Rhodium-technetium catalysts in the dehydrogenation of cyclohexane

G. N. Pirogova^{*} and N. N. Rimar'

Institute of Physical Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 117915 Moscow, Russian Federation. Fax: +7 (095) 952 7514

The catalytic properties of a Rh–Tc/support (γ -Al₂O₃, SiO₂, or MgO) system in the dehydrogenation of cyclohexane have been investigated. A nonadditive increase in the catalytic activity of bimetallic catalysts in comparison with monometallic systems has been established. This effect depends on the ratio of the amounts of the supported metals and on the nature of the support. Diffuse reflectance spectra showed the presence of ionic forms of the metals in the bimetallic catalysts. Analysis of the catalytic and optical properties allowed one to draw the conclusion that the synergistic effect is explained by the formation of Rh_xTc_y clusters.

Key words: cyclohexane, dehydrogenation, bimetallic catalysts; diffuse reflectance spectra; synergistic effect.

It has been shown previously^{1,2} that the introduction of technetium to supported platinum, palladium, and nickel catalysts results in a nonadditive increase in the activity of the bimetallic catalysts over the monometallic catalysts. In the present work, the study of the properties of bimetallic catalysts is continued for the Rh—Tc/support system. Dehydrogenation of cyclohexane is used as the model reaction.

Experimental

Catalysts were prepared by impregnating the support with aqueous RhCl₃ and NH₄TcO₄ solutions. γ -Al₂O₃, SiO₂, and MgO were used as supports. Samples were dried in air at 80 °C and calcinated in a flow of hydrogen for 2 h at 300 °C and then for 6 h at 700 °C. The amount of technetium applied was determined by radiometry, and the amount of rhodium was determined by spectrophotometry.

Catalytic dehydrogenation was performed in a pulse microcatalytic apparatus, and helium was used as the carrier gas. The catalyst (0.5 g, 1 cm^3) was placed in a reactor, and cyclohexane was introduced in 0.015-cm^3 portions. The reaction products were analyzed by GLC on a Biokhrom-1 chromatograph. Capillary glass columns with polyethylene glycol (PEG-40M) were used for separation of the hydrocarbons.

The specific surface area of the samples was determined by the **BET** method from the low-temperature adsorption of krypton.

Diffuse reflectance spectra were recorded on a Specord M-40 spectrophotometer.

Results and Discussion

The conversion of cyclohexane on supported monometallic technetium-containing catalysts follows the dehydrogenation pathway: benzene and hydrogen are the reaction products. On rhodium catalysts, in addition to these products, a small amount of lower hydrocarbons (C_1-C_5) is formed at temperatures >400 °C.

The results of the dehydrogenation of cyclohexane on a Rh–Tc/Al₂O₃ system are presented in Fig. 1. It is seen that the Tc(0.05 %)/Al₂O₃ catalyst is inactive at temperatures <300 °C, however, the introduction of the same amount of technetium to the rhodium catalyst results in a considerable increase in the yield of benzene.



Fig. 1. Yield of benzene in the dehydrogenation of cyclohexane on the catalysts: $Tc(0.05 \%)/Al_2O_3 (1)$; $Rh(0.05 \%)/Al_2O_3$ (2); Rh(0.05 %)— $Tc(0.05 \%)/Al_2O_3 (3)$; a mechanical mixture of $Rh(0.1 \%)/Al_2O_3 + Tc(0.1 \%)/Al_2O_3 (4)$.



Fig. 2. Yield of benzene in the dehydrogenation of cyclohexane on the Rh-Tc catalysts at 260 °C vs. the Tc/Rh ratio for the samples: Rh(0.2 %)-Tc/Al₂O₃ (1); Rh(0.1 %)-Tc/Al₂O₃ (2); Rh(0.05 %)-Tc/Al₂O₃ (3). [Rh] = const, the Tc content varies.

The activity of a mechanical mixture of Rh(0.1 %)/Al₂O₃ + Tc(0.1 %)/Al₂O₃ (0.5 cm³ + 0.5 cm³) containing the same amount of metals as the impregnated bimetallic catalyst at temperatures <270 °C is the same as that of the rhodium catalyst. The yield of benzene sharply increased at higher temperatures. It is likely that the metals interact at the sites of contact under these conditions, which results in an increase in the activity. It should be mentioned that the change in the activity of rhodium catalysts promoted by various metals has also been observed previously.^{3,4}

The nonadditive increase in the activity of bimetallic catalysts is the most pronounced for samples with a low



Fig. 3. Yield of benzene in the dehydrogenation of cyclohexane on catalysts containing 0.1 % Rh and 0.1 % Tc on different supports: Al_2O_3 (1); SiO_2 (2); MgO (3).

content of metals. The dependence of the yield of benzene on the concentration and the ratio of metals supported on Al_2O_3 is presented in Fig. 2.

The maximum synergistic effect was manifested at the Tc/Rh ratio equal to 1. An increase in the yield of benzene on bimetallic catalysts is accompanied by an increase in the yield of lower hydrocarbons, especially when the concentration of the supported metals is increased. For example, the yield of C_1-C_5 hydrocarbons reaches 7-8 % at 340 °C when the overall metal content in a sample equals 0.4 %. It is known that the nature of the support affects the activity of rhodium catalysts.⁵ A similar effect was observed for the bimetallic samples, on which the yield of benzene decreased in the series Rh-Tc/Al₂O₃ > Rh-Tc/SiO₂ > Rh-Tc/MgO (Fig. 3).

The results of a comparative study of the two latter systems are presented in Table 1. The results of testing Tc(0.05 %)/MgO and Tc(0.2 %)/SiO₂ are not presented, because these catalysts are inactive in the 260-350 °C

Catalyst			$S_{\rm sp}$	$T_{\rm exp}$	Yield (%)	
support	[Rh] (%)	[Tc] (%)	$/m^{2} g^{-1}$	/°Ĉ	benzene	C_1 - C_5 -hydrocarbons
SiO ₂	0.2	0	200	260 300 350	20 30 34	0 0 1.0
SiO ₂	0.2	0.2	219	260 300 350	42 65 75	1.0 2.0 7.0
MgO	0.05	0	2	260 300 350	3 4 5	0 0 0
MgO	0.05	0.05	5	260 300 350	10 17 24	0 0 0.1

Table 1. Catalytic properties of the Rh-Tc catalysts



Fig. 4. Yield of benzene in the dehydrogenation of cyclohexane on Rh—Tc catalysts vs. the Tc/Rh ratio: on MgO at 360 °C (1) and on SiO₂ at 260 °C (2). [Rh] = const = 0.1 %, the Tc content varies.

range. It can be seen from the data in Table 1 that the introduction of small amounts of technetium to the rhodium catalysts applied on SiO₂ or MgO results in a two- to fivefold increase in the yield of benzene. Lower hydrocarbons appear at high temperatures like in the case of samples based on Al₂O₃. For Rh–Tc/SiO₂ their yield was 1-2 % at 300 °C and reached 15 % for some samples at 400 °C. The yields of benzene and lower hydrocarbons on Rh–Tc/MgO catalysts were significantly lower than on other systems. For example, the amount of C₁–C₅ hydrocarbons did not exceed 1 % at 350 °C and reached 6-7 % only at 450 °C. This is probably associated not with the nature of the support, but rather with the low specific surface area of these catalysts (see Table 1).

Like in the case of the samples based on Al_2O_3 , the effect of an increase in the activity of the catalysts containing SiO₂ or MgO depends on the ratio of the concentrations of the supported metals. For the Rh-Tc/SiO₂ system, the maximum catalytic activity is observed at the Tc/Rh ratio equal to 3/4, whereas for Rh-Tc/MgO it is at Tc/Rh = 3/2 (Fig. 4).

Thus, the nature of the carrier affects the yields of the reaction products and the optimum ratio of the supported metals.

The optical properties of the Rh— Tc/Al_2O_3 system were studied together with the catalytic activity. Spectra of the catalysts are presented in Fig. 5 as increments of the "optical reflectance density" (minus the optical density of Al_2O_3). After impregnation of Al_2O_3 with an aqueous solution of NH_4TcO_4 and drying, two bands at 247 and 294 nm appear in the diffuse reflectance spectrum, whose positions are almost the same as those of the bands of an aqueous solution of NH_4TcO_4 . After



Fig. 5. Diffuse reflectance spectra of the catalysts reduced at 700 °C (1, 4) and the initial catalysts (2, 3): Tc/Al₂O₃ (1); RhCl₃/Al₂O₃ (2); RhCl₃-NH₄TcO₄/Al₂O₃ (3); Rh-Tc/Al₂O₃ (4).

high-temperature treatment with hydrogen, the bands that are characteristic of pertechnetate remain in the spectrum (see Fig. 5). The absorption in the visible region increases, which is caused by the d-d transition of the reduced technetium.

The spectrum of Al_2O_3 impregnated by an aqueous solution of $RhCl_3$ and then dried contains bands at 343 and 448 nm (see Fig. 5, curve 2), whose positions differ from those of the absorption bands in the spectrum of an aqueous solution of $RhCl_3$ (381 and 480 nm). Most probably, the valence of rhodium changes after application of $RhCl_3$ to the support, and the bands shift to the UV region. It has been previously reported⁶ that Rh^{3+} can be transformed to lower valent states. The spectrum of the rhodium catalyst does not contain any absorption bands in the region mentioned after reduction with hydrogen at 700 °C.

The studies of the diffuse reflectance spectra at all of the stages of preparation of bimetallic catalysts showed that the ionic forms of the metals are retained both after impregnation of Al_2O_3 with the corresponding solutions and after high-temperature reduction. This is especially characteristic of the ionic forms of technetium (247 and 294 nm). The band caused by the presence of the rhodium ions (425 nm) lies in a shorter wave position than in the spectrum of the monometallic rhodium catalyst. High-temperature reduction results in the subsequent shift of the band of rhodium to the UV region (to 417 nm). The overall increase in the optical density in the visible region is caused by the appearance of the metallic phase. Similar results were obtained in the studies of the catalysts on other supports.

The maintenance of the absorption bands typical of the ionic forms of rhodium and technetium and their shift during the preparation of the bimetallic catalysts allow one to draw the conclusion that the supported metals interact both with each other and with the support. Cluster compounds of the Rh_xTc_y type may be the products of the interaction.

Analysis of the experimental results on the activity of the bimetallic catalysts and the mechanical mixture and the optical properties of the samples studied makes it possible to suggest the reason for the synergistic effect. Like in the case of the Pt—Tc, Pd—Tc, and Ni—Tc systems, the compounds of metals formed (Rh_xTc_y) generate additional active centers that cause a nonadditive increase in the activity of the bimetallic catalysts over that of the monometallic samples.

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