AB are observed at 1440, 1490, 1540, 1590, and 1630 cm<sup>-1</sup> after adsorption of pyridine on the Rh-containing catalyst with an H-pentasil support (M = 29) (Fig. 3b). Desorption of pyridine at 350°C results in the disappearance of the 1590 cm<sup>-1</sup> AB from the spectrum, and the intensity of the other AB decreases significantly, but pyridine cannot be totally desorbed even at 450°C. The 1540 and 1630 cm<sup>-1</sup> AB belong to the  $C_5H_5NH^+$  pyridinium ion, the 1490 cm<sup>-1</sup> AB can be assigned to both coordination-bound pyridine and to pyridinium ions, and the AB at 1440 cm<sup>-1</sup> belongs to coordination-bound pyridine. As a consequence, L and B acid sites are present on the Rh/H-pentasil sample (M = 209).

The spectral picture on the Rh/Na-pentasil sample (M = 37) (Fig. 3c) is similar to the picture described above for the Rh/H-pentasil sample (M = 29). However, the intensity of the AB characterizing coordination-bound pyridine and the pyridinium ion decreases for the Rh/Na-pentasil sample (M = 37) in comparison to the Rh/H-pentasil sample (M = 29), which suggests a lower concentration of L and B sites. In addition, desorption of pyridine from the Rh/Na-pentasil sample (M = 37) takes place at lower temperatures, which indicates the weaker acid sites on the surface of this catalyst.

The IR spectroscopic study of the acidty of the catalysts based on adsorption of pyridine makes it possible to hypothesize that there is a correlation between the activity of the catalysts and their acid properties. A decrease in the concentration and strength of the acid sites on the surface of the catalysts results in a decrease in the activity in formation of pyridines. The samples with a higher concentration of L sites are more active in this reaction.

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# EFFECT OF THE REDUCTION TEMPERATURE ON THE FORMATION

AND ACTIVITY OF BIMETALLIC Ni-Tc CATALYSTS

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The effect of the temperature on the formation, surface state, and catalytic activity in the reactions of dehydrogenation of cyclohexane and dehydrocyclization of n-hexane by Ni-Tc/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mono- and bimetallic catalysts was investigated. TcO<sub>2</sub>, NiCl<sub>2</sub>, and metal phases, and at a high temperature (500-700°C), NiAl<sub>2</sub>O<sub>4</sub> spinel and Ni-Tc clusters, were found on the surface of all of the catalysts. It was shown that the maximum activity is observed in reduction of monometallic catalysts at 500°C and bimetallic catalysts at 700-800°C. Synergism appeared in the bimetallic catalysts due to the formation of Ni-Tc clusters.

Incorporation of Tc in supported platinum catalysts causes a nonadditive increase in the activity of bimetallic catalysts in comparison to nonmetallic catalysts [1]. The form-

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Fig. 1. Effect of the reduction temperature on the yield of benzene in dehydrogenation of cyclohexane at 360°C on the catalysts: 1) 0.1% Tc/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; 2) 2% Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; 3) 2% Ni-1% Tc/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Fig. 2. Yield of benzene in dehydrogenation of cyclohexane on Ni-Tc/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. 1-3) catalyst not treated with H<sub>2</sub> (the numbers 1-3 correspond to the cycle numbers); 4) catalyst with T<sub>red</sub> = 20°C (first cycle); 5, 6) catalyst with T<sub>red</sub> = 100°C [5) first cycle, 6) second cycle].

Fig. 3. Dependence of the yield of benzene at 340°C on the ratio of Ni and Tc for 2% Ni-Tc/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

	100°		500°	700°
Phase	before the experiment	after the experiment	-	
Ni	1,00(8) 0,81(7)	0,98(10) 0,80(25)	1,02(5) 0,82(30)	1,00(10)
Τc	1,10(10) 1,64(8) 1,22(25)	1,13(60)	1,10(20) 1,61(30) 1,20(20)	<b>1</b> ,08 (30) <b>1</b> ,60 (5) <b>1</b> ,26 (65)
$\rm NiCl_2$	1,16(35)	1,18(10)		1,17(5)
TcO <sub>2</sub>	<b>1,22 (2)</b> <b>1,35 (70)</b> <b>1,42 (50)</b>	- - -	1,23 (15) 1,30 (25) 1,51 (15)	1,21(45) 4,30(40) 4,47(45)
Ni – Tc	-	_	2,08(5) 1,26(5) 1,07(15)	2,07 (25) 1,26 (65) 1,08 (30)
NiAl <sub>2</sub> O <sub>4</sub>	_			2,43(5) 1.20(5)

TABLE 1. Interplanar Distances (Å) in the 2% Ni-1%  $Tc/\gamma$ -Al<sub>2</sub>O<sub>3</sub> System as a Function of the Reduction Temperature

ation and activity of the Ni-Tc/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalytic system were investigated in the present study. The data obtained in dehydrogenation of cyclohexane were compared with the results of studying the phase composition of the surface of catalysts reduced under different temperature conditions.

#### EXPERIMENTAL

The catalysts were prepared by impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with solutions of NiCl<sub>2</sub> and NH<sub>4</sub>TcO<sub>4</sub>. After drying at 80-90°C, reduction with H<sub>2</sub> was conducted for 6 h at 25-900°C. The data on the catalytic activity were obtained in a pulsed microcatalytic setup at atmospheric pressure. Helium was the carrier gas. The products of the reaction were analyzed by GLC. Columns packed with Chromosorb with applied squalane (5%) were used for separation. The amount of catalyst was 0.5 g. The electron microscopic studies and electron microdiffraction were conducted on an EM-301 transmission electron microscope. The samples were prepared by the method in [2]. Photography was conducted in the dark field based on the reflections identified. Histograms of the particle size distribution were calculated from



Fig. 4. Histograms of the particle size distribution in the catalysts: a) 1% Tc/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; b) 3% Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; c) 2% Ni-1% Tc/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (prepared at 500°C); d) 2% Ni-1% Tc/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (prepared at 700°C); d<sub>av</sub>(average diameter), Å: a) 23; b) 24; c) 40; d) 33.

the electron photographs. The size of 1000-1400 particles was determined in plotting the histograms.

## RESULTS AND DISCUSSION

The effect of the reduction temperature  $(T_{red})$  on the activity of mono- and bimetallic catalysts in the reaction of dehydrogenation of cyclohexane was investigated to establish the optimum conditions of formation of the catalysts; only benzene was formed in the reaction on all of the catalysts. The data on the yield of benzene (X) as a function of  $T_{red}$ are shown in Fig. 1. The comparative data were obtained for 360°C, where all of the catalysts exhibited pronounced activity. Note that even at  $T_{red} = 20$  °C, Tc catalysts drive the reaction. The maximum yield of benzene on the monometallic catalysts is observed at  $T_{red}$  = 500°C. In the case of bimetallic catalysts, the maximum activity is attained at temperatures of 700-800°C. The detection of activity in the catalysts reduced at low temperatures was an unusual finding: reduction of  $NH_4TcO_4$  to the metal takes place at T > 300°C. The question of what is responsible for the formation of active sites of dehydrogenation arises. A special study was conducted to explain the cause of these phenomena. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was impregnated with solutions of NH4TcO4 and NiCl2 and dried, then three cycles of experiments on dehydrogenation of cyclohexane were conducted. The cycle consisted of 15 experiments conducted in the 100-400°C range. After termination of each cycle, the temperature was decreased to ~20°C, and then a new cycle of experiments was begun with gradual elevation

	[ <b>T</b> c], %	Yield, %			
[Ni], %		benzene	light hydrocarbons		
Dehydrogenation of cyclohexane 420°C					
$\frac{2}{-}$	0,1	25 3			
2	0,1 Dehvdrogenation	of n-hexane 48	– ۱ ٥°C		
1		2,0	4,3		
- 1	0.1 0,1	12,6	12,0		

TABLE 2. Catalytic Activity of Mono- and Bimetallic Ni-Tc Samples

of the temperature. In the first cycle, the reaction was pronounced at >260°C (Fig. 2). At 300°C, the yield of benzene was equal to ~5%, but after 380°C, the yield of benzene increased sharply and attained 50% at 420°C. A second cycle of experiments on dehydrogenation of cyclohexane was conducted with the same catalyst. It was found that the temperature at the onset of the reaction decreased: a 5% yield of benzene was obtained at 200°C. Finally, a third cycle of experiments was conducted with the same catalyst. The yield of benzene increased again. The same series of experiments was then conducted with catalysts prepared at  $T_{red}$  = 20 and 100°C. The curves for the first cycle of experiments characteristically coincided for all three catalysts. The repeated cycles also caused an increase in the activity. The data obtained in these experiments are a typical example of the effect of the reaction medium on the activity of the catalysts [3]. The activity becomes marked in the first cycle at 300°C, when decomposition of the supported salts begins. The TcO<sub>2</sub> formed, for example, can drive the dehydrogenation reaction. The subsequent sharp increase in the activity of the catalysts is due to the fact that the hydrogen formed in the reaction causes reduction of the catalyst. A metal phase appears, i.e., in the second cycle we have a catalyst with another phase composition and another (higher) activity. Further reduction of the catalyst takes place during the second cycle of experiments and, for this reason, the activity in the third cycle is higher than in the second cycle. The catalytic activity also increases with an increase in the degree of reduction.

The surface phase composition was also investigated by electron microdiffraction. The data on the interplanar distances for the different phases are reported in Table 1. The intensities of the reflections in the electron diffraction patterns used to calculate the interplanar distances are given in parentheses. The surface phase composition of both the starting catalyst and after the dehydrogenation reaction is reported for the catalyst with  $T_{red} = 100$ °C. The data show that Tc, TcO<sub>2</sub>, Ni, and NiCl<sub>2</sub> are present on the surface of all catalysts regardless of  $T_{red}$ . The difference only consists of the amount of the corresponding phase. A Ni-Tc solid solution is detected in the bimetallic catalysts, and NiAl<sub>2</sub>O<sub>4</sub> spinel is found in the samples with  $T_{red} = 700$  °C. The amount of metal phases increases, and the concentration of NiCl<sub>2</sub> and TcO<sub>2</sub> decreases with an increase in  $T_{red}$ . The amount of Tc and Ni metal phases increases in the sample with  $T_{red} = 100$  °C after conducting the experiment, while the amount of NiCl<sub>2</sub> decreases; TcO<sub>2</sub> disappears in general. These results are in agreement with our conclusions concerning the effect of the reaction medium on the phase composition of the catalyst. It is necessary to note that the formation of a small amount of Ni and Tc metal phases takes place at  $T_{red}$  = 100°C. This finding indicates the mutual effect of the Ni and Tc on the surface of the support, which results in a reduction in Tred. However, the amount of reduced phases is small and, for this reason, the catalytic activity is also insignificant at  $T_{red} = 100$  °C.

As the data in Fig. 1 shows, the most active bimetallic catalysts are obtained at  $T_{red}$  = 700-800°C. For this reason, all subsequent catalytic studies were conducted with catalysts prepared at 700°C. For bimetallic Ni-Tc catalysts synergism was detected as in the case of Pt-Tc catalysts. In comparison to the monometallic catalysts, the temperature at the beginning of the reaction is reduced and the yield of aromatic product in the reactions of dehydrogenation of cyclohexane and hydrocycliczation of n-hexane is increased (Table 2). The effect is a function of the ratio between the supported metals. The catalysts with an atomic ratio of Ni:Tc = 11:1 are the most active (Fig. 3). The electron microscopic studies showed that the dispersion and average particle diameter are almost the same in the mono- and bimetallic catalysts (Fig. 4). The formation of Ni-Tc solid solutions, which create more active sites of dehydrogenation of cyclohexane and n-hexane, is the most probable cause of the synergism.

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