Cyclohexane transformations over metal oxide catalysts
1. Effect of the nature of metal and support on the catalytic activity in cyclohexane ring opening

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The activities of monometallic Pt-, Ru-, and Rh-containing catalysts supported on Al_2O_3, Al_2O_3—F, SiO_2, WO_3/ZrO_2, and La_2O_3/ZrO_2, in cyclohexane ring opening to form *n*-hexane were studied. The most active catalyst is Rh/Al_2O_3. Cyclohexane hydrogenolysis to *n*-hexane also occurs over the Pt/Al_2O_3 and $Pt/La_2O_3/ZrO_2$ catalysts. Ring opening over the Ru catalysts proceeds at significantly lower temperatures (210—230 °C) than over the Pt and Rh catalysts (350—400 °C), but the ruthenium systems are less selective for *n*-hexane formation than Rh/Al_2O_3 catalysts. The effects of acid-basic properties of the support and the reaction conditions on the activities of the catalytic systems in cyclohexane ring opening was studied.

Key words: cyclohexane, methylcyclopentane, *n*-hexane, ring opening, hydrogenolysis, dehydrogenation, isomerization, heterogeneous catalysis, platinum, rhodium, ruthenium.

Selective ring opening of naphtene hydrocarbons to form normal and low branched paraffins improves the quality of diesel fuel due to enhancement of the cetane number of the fuel, whereas skeletal isomerization leads to a marked improvements in quality of gasoil fractions.

Ring opening of cyclopropane, cyclobutane, and cyclopentane hydrocarbons has been reported earlier.[1—5] Ring opening of cyclohexane to form *n*-hexane was studied to a lesser extent.[6,7]

Dehydrogenation, isomerization to methylcyclopentane (MCP), and hydrocracking to C_1—C_5 hydrocarbons are the main reactions of cyclohexane and its alkyl derivatives over oxide catalysts containing Pt, Rh, Ru, Ir, Re, and U.[1,7—11] Under specific conditions, *n*-hexane can be formed from cyclohexane over oxide catalysts containing Rh, Ru, Ni, and Pt.[6,7,12]

From the study of the mechanisms of hydrogenolysis of cyclopentane and cyclohexane,[7] it can be inferred that Pt significantly differs from other VIII group metals in its catalytic behavior. Whereas cyclohexane transforms to *n*-hexane over the activated carbon-supported Rh, Ru, Ir, and Os catalysts, this reaction does not occur over Pt/C, although the corresponding alkanes can be formed from cyclopentane and C_7—C_{15} cycloalkanes.

Isomerization to alkylcyclopentanes is the main pathway of the cyclohexane[8] and methylcyclohexane[13] transformations over bifunctional Pt catalysts containing metal oxides modified with SO_4^{2-} or WO_4^{2-} anions and exhibiting strong acid and superacid properties ($Pt/WO_3/ZrO_2$ and $Pt/SO_4/ZrO_2$). When alkylcyclopentanes undergo hydrogenolysis over electron-deficient metal particles, isoalkanes are formed along with *n*-alkanes C_6 and C_7.

The type of cyclohexane or methylcyclohexane transformations over Ru- and Ir-containing catalysts[9—11,14] depends on the metal dispersion. When the dispersion is low, cyclohexane hydrogenolysis (hydrocracking) to form light alkanes, mainly methane, prevails, whereas dehydrogenation to benzene is the main reaction over highly dispersed catalysts.[9]

The effects of the metal nature (Pt, Rh, Ru), acid-basic properties of the support (SiO_2, Al_2O_3, Al_2O_3—F, WO_3/ZrO_2, and La_2O_3/ZrO_2), and the reaction conditions on the activity and selectivity of the metal oxide catalysts in the cyclohexane ring opening to form *n*-hexane were studied in this work.

Experimental

We used γ-Al_2O_3, Al_2O_3—F (F content was 0.3 or 3.5 wt.%) and SiO_2 with the specific surface area (S_{sp}) of 250, 150—160, and 300 $m^2 g^{-1}$, respectively, as the catalyst supports. The support 15% WO_3/ZrO_2 was prepared according to the known procedure,[15] and 3% La_2O_3/ZrO_2 was prepared by impregnating zirconium hydroxide with an aqueous solution of lanthanum

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nitrate followed by calcination at 500 °C for 4 h. The metals (Pt, Rh, and Ru) were introduced from dilute aqueous solutions of H_2PtCl_6, $RhCl_3$, and $[Ru(NH_3)_6](NO_3)_3$, respectively, by impregnation of the support at 20 °C followed by evaporation on a rotary evaporator. Then the samples were dried for 2 h at 130 °C. Before runs, the catalysts were reduced in an H_2 flow for 3 h at 450 °C. The concentrations of Pt, Ru, and Rh in the catalysts were 1.0 wt.%.

The cyclohexane transformations were studied in a flow setup at 180—400 °C and a pressure of 0.7—5.0 MPa. The catalyst volume was 1—3 cm^3, the cyclohexane feed rate was 1—2 h^{-1} at the molar ratio $H_2 : C_6H_{12} = (5—10) : 1$. The reaction products were analyzed by GLC without preliminary separation of gaseous and liquid hydrocarbons on a column (l = 3 m) packed with polymethylphenylsiloxane on Celite C-22. The selectivity for each product was evaluated as the ratio of its yield to the overall cyclohexane conversion.

Results and Discussion

Pt catalysts. Dehydrogenation to benzene is the main reaction involved in cyclohexane transformations in the presence of Pt/SiO_2 at 340 °C and a pressure of 0.7 MPa (Table 1). In this case, cyclohexane does not undergo hydrogenolysis and the yield of *n*-hexane was <1%. Over the Pt/Al_2O_3—F catalyst (0.3 wt.% F) under similar conditions, cyclohexane is predominantly dehydrogenated to benzene but the yields of *n*-hexane and MCP are one order of magnitude higher than those over Pt/SiO_2. Less than 1% of cyclohexane is hydrocracked to C_1—C_5 hydrocarbons.

At a low cyclohexane conversion (11.6%) only benzene and a small amount of *n*-hexane are obtained over the Pt/Al_2O_3 catalyst without F (see Table 1). With increasing temperature and conversion of cyclohexane, the selectivity for benzene decreases, while MCP and isohexanes appear in the reaction products. A pressure increase at the constant temperature leads to a decrease in both the cyclohexane conversion and selectivity for benzene, and the *n*-hexane yield increases. The $n\text{-}C_6H_{14} : i\text{-}C_6H_{14}$ ratio in the products of cyclohexane transformation varies from 5 to 13, and this is significantly higher than that found in MCP hydrogenolysis under similar conditions (see Ref. 4). Hence, *n*-hexane can be formed over Pt/Al_2O_3 through the direct opening of the cyclohexane ring.

As is known, treatment of the Al_2O_3 surface with halides induces the appearance of proton acidity and, as a result, the enhancement of catalytic activity in skeletal isomerization. Cyclohexane is mainly dehydrogenated to benzene over the Pt/Al_2O_3—F catalyst (3.5 wt.% F) at 320—420 °C and a pressure of 0.7 MPa (Fig. 1, *a*). However, as pressure is increased to 2.0 MPa, the product distribution substantially changes: despite a decrease in the molar ratio $H_2 : C_6H_{12}$ from 10 : 1 to 5 : 1, the benzene yield is at most 6 wt.%, and simultaneously, the contribution from isomerization of cyclohexane to MCP increases (Fig. 1, *b*). With an increase in temperature from 350 to 400 °C, the MCP yield passes through a maximum, the *n*-hexane yield increases up to 22.9 wt.%, and that of isohexanes reaches 42.4 wt.% (see Fig. 1, *b*).

The introduction of 3.5 wt.% F in the Pt/Al_2O_3 catalyst changes the pattern of cyclohexane transformation: at the conversion of <15%, only MCP and benzene are

Table 1. Effect of reaction conditions on the conversion and selectivity of cyclohexane transformations over the Pt- and Rh-containing oxide catalysts (molar ratio $H_2 : C_6H_{12} = 10 : 1$)

Catalyst	υ_{vol} /h^{-1}	p /MPa	T /°C	X (%)	Y (wt.%)	S (%))				
						C_1—C_5	$i\text{-}C_6H_{14}$	$n\text{-}C_6H_{14}$	MCP	C_6H_6
Pt/SiO_2	1	0.7	340	38.9	0.4	—	—	1.0	0.2	98.8
Pt/Al_2O_3—F (0.3 wt.% F)	1	0.7	340	37.6	3.2	0.5	0.8	8.5	4.3	85.9
Pt/Al_2O_3	2	1	350	11.6	1.5	—	—	12.9	—	87.1
	2	1	370	34.1	2.7	—	0.9	7.9	5.3	85.9
	2	2	370	14.7	5.2	—	2.7	35.4	9.5	52.4
	2	2	400	49.6	12.4	1.2	3.2	25.0	4.6	65.9
	2	3	400	41.4	17.5	2.9	8.0	42.3	8.9	37.9
Pt/Al_2O_3—F (3.5 wt.% F)	2	1	350	14.5	—	—	—	—	60.7	39.3
Rh/SiO_2	2	5	320	92.7	51.9	44.0	—	56.0	—	—
Rh/Al_2O_3	2	1	280	33.2	24.9	23.2	1.8	75.0	—	—
	2	1	350	100	—	100	—	—	—	—
	2	3	300	91.0	59.3	34.1	0.7	65.2	—	—
	2	5	280	55.9	49.0	12.3	—	87.7	—	—

Note. The following designations were used here and in Tables 2, 3: υ_{vol} is the cyclohexane space feed rate, X is the cyclohexane conversion, Y is the *n*-hexane yield, S is the selectivity for products.

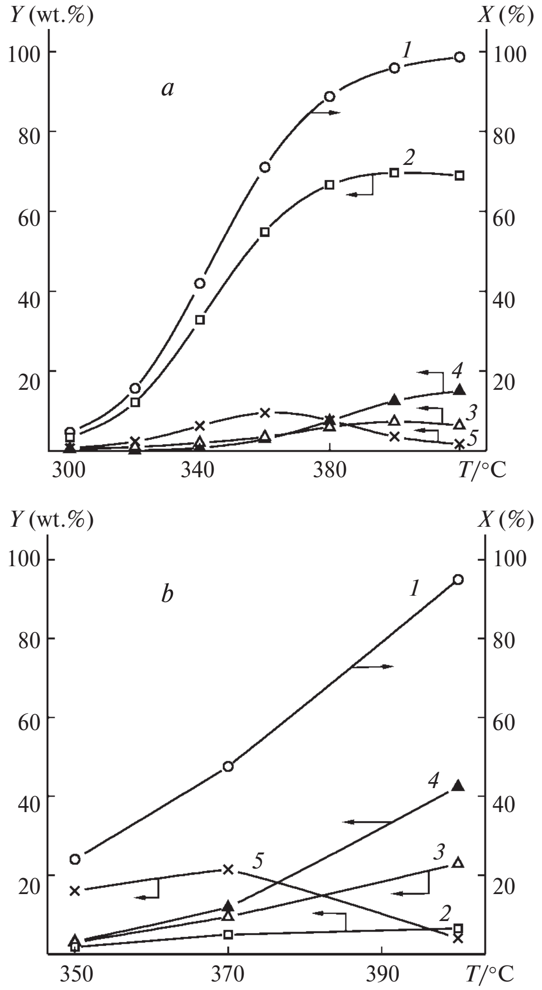


Fig. 1. Effect of reaction conditions on the cyclohexane conversion (X) (*1*) and yields (Y) of benzene (*2*), *n*-hexane (*3*), isohexanes (*4*), and methylcyclopentane (*5*) over $Pt/Al_2O_3—F$ (3.5 wt.% F): pressure 0.7 MPa (*a*), 2.0 MPa (*b*), molar ratio $H_2 : C_6H_{12}$ = 10 : 1 (*a*) and 5 : 1 (*b*), cyclohexane space feed rate, 2 h^{-1}.

formed with the selectivity for MCP 1.5 times higher than that for benzene (see Table 1). At pressures above 1 MPa, the main reaction accompanying cyclohexane transformation over the catalyst becomes isomerization to MCP followed by hydrogenolysis to isohexanes and *n*-hexane rather than dehydrogenation to benzene (see Fig. 1, *b*).

In the presence of the $Pt/WO_3/ZrO_2$ bifunctional system containing strong acid sites, cyclohexane predominantly isomerizes to MCP (Fig. 2, *a*). At temperatures $\geq$350 °C, isohexanes and *n*-hexane are formed in small quantities with total yields not exceeding 10 wt.% (Table 2, Fig. 2, *a*).

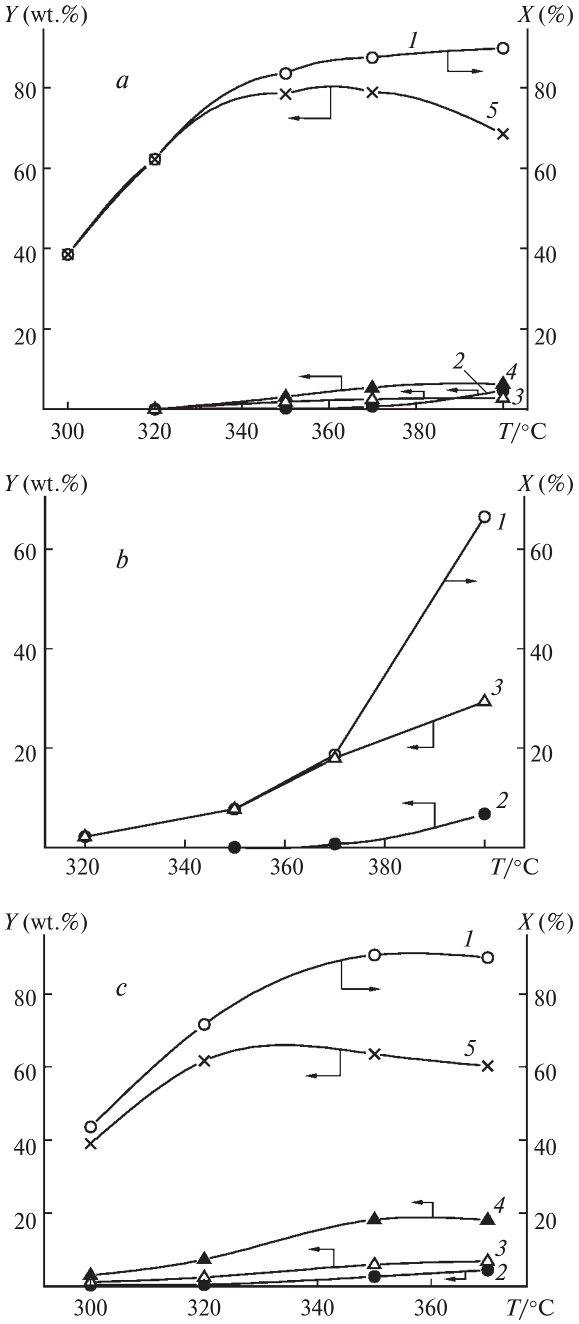


Fig. 2. Dependence of the cyclohexane conversion (X) (*1*) and yields (Y) of alkanes $C_1—C_5$ (*2*), *n*-hexane (*3*), isohexanes (*4*), and methylcyclopentane (*5*) over the catalysts $Pt/WO_3/ZrO_2$ (*a*), $Pt/La_2O_3/ZrO_2$ (*b*), and $Rh/WO_3/ZrO_2$ (*c*) on temperature (T) (pressure 2.0 MPa, molar ratio $H_2 : C_6H_{12}$ = 10 : 1, cyclohexane space feed rate, 2 h^{-1}).

Selectivity for *n*-hexane is very high for the $Pt/La_2O_3/ZrO_2$ system possessing the basic properties (see Table 2). With increasing temperature and pressure, the cyclohexane conversion increases and selectivity for *n*-hexane decreases. Simultaneously, the yield of the $C_1—C_5$ hydrocarbons increases and formation of isohexanes and benzene is detected (see Table 2, Fig. 2, *b*).

Table 2. Effect of the acid-basic properties of the support in Pt- and Rh-containing catalysts on the selectivity of cyclohexane transformations (molar ratio $H_2 : C_6H_{12} = 10 : 1$, $\upsilon_{vol} = 2\ h^{-1}$)

Catalyst	p /MPa	T /°C	X (%)	Y (wt.%)	S (%)				
					C_1—C_5	i-C_6H_{14}	n-C_6H_{14}	MCP	C_6H_6
$Pt/WO_3/ZrO_2$	1	300	33.0	—	—	—	—	100	—
	2	300	38.5	—	—	—	—	100	—
	2	400	89.8	2.8	5.2	7.0	3.1	76.3	8.4
$Rh/WO_3/ZrO_2$	1	300	43.0	1.2	0.7	6.5	2.8	90.0	—
	2	300	43.6	1.2	0.7	7.1	2.8	89.4	—
	2	350	90.6	6.0	3.0	20.2	6.6	70.2	—
	2	370*	67.9	—	—	—	—	54.5	45.5
$Pt/La_2O_3/ZrO_2$	2	370	18.7	18.0	3.7	—	96.3	—	—
	2	400	66.6	29.4	10.0	5.2	44.1	2.7	38.0
	3	370	19.8	17.1	2.5	11.4	88.6	—	—
	3	380	36.5	25.9	7.7	9.9	71.0	—	11.5
	3	400	83.3	43.4	31.5	10.7	52.1	—	5.8
	4	380	57.5	38.5	19.8	13.2	67.0	—	—
$Rh/La_2O_3/ZrO_2$	1	280	33.8	21.3	37.0	—	63.0	—	—
	2	280	41.7	30.0	28.1	—	71.9	—	—
	3	280	47.9	34.1	28.8	—	71.2	—	—
	3	300	100	—	100	—	—	—	—

* Replacement of H_2 for N_2 (molar ratio $N_2 : C_6H_{12} = 10 : 1$).

Hence, depending on the acid-basic properties of the support and reaction conditions, cyclohexane transforms over the Pt-containing catalysts through the following pathways: dehydrogenation to benzene, isomerization to MCP, opening of the cyclohexane ring to *n*-hexane, and hydrogenolysis to C_1—C_5 alkanes. When Pt is supported on SiO_2 or Al_2O_3, dehydrogenation of cyclohexane to benzene prevails. Cyclohexane ring opening to form *n*-hexane occurs over the Pt/Al_2O_3 and $Pt/La_2O_3/ZrO_2$ systems. The Broensted acid sites (B-sites) likely participate in the formation of the isomerization products (MCP, isohexanes) over the acid catalysts (Pt/Al_2O_3—F, $Pt/WO_3/ZrO_2$). Isohexanes found over Pt/Al_2O_3 seem to be the products of secondary reactions.

Rh catalysts. The Rh/Al_2O_3 catalysts have been shown earlier[12] to be the most active and selective in cyclohexane ring opening to form *n*-hexane. As can be seen in Table 1, cyclohexane hydrogenolysis over the Rh catalysts occurs at temperatures of 280—320 °C, that is, 50—100 °C lower than that over the Pt/Al_2O_3 systems. The reaction conditions strongly affect the pathway of the cyclohexane transformation over Rh/Al_2O_3 and Rh/SiO_2: both selective ring opening to form *n*-hexane and complete hydrogenolysis to C_1—C_5 hydrocarbons can take place depending on the temperature and/or pressure. This catalytic behavior is determined not only by the support nature (Al_2O_3, SiO_2) but also by the properties of supported Rh clusters,[16] since this behavior is due to differences in the activation energies for cracking and ring opening. For example, the *n*-hexane yield over Rh/Al_2O_3 at 280 °C (pressure 1.0 MPa) is 24.9 wt.% at selectivity of 75%, whereas cyclohexane transforms to C_1—C_5 hydrocarbons at 350 °C with the 100% conversion and selectivity. The highest *n*-hexane yield (59.3 wt.%) was obtained over Rh/Al_2O_3 at 300 °C and 3.0 MPa. The yield of isohexanes is at most 1.8 wt.%. Benzene and MCP are not formed over the Rh/Al_2O_3 and Rh/SiO_2 catalysts under conditions of our experiments (see Table 1).

The data of Table 2 and Fig. 2, *c* clarify the activity and selectivity of the Rh-containing systems with the acid (WO_3/ZrO_2) and basic (La_2O_3/ZrO_2) properties.

Isomerization to MCP is the main pathway of cyclohexane transformation over the $Rh/WO_3/ZrO_2$ and $Pt/WO_3/ZrO_2$ catalysts. With an increase in temperature, the yield of MCP passes through a maximum, while the yields of isohexanes, *n*-hexane, and alkanes C_1—C_5 steadily increase (see Fig. 2). At similar cyclohexane conversions, the selectivity for MCP is lower over $Rh/WO_3/ZrO_2$ and those for isohexanes and *n*-hexane are substantially higher than over $Pt/WO_3/ZrO_2$ (see Table 2). When N_2 is used instead of H_2, the cyclohexane conversion decreases and the MCP and benzene are the transformation products. Hence, cyclohexane isomerization to MCP occurs predominantly over the Pt- and Rh-containing catalysts supported on the acid oxides (Al_2O_3—F, WO_3/ZrO_2). Isohexanes and *n*-hexane are produced upon the hydrogenolysis of MCP and cyclohexane (see Table 2, Fig. 2).

On the contrary, the cyclohexane ring opening to form *n*-hexane and the hydrogenolysis of cyclohex-

Table 3. Cyclohexane transformations over the Ru catalysts (molar ratio $H_2 : C_6H_{12} = 10 : 1$, $p = 1.0$ MPa, $\upsilon_{vol} = 2\ h^{-1}$)

Catalyst	T /°C	X (%)	$S_{n\text{-}C_6H_{14}}$ (%)	Yield of products (wt.%)		
				C_1—C_5	i-C_6H_{14}	n-C_6H_{14}
Ru/Al_2O_3	200	11.9	66	4.1	—	7.8
	210	29.4	53	13.4	0.3	15.7
	230	100	0	100	—	—
Ru/Al_2O_3—F	190	5.5	65	1.9	—	3.6
(3.5 wt.% F)	210	30.9	44	17.3	—	13.6
	230	100	0	100	—	—

ane to C_1—C_5 alkanes prevail over the basic catalysts ($Rh/La_2O_3/ZrO_2$ and $Pt/La_2O_3/ZrO_2$). The n-hexane yield over $Rh/La_2O_3/ZrO_2$ reaches 34.1 wt.% with selectivity of 71.2%.

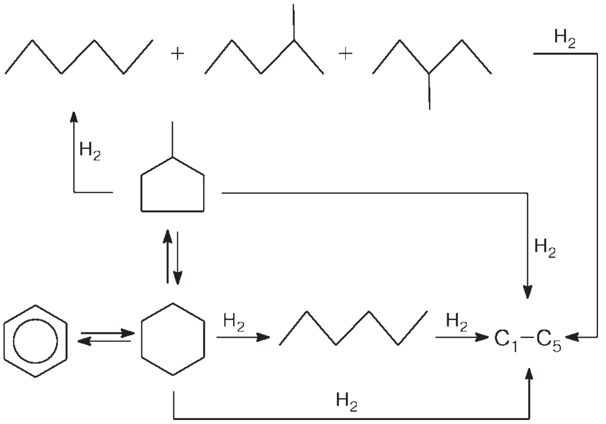
It has been shown earlier[13] that the B-sites and metallic particles participate in cyclohexane ring opening over bifunctional catalysts and this process involves alkylcyclopentanes. When the support has no B-sites,[7,12] ring opening occurs through the C—C bond rupture over the metal (Pt, Rh, Ru) and n-hexane and alkanes with lower molecular weights are formed.

Considerable differences in selectivity of Pt- and Rh-containing catalysts on the acid and basic supports can be due not only to the support properties but also the different dispersion of the metal particles. The difference in sizes of the metal particles causes a change in the metal charge during the formation of specific active sites at the metal—support interface.[16] For example, a bifunctional site, a positively charged adduct of the metal particle with a proton, can be formed upon interaction between the Rh (or Pt) small particles and B-sites.[16,17] These sites are capable of catalyzing C—C bond hydrogenolysis.

Ru catalysts. The Ru systems are active in cyclohexane hydrogenolysis at lower temperatures than the Rh and Pt catalysts (*cf.* the data of Tables 1—3). The hydrogenolysis of cyclohexane to form n-hexane and alkanes with lower molecular weights is the main pathway of cyclohexane transformation over Ru/Al_2O_3 and Ru/Al_2O_3—F (see Table 3).

The cyclohexane conversion at temperatures of 210—230 °C over the Ru catalysts varies from 30 to 100%, whereas the Pt and Rh-containing catalysts are inactive in fact. The yield of n-hexane and selectivity of its formation strongly depend on the reaction temperature. When the temperature increases from 190—200 to 230 °C the selectivity drops from 65% to 0. The maximal yield of n-hexane over Ru/Al_2O_3 was 15.7 wt.% at the selectivity of 53%. The yield of C_1—C_5 hydrocarbons changes in parallel to the cyclohexane conversion, and only C_1—C_5 alkanes, mainly methane, are formed at 230 °C. Neither benzene nor MCP were formed over Ru/Al_2O_3 and Ru/Al_2O_3—F under the above conditions.

Summing up, the overall scheme of cyclohexane transformations over the metal oxide catalysts can be presented as follows.



A preferable reaction path depends on the metal nature, acid-basic properties of the support, and the reaction conditions.

Dehydrogenation of cyclohexane to benzene occurs over Pt/SiO_2 and Pt/Al_2O_3, and cyclohexane ring opening to form n-hexane, whilst to a lesser extent, takes place over Pt/Al_2O_3. Depending on the reaction conditions, dehydrogenation of cyclohexane to benzene or its isomerization to MCP followed by C_5 cycle opening and formation of a mixture of hexane isomers prevails over Pt/Al_2O_3—F.

The catalysts containing Pt and Rh on the solid superacid WO_3/ZrO_2, are characterized by the high yield and selectivity to MCP. When the basic support is used (La_2O_3/ZrO_2), a high selectivity in cyclohexane ring opening to form n-hexane was found. The opening of the C_6 ring to form n-hexane and hydrogenolysis to C_1—C_5 alkanes are the main reactions over the Rh/Al_2O_3, Rh/SiO_2, and Ru catalysts.

In terms of the maximal yield of n-hexane formed upon cyclohexane ring opening, the catalysts studied can be arranged in the following sequence: $Rh/Al_2O_3 \geq$ $\geq Rh/SiO_2 > Pt/La_2O_3/ZrO_2 \geq Rh/La_2O_3/ZrO_2 \gg$ $\gg Pt/Al_2O_3 \approx Ru/Al_2O_3$.

The most active and selective catalyst in this reaction is Rh/Al_2O_3.

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