- A. Yu. Stakheev, A. A. Yuffa, E. S. Shpiro et al., Kinet. Katal., <u>25</u>, No. 3, 750 (1984).
- 8. K. T. Ng and D. M. Hercules, J. Phys. Chem., <u>80</u>, 2094 (1976).
- 9. A. Takeuchi, K. Tanaka, and K. Miyahara, Bull. Chem. Soc. Jpn. Chem. Lett., No. 2, 171 (1974).
- 10. A. Takeuchi, K. Tanaka, J. Toyoshima, and K. Miyahara, J. Catal., <u>40</u>, No. 1, 94 (1975).
- K. H. Bourne, P. D. Holmes, and R. C. Pithketly, 3rd Int. Congr. Catalyse, II/16, Amsterdam (1964), p. 12.

SYNERGISTIC EFFECT IN THE DEHYDROGENATION OF HYDROCARBONS ON Pd-Tc CATALYSTS

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Palladium catalysts are used for many processes in the chemical and petrochemical industries [1]. One of the methods for increasing the activity of metal catalysts is the introduction of a second metal [2]. Small additions of Tc increase the activity of Pt catalysts considerably [3]. The goal of this work was to study the catalytic properties of Pd-Tc/carrier in the dehydrogenation of cyclic hydrocarbons and n-hexane.

### EXPERIMENTAL

Catalysts were obtained by impregnating a carrier with solutions of  $PdCl_2$  and  $NH_4TcO_4$ . After drying, the samples were reduced in  $H_2$  at 700°C for 12 h.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>, SiO<sub>2</sub>, and  $Y_2O_3$  were used as carriers. The amount of Tc deposited was determined radiometrically, and the amount of Pd spectrophotometrically. The investigation of catalytic activity was carried out in a microcatalytic impulse device under atmospheric pressure. The carrier gas was He. Products were analyzed by GLC on a column filled with Chromosorb, which was coated with squalane (5%). The volume of the catalyst was 0.5-1 cm<sup>3</sup>, and its specific surface area  $S_{sp}$  was determined by a BET isotherm with low temperature Kr adsorption. Chemisorption of CO was carried out in a volumetric adsorption apparatus.



Fig. 1. Yield of benzene from the dehydrogenation of cyclohexane on catalysts: 1) 0.1% Pd/MgO; 2) 0.2% Tc/MgO; 3) 0.1% Pd-0.15% Tc/MgO; 4) a mixture of 0.5 cm<sup>3</sup> of 0.1% Pd/MgO and 0.5 cm<sup>3</sup> of 0.2% Tc/MgO. Catalyst volume was 1 cm<sup>3</sup>.

Fig. 2. Yield of AH as a function of Tc content at 390°C for the dehydrogenation of cyclohexane: 1) 0.2% Pd-Tc/MgO; 2) 0.1% Pd-Tc/MgO; for the dehydrogenation of methylcyclohexane: 3) 0.2% Pd-Tc/MgO.

Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1482-1485, July, 1989. Original article submitted May 16, 1988.

1354 0568-5230/89/3807-1354\$12.50 © 1990 Plenum Publishing Corporation

TABLE 1. Dehydrogenation of Cyclohexane on 0.2% Pd-0.2% Tc/ carrier catalysts at 340°C

Carrier	s <sub>sp</sub> , m <sup>2</sup> /g	Conversion,	Carrier	S <sub>sp</sub> , m <sup>2</sup> /g	Conversion,
γ-Al <sub>2</sub> O <sub>3</sub> MgO TiO <sub>2</sub>	60 9 4	77 45 40	$Y_2O_3$ SiO <sub>2</sub>	7 168	37 6

TABLE 2. Comparison of Catalytic Activity of Mono- and Bimetallic Catalysts for the Dehydrogenation of Cyclohexane at 320°C (0.5 g catalyst)

	[M], %		Yield	[M], %		Yield of ben-	Car-	[M], %		Yield of ben-	
Carrier	Pd	Тс	zene, %	Carrier	Pd Tc	zene, %	rier	Pd	Тс	zene, %	
γ-Al <sub>2</sub> O <sub>3</sub>	0,1 0,1	0,1 0,1	2 2 33	TiO2	0,1 0,1	0,1 0,125	0 9 28	Y <sub>2</sub> O <sub>3</sub>	0,2 	$0,2 \\ 0,2 \\ 0,2$	0 0 26,5

TABLE 3. Comparison of the Ability of Different Hydrocarbons to Undergo Dehydrogenation on 0.2% Pd-0.25% Tc/MgO (0.5 g catalyst)

Triticl budge earlier	т,°С	Yield, %					
Initial hydrocarbon		principal AH	other products				
Cyclohexene	160 200 240	Benzene 65,35	Cyclohexane 34,65 » 11,46 » 6,72				
Cyclohexane	240 360 400 440	Benzene 2.23					
Methylcyclohexane	360 400 440	Toluene 39,76	Benzene 1.64				
Ethylcyclohexane	520 580	Ethylbenzene <sub>5,83</sub> » 5,82	Foluene 3.41 Toluene 3.27, cyclohexane 4.73				
n-Hexane	600 440 520 580	» 19,56 Benzene 1,41 » 4,33 » 17,93	Cyclohexane 2.34  Hexene 10.01				

### RESULTS AND DISCUSSION

As in the case of Pt-Tc catalysts, the introduction of Tc into Pd catalysts causes a nonadditive increase in activity; i.e., a synergistic effect is observed. Figure 1 presents data on the yield of benzene from the dehydrogenation of cyclohexane on mono- and bimetallic catalysts. At the start of the reaction, the temperature was about 100°C lower at the bimetallic catalyst than at the monometallic catalysts, but the yield of benzene still increased by 6-7 times. Similar results were obtained with alkyl derivatives of cyclohexane.

This increase in activity through promotion depends on the nature of both the carrier and reagent. Figure 2 presents data on the yield of aromatic hydrocarbons (AH) as a function of the ratio of the metals. The greatest conversion of naphthenes was observed with 50-60% Tc in the active phase.

Table 1 shows that there is no apparent connection between  $S_{sp}$  and activity, which is determined by the chemical nature of the carrier. It has been demonstrated [1, 4, 5] that



Fig. 3. CO chemisorption as a function of the amount of deposited metal for the catalysts: 1) Pd/MgO; 2) Tc/MgO; 3) 0.2% Pd-Tc/MgO (Pd content is constant, but that of Tc varies).

the ionic form of the metal is present in the most active Pd- and Tc-deposited catalysts and results from an interaction between the active phase and the carrier. A similar process apparently also takes place in bimetallic catalysts. The least activity occurred with a catalyst on the inert carrier  $SiO_2$ . For the remaining carriers, their interaction with the deposited metal compounds was possible, and the activity of these catalysts was greater than that with  $SiO_2$ . As in the case of MgO, a synergistic effect for dehydrogenation on Pd-Tc/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pd-Tc/Y<sub>2</sub>O<sub>3</sub>, and Pd-Tc/TiO<sub>2</sub> was observed. Table 2 lists the percent yields of benzene on mono- and bimetallic catalysts deposited on different carriers. It can be seen that introducing a second metal substantially increases the yield of benzene.

For catalysts deposited on  $\text{TiO}_2$ , the influence of calcination temperature on activity was studied. In the dehydrogenation of cyclohexane, no perceptible difference was detected in the activity of samples reduced at 500°C, 700°C, and 900°C. This indicates that interaction of the deposited Pd and Tc compounds with the carrier takes place during the initial stages of preparation.

A comparison of the reactivity of cyclohexene, cyclohexane, methylcyclohexane, ethylcyclohexane, and n-hexane was carried out on the most active Pd-Tc catalysts (Table 3). The conversion of cyclohexene occurs most easily and exhibits a maximum in the yield of AH as a function of temperature. The temperature corresponding to maximum conversion depends on the composition of the catalyst. The liquid fraction in this case contains benzene and cyclohexane, whereas only benzene is formed in the dehydrogenation of cyclohexane on all Pd-Tc catalysts, though the formation of light hydrocarbons (1-2%) was observed above 500°C. The dehydrogenation of alkyl derivatives of cyclohexane occurs at higher temperatures and is accompanied by secondary reactions. The cyclization of n-hexane also occurs at high temperatures.

In all probability, the observed synergistic effect is related to Pd-Tc interaction, which results in the formation of new active centers for dehydrogenation. Experiments with mechanical mixtures of monometallic catalysts confirm this assumption. As seen in Fig. 1, the yield of benzene up to  $500^{\circ}$ C is the same in the mechanical mixture (curve 4) as on Tc catalysts (curve 2). Above  $500^{\circ}$ C the yield of benzene is greater in the mechanical mixture than on the monometallic catalysts, possibly the result of a topochemical reaction forming compounds of the type  $Pd_{x}Tc_{y}$ .

Figure 3 shows the change in CO chemisorptive capacity of mono- and bimetallic catalysts as a function of the amount of deposited metal. For monometallic catalysts, the largest amount of CO is observed at low metal content because of the spillover effect. The introduction of a second metal markedly decreases the adsorptive capacity of the samples. This suppressed CO chemisorption indicates a change in the nature of the active phase in bimetallic catalysts. A comparison of the data on catalytic and chemisorptive properties leads to the conclusion that an interaction of deposited Pd and Tc compounds takes place during the preparation of the catalysts, and that this results in the formation of highly active centers for dehydrogenation. Apparently, compounds of the type  $Pd_xTc_y$  and the surface ions of the carrier enter into the structure of such centers.

# CONCLUSIONS

1. The existence of synergism is demonstrated; the activity of Pd-Tc/carrier catalysts in the dehydrogenation of hydrocarbons considerably exceeds that of monometallic catalysts. The most active catalysts are those with Pd:Tc ratios from 1:1 to 2:3.

2. In terms of reactivity on Pd-Tc catalysts, the hydrocarbons are arranged as follows: cyclohexene > cyclohexane > methylcyclohexane > ethylcyclohexane > n-hexane.

3. Activity in the dehydrogenation of cyclohexane varies as follows:  $Pd-Tc/\gamma-Al_2O_3 > Pd-Tc/MgO > Pd-Tc/TiO_2 > Pd-Tc/Y_2O_3 > Pd-Tc/SiO_2$ .

4. A decrease in CO chemisorptive capacity on bimetallic catalysts compared to monometallic catalysts is established.

# LITERATURE CITED

- 1. Metallic Catalysts [in Russian], Nauka, Alma-Ata (1982), p. 132.
- L. B. Babenkova, I. N. Blagoveshchenskaya, V. N. Vorob'ev, and K. M. Kubanova, Kinet. Katal., <u>28</u>, No. 5, 1132 (1987).
- V. I. Spitsyn, G. N. Pirogova, N. N. Popova, and G. E. Kalinina, Dokl. Akad. Nauk SSSR, 292, No. 1, 103 (1987).
- 4. Z. V. Luk'yanova, V. I. Shekhobalova, and V. S. Boronin, Vestn. Mosk. Univ., No. 3, 263 (1978).
- 5. G. N. Pirogova, N. M. Prokhorets, R. I. Korosteleva, and Yu. V. Voronin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 288 (1986).

#### ALKYLAROMATIC CARBENE IONS ON H-TsVK ZEOLITES

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In spite of the popularity of the hypothesis of the carbene-ion mechanism in the conversion of hydrocarbons on acidic catalysts, there is little evidence of the formation of such ions, particularly of an aromatic character. In [1], diffuse reflectance spectroscopy (DRS) was used to establish the formation of alkylaromatic carbocations on aluminosilicates. The formation of aromatic carbocations is assumed in the case of the adsorption of olefins and methanol on H-ZSM-5 zeolite [2]. At the same time, the appearance of a corresponding band at 370 nm for H-TsVK treated in a similar manner is connected, on the basis of DRS and IR spectroscopy, with the formation of carbocations of nonaromatic character [3].

The aim of the present work was to elucidate possible routes to the formation of alkylaromatic carbocations and to determine their spectroscopic manifestations and thermal stability.

#### EXPERIMENTAL

Zeolite H-TsVK, which is an analog of H-ZSM-5 [4] with  $SiO_2/Al_2O_3 = 30$ , was used in the present work. Ageing of the samples was effected in  $O_2$  and in vacuum at 773-823 K. IR and DRS spectra were recorded on UR-20 and UV-300 instruments respectively, in the latter case using the standard extension for reflectance. Aromatic hydrocarbons were adsorbed under the pressure of the saturated vapor.

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