Russian Chemical Bulletin, International Edition, Vol. 51, No. 2, pp. 255—258, February, 2002

Cyclohexane transformations over metal oxide catalysts
2.* Selective cyclohexane ring opening to form *n*-hexane over mono- and bimetallic rhodium catalysts

T. V. Vasina,[a] O. V. Masloboishchikova,[a] E. G. Khelkovskaya-Sergeeva,[a] L. M. Kustov,[a★] and P. Zeuthen[b]

[a]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: lmk@ioc.ac.ru
[b]*Haldor Topsoe A/S, DK-2800 Lyngby, Denmark*

The activity of monometallic Rh and Pt catalysts and bimetallic Pt—Rh catalysts on oxide supports in cyclohexane ring opening to form *n*-hexane was studied. The Rh-containing catalysts are highly active and selective in this reaction. Cyclohexane dehydrogenation predominates in the case of the Pt catalysts. The use of the bimetallic alumina-supported Pt—Rh catalysts allows one to minimize the contribution of cyclohexane cracking and to enhance the selectivity for *n*-hexane with the yield of the latter slightly depending on the metal ratio in the bimetallic system under the experimental conditions.

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

As shown earlier,[1—6] depending on the metal nature, acid-basic properties of a support, and reaction conditions, cyclohexane can undergo dehydrogenation to benzene, isomerization to methylcyclopentane (MCP), or hydrogenolysis (hydrocracking) to form *n*-hexane and alkanes C_1—C_5 over metal oxide catalysts. Cyclohexane ring opening to form *n*-hexane occurs mainly over Rh- and Pt-containing oxide catalysts under specific conditions,[1—3] and the *n*-hexane yield over the Rh catalysts is significantly higher than that over the Pt catalysts.

Bimetallic systems are often used as selective and stable catalysts, which are more resistant to deactivation than monometallic catalysts based on VIII group metals. The properties of the bimetallic catalysts substantially depend on the mode of metal introduction, component ratio, support nature, and activation conditions.[7—10]. For example, addition of Ag to the Rh/TiO_2 system enhances selectivity of MCP hydrogenolysis to *n*-hexane likely due to a change in the mechanism of cyclopentane ring opening.[7]

Cyclohexane ring opening to form *n*-hexane over the monometallic Rh- and Pt-containing catalysts and bimetallic Pt—Rh catalysts on oxide supports as well as the effect of the Pt : Rh ratio and reaction conditions (temperature and pressure) on the yield of *n*-hexane and selectivity were studied in this work.

Experimental

The Al_2O_3 and SiO_2 supports with the specific surface areas (S_{sp}) of 250 and 300 $m^2 g^{-1}$ were used. The metals (Pt, Rh, and Pt—Rh) were introduced from dilute aqueous solutions of H_2PtCl_6, $RhCl_3$, and mixed $H_2PtCl_6 + RhCl_3$ solutions, respectively. The supports were impregnated at 20 °C, evaporated on a rotary evaporator, and dried at 130 °C. Before operation, the catalysts were reduced for 3 h in an H_2 flow at 450 °C and sometimes at 500—600 °C. Some samples were treated only with air at 500 °C or initially with air at 500 °C and then with H_2 at 450 °C. The Pt and Rh concentrations in the monometallic catalysts were 1.0—2.0 wt.% and 1 wt.% in the bimetallic systems (total metal content) at the ratios Pt : Rh = 1 : 3, 1 : 1, and 3 : 1.

The reaction was carried out in a flow setup at temperatures of 210—400 °C and pressures of 1.0—5.0 MPa, a volume of the catalyst was 3 cm^3, cyclohexane space feed rate was 2 h^{-1}, and molar ratio was $H_2 : C_6H_{12} = 10 : 1$. Analysis of the reaction products was described previously.[1]

Results and Discussion

The cyclohexane transformations were studied over two groups of catalysts, monometallic (Pt/Al_2O_3, Rh/Al_2O_3, Rh/SiO_2) and bimetallic ($Pt—Rh/Al_2O_3$) with various metal ratios.

Monometallic catalysts. The data of Table 1 show that cyclohexane transformations over the 1% Pt/Al_2O_3 cata-

---

* For Part 1, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 242—245, February, 2002.

Table 1. Effects of pressure (p) and temperature (T) on cyclohexane conversion over the Pt- and Rh-containing oxide catalysts

Catalyst	p /MPa	T /°C	X (%)	S (%)	Yield of products (wt.%)					
					C_1—C_4	C_5H_{12}	i-C_6H_{14}	n-C_6H_{14}	MCP	C_6H_6
1% Pt/Al_2O_3	2	370	14.7	35.4	—	—	0.4	5.2	1.4	7.7
	2	400	49.6	25.0	0.2	0.4	1.6	12.4	2.3	32.7
	3	400	41.4	42.3	0.3	0.9	3.3	17.5	3.7	15.7
1% Rh/Al_2O_3	3	280	39.1	90.0	2.1	1.8	—	35.2	—	—
	5	280	55.9	87.7	4.9	2.0	—	49.0	—	—
	3	300	91.0	65.2	21.2	9.9	0.6	59.3	—	—
2% Rh/Al_2O_3	3	280	89.0	78.0	8.8	10.2	0.6	69.4	—	—
	5	280	83.0	84.9	6.9	5.3	0.3	70.5	—	—
1% Rh/SiO_2	3	320	80.8	35.4	19.6	32.6	—	28.6	—	—
	5	320	92.7	56.0	18.6	22.2	—	51.9	—	—

Note. The following designations are used here and in Tables 2, 3: X is the cyclohexane conversion, S is selectivity for n-hexane.

lyst occur at relatively high temperatures (370—400 °C). Cyclohexane is mainly dehydrogenated to benzene despite the elevated H_2 pressure in the system (1—3 MPa). The cyclohexane conversion increases from 14.7 to 49.6% with an increase in temperature from 370 to 400 °C. The yield of n-hexane reaches 17.5 wt.% at the selectivity of 42.3% (400 °C, 3 MPa). The number of reaction products is increased with an increase in temperature because of the formation of MCP and isohexanes but the yield of C_1—C_5 alkanes is low.

The Rh/Al_2O_3 and Rh/SiO_2 catalysts are more active and selective in cyclohexane ring opening. The reaction occurs at 280—320 °C, *i.e.*, at significantly lower temperatures compared to the platinum-alumina catalyst. The maximal yield of n-hexane (1% Rh/Al_2O_3, 300 °C, 3 MPa) was 59.3 wt.% at selectivity of 65.2%. Benzene and MCP were not found in the reaction products, and the yield of isohexanes did not exceed 1 wt.%. Cyclohexane hydrogenolysis to form C_1—C_5 alkanes was the only side reaction.

The main channel of cyclohexane transformation over the Rh catalysts strongly depends on temperature and pressure (Fig. 1). The yield of n-hexane was 7—14 wt.% at a pressure of 1 MPa and 240—260 °C (at selectivity up to 90%) and increased to 32—34 wt.% with an increase in temperature to 300—320 °C. A further increase in temperature up to 350 °C results in a drop of the n-hexane yield, and hydrogenolysis to form C_1—C_5 hydrocarbons becomes the major reaction path (see Fig. 1, *a*).

The yield of n-hexane gradually increases with an increase in the pressure from 1 to 5 MPa at a constant temperature (280 °C) and reaches 49 wt.% (see Fig. 1, *b*), whereas selectivity for n-hexane initially increases reaching a 88% value and then remains unchanged. The plots of the n-hexane yield and selectivity of its formation at 300 °C versus pressure pass through a maximum at 3 MPa. When pressure increases to 5 MPa, cyclohexane hydrogenolysis to C_1—C_5 alkanes becomes prevailing and the yield of n-hexane is halved. Hence, the optimal combination of the selectivity and n-hexane yield can be achieved by the proper choice of temperature and pressure.

When the Rh content in the catalyst increases from 1 to 2 wt.%, the cyclohexane conversion substantially increases but selectivity to n-hexane changes insignificantly (see Table 1). The highest yield of n-hexane over the

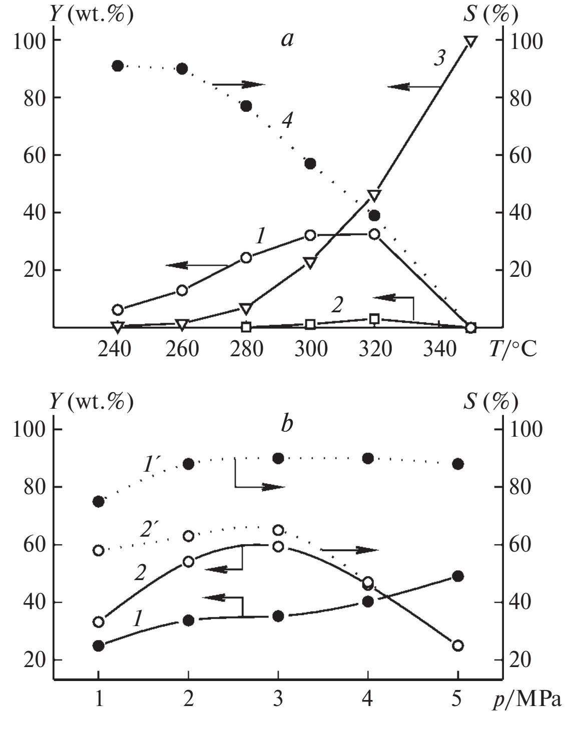

Fig. 1. *a*. Temperature (T) dependence of the yield (Y) of n-hexane (*1*), overall yield of isohexanes (*2*) and hydrocarbons C_1—C_5 (*3*), as well as selectivity (S) to n-hexane (*4*) over the 1% Rh/Al_2O_3 catalyst at a pressure of 1 MPa. *b*. Pressure dependence of the yield of n-hexane (*1*, *2*) and selectivity to n-hexane (*1′*, *2′*) over the 1% Rh/Al_2O_3 catalyst at 280 (*1*, *1′*) and 300 °C (*2*, *2′*).

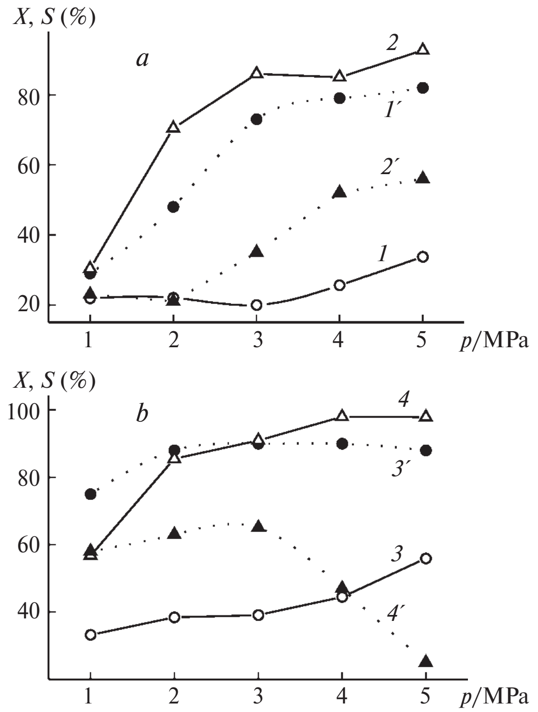

Fig. 2. Pressure dependence of the cyclohexane conversion (*X*) (*1*, *2*, *3*, *4*) and selectivity (*S*) to *n*-hexane (*1*′, *2*′, *3*′, *4*′) over the 1% Rh/SiO_2 (*a*) and 1% Rh/Al_2O_3 (*b*) catalysts at temperatures 280 (*3*, *3*′), 300 (*1*, *1*′, *4*, *4*′), and 320 °C (*2*, *2*′).

2% Rh/Al_2O_3 catalyst at 280 °C and a pressure of 5 MPa is 70.5 wt.% at selectivity of 84.9%.

Hence, depending on the process conditions, selective cyclohexane ring opening to form *n*-hexane or hydrogenolysis to C_1—C_5 hydrocarbons are the main paths of cyclohexane transformation over Rh/Al_2O_3 (see Fig. 1, Table 1).

The temperature and pressure at which the 1% Rh/SiO_2 catalyst shows the highest activity in cyclohexane ring opening to form *n*-hexane are higher than those for the alumina-based system.[1,3] The temperature of 320 °C is an optimal temperature for the reaction over Rh/SiO_2 (it is 40 °C higher than over Rh/Al_2O_3) (see Table 1) as well as a pressure of 5 MPa (Fig. 2). The maximal yields of *n*-hexane over the 1% Rh/SiO_2 and 1% Rh/Al_2O_3 catalysts are comparable. However, selectivity of cyclohexane ring opening is higher over the latter, since C_1—C_5 hydrocarbons are formed over 1% Rh/SiO_2 in the amount of up to 50 wt.%.

In contrast to Pt/Al_2O_3 catalysts, cyclohexane dehydrogenation to benzene and isomerization to MCP do not occur over Rh/Al_2O_3 and Rh/SiO_2 catalysts under the experimental conditions used (240—350 °C, 1—5 MPa). A possible reason for this is that hydrogenating-dehydrogenating properties are typical of the Pt catalysts, while the Rh-containing systems are characterized by strong cracking activity, which manifests itself in the hydrogenolysis of the C—C bond in cycloalkanes. An electron deficiency arises on the metal clusters because of strong interaction of Pt and Rh with the support, thus favoring the formation of particles with various charges, dispersion, *etc.*, thereby affecting[11] the catalytic properties of the whole system.

Table 2. Effect of pretreatment conditions on activity of the 1% Rh/Al_2O_3 catalyst in cyclohexane ring opening at 300 °C

Pretreatment conditions		*p* /MPa	*X* (%)	*S* (%)	Yield of *n*-hexane (wt.%)
Medium	*T*/°C				
H_2	450	2	85.5	63.3	54.1
		3	91.0	65.2	59.3
H_2	520	2	87.1	63.6	55.4
		3	97.1	51.6	50.1
H_2	600	2	89.5	62.7	56.1
Air	500	2	67.7	64.5	43.7
		3	100	—	—
Air	500	2	48.1	73.2	35.2
Air + H_2	500[a], 450[b]	3	60.4	71.5	43.2

[a] Air.
[b] H_2.

Hence, the activation conditions are important for the formation of the active catalyst surface because they affect the acid-basic properties of the system, the electron state of the metal, the dispersion, and the morphology of metal particles. Table 2 presents the data on the influence of the pretreatment conditions on cyclohexane transformations on the 1% Rh/Al_2O_3 catalyst. Reduction in an H_2 atmosphere produces the catalytic system that is the most active and selective in cyclohexane ring opening. Variation of the temperature of catalyst treatment (within the range of 450—600 °C) does not affect the activity in fact. The system formed during catalyst activation in an oxidative medium exhibits the enhanced activity in cyclohexane hydrocracking to form C_1—C_5 alkanes. The successive treatment of the catalyst with air and H_2 is more efficient than the treatment only with air but significantly less efficient than activation in the H_2 flow. The larger the Rh particles or RhO_x phase are likely formed in the oxidative medium, facilitating cyclohexane hydrogenolysis to form light alkanes (see Table 2). The electron state of the metal also depends on the activation conditions.

Bimetallic catalysts. The introduction of the second metal into the system is often used to enhance selectivity and stability of the catalyst. We studied the effect of Pt on activity and selectivity of the Pt—Rh bimetallic systems in cyclohexane ring opening (Fig. 3, Table 3). As can be seen in Fig. 3, the addition of Pt to Rh/Al_2O_3 decreases the contribution of hydrogenolysis to C_1—C_5 alkanes and increases selectivity of cyclohexane transformation for

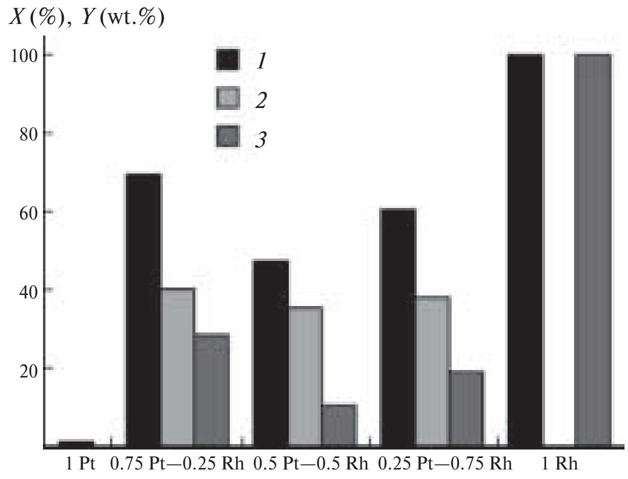

Fig. 3. Effect of the Pt and Rh contents (wt.%) in the bimetallic Pt—Rh/Al_2O_3 catalysts on the cyclohexane conversion (X) (*1*) and yields of *n*-hexane ($Y_{n\text{-}C_6H_{14}}$) (*2*) and hydrocarbons C_1—C_5 ($Y_{C_1-C_5}$) (*3*) in cyclohexane hydrogenolysis (320 °C, 2 MPa).

Table 3. Cyclohexane transformation over the bimetallic catalysts Pt—Rh/Al_2O_3

Metal content	p /MPa	T /°C	X (%)	S (%)	Yield of *n*-hexane (wt.%)
0.5% Pt + 0.5% Rh	3	280	9.1	96.7	8.8
	5	320	65.0	81.8	53.2
0.5% Pt + 1.0%Rh	3	280	64.8	83.2	53.9
	5	280	47.9	89.8	43.0
1% Rh	3	280	39.1	90.0	35.2
	5	280	55.9	87.7	49.0

n-hexane (320 °C, 2 MPa). The cyclohexane conversion on the monometallic catalyst 1% Pt/Al_2O_3 under these conditions is $\geq$1%, whereas cyclohexane completely transforms to the C_1—C_5 gaseous cracking products over the 1% Rh/Al_2O_3 catalyst. The yield of *n*-hexane over the bimetallic catalysts slightly depends on the Pt : Rh ratio, but the selectivities for *n*-hexane over these catalysts significantly differ. The (0.5 wt.% Rh—0.5 wt.% Pt)/Al_2O_3 system is the most selective, and the yield of the C_1—C_5 cracking products is 2—3 times lower than that over the Pt—Rh catalysts with a different composition.

The yield of *n*-hexane over the bimetallic catalysts (3—5 MPa, 300—320 °C) reaches 53 wt.% at selectivity of up to 83% (see Table 3). The optimal temperature of cyclohexane ring opening over the Pt—Rh bimetallic catalysts is 20—30 °C higher than that over 1% Rh/Al_2O_3 but essentially lower than that over 1% Pt/Al_2O_3. A weak dependence of the *n*-hexane yield on the Pt : Rh ratio over the bimetallic alumina-based catalysts is likely due to the formation of the Pt—Rh alloy phase enriched in Rh,[10] which decreases the concentration of free electrons. This can lead to weakening the substrate—metal bond and, as a sequence, to a lesser probability of the rupture of the C—C bonds in the substrate molecule.[12]

Hence, the Rh-containing alumina catalysts are the most active and selective in cyclohexane ring opening to form *n*-hexane.

References

1. O. V. Masloboishchikova, T. V. Vasina, E. G. Khelkovskaya-Sergeeva, L. M. Kustov, and P. Zeuthen, *Izv. Akad. Nauk, Ser. Khim.,* 2002, 237 [*Russ. Chem. Bull, Int. Ed.*, 2002, **51**, 249].
2. L. M. Kustov, T. V. Vasina, O. V. Masloboishchikova, E. G. Khelkovskaya-Sergeeva, and P. Zeuthen, *Stud. Surf. Sci. Catal.*, 2000, **130A**, 227.
3. Ger. Offen 2.127.624; *Chem. Abstrs.*, 1972, **76**, 50630v.
4. O. V. Bragin and A. L. Liberman, *Prevrashchenie uglevodorodov na metallsoderzhashchikh katalizatorakh* [*Transformations of Hydrocarbons over Metal-containing Catalysts*], Khimiya, Moscow, 1981, 264 pp. (in Russian).
5. Y. L. Lam and J. H. Sinfelt, *J. Catal.*, 1976, **42**, 319.
6. L. I. Ali, A.-G. A. Ali, S. M. Aboul-Fotouh, and A. K. Aboul-Gheit, *Appl. Catal. A: General*, 1999, **177**, 99.
7. R. J. Fenoglio, G. M. Nunez, and D. E. Resasco, *Appl. Catal. A: General*, 1990, **63**, 319.
8. G. M. Nunez and A. J. Rouco, *J. Catal.*, 1988, **111**, 41.
9. J. M. Dumas, C. Geron, H. Hadrane, P. Marecot, and J. Barbier, *J. Mol. Catal.*, 1992, **77**, 87.
10. R. E. Lakis, C. E. Lyman, and H. G. Stenger, *J. Catal.*, 1995, **154**, 261.
11. A. Yu. Stakheev and L. M. Kustov, *Appl. Catal. A: General*, 1999, **188**, 3.
12. R. Montarnal and G. Martino, *Rev. Inst. Petrol.*, 1977, **32**, 367.

Received July 26, 2001;
in revised form October 11, 2001