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Hydrogenation of Benzene in the Presence of Ruthenium on a Modified Montmorillonite Support

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Abstract—Liquid-state hydrogenation of benzene on a supported ruthenium catalyst is studied. The degree of utilization of the inner surface of the porous system is determined. In the presence of water, hydrogenation occurs with the formation of cyclohexene along with cyclohexane.

Keywords: benzene, hydrogenation, catalysts, montmorillonite, modification, benzopyrene.

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INTRODUCTION

Reducing the content of aromatic hydrocarbons and especially benzene in motor fuels continues to be an important challenge. Accumulated in the environment, the toxic compound benzene and the carcinogenic product of its partial oxidation benzopyrene adversely affect human and animal biological activity [1]. We must therefore improve oil-refining technology and some of its stages in order to lower the content of benzene and its derivatives. One such process is the catalytic hydrodearomatization of aromatic hydrocarbons into naphthenes. However, the presence of catalyst-deactivating heteroorganic compounds in oil distillates necessitates the further development of catalysts and detailed studies of the mechanism of the catalytic transformation of hydrocarbons [2–5].

The hydrogenation and dehydrogenation of six-membered cyclic hydrocarbons are of great interest to hydrogen technology. Benzene and its derivatives are unique compounds in the storage and transportation of hydrogen. It is therefore necessary to develop catalysts for hydrogenation and dehydrogenation under relatively mild conditions.

The aim of this study was to investigate the hydrodearomatization of benzene (a component of motor fuels) in the presence of ruthenium catalysts on a support of montmorillonite of bentonite clay with a columnar structure.

EXPERIMENTAL

Preparation of Catalysts

Ruthenium catalyst (0.5–1.0 wt % Ru) was prepared on a support of modified montmorillonite of bentonite clay. The natural clay was modified into a columnar structure using aluminum polyhydroxo complexes [5]. A sodium hydroxide solution was gradually poured into aqueous aluminum hydroxochloride while constantly stirring the mixture to pH ~3 or 4. The concentration of hydroxo complexes was calculated on the basis of 5–30 mg-equiv of Al^{3+} per 1 g of clay. A suspension of bentonite (~1.0 wt %) was prepared by vigorously stirring bentonite in water for 4 h; the pH of the suspension was ~8 or 9. The medium acidity was monitored with an OR-208/1 pH-meter. The suspension of clay was slowly added to the solution of the aluminum polyhydroxo complex to avoid its coagulation.

The coagulation-preventing basicity reserve of Al^{3+}/OH^- was 1/3. The suspension of clay treated with aluminum hydroxochloride was stored for 24 h. The precipitate was washed with water and condensed by centrifuging. The sample was separated from the liquid and dried at room temperature and then at 110°C (2 h) and 180°C (4 h). The solid was cooled, ground, and sieved. Fractions with definite grain sizes were impregnated with aqueous ruthenium hydroxochloride $Ru(OH)Cl_3 \cdot 4H_2O$ of pure grade (0.5–1.0 wt % Ru). The resulting thick mass was dried on a water bath. It was then calcinated at 180°C for 6 h.

Determining Catalytic Activity

A catalyst sample (0.1 g) was reduced with hydrogen at 250°C for 4 h before each experiment. After reduction, the catalyst was cooled to room temperature under hydrogen. It was then transferred under a layer of cyclohexane to a steel autoclave (working capacity, 100 cm^3) equipped with a stirrer and sampling unit. A mixture (50 cm^3) of benzene and cyclohexane of pure grade was used for hydrodearomatiza-

Table 1. Dependence of the adsorption structural parameters of montmorillonite on the content of modifying aluminum

$[Al^{3+}]$, mg-equiv/g of clay	S_{sp}, m^2/g	d_{001}, nm	V, cm^3/g	Loss of thermal stability	
				t, °C	S_{sp}, m^2/g
–	60	0.9	0.19	160	40
5	140	1.36	0.46	340	110
10	180	1.64	0.54	500	140
15	270	2.00	0.56	600	210
20	280	2.06	0.58	600	220
30	260	1.90	0.54	600	200

Note: $[Al^{3+}]$ is the content of aluminum ions and V is the total pore volume.

tion $[V(C_6H_6) : V(C_6H_{12}) = 1 : 1]$. Dilution with cyclohexane was needed to scatter the heat that evolved during the hydrogenation of benzene in order to conduct the process under ideal mixing conditions. The initial rate of hydrogenation was determined differentially from the plot of the time dependence of benzene concentration $-dc/d\tau = \tan\alpha$. The hydrogen pressure was measured with a manometer and varied from 0.5 to 6.0 MPa; the reaction temperature was varied from 120 to 200°C.

X-ray Diffraction and Chromatographic Analysis

The XRD patterns of the samples were recorded on a DRON-3 diffractometer (CuK_α radiation). The specific surface of the catalysts was determined by BET and by gas chromatography from the retained volume of the familiar γ-Al_2O_3 adsorbent.

The catalyst was analyzed on a Chrom-4 chromatograph equipped with a flame ionization detector. The column (length 3 m, diameter 3 mm) was filled with solid Khromaton-N treated with liquid polyethyleneglycol adipate (15% of the mass of the substrate). The column temperature was 100°C; the evaporator temperature was 150°C. Argon was used as the carrier gas (flow rate, 50 cm^3/min).

RESULTS AND DISCUSSION

The use of adsorbents with a layered column structure in catalytic and sorption processes has stimulated the development of methods for synthesizing them from natural aluminosilicates. Table 1 presents selected physicochemical characteristics of ruthenium catalysts on columnar montmorillonite substrates obtained from bentonite clays from the southern region of the Kazakh Republic.

Modification of bentonite clays with Al(III) polyhydroxo complexes increased the specific surface from 60 to 280 m^2/g; the total pore volume grew from 0.19 to 0.50–0.58 cm^3/g; the interlayer distance d_{001}, from 0.9 to 2.06 nm.

The maximum distance of 2.00–2.06 nm corresponds to an aluminum concentration of 15–20 mg-equiv/g of clay with oligomer aluminum ions on ion-exchange centers [6]. At aluminum concentrations of over 20 mg-equiv/g of clay, the distance did not grow because of the emergence of nonhydrolyzed aluminum salts, which do not affect the formation of a layered columnar structure in solution. A similar effect was reported for iron(III) polyhydroxo complexes [7].

Modifying montmorillonites of bentonite clays makes them thermally stable. The specific surface 270–280 m^2/g, determined after calcination at 180°C, shrank to 210–220 m^2/g, respectively, at 600°C. The nonmodified bentonite clays collapsed at 160°C, their specific surface being 40 m^2/g. The obtained modified montmorillonites were used to prepare supported ruthenium catalysts (0.5–1.0 wt % Ru) on which the hydrogenation of benzene was studied.

The catalytic systems in question have a quite developed specific surface. In the first series of experiments, the utilization of the inner surface of the catalysts was determined. The Tile–Zeldovich criterion φ

Table 2. Dependence of efficiency on the particle size of 0.5% Ru–substrate catalyst

d_{av}, mm	φ	$\tanh\varphi$	η
0.2	0.14	0.15	0.99
0.4	0.31	0.30	0.98
0.6	0.47	0.44	0.94
0.8	0.62	0.55	0.90
1.0	0.75	0.64	0.84
2.0	1.56	0.97	0.63

Note: $m_{cat} = 0.1$ g, $t = 120°C$, $p_{H_2} = 40$ atm, $c_{0C_6H_6} = 5.6$ M; d_{av} is the average diameter of the catalyst particles.

Table 3. Hydrogenation of benzene in the presence of water on the 0.5% Ru–substrate catalyst

Initial mixture, mL			Yields of hydrogenation products (mol %) after different periods of time (min)							
			C_6H_{10}	C_6H_{12}	C_6H_{10}	C_6H_{12}	C_6H_{10}	C_6H_{12}	C_6H_{10}	C_6H_{12}
C_6H_6	C_6H_{14}	H_2O	5		10		20		30	
25	25	–	–	16.0	–	30	–	58	–	74
25	20	5	1.0	11.0	2.5	20	4.0	36	3.0	48
25	15	10	2.0	9.0	3.0	18	6.0	31	5.0	41
25	10	15	1.5	8.0	2.0	14	3.0	24	3.0	30
25	5	20	0.5	6.0	1.0	10.0	2.0	14	2.0	18

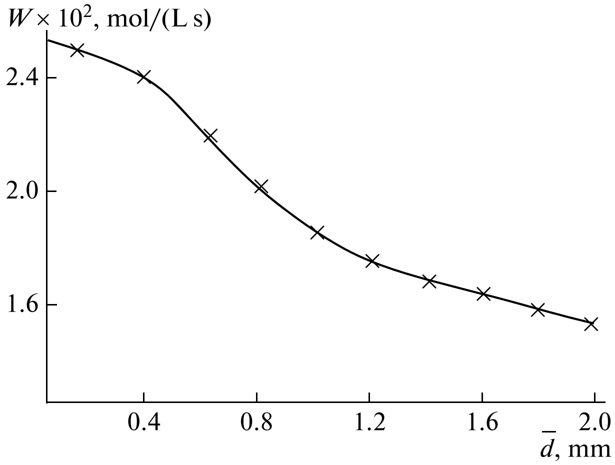
Note: $m_{cat} = 0.1$ g, $t = 120°C$, and $p_{H_2} = 40$ atm.

was included in our calculations. This criterion is in direct proportion to the reduced radius of the catalyst:

$$\varphi = R_0 (k/D)^{1/2},$$

where R_0 is the reduced radius of the catalyst particle ($R_0 = R/3$ for spherical particles), k is the reaction rate constant, and D is the effective diffusion coefficient of reactant molecules on the inner surface of pores.

For gases, the diffusion coefficient is ~0.1 cm^2/s; the molecular diffusion in liquid is ~10^{-5} cm^2/s [8]. The diffusion coefficient of the gas dissolved in the liquid is on the same order of magnitude as the liquid itself, ~10^{-5} cm^2/s. At 120°C, the pressure of saturated benzene vapors determined from the Kocks plot is 2 atm [9]. If we include the critical values of benzene ($t_{cr} = 288.6°C$ and $p_{cr} = 48.6$ atm), the fugacity of benzene vapors is $f^v = 0.80$ atm. At 120°C, saturated vapor pressure 2 atm, and constant pressure of the system 40 atm, the fugacity of liquid benzene is $f^l = 38$ atm. The phase equilibrium constant is $k = f^l/f^v = 47.5$, suggesting that the benzene was mainly in the liquid phase.



Dependence of the rate of hydrogenation on the catalyst particle size.

The rate constant of liquid-state hydrogenation of benzene was determined using catalyst powder with a mean particle size of <0.1 mm (2.3×10^{-2} s^{-1} for the given case). The efficiency (the degree of utilization of the inner surface of pores) was determined with the equation

$$\tanh\varphi = [\exp(\varphi) - \exp(-\varphi)]/[\exp(\varphi) + \exp(-\varphi)].$$

The calculated parameters of benzene hydrogenation in the presence of porous catalysts are summarized in Table 2.

It follows from the data of Table 2 that the efficiency is 0.84 for a particle with an average diameter >1 mm and 0.63 for 2 mm. These data suggest that the inner surface of pores during liquid-state hydrogenation is utilized effectively when the catalyst particle size is less than 0.8 mm. For larger particles, the observed rate diminished linearly (see figure).

In subsequent experiments, we used catalysts with average particle sizes of <0.4 mm. Since the experiments were performed with vigorous stirring (2000 rpm), the effect of external diffusion was ignored.

The sole reduction product in the hydrogenation of benzene under the given conditions was cyclohexane. As is well known, varying the acidity of solid catalysts often changes their selectivity. An important role is played here by the preadsorbed water of the adsorbent, which favors the formation of Brønsted and Lewis acid centers on the aluminosilicate surface [3].

It was therefore of interest to study the behavior of ruthenium catalysts on a columnar montmorillonite substrate in the hydrogenation of benzene in the presence of water. Table 3 presents data on the reduction of the aromatic ring by hydrogen.

According to Table 3, the presence of water in the system during the hydrogenation of benzene after 20 min led to the formation of 6 mol % cyclohexene and 31 mol % cyclohexane at a water content of

10 mL. A further increase in the volume of water reduced the yield of hydrogenation products.

After the addition of four hydrogen atoms, the benzene ring is believed to have been hydrogenated to cyclohexane without leaving the catalyst's surface. In addition, we think that the resulting cyclohexene was ousted by water molecules; i.e., the rate of cyclohexene desorption was comparable to that of hydrogenation [10–12]. This is indicative of the sequential addition of hydrogen to the benzene ring.

However, the reaction mixture did not contain cyclohexadiene, which would also have been displaced by water molecules from the catalyst's surface. The rate of cyclohexadiene hydrogenation is obviously higher than the rate of its desorption. We may assume that the formation of intermediate cycloolefins is favored by the character of benzene adsorption, which can be either planar or of the edge type. Ruthenium on columnar montmorillonite in the presence of water molecules creates favorable conditions for the decomposition of the delocalized π system of the aromatic ring (edge adsorption of benzene). It is possible that in the activated complex, the benzene participates with the 4*p* electrons of the ring, which consequently join four hydrogen atoms. This assumption is consistent with Sedgwick's 18-electron rule [13, 14].

CONCLUSIONS

We studied the hydrogenation of benzene on a supported ruthenium catalyst and calculated its efficiency for determining the observed rate. The presence of water in the system led to stepwise reduction of benzene on the catalyst's surface, forming cyclohexane and cyclohexene. The results from our experiments can be used for the hydrodearomatization of motor fuels, especially the transformation of aromatic hydrocarbons into naphthenes.

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