.98
NaK	4.43	7.16	
MgK	1.50	2.06	1.06
AlK	16.07	16.92	3.55
SiK	20.75	23.25	20.82
KK	8.10	9.01	
FeK	1.59	0.99	
CoK	3.44		
RhL		0.92	0.49

Desired product in the hydrogenation of benzene is predominantly cyclohexane. The resulting product can be used as a high-octane component of motor fuels, and as feedstock for petrochemical processes. Table 2 shows the hydrogenation of benzene to produce pure zeolite at a hydrogen under 20 atm. pressure. As seen from the results for pure zeolite conversion of about 7%. The presence of 2, 2 DMB products, CH, MCP means that in the pure zeolite present isomerizes centers.

Table - 2 The hydrogenation of benzene to produce pure zeolite at a hydrogen pressure of 20 atm.

Hydrocarbon name	250 °C	280 °C	300 °C	320 °C
2,2 DMB	2,3	2,3	2,0	2,0
Methylcyclopentane	0,9	1,0	06	06
Cyclohexane	1,3	1,5	1,2	2,2
Hexane	0,7	0,8	-	-
Benzene	93,3	93,4	95,4	94,4
Toluene	1,0	1,0	0,8	0,8

Tables 3-5 show the results of hydrogenation of benzene over different catalysts. Table 3 shows the results of the hydrogenation of benzene over a zeolite catalyst with the addition of Tonkerisskaya clay and 1% rhodium at a hydrogen pressure of 20 atm. depending on the temperature. As can be seen from Table 3 the content of 2, 2-

dimethylbutane and methylcyclopentane increases at a temperature of 280 °C. This characteristic of the fact that this catalyst had an activity in the isomerization reaction of cyclohexane to methylcyclopentane.

Table 3 - hydrogenation products of benzene of 1% rhodium clay containing zeolite at hydrogen pressure of 20 atm. depending on the temperature °C

Hydrocarbon name	250 °C	280 °C	300 °C	320 °C
2,2 DMB	16,2	17,5	14,9	13,2
Methylcyclopentane	25,3	16,4	21,3	19,1
Cyclohexane	37,0	40,0	41,2	42,5
Hexane	5,6	7,9	8,0	10,3
Benzene	19,1	15,8	12,1	12,0
Toluene	1,3	1,2	1,3	1,4
Cyclohexene	0,5	1,2	1,2	1,5

Table 4 shows the results of the hydrogenation of benzene over various catalysts. An unmodified zeolite at a hydrogen pressure of 20 atm. conversion is very low. As seen from Table pure zeolite benzene hydrogenation reaction is not.

Table - 4 hydrogenation products of benzene 0.5% rhodium zeolite at a hydrogen pressure of 20 atm.

Hydrocarbon name	Zeolite	Zeolite + 0,5 % Rh
2,2 DMB	2,3	9,2
Methylcyclopentane	0,9	23,8
Cyclohexane	1,3	42,4
Hexane	0,7	8,2
Benzene	93,3	15,3
Toluene	1,0	1,1

The hydrogenation of benzene was investigated on the modified zeolite catalysts in the temperature range of 250 to 450 °C and a pressure of 25 atm. In the hydrogenation reaction, benzene conversion was 100% and the selectivity is close to 85%. The advantages of rhodium catalysts based on zeolite, should be attributed to their lesser sensitivity sulfur compounds and the possibility of catalyst regeneration.

Table 5 shows the hydrogenation products of benzene on the catalyst 0.5% rhodium carbonized zeolite at a hydrogen pressure of 20 atm.

Table 5 - The hydrogenation products of benzene over 0.5% Rh zeolite at a hydrogen pressure of 20 atm.

Hydrocarbon name	250 °C	280 °C	300 °C	320 °C
2,2 DMB	8,5	9,2	12,4	11,0
Methylcyclopentane	23,2	23,8	26,7	20,2
Cyclohexane	41,3	42,4	39,2	45,2
Hexane	7,5	8,2	7,5	10,2
Benzene	18,3	15,3	13,0	12,0
Toluene	1,2	1,1	1,2	1,4

Figure 3 shows the dependence of temperature on the conversion of a rhodium catalyst at a pressure of 25 atm. At a pressure of 25 atm. over Rh zeolite catalyst shows high conversion. It is evident that among all the smallest modified catalysts, the catalyst exhibits catalytic activity of the clay containing 0.5% rhodium. Pressurization in such cases decreases the conversion. In the temperature ratio 280-320 °C at a conversion of 54% increases the selectivity of 2, 2 DMB and cyclohexane.

Yield isomers of benzene in liquid catalysts supply of the process depend on the temperature over zeolite catalyst. Rh-promoted zeolite at 350 °C with a yield of 62%, a liquid catalyst RON 92.9 points. It is worth noting that in the process carbonized catalyst compared to the process without pretreatment of the catalyst is observed a lower yield of cyclohexane.

When the hydrogenation of benzene side products formed, this increases the octane number of from 6 to 12 points. Moreover, as shown by chromatographic analysis catalyst, which is a component of gasoline, increased knock resistance, is mainly due to the formation of Naphthenes.

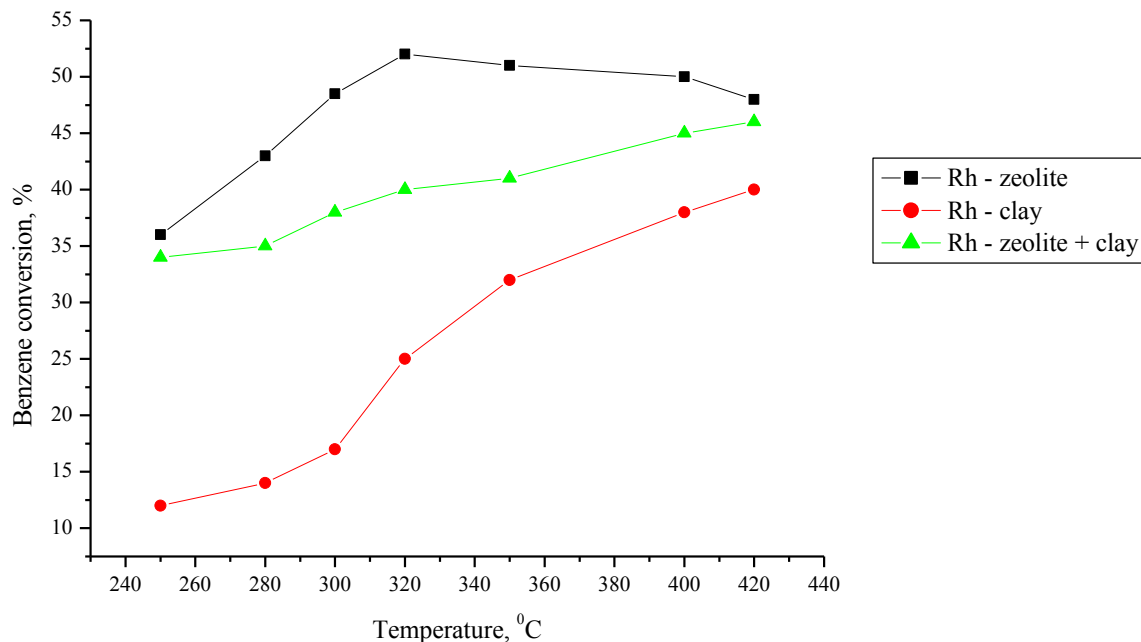


Figure 3 – Relationship between benzene conversion and temperatures over different catalysts

Figure 4 shows the conversion of benzene to catalyst is rhodium on aluminum oxide at a temperature of 25 atm pressure. Of all the catalysts synthesized lowest rhodium catalytic activity of the catalyst showed on alumina

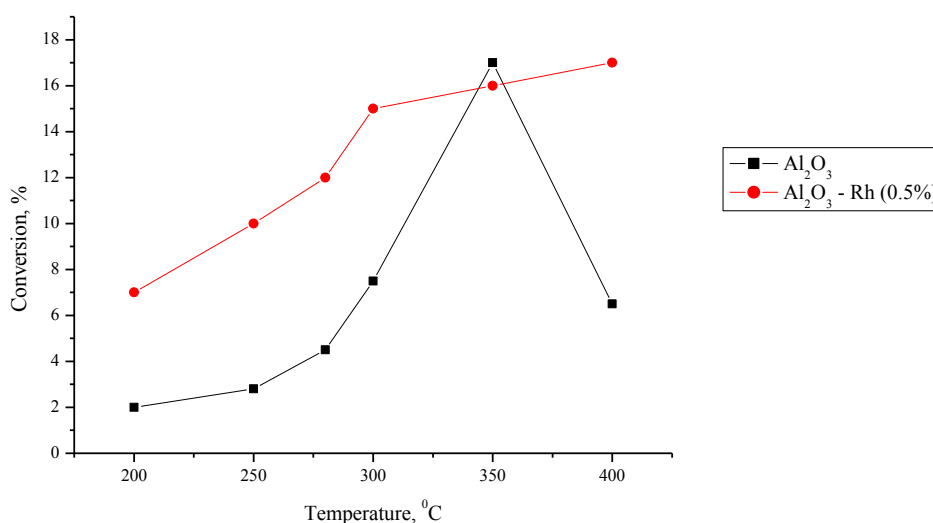


Figure 4 - Relationship between benzene conversion and temperatures over Rh-promoted aluminum oxide catalyst under 25 atm. pressure.

Figure 5 shows the dependence of the yield of cyclohexane at different catalysts. Studies have shown that the isomerization of cyclohexane to methylcyclopentane active rhodium zeolite proceeds at a temperature of 320 °C, than catalysts previously investigated.

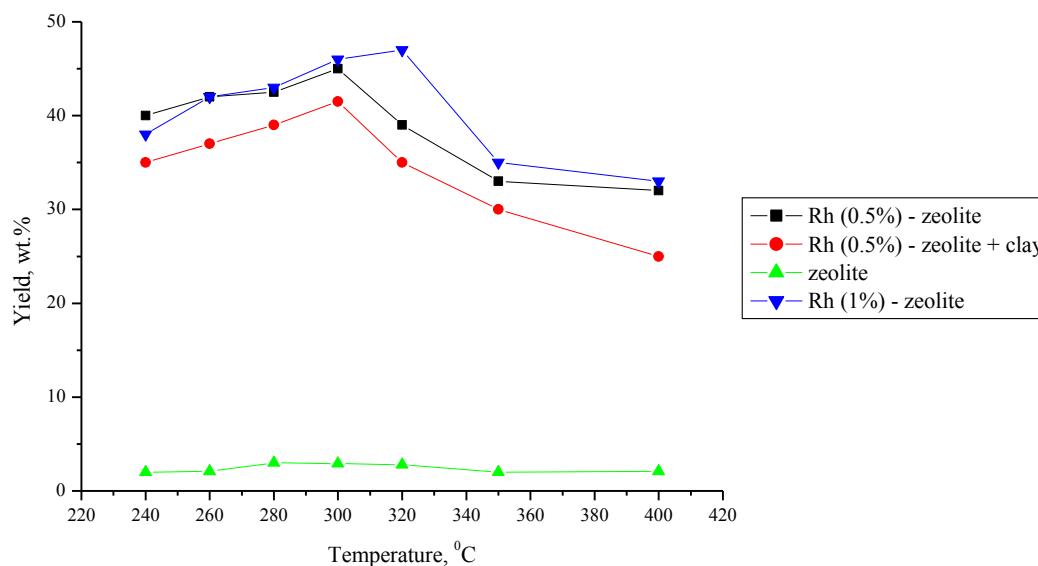


Figure 5 - Relationship between yield of cyclohexane and temperature over various catalysts

Ratio of methylcyclopentane in cyclohexane mixture reaches 54.6% over 1% Rh zeolite catalyst.

Figure 6 shows the effect of the ratio of hydrogen to benzene output DMB and cyclohexane. The most optimal ratio for output DMB and cyclohexane is 6: 1.

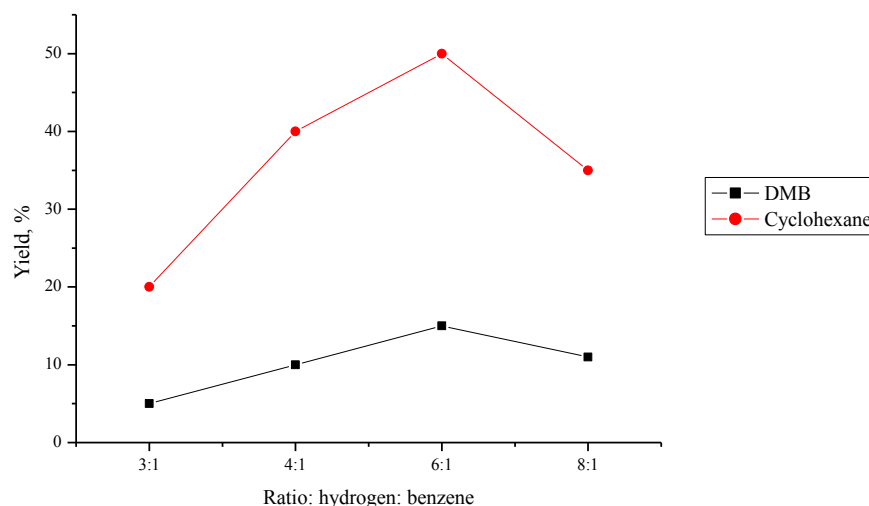


Figure 6 - Effect of the ratio hydrogen: benzene on yield of DMB and cyclohexane

When modifying zeolite by 1% rhodium increased catalytic activity in the hydrogenation of benzene. As noted above, the modified zeolite is 0.5 rhodium allows to obtain a mixture of isomers - dimethylbutane (2, 2-DMB), methylcyclopentane and cyclohexane. Comparative physico-chemical analysis carbonized modified rhodium zeolite showed that the catalytic activity in the hydrogenation of benzene to produce the desired products.

Conclusion

The results showed that the study of the catalytic activity of Rh- promoted catalysts are active and selective catalyst is from 1% rhodium zeolite-clay in the test reaction mixture, in which there is the maximum formation amount of the target products.

It has been established that the zeolite containing 0.5% of rhodium and 10% clay exhibits catalytic activity in hydrogenation of benzene in the temperature range 280-350 °C, and also has high selectivity to yield of CH, DMB. From the elemental analysis results show that all active phase deposited lossless deposited on carriers.

As a result, unable to significantly improve the environmental performance of motor fuel to achieve the parameters corresponding to Euro-4 standards.

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