656 Russian Chemical Bulletin, International Edition, Vol. 55, No. 4, pp. 656—660, April, 2006

Transformations of cyclohexane and benzene on the bimetallic Ru—Pt oxide catalysts

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The bimetallic Ru-Pt/Al_2O_3 catalysts with an overall metal content of 1 wt. % and Pt : Ru weight ratios from 1 : 3 to 3 : 1 were studied. The catalytic activity for cyclohexane and benzene transformations, including hydrogenation, hydrogenolysis, and skeletal isomerization of the initial substrates and products of intermediate transformations, was studied at temperatures 180—350 °C and H_2 pressures from 1.0 to 5.0 MPa. The maximum yield of *n*-hexane from cyclohexane and benzene was obtained on the catalysts with a ruthenium content of 0.75—1.0%, being ~29—30 wt.% at 40% selectivity. The selectivity to form *n*-hexane decreases with an increase in the cyclohexane conversion and is almost independent of the composition of the Ru—Pt system. On the catalysts under study, benzene is converted to the same products but at temperatures by 60 °C lower as compared to cyclohexane conversion.

Key words: bimetallic catalysts, platinum, ruthenium, cyclohexane, benzene, *n*-hexane, ring opening, hydrogenation, hydrogenolysis.

Stringent levels imposed on the content of aromatic hydrocarbons, in particular, benzene, in motor fuels can only be met by improving the quality of fuels. One of the ways to solve this problem can be the selective ring opening of aromatic and naphthenic hydrocarbons to form alkanes with the same number of carbon atoms as in the initial hydrocarbon.

It has previously been shown[1—4] that the reaction of cyclohexane ring opening forming *n*-hexane occurs, under certain conditions, on the oxide catalysts containing Rh, Ru, or Pt. The six-membered ring opening on the Ru catalyst occurs at much lower temperatures (210—230 °C) than on the Rh and Pt catalysts (350—400 °C).[2] However, the Ru-oxide systems are characterized by high activity in the hydrogenolysis of alkanes and naphthenes forming methane and other low alkanes. The activity of the Ru catalysts depends, to a great extent, on the initial compound from which Ru is introduced and on the support nature (SiO_2, Al_2O_3, TiO_2, ZrO_2).[2,5,6]

The properties of the Ru catalysts also change considerably when the second metal is introduced, for instance, Pt, Pd, Ir, or Re. The influence of the structure of the bimetallic Ru—Pt system on its catalytic activity and selectivity has been studied earlier for the deep hydrogenolysis of alkanes and naphthenes, hydrogenation of benzene, and isomerization of hexanes.[7—12] The properties of the bimetallic Ru—Pt catalysts depend strongly on the nature of the support and the initial salt (chlorides or ammoniates), a sequence of introduction of metals, and conditions of preliminary activation.[9—13] For instance, in terms of activity in methylcyclopentane (MCP) hydrogenolysis,[9] the bimetallic Pt—Ru system is substantially different from the monometallic Ru/Al_2O_3 catalyst, because the introduction of Pt decreases the formation of light hydrocarbons, namely, the predominant direction of MCP conversion on Ru/Al_2O_3.

The present work is aimed at enhancing the selectivity of the Ru catalyst in the reaction of six-membered ring opening. For this purpose, we studied the influence of the second metal (Pt) in the bimetallic Ru—Pt/Al_2O_3 catalysts with different compositions on the regularities of *n*-hexane formation by cyclohexane hydrogenolysis and benzene hydrogenation followed by the hydrogenolysis of cyclohexane.

Experimental

The support for catalysts was γ-Al_2O_3 (Haldor Topsoe, Denmark) with the specific surface S_{sp} = 250—300 $m^2 g^{-1}$. Metals (Ru, Pt) were introduced from dilute 1 *M* aqueous solutions of H_2PtCl_6, $Ru(CH_3COO)_3$, or $RuCl_3$ (analytical grade). To prepare the bimetallic catalysts, first Pt and after drying Ru were introduced. The support was impregnated at 20 °C, the solvent was removed on a rotary evaporator, and the samples were dried at 130 °C. Before experiments, the catalysts were reduced for 3 h in a hydrogen flow at 450 °C. The content of the metals in the monometallic samples and the total content of Pt and Ru in the bimetallic systems was 1 wt.% at the metal ratio Pt : Ru equal to 1 : 3, 1 : 1, and 3 : 1. The metal content was

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 633—637, April, 2006.

Table 1. Transformation of cyclohexane on Ru(1%)/Al_2O_3 (P = 2.6 MPa)

T /°C	X (%)	S (%)	Yield of products (wt.%)				
			CH_4—C_3H_8	ΣC_4H_8	ΣC_5H_{12}	i-C_6H_{14}	n-C_6H_{14}
230	7.7	71.4	0.1	0.2	1.9	0	5.5
240	13.6	69.1	0.3	0.5	3.4	0	9.4
260	43.1	55.2	2.1	3.4	12.8	1.0	23.8
270	48.5	39.0	13.0	9.5	23.2	2.2	30.6
280	100	0	100	0	0	0	0

Note. The following designations were used here and in Table 2: X is conversion, and S is selectivity of n-hexane formation.

determined by the atomic absorption method on an AAC-3 instrument.

The transformations of cyclohexane and benzene were studied in a flow-type setup at temperatures 180—350 °C and a pressure of 1.0—5.0 MPa. The load of the catalyst was 3 cm^3, the volumetric feed rate of hydrocarbon (cyclohexane, benzene) was v = 2 h^{-1}, and the molar ratio H_2 : hydrocarbon was 10 : 1. The reaction products were analyzed on LKhM-80 and Chrom-5 chromatographs without preliminary separation using GLC on a column with 15% polymethylphenylsiloxane on Celite S-22 and on a PONA column (50 m). The activity of the catalysts was estimated from the hydrocarbon conversion and selectivity of formation of hydrogenation, ring opening, and hydrogenolysis products.

Results and Discussion

Cyclohexane conversion. The transformation of cyclohexane has previously[2] been studied on the monometallic Pt(1%)/Al_2O_3 and Ru(1%)/Al_2O_3 catalysts. The Ru catalyst was shown to be active in cyclohexane hydrogenolysis at much lower temperatures (200—230 °C) than Pt/Al_2O_3. The main direction of the cyclohexane conversion on Ru/Al_2O_3 was hydrogenolysis to form alkanes C_1—C_6, while no dehydrogenation of naphthene to benzene was observed. On the contrary, on Pt/Al_2O_3 at temperatures 180—350 °C and a pressure of 2.6 MPa the cyclohexane conversion does not exceed 1%, and benzene becomes the main transformation product as the conversion was increased at temperatures >350 °C.

The results of cyclohexane hydrogenolysis on the Ru catalyst prepared from $Ru(CH_3COO)_3$ are presented in Table 1. It is seen that the naphthene conversion at 230 °C is lower than 10%. With an increase in the temperature of the reaction, the conversion increases and the yield of n-hexane passes through a maximum and then decreases almost to zero. In this case, the main direction of cyclohexane transformation becomes hydrogenolysis with the formation of alkanes C_1—C_5. When the temperature increases from 270 to 280 °C, the conversion increases jumpwise from 48.5 to 100% and the selectivity with respect to the ring opening products decreases simultaneously almost to zero. At 280 °C the substrate is completely transformed into lower alkanes, predominantly methane. The maximum yield of n-hexane on Ru(1%)/Al_2O_3 is 30.6 wt.% at a selectivity of 39%.

The influence of the Pt content on the activity of the bimetallic Ru—Pt catalysts at temperatures 230—350 °C and a pressure of 2.4 MPa is illustrated in Figs 1 and 2. The temperature dependences of the cyclohexane conversion and the yield of n-hexane have the same pattern for the Ru/Al_2O_3 and Ru—Pt/Al_2O_3 catalysts with different compositions. The temperature at which the maximum yield of n-hexane is observed depends on the ruthenium content. A decrease in the Ru content from 1.0 to 0.25% and, correspondingly, an increase in the Pt content in the catalyst from 0 to 0.75% result in an increase in the temperature needed for the reaction to occur. Accordingly, the n-hexane yield decreases, and the maximum of the n-hexane yield is shifted to higher temperatures (see Fig. 1). The results obtained on the bimetallic catalysts can be related to a change in the dispersion and electronic state of ruthenium caused by a decrease in its concentration upon the introduction of the second metal

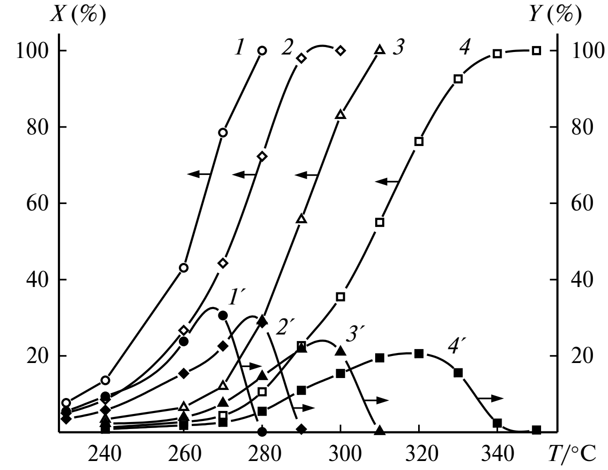

Fig. 1. Conversion (*1—4*) of cyclohexane (X) and the yield (*1′—4′*) of n-hexane (Y) *vs.* temperature on the catalysts Ru(1%)/Al_2O_3 (*1*, *1′*), Ru(0.75%)—Pt(0.25%)/Al_2O_3 (*2*, *2′*), Ru(0.5%)—Pt(0.5%)/Al_2O_3 (*3*, *3′*), and Ru(0.25%)—Pt(0.75%)/Al_2O_3 (*4*, *4′*) at 2.6 MPa.

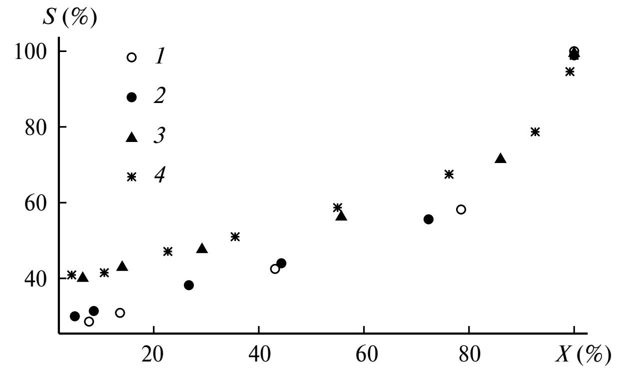

Fig. 2. Selectivity of formation of alkanes $C_1—C_5$ (S) *vs.* cyclohexane conversion (X) on Ru(1%)/Al_2O_3 (*1*) and the bimetallic catalysts Ru(0.75%)—Pt(0.25%)/Al_2O_3 (*2*), Ru(0.5%)—Pt(0.5%)/Al_2O_3 (*3*), and Ru(0.25%)—Pt(0.75%)/Al_2O_3 (*4*) at 2.6 MPa.

into the system. It is known[14] that cyclohexane hydrogenolysis is a structure-sensitive reaction and depends on the dispersion of ruthenium. The data obtained by us for the hydrogenolysis of this hydrocarbon on the bimetallic catalysts indicate that the size of the ruthenium particles decreases, most likely, when Ru is partially replaced by Pt and, as a consequence, the catalytic activity of the bimetallic catalysts in hydrogenolysis decreases. The catalytic activity of the supported Ru catalysts also decreased with an increase in the metal dispersion for the hydrogenolysis and hydrogenation of benzene.[15] When the size of the ruthenium crystallites decreases, the decrease in the activity of hydrogenolysis is much more pronounced than that for benzene hydrogenation.

The plots of the selectivity of formation of alkanes $C_1—C_5$ as a function of the substrate conversion are presented in Fig. 2 and serve to estimate the influence of the platinum content in the bimetallic catalysts on the hydrogenolysis of cyclohexane to low alkanes. As can be seen, the selectivity increases with an increase in the cyclohexane conversion and is virtually independent of the catalyst content. A decrease in the ruthenium concentration and, correspondingly, an increase in the platinum concentration in the catalyst has no substantial effect on the selectivity to hydrogenolysis. Only reactions of ring opening of cyclohexane to *n*-hexane and hydrogenolysis to light hydrocarbons occur on the catalysts under study and, hence, an increase in the selectivity with respect to alkanes $C_1—C_5$ results in a decrease in the selectivity to form *n*-hexane.

Benzene conversion. The hydrogenation of benzene on the Group VIII metals is studied in rather detail.[16,17] Much less works deal with deeper transformations including the subsequent hydrogenolysis and ring opening of cyclohexane, which is formed as the primary product of benzene hydrogenation. The hydrogenation and hydrogenolysis of benzene were studied on the bulky and supported Ru catalysts.[15] We studied benzene transformation on the mono- and bimetallic Ru catalysts at temperatures 180—340 °C and a hydrogen pressure of 2.4—5.0 MPa. Under these conditions, the benzene conversion is 100%. The main directions of benzene transformation are hydrogenation to cyclohexane, ring opening with *n*-hexane formation, and hydrogenolysis to alkanes $C_1—C_5$. At low temperatures (<200 °C), the products of benzene transformation contain predominantly cyclohexane. The products of ring opening and hydrogenolysis, namely, *n*-hexanes and alkanes $C_1—C_5$, are also formed at increased reaction temperatures. To compare the results of hydrogenolysis of benzene and cyclohexane, the selectivity of *n*-hexane formation in the hydrogenolysis of benzene was calculated from the ratio of the *n*-hexane yield to the total yield of the products of ring opening and hydrocracking (formation of light products $C_1—C_5$): $S^* = Y_{C_6H_{14}}/Y_{C_1-C_5} + Y_{C_6H_{14}}$.

The results of benzene transformation on two Ru catalysts prepared from different ruthenium salts, *viz.*, $Ru(CH_3COO)_3$ (**I**) and $RuCl_3$ (**II**), are given in Table 2. As the data obtained show, the activity and selectivity of *n*-hexane formation in the presence of catalyst **I** are higher

Table 2. Transformation of benzene on Ru(1%)/Al_2O_3

Catalyst (initial ruthenium salt)	T /°C	P /MPa	S^* (%)	Yield of products* (wt.%)					
				$CH_4—C_3H_8$	ΣC_4H_{10}	ΣC_5H_{12}	*i*-C_6H_{14}	*n*-C_6H_{14}	*cyclo*-C_6H_{12}
I ($Ru(CH_3COO)_3$)	220	2.4	44.7	6.1	5.6	16.3	1.2	23.6	47.2
	220	3.5	51.4	3.7	3.9	13.0	0.8	22.6	56.0
	220	5.0	49.3	4.0	3.0	9.8	0.4	17.1	65.7
II ($RuCl_3$)	220	2.4	27.2	17.2	7.8	15.9	1.1	15.8	41.9
	220	3.5	45.0	2.5	3.0	11.9	0.7	15.0	66.7
	230	3.5	33.1	13.3	7.4	21.0	1.1	21.2	36.0

* The conversion of benzene under the studied conditions is 100%. The selectivity of *n*-hexane formation is calculated from the ratio of the yield of *n*-hexane to the total yield of the products of C_6-ring opening and hydrogenolysis to light products. The yield of methylcyclopentane is 0.2—0.3 wt.%.

than those on sample **II**, whereas the yield of alkanes C_1—C_5, by contrast, is higher on catalyst **II**. This can be related to differences in the dispersion and state of the metal in the catalysts with and without chlorine. As shown earlier,[5] the residual chlorine and ruthenium dispersity are the main factors affecting the selectivity of cyclohexane on Ru/Al_2O_3.

The influence of the pressure on the direction of the reaction, namely, C_6-ring opening to form *n*-hexane or hydrocracking to alkanes C_1—C_5, was studied on catalysts **I** and **II**. The pressure increase from 2.4 to 3.5 MPa suppressed the hydrocracking reactions on the both catalysts and exerted almost no effect on the C_6-ring opening (see Table 2). The cyclohexane content in the reaction products increases simultaneously. The further increase in the pressure to 5 MPa on sample **I** decreases the yields of both alkanes C_1—C_5 and *n*-hexane.

The temperature dependences of the yields of *n*-hexane and alkanes C_1—C_5 during benzene hydrogenolysis on $Ru(1\%)/Al_2O_3$ are similar to the results obtained for cyclohexane hydrogenolysis (Figs 1 and 3). However, the hydrogenolysis of benzene occurs at lower temperatures than cyclohexane hydrogenolysis. The maximum yield of *n*-hexane from benzene is observed at 220 °C, while that from cyclohexane is observed at 260—270 °C.

Let us consider how the platinum content affects the activity of the Ru—Pt catalysts in benzene hydrogenolysis at temperatures 180—340 °C and a pressure of 2.4—5.0 MPa (Figs 3 and 4). The features of benzene transformation are similar for the bimetallic catalysts with a ruthenium content of 0.5 and 0.75%. They are similar to the results obtained for cyclohexane hydrogenolysis, although all parameters are shifted to the region of lower temperatures (see Figs 1 and 3). For instance, on the $Ru(0.75\%)$—$Pt(0.25\%)/Al_2O_3$ catalyst, benzene is predominantly hydrogenated to cyclohexane at 180 °C, while the conversion of benzene to the products of ring opening and hydrocracking is lower than 10%. When the temperature increases, the yield of *n*-hexane passes through a maximum, and the 100% conversion of benzene to low alkanes is observed at 230—240 °C. Under the same conditions (230 °C), the conversion of cyclohexane does not exceed 14%. At the reaction temperatures below 240 °C benzene is mainly hydrogenated to cyclohexane on the bimetallic catalysts with the lowest ruthenium content, *viz.*, $Ru(0.25\%)$—$Pt(0.75\%)/Al_2O_3$. With the temperature increase, the yields of C_6-ring opening products and light products increases slowly, and even at 340 °C their total yield does not exceed 70 wt.%, which is much lower than the yields on the bimetallic catalysts containing a larger amount of ruthenium. At reaction temperatures above 340 °C, the benzene conversion decreases. The reason can be either the catalyst deactivation or the equilibrium shift in the benzene $\rightleftarrows$ cyclohexane system toward benzene at high temperatures. The observed differences in temperatures needed to effect the cyclohexane and benzene transformations can be related to the fact that benzene, probably, more easily forms surface chemisorbed compounds, whose further transformations afford alkanes C_1—C_6.

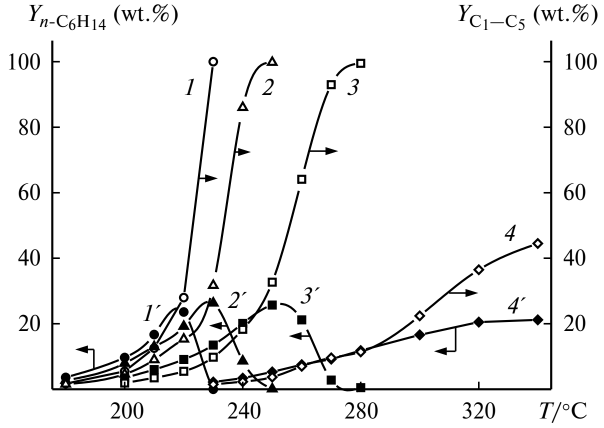

Fig. 3. Yields (*Y*) of *n*-hexane (*1—4*) and alkanes C_1—C_5 (*1′—4′*) *vs.* temperature on the catalysts $Ru(1\%)/Al_2O_3$ (*1, 1′*), $Ru(0.75\%)$—$Pt(0.25\%)/Al_2O_3$ (*2, 2′*), $Ru(0.5\%)$—$Pt(0.5\%)/Al_2O_3$ (*3, 3′*), and $Ru(0.25\%)$—$Pt(0.75\%)/Al_2O_3$ (*4, 4′*) during benzene hydrogenolysis (pressure 2.4 MPa).

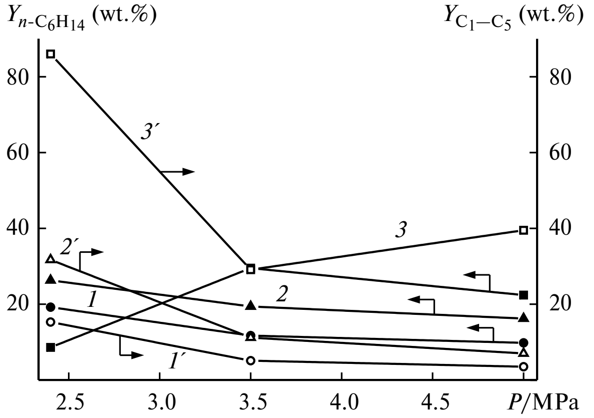

Fig. 4. Yields (*Y*) of *n*-hexane (*1—3*) and alkanes C_1—C_5 (*1′—3′*) *vs.* pressure during benzene hydrogenolysis on $Ru(0.75\%)$—$Pt(0.25\%)/Al_2O_3$ at 220 (*1, 1′*), 230 (*2, 2′*), and 240 °C (*3, 3′*).

The pressure effect on the yield of the main products of benzene transformation on the bimetallic $Ru(0.75\%)$—$Pt(0.25\%)/Al_2O_3$ catalyst is presented in Fig. 4. At low reaction temperatures (≤230 °C), the pressure increase from 2.4 to 5.0 MPa decreases the yields of both *n*-hexane and alkanes C_1—C_5. In this case, the benzene conversion is suppressed mainly due to a decrease in the yield of alkanes C_1—C_5. At temperatures >230 °C the pressure increase from 3.5 to 5.0 MPa, on the contrary, results in an increase in the *n*-hexane yield. The optimal conditions for the reaction on this catalyst are 240 °C and 3.5 MPa under which the *n*-hexane yield is 29.5 wt.%.

Thus, the activity of the bimetallic Ru—Pt/Al_2O_3 catalysts in the hydrogenolysis of cyclohexane and benzene depends strongly on the ruthenium content. The selectivity of *n*-hexane formation decreases with an increase in the cyclohexane conversion and is virtually independent of the catalyst composition. Under the conditions studied, the maximum yield of *n*-hexane from cyclohexane and benzene is 29—30 wt.% at 40% selectivity and was obtained on the catalysts with a ruthenium content of 0.75—1.0%. The temperature of the benzene hydrogenolysis reaction is by 50—60° lower than that for cyclohexane hydrogenolysis.

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Received July 25, 2005;
in revised form March 15, 2006