

# Rh-Promoted Carbon Catalysts to Obtain Clean Components of Motor Fuels

S. K. Tanyrbergenova, A. Temirkhan, Z. A. Mansurov, N. K. Zhylybayeva, and G. M. Naurzbayeva

**Abstract**—In this work were selected the optimal conditions of the dearomatization reaction based on the hydrogenation of benzene to cyclohexane over Rh catalyst, which increases the octane number. The results showed that the study of the catalytic activity of 1% Rh catalysts were active and selective. Carbonized apricot pits 0.5% Rh-promoted exhibits catalytic activity in hydrogenation of benzene in the temperature mode, but by increasing the space velocity rapidly loses activity. Rh catalyst on calcined  $\text{Al}_2\text{O}_3$  at 550 °C showed markedly less stability in comparison to the other samples. 0.5% Rh-promoted clay-containing zeolite exhibits catalytic activity in the hydrogenation of benzene in the temperature range 280-350 °C, and also has high selectivity to yield of cyclohexane and DMB. As a result, turned improve the environmental performance of motor fuel to achieve the parameters corresponding to Euro-4 standards.

**Index Terms**—Benzene, carbon catalysts, hydrogenation, rhodium.

## I. INTRODUCTION

The present level of quality requirements for motor fuels is determined not only by the need to ensure their performance, but also the prerequisite for environmental safety of vehicle engines. In particular, European standards tightened requirements to the contents of alkenes and aromatic hydrocarbons and sulfur in commercial diesel fuel and gasoline.

The problem of ecological fuel acquired independent significance in connection with the tightening requirements for ecological safety of diesel fuel, in particular to the content of diesel fuel with low arenas content. 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) [1].

To obtain high-octane gasoline with a low content of

aromatic hydrocarbons in their composition traditionally use alkylation and hydroisomerization processes, also oligoizomerization processes [2]. The structure of high-octane gasoline input gasoline fraction of catalytic cracking products, as well as isobutane alkylation products and hydroisomerization of  $\text{C}_5\text{-C}_6$  alkanes [3]. All of these technologies make it possible to obtain not cause environmental problems saturated hydrocarbons - alkanes and cycloalkanes, which, although not fully, but significantly reduced the proportion of arenes in gasoline [4].

In order to the oil fraction can be used as a diesel fuel component, fraction must meet certain requirements: for it also imposes limits on the content of sulfur and aromatic compounds [5]. This limitation is due to the fact that the above fraction in the final product contains a certain amount, and at a deviation from the requirements of compounding will not yield commercial product that complies with the regulations [6].

In this work were selected the optimal conditions of the dearomatization reaction based on the hydrogenation of benzene to cyclohexane over Rh catalyst, which increases the octane number. Rh catalysts operate under milder conditions and have greater selectivity for compounds with a terminal double bond than conventional systems based on Co.

The aim of this work was development Rh catalyst for hydrogenation of benzene and studies the effect of the phase composition of the active phase to their catalytic properties in the study process.

## II. EXPERIMENTAL

As a basis for growth and formation of nano-carbon composites used apricot pits and clay from Tonkerisskaya field (Kazakhstan).

Selection of this clay due to the fact that the composition of this clay were detected oxides  $\text{Fe}_3\text{O}_4$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{Cr}_2\text{O}_3$ , which must promote the formation in carbonization carbon fiber and nanostructure. This causes an increase in the catalytic carbon surface area and porosity, resulting in the formation of transport pores.

Rh catalysts based on apricot seed were prepared as follows: AS-impregnated with salts of metals was reduced at 500 °C in an atmosphere of hydrogen. Carbonized apricot pits as solid carbon matrix is a durable material which has a porous structure. Prepared samples were loaded into the hydrocracking reactor and tested in hydrocracking, hydroisomerization and hydrogenation of hydrocarbons processes.

Rh catalysts based on zeolite were prepared by impregnation followed by calcinations. The impregnation was

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performed by immersing the matrix in a concentrated solution of a rhodium salt. The impregnated zeolite was subjected to carbonization process for 3-5 hours. The obtained catalyst containing 0.5-1% of rhodium using for hydrogenation.

Investigation of carbonized materials structure using SEM (Microscope Quanta 3D 200i CEI, made in USA, with an accelerating voltage of 30 kV) have shown that the obtained samples have a structure with varying wall thickness and pore size, as a result of which appear to be drastically reduced the activation energy of different chemisorptions reactions. When this does not change the morphology of the material and the surface structure is dense.

Investigation of activity of synthesized catalysts were performed in the high-pressure laboratory flow in the temperature range 50-300 °C, pressure 0.1-3.0 MPa, and a volume rate of 1.0-4.0 h<sup>-1</sup>. The hydrogen feed rate was 30-60 ml / min.

Electron microscopic study of the samples was carried out on the JEM-100SKH device at an accelerating voltage of 100 kV. The device allows us to study objects at high resolution (3.0 Å).

Determination of the composition of the gas phase was carried out by gas chromatography on a Chromatograph type 3700, Chrome- 5. Content was determined in the pyrolysis products of carbon monoxide, oxygen, hydrogen and hydrocarbons.

Carbohydrate moiety analyzed on chromatography. Detector - flame ionization. Carrier gas – nitrogen, stainless steel column of 3 m length and 3 mm in diameter, the sorbent  $\gamma$  - Al<sub>2</sub>O<sub>3</sub> temperature from 90 to 180 °C.

### III. RESULTS AND DISCUSSION

The work investigated the hydroisomerization reaction of benzene comprising a stage of hydrogenation to cyclohexane (CH), followed by isomerization to methylcyclopentane (MCP) on Rh-promoted carbon catalyst. As a matrix used a pure zeolite and its mixture with clay,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, with their ratio was varied within wide limits. Rhodium deposited by impregnation of solutions of rhodium nitrate salts.

A different concentration of rhodium was applied to a series of matrix: Al<sub>2</sub>O<sub>3</sub>, zeolite, clay, carbonized apricot pits. We also produced Co- promoted catalysts for comparison of catalytic activity.

The physical and chemical characteristics of the produced catalysts (see Table I). To create the carbon catalyst for hydrogenation deposited rhodium salts on matrix. Supported rhodium metal centers allow equilibrium to maintain a low concentration of olefins in the reaction mixture and prevent coking of the catalyst surface. Carbonization of zeolite samples lasted 5 hours, with the purpose of increasing the carbon content.

Among of all the tasted samples, Rh- promoted catalyst on a zeolite characterized by highest activity. It is considered that for the efficient operation of bifunctional metal catalysts metal centers should be as close as possible to the acid sites. So often a metal component is applied directly to the surface of the zeolite. Nevertheless, the catalyst containing 10% clay and zeolite promoted by Rh demonstrated high activity and

selectivity in the hydrogenation of benzene.

TABLE I: BASIC PHYSICAL AND CHEMICAL CHARACTERISTICS OF RH-PROMOTED CARBON CATALYST ON DIFFERENT MATRIX

Indicators	Zeolite	Zeolite	Clay	CAP	Zeolite + Clay	Al <sub>2</sub> O <sub>3</sub>
Rhodium content (% wt.)	-	0.5	0.5	0.5	0.5	0.5
Carbon content (% wt.)	-	5.0	15.0	21.0	12.0	9.0
Specific surface (m <sup>2</sup> /g)	112.0	122.0	106.0	452.0	156.0	96.0
Carbonization (hour)	1.0	3.0	1.0	45.0	3.0	2.0

It was established experimentally that 0.5% Rh-promoted carbonized apricot pits (CAP) are catalytically active in the hydrogenation of benzene. According to the chromatographic analysis data the optimal temperature of 430 °C and pressures of 20 atm. for the benzene hydrogenation, benzene conversion is 64% (Table II). In hydrogenation of benzene reaction over rhodium catalysts hydrogen feed rate 60 ml /min and feed rate of benzene with 0.1 ml /min. By increasing the hydrogen feed over rhodium catalyst at temperatures above 480 °C in the reaction products is found small amounts of hexane. Under given conditions, the isomerization of cyclohexane to methylcyclopentane not observed.

Results of the hydrogenation of benzene over cobalt and rhodium carbon catalyst at a temperature of 450 °C and 25 atm. (see Table II) Composition benzene hydrogenation products depends not only on the activity of the catalyst, and the conditions of supply of hydrogen and benzene. From the experimental results that with the increase in the initial feed mixture of benzene, cyclohexane yield gradually decreases due to the lack of hydrogen. Over Co- promoted catalysts benzene conversion 51% at a temperature of 430 °C.

TABLE II: BENZENE CONVERSION AT VARIOUS CATALYSTS (CAP)

T, °C	Benzene conversion, %		
	0.5 % Rh	5 % Co	7 % Co
350	47	24	27
380	49	29	32
400	59	33	35
430	64	41	42
450	65	42	45
480	65	45	48

Identified the optimal conditions for the benzene hydrogenation over Rh catalyst. The maximum yield of cyclohexane over Rh-promoted catalyst at a temperature of 430 °C, over Co-promoted catalyst the maximum yield of cyclohexane at a temperature of 480 °C and a pressure of 20 atm. Aromatics feed of 10 ml /min, and the hydrogen 60 ml /min.

Widely studied changing of the hydrogen: benzene molar ratio. Increasing hydrogen partial pressure reduces the coking rate of Rh-promoted zeolite catalysts.

Impact of hydrogen: benzene ratio to the result in the

benzene hydrogenation processes (see Table III). Increase the ratio of hydrogen above 8: 1 is impractical because the reaction products, a large number of hexane.

Investigation of the catalytic activity of the synthesized series Rh-promoted catalysts on different matrix in the hydrogenation reaction of benzene showed that yield of cyclohexane and targeted products is optimal catalyst supported on synthetic zeolite composition 1% Rh.

The catalytic activity of the product yield in the conversion of benzene to cyclohexane carriers arranged in a row: zeolite > zeolite + clay ≥ clay > Al<sub>2</sub>O<sub>3</sub> > CAP.

TABLE III: IMPACT OF HYDROGEN: BENZENE RATIO

Indicators	Ratio hydrogen: benzene			
	3:1	4:1	6:1	8:1
Benzene conversion	32	68	74	81
Yield 2.2 DMB	5	10.2	14.9	11.2
Yield cyclohexane	20	40	49	39

At the initial zeolite hydrogenation of benzene is very low. Over 1% Rh zeolite reaction begins at a temperature of 250 °C and at 380 °C and higher temperature formed benzene isomers. To by-products are isomeric hydrocarbons - methylcyclohexane, ethylcyclohexane and small quantities of hydrogen. With increasing temperature of the process increasing benzene conversion and selectivity of isomers of aromatic hydrocarbons. By increasing the space velocity decreases the conversion and selectivity of the target products. Thus, over 1% Rh zeolite main direction of the process when hydrogenating benzene to cyclohexane followed by subsequent isomerization reactions in such cases would require additional amounts of hydrogen.

As is known, isoparaaffinic hydrocarbons in gasoline octane number average determined within 72-76 points, and aromatic hydrocarbons have octane in the range 96-120 points, and characterized by a significant increase in refractive index and reduced aniline point gasoline. Thus, we must determine the favorable conditions for the hydrogenation of aromatic hydrocarbons, which increase the octane number.

In order to elucidate the nature of the catalytic activity, as well as factors affecting the stability was investigated the influence of the environment on the reaction of benzene hydrogenation. Fig. 1 shows relationship between temperature and benzene conversion over Rh catalysts of hydrogenation over 0.5% Rh catalyst at a pressure of 18 atm. conversion of benzene depending on temperature.

In case the catalyst system is recovered in a hydrogen atmosphere, the benzene hydrogenation proceeds with a high yield and can reduce the temperature to 300 °C. It can be seen that the maximum activity observed for the composition, wherein the rhodium is present in an amount of 1% on the carbon support (CAP).

Thus, it is shown that the regeneration of the catalysts in a hydrogen atmosphere restores the activity of the studied catalysts in benzene hydrocracking.

Fig. 2 shows the results of the study relationship between benzene conversion and time under the pressure of 30 atm. and temperature at 400 °C. The experimental data shows that

the Rh-promoted zeolite catalyst (carburized 3 hours) loses the catalytic activity, worked 22 hours. A Rh- promoted CAP worked under the same conditions of 26 hours.

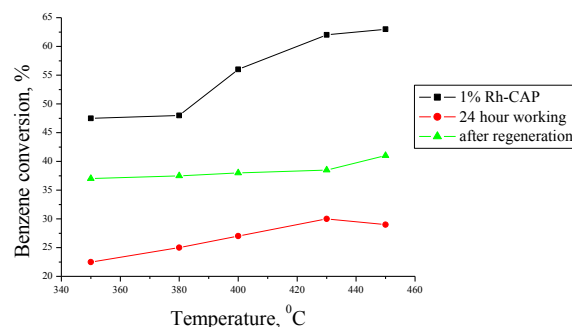


Fig. 1. Relationship between temperature and benzene conversion over Rh catalysts.

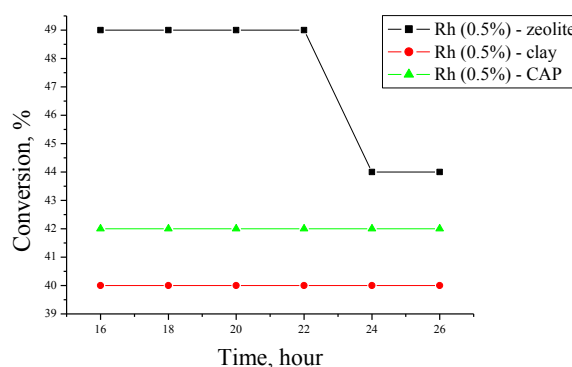


Fig. 2. Relationship between benzene conversion and time under the pressure of 30 atm.

Investigation of valuable by-products of benzene hydrogenation over Rh catalyst was developed for the installation of running at pressures of 18 -25 atm. and temperatures 250 - 320 °C. As catalysts, Rh- promoted catalysts are used on carbon (CAP), zeolite and a zeolite with the addition of clay.

Catalysts activity in the benzene hydrogenation reactions determined by two parameters - the proportion of 2, 2 - dimethylbutane (2,2-DMB) in the mixture of isomers and the proportion of methylcyclopentane in its mixture with cyclohexane. This indicator characterizes catalyst activity in the isomerization reaction of cyclohexane to methylcyclopentane. Fig. 3 shows the yield of 2, 2 - DMB over different catalysts depending on the temperature. As seen in Fig. 3 yield of 2, 2 DMB over 0.5% Rh zeolite was 12.4%, and high yield on catalyst zeolite + clay + 1% rhodium - 17%.

Based on the experimental data, we assume that the structural characteristic, the particle size distribution and bulk density of the clay as a dispersant have some influence on the catalyst productivity.

Clay-containing zeolite catalyst with a lower surface area has better stability. According to the mechanism of benzene hydrogenation small surface area prevents complete benzene hydrogenation. And inhibits further hydrogenation of cyclohexene into cyclohexane, and thus increases the selectivity of a cyclohexene. Homogeneous chemical

environment for the selective hydrogenation of benzene, as provided with a smaller particle size and narrow particle size distribution enhance stability of cyclohexene selectivity and catalyst stability. Large pore diameters useful for desorption and increases cyclohexene selectivity.

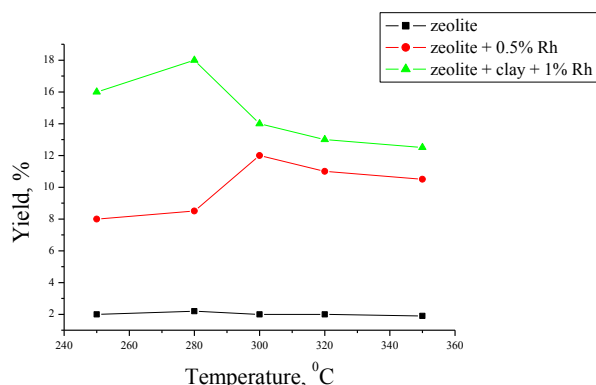


Fig. 3. Yield of 2, 2 – DMB over different catalysts depending on the temperatures.

Fig. 4 shows relationship between benzene conversion and pressure at 280 °C over 0.5% Rh catalyst based on different matrix. As seen from the experimental data benzene conversion is 60% under 30 atm. pressure over zeolite catalyst, clay-containing zeolite to 65% under 35 atm. pressures.

Important role in the synthesis of zeolite playing structure-forming additive, as are most commonly used toxic and explosive compounds, which creates certain difficulties in the industrial production of catalysts. In this regard, great importance is the development of methods for the synthesis of high-silica zeolite using inexpensive and non-toxic compounds as structure-forming. We have synthesized Rh zeolite using clay as a structure-forming compound.

For use of zeolite catalysts in industrial installations necessary to increase its mechanical strength by introducing into the zeolite binder.

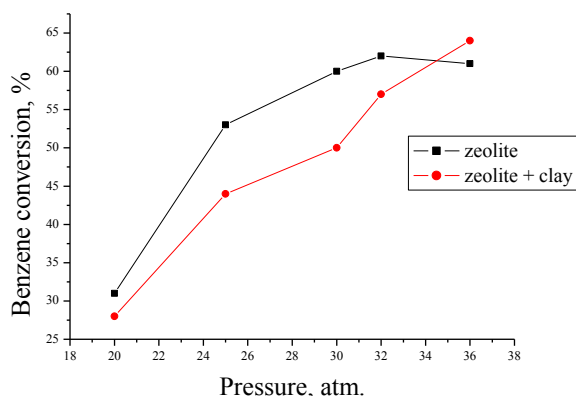


Fig. 4. The relationship between benzene conversion and under the 30 atm. Pressure.

For these purposes we select clay, content in the catalyst varies from 10 to 30 wt%. Mixing of sample clay reduces its acidity, but the specific surface increased. Particularly significant effect on the structure of zeolite provides clay (10%) and also on the yield of desired products at higher

temperatures and pressures. This means that the clay-containing zeolite structure during carbonization undergoing structural changes, and becomes resistant to coking processes. Further increase clay in catalyst reduces the mechanical strength under carbonization. Samples containing 20 and 30% of clay, characterized fragile structure. Therefore, the further addition of clay into the zeolite is not appropriate. Since the resulting granules quickly disintegrate.

Target product in benzene hydrogenation process is preferably cyclohexane. The resulting product can be used as a high-octane component of motor fuels, and as feedstock for petrochemical processes.

#### IV. CONCLUSION

The results showed that the study of the catalytic activity of Rh catalysts were active and selective 1% Rh zeolite catalyst. In the reaction mixture were desired the formation of the maximum amount of the targeted products. At higher temperatures, largely derived benzene alkylation, resulting in reduced yield of cyclohexane.

Carbonized apricot pits 0.5% Rh-promoted exhibits catalytic activity in hydrogenation of benzene in the temperature mode, but by increasing the space velocity rapidly loses activity.

Rh catalyst on calcined  $\text{Al}_2\text{O}_3$  at 550 °C showed markedly less stability in the hydrogenation of benzene in comparison to the other samples.

0.5% Rh-promoted clay-containing zeolite exhibits catalytic activity in the hydrogenation of benzene in the temperature range 280-350 °C, and also has high selectivity to output cyclohexane and DMB.

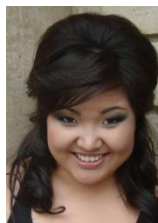
As a result, turned improve the environmental performance of motor fuel to achieve the parameters corresponding to Euro-4 standards.

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