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HYDRODEAROMATIZATION OF GASOLINE FRACTIONS OF ATYRAU OIL REFINERY OF THE REPUBLIC OF KAZAKHSTAN

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ABSTRACT

Benzene hydrogenation over mono- and bimetallic catalysts based on Group 8 metals on various supports in the temperature range 25-200°C and pressures of 0.5-4 MPa has been investigated. Bimetallic catalysts were tested in the hydrodearomatization of gasoline fractions from Atyrau Refinery plant. It is shown that after the reaction of benzene was completely removed from gasoline, content of aromatics, olefins and paraffins is significantly decreased and isoparaffins content increased.

Key words: Benzene hydrogenation, Pt/Al_2O_3, Pd/Al_2O_3, Hydrodearomatization.

INTRODUCTION

Fuel quality substantially depends on the hydrocarbons composition. Aromatic hydrocarbons in fuel are represented by monoaromatic compounds: benzene, toluene, xylene isomers, ethyl benzene and other aromatic compounds. High concentration of aromatic hydrocarbons especially bicyclic leads to a decrease in the speed and completeness of combustion, contributes to the carburization of the combustion system and degrades the environmental situation in the world. Decline in the proportion of aromatic hydrocarbons in petroleum and petroleum products can be achieved by different methods - the principal process is the catalytic hydrogenation of aromatic hydrocarbons to alter the chemical structure of hydrocarbons in the proper direction. Development and implementation of hydrodearomatization of oil fuel fractions improve fuel performance characteristics of domestic gasoline and environmental situation in the Republic.

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The running characteristics of fuel oil and raw materials for the petrochemical refining are improved in the process of hydrogenation of straight-run gasoline distillates in the presence of high-performance catalysts providing the hydrogenation of benzene and polycyclic aromatic hydrocarbons[1-8].

Hydrogenation process of aromatics hydrocarbons plays an important role in the petrochemical industry, since benzene and other aromatic hydrocarbons concentrations in fuels should be reduced due to stricter environmental laws. Fuel aromatic hydrocarbons contribute to carburization of the combustion system, which leads to an increase in the content of the exhaust gases NO_X.

In the petroleum refining industry hydrogenation process is carried out in severe conditions (high temperature and hydrogen pressure) by metal oxide catalysts, where the metal is Co, Mo, Ni, Cu, W, and other transition metals. The most effective and selective catalysts for the hydro-dehydrogenation reactions are catalytic systems based on metals of the platinum group especially Pt, Pd, Rh and Ru.

The purpose of present work is the synthesis of selective catalysts for the hydrogenation of benzene and aromatics hydrodearomatization in gasoline fractions to produce fuels that meet international standards.

EXPERIMENTAL

Experiments were carried out on kinetic high-pressure installation consisting of improved autoclave of Vishnevsky with rapid mixing and measuring part. In work were used Pd, Rh Pt and Ru catalysts on various carriers: Al_2O_3, Sibunit, charcoal, zeolites, aluminosilicate, $CaCO_3$, SiO_2.

The developed catalysts were investigated by the following methods of the analysis: measurement of a surface of the catalyst (BET) and electronic microscopy (TEM and SEM). The hydrogenation of model compound-benzene on mono-and bimetallic catalysts was previously studied for the developing catalysts for hydrodearomatization. Alcohols (ethanol, isopropanol) and hexane of "reagent grade" were used as solvents. Analysis of the initial substances and reaction products was carried out by gas chromatography.

RESULTS AND DISCUSSION

Monometallic catalysts based on platinum metals (Table 1) displayed different activity and selectivity in the hydrogenation of aromatic compounds. The highest rate of benzene hydrogenation reaction is observed in Pt-and Pd-catalyst (Table 1). Conversion of benzene and yield of cyclohexane are also the maximum on Pt/Al_2O_3 and Pd/Al_2O_3.

Table 1: Hydrogenation of benzene on catalysts based on metals of group 8 at 1.5 MPa and 100°C

Consecutive number	Catalyst	Conversion (%)	Molar flow rate (mole per min)	Yield of cyclohexane (%)
1	Pt/Al_2O_3	78	34.2	76
2	Pd/Al_2O_3	76	28.2	75
3	Rh/Al_2O_3	72	23.7	65
4	Ru/Al_2O_3	60	12.2	40 + 15*

Note: *Yield of cyclohexane

On Ru-catalysts there is the process of incomplete recovery of benzene to cyclohexane (15%), the yield of cyclohexane is only 40%.

According to the conversion and yield of cyclohexane, catalysts form series:

$$Pt > Pd > Rh >> Ru$$

The effect of nature of the support on reaction rate, benzene conversion and yield of cyclohexane on monometallic catalysts was studied (Table 2). It was found that in the hydrogenation of benzene most active catalysts are catalysts deposited on an aluminosilicate, various modifications of Al_2O_3, γ-Al_2O_3 and SiO_2, and different carriers are optimal for metals different by the nature. Thus Pt and Pd-catalysts are more active when deposited on aluminum oxides and aluminosilicate and Rh-catalysts are more active when deposited on silicon oxide.

For all catalysts mainly complied following dependence of the reaction rate and outputs of napthenes:

$$AC > Al_2O_3 > C > Sibunit > CaCO_3 > SiO_2$$

It should be noted that reaction rate among the carriers except coal is correlated with a decrease in the acidity of the carrier. In the reaction products on zeolite carriers the cracking products (opening of aromatic ring) were detected (upto 5%).

Table 2: Effect of Pt-catalyst support on hydrogenation of benzene at 15 atm and 200°C

Support	Conversion (%)	Molar flow rate (mmol/min)	Yield of cyclohexane (%)
C	57	27.9	54
SiO_2	54	25.8	52
γ-Al_2O_3	78	34.2	76
Sibunit	58	26.7	54
Aluminosilicate (AS)	80	36.8	78
$CaCO_3$	56	24.7	53

The bimetallic catalysts based on of Group VIII metals display higher activity than the monometallic. Among them, the maximum rate of conversion (91%) and naphthene hydrocarbon yield (88%) observed on Pt-Pd/Al_2O_3 and Pt-Rh/Al_2O_3 (Table 3). According to the reduction of reaction rate, change rate of benzene and toluene, cyclohexane output (methylcyclohexane) catalysts arranged in following series:

$$\text{Pt-Pd}/Al_2O_3 = \text{Pt-Rh}/Al_2O_3 > \text{Rh-Pd}/Al_2O_3 > \text{Pt-Ru}/Al_2O_3 > \text{Ru-Pd}/Al_2O_3$$

Table 3: Hydrogenation of benzene on bimetallic catalysts based on metals of group VIII in ethanol at 100°C and 1.5 MPa

Catalyst	Conversion (%)	Molar flow rate (mole/min)	Yield of cyclohexane (%)
Pt-Pd/Al_2O_3 (2:8)	90	49.8	88
Rh-Pd/Al_2O_3 (2:8)	78	42.1	73
Ru-Pd/Al_2O_3 (2:8)	70	35.2	62
Pt-Rh/Al_2O_3 (2:8)	91	49.2	88
Pt-Ru/Al_2O_3 (2:8)	81	38.4	75

Pd has a high sorption capacity relative to hydrogen (from 600 to 4580 volumes) depending on the type-compact or black. Palladium when applied on a carrier in small amounts loses its characteristic properties due to the presence of a large amount of dissolved hydrogen. In the system, Pt-Pd components are similar in electronic structure: both have free s-and d-levels, capable of forming a continuous series of solid solutions. When you change the ratio of platinum-palladium, the ratio of dissolved and adsorbed forms of hydrogen in catalyst is also changing: when the platinum content is increased, it decreases the amount of dissolved hydrogen at 30 atm. % Pt solubility of hydrogen becomes equal to zero; the amount of adsorbed hydrogen grows and the binding energy of N-Me decreases. A mixed platinum-palladium catalyst has greater adsorption capacity relative to hydrogen than platinum and palladium separately.

Increasing temperature in the range of 25-120°C and at pressure of 1.5 MPa increases the speed of reaction, the change ratio of benzene and toluene, cyclohexane and methyl cyclohexane yield (Table 4). The apparent activation energy calculated by the Arrhenius equation and from the dependence of log k and 1/T in the studied temperature range is 65.0 kJ/mole for benzene and 68.5 kJ/mole for toluene.

Table 4: Effect of hydrogen pressure and temperature on the conversion of benzene and toluene, yield of naphthenes on Pd-Pt/Al_2O_3

Hydrogen pressure, temperature	**Convertion (%)**		**Yield (%)**	
	Benzene	**Toluene**	**Cyclohexane**	**Methyl cyclohexane**
0.5 MPa	58	51	55	48
1.0 MPa	80	76	75	72
4.0 MPa	95	91	92	87
6.0 MPa	99	97	96	92
25°C	80	51	75	48
70°C	94	90	91	86
120°C	99	97	95	89

Effect of hydrogen pressure and temperature on the conversion of benzene and toluene was researched (Table 4). The pressure varied from 0.5 to 6.0 MPa, at a temperature of 100°C. Reaction order with respect to hydrogen calculated from the logarithmic dependence of the hydrogenation rate on the pressure is close to unity.

The process of hydrogenation of benzene on bimetallic catalysts was researched (Fig. 1). The reaction was studied at temperatures of 50-200°C and hydrogen pressures of 0.5-3.0 MPa. It was established that in the hydrogenation of benzene Pt-Rh-supported catalysts on AC, Al_2O_3, SiO_2 displayed the greatest activity. At a pressure of 2.0-3.0 MPa and a temperature of 150-200°C the conversion of benzene reaches 90-99%, and the yield of cyclohexane is 85-95%.

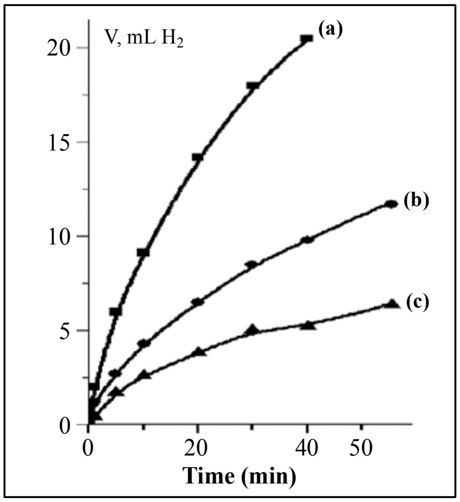
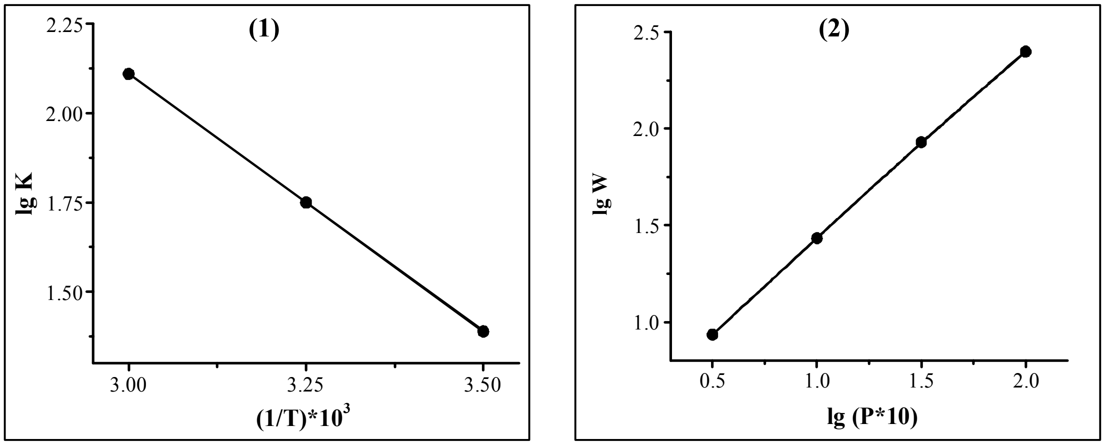


Fig. 1: Hydrogenation of benzene on Rh-Pt (9:1) catalyst at 25°C and 1-0.5 MPa and 2-2.5 MPa; 3-4.0 MPa

The temperature dependence of recovery rate is described by the Arrhenius equation [Fig. 2(1)]. The value of the apparent activation energy is 32 kJ/mol.

The reaction order with respect to hydrogen, as determined from the logarithmic dependence of the rate on pressure is 1 [Fig. 2(2)].

By increasing the sample of benzene from 17.8 to 71.2 mmol, recovery rate increases by 4 times. Order of reaction on the substrate, determined by the logarithmic dependence of the rate on the sample of substrate is close to 1 [Fig. 2(3)].



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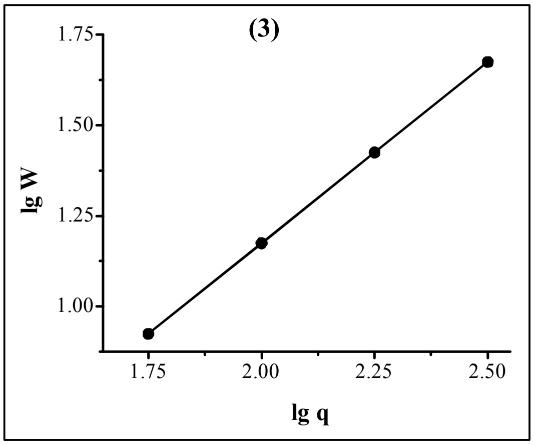

Fig. 2: Hydrogenation of benzene on Rh-Pt/Al_2O_3, 1-dependence of lgK on 1/T, 2-dependence of lgW-lgP_{H2}, 3-dependence of lg W – lg q

Thus, active catalysts of Pt-Rh-and Pd-Pt/Al_2O_3 and optimal conditions (2.0-4.0 MPa and 25-100°C) were developed for the hydrogenation of benzene. These catalysts were tested in the process of hydrodearomatization of gasoline fractions: 1-hydrogenate gasoline, 2-stable catalysate derived from LLP "Atyrau Oil Refinery".

Table 5 presents data on the group composition of organic substances in raw gasoline fractions and after hydrogenation on Rh-Pt/Al_2O_3. In the initial hydrogenates there was 2.22% of benzene, after the hydrogenation no benzene were found in the catalysate – i.e. it fully hydrogenated. The content of aromatics in initial gasoline was 13,70%, and after the hydrogenation it shows 2,26%.

It should be noted that the amount of olefin was reduced by almost 2-fold from 0.47% to 0.28%, which is very favorable for gasolines because the presence of olefins leads to instability (in chemical expression, reaction of oligomerization and polymerization occurs).

Also the content of isoparaffins increased from 35.79% to 44.26%, which is favorable for the octane number. For stable catalysate content of benzene in the initial state was 4.53%, after the reaction, the benzene content was of 0.15%, i.e. benzene conversion is 97%. The toluene content decreased from 19.65% to 12.99% after hydrogenation. Number of aromatics decreased from 51.5% to 22.96%.

The amount of paraffins also decreased from 16.17% to 14.71%. And the content of isoparaffins increased from 29.57% to 51.75%. Perhaps reaction of paraffin isomerization into isoparaffins occurred.

The amount of olefins is almost not changed. Content of naphthenes increased sharply from 1.95% to 12.08%.

Table 5: Composition of gasoline fractions, row and after hydrogenation by Rh-Pt/Al_2O_3 catalysts at 3 MPa and 25°C

Sample name	Content of determined indicator, weight %					
	Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Benzene
Hydrogenate gasoline (initial)	30.44	35.79	0.47	30.03	13.70	2.22
After hydrogenation	29.47	44.26	0.28	23.77	2.26	-
Stable catalysate (initial)	16.17	29.57	0.78	1.95	51.5	4.53
After hydrogenation	14.71	51.75	0.74	12.08	22.96	0.15

The specific areas of the prepared catalysts are presented in Table 6, from which it is possible to draw a conclusion that at bimetallic catalysts the surface is much lower, than at the monometallic.

Table 6: The specific area of prepared supported catalysts

Catalyst	S^* m^2/g
Pt/Al_2O_3	285
Pd/Al_2O_3	268
Rh/Al_2O_3	277
Ru/Al_2O_3	256
Pt-Pd/Al_2O_3 (2:8)	209
Rh-Pd/Al_2O_3 (2:8)	162
Ru-Pd/Al_2O_3(2:8)	186
Pt-Rh/Al_2O_3(2:8)	157
Pt-Ru/Al_2O_3(2:8)	170

Figure 3 shows electron micrographs of the Pd/Al_2O_3. The catalyst is presented by extensive congestions of disperse particles of 25 Å in size, and also large crystals of 150-200Å in size with signs of cubic and tetrahedral motive of a facet (SEM) and uniform distribution of particles on the carrier surface is seen on the TEM image. Microdiffraction pictures correspond to metallic Pd, besides at a small amount (upto 5%) there are PdO particles.

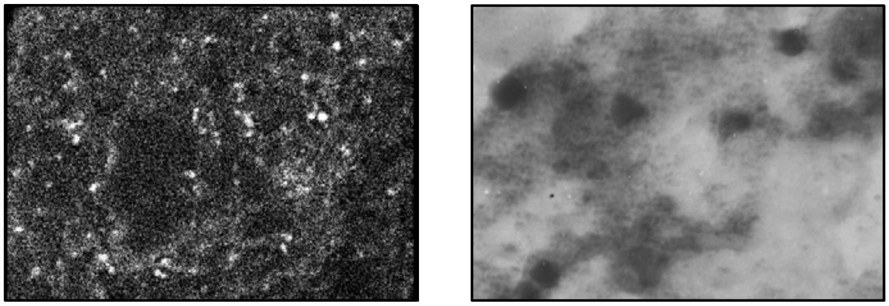
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Fig. 3: Electron micrographs of the Pd/Al_2O_3: 1-SEM (zoom 160000), 2-TEM (1 micron)

On SEM pictures of Pt-Pd/Al_2O_3 (Fig. 4) the catalyst is presented by fine particles of 20-25 Å in size and a small amount of more dense and large particles 50 Å, which microdiffraction pictures are presented by the diffusion rings corresponding to metals (Fig. 4, image 1). Particles of the Pt-Pd composition have sizes of 2-2.5 nm (Fig. 4, image 2).

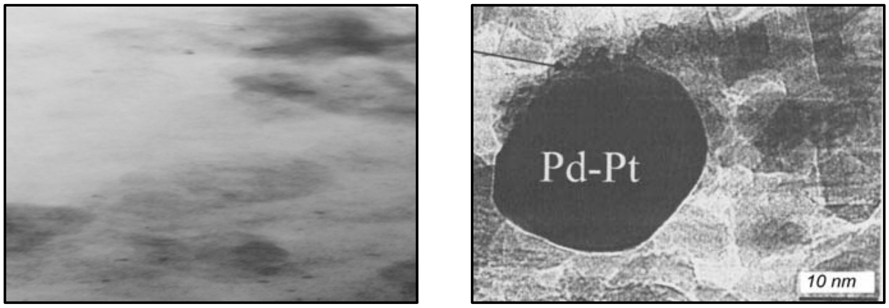

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Fig. 4: SEM images of the Pt-Pd/Al_2O_3: 1-(zoom 160000), 2-Pt-Pd particle

CONCLUSION

Thus, study of the hydrogenation of benzene over mono- and bimetallic catalysts based on metals Group 8 on various supports in the temperature range 25-200^{o}C and pressures of 0.5-4 MPa have been conducted. Bimetallic catalysts were tested in the process of hydrodearomatization of gasoline fractions of Atyrau Oil Refinery. It is indicated that benzene was completely removed from gasoline during reaction and aromatic content, olefins and paraffins is significantly decreased and increased isoparaffins.

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