CONVERSIONS OF HEXANES ON ALUMINA—RHODIUM CATALYST

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In [1], we described an unusual course of catalytic conversions of hexanes in the presence of alumina—rhodium catalyst obtained by the decomposition of the complex $[(CH_3)_2S]_3RhBr_3$; the main reaction products were isomeric hexanes and methylcyclopentane (MCP). According to data reported in [2-6], alkanes on Rh catalysts undergo intense methane decomposition, aromatization, and coke formation.

Here we are reporting on a study of the influence of the catalyst preparation method and composition on the activity and selectivity of Rh/Al_2O_3 in the conversion of certain alkanes; chemisorption and thermal desorption characteristics have been obtained for Rh catalysts of different genesis.

EXPERIMENTAL

The catalysts were prepared by the following procedure. To a benzene solution of 0.0259 g of $[(CH_3)_2S]_3RhBr_3$ (Rh content 19.32%), 0.995 g of γ-Al_2O_3 (S_{sp} = 200 m^2/g) was added; the mixture was held for 1 h at ~20°C, the benzene was evaporated, and, after heating for 3 h at 110°C, an Al_2O_3-anchored complex was obtained, containing 0.5% Rh (relative to Rh/Al_2O_3); this was designated Rh-1. Specimens of Rh/Al_2O_3 with 0.6% and 3.5% Rh contents (designated Rh-2 and Rh-3, respectively) were prepared by impregnating the support with an $RhCl_3$ solution, as in [3].

As the initial hydrocarbons we used 2- and 3-methylpentanes and n-hexane (designated 2- and 3-MP, and n-C_6, respectively) and 2,2,4-trimethylpentane. The hydrocarbons were purified by distillation in high-efficiency columns. The purity of these alkanes and the composition of the reaction products were determined by GLC [7].

The experiments were performed in the pulse regime in a unit described in [7]. A 30-mg quantity of catalyst was treated with H_2 in a microreactor heated for 15 min each at 250, 350, and 450°C, then 1 h at 500°C. These prepared catalysts were Rh-1, 0.5% Rh/Al_2O_3 from $[(CH_3)_2S]_3RhBr_3$, Rh-2, 0.6% Rh from $RhCl_3$—Al_2O_3. The H_2 flow rate in the experiments was 200 or 100 ml/min, and each pulse was 0.7 ± 0.5 µl.

The coke formation, as determined from the difference in quantities of hydrocarbons passing through the system by two paths (analytical column, or catalyst plus analytical column), was 2-3% with the Rh-1. This is within the limits of accuracy of pulse metering.

The dispersity of the Rh was determined in accordance with [8] by the adsorption of O_2, with GLC analysis. Before performing the chemisorption measurements, the catalysts were reduced for 1 h at 500°C, pumped down to 10^{-3} torr at this temperature, cooled to 25°C under vacuum, and then used in the experiments on O_2 adsorption. The average size of the Rh particles was calculated in accordance with [8].

DISCUSSION OF RESULTS

The Rh/Al_2O_3 catalysts prepared by the different methods showed substantial differences in catalytic activity and selectivity in alkane conversion (Table 1).

The distinctive feature of the Rh-1 is its capability for C_5-dehydrocyclization (C_5-DHC) of alkanes (Fig. 1). Under the conditions that were studied, the structure of the hydrocarbon does not have any great influence on its capability for C_5-DHC; the yields of MCP from n-C_6 and 3-MP are practically identical over the entire range of temperatures studied, and only from

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TABLE 1. Distribution of Products from Conversion of n-C_6 on Rh/Al_2O_3 with Different Methods of Preparation

Catalyst	T., °C	Conversion, %	Composition of conversion products, %									
			C_1+C_2	C_3	i-C_4	n-C_4	i-C_5	n-C_5	2-MP	3-MP	MCP	benzene
Rh-1	400	17,0	14,0	12,0	<0,1	10	1,8	13	20	13	12	7
	450	52,5	19,8	8,4	1,3	11	5,9	16,6	12	8	5,5	11
	500	94,7	45	15,7	1,1	11,6	2,7	4,9	0,8	0,6	0,2	16,3
	400 *	8,8	17	9,1	<0,1	8,0	0,7	12,5	17,0	19,3	14,8	6,8
Rh-2	200	16,5	22	29	<0,1	3,2	<0,1	7	4	6	–	–
	225	47,8	24,9	27,2	<0,1	33,9	<0,1	9,4	2,3	2,3	–	–
	250	98,5	35,9	32,8	1,3	23,8	1,6	3,6	0,5	0,5	–	–
Rh-3	200	29,8	22,1	29,8	<0,1	32,2	<0,1	6,3	4,8	4,8	–	–

*Carrier gas flow rate 200 ml/min; in all other cases, 100 ml/min.

TABLE 2. Composition of Products from Conversion of MCP on Rh-1, %

T., °C	Conversion, %	$\Sigma\, C_1-C_4$	i-C_5	n-C_5	2-MP	3-MP	n-C_6	Benzene
450	75	21	9	7	29	8	15	11
550	84	63	4	5	2	Trace	5	21

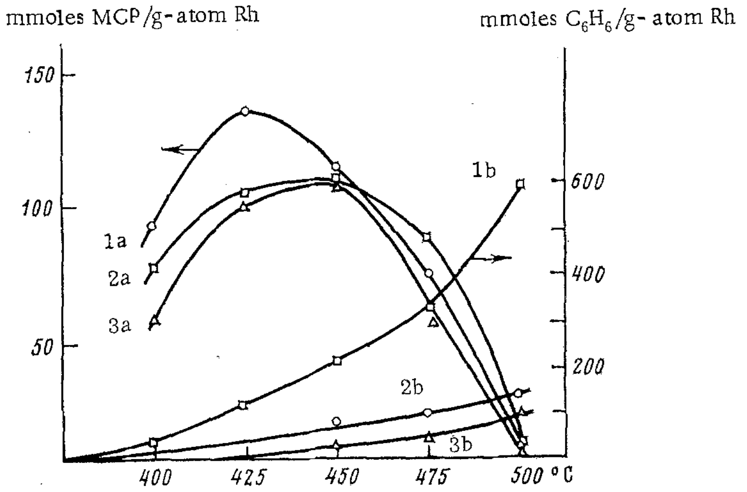

Fig. 1. Temperature dependence of yields of MCP (1a-3a) and C_6H_6 (1b-3b) from n-C_6, 2-MP, and 3-MP, respectively.

the 2-MP are the yields slightly higher than from the other two hexanes that were investigated. A change in the carrier gas flow rate or in the Rh-1 reduction temperature does not have any substantial effect on the selectivity of the reaction with respect to MCP. As can be seen from Fig. 2 (curves 3 and 4), an increase in the Rh-1 reduction temperature from 500°C to 575°C gives only a slight shift in the temperature at which the maximal MCP yield was observed.

These results suggest that the yields of MCP from 2-MP and 3-MP at $\geqslant$450°C are somewhat lowered because of dehydroisomerization of MCP to benzene. Actually, when we compare the temperature dependences of the yields of benzene and MCP (Fig. 1), it is evident that as the temperature is increased, the MCP yield curve passes through a maximum (425-450°C), whereas the benzene yield becomes perceptible above this temperature. Direct experiments on the dehydroisomerization of MCP to benzene provide further support for this view (Table 2).

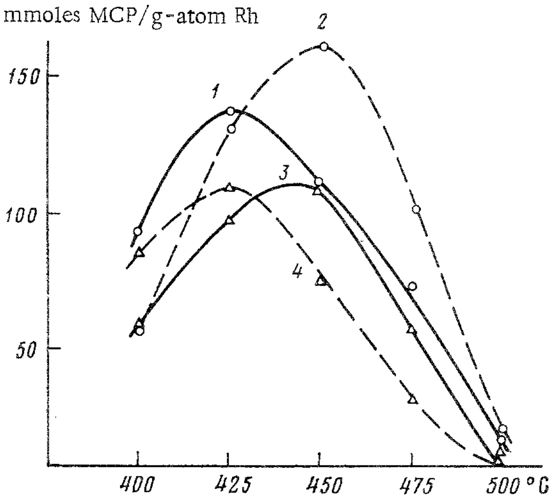

Fig. 2. Influence of reduction temperature and carrier gas flow rate on yields of MCP from 2-MP and 3-MP. Carrier gas flow rate, ml/min: 1) 100; 2) 200. Catalyst reduction temperature, °C: 3) 500; 4) 575.

Along with the isomeric hexanes, the catalytic conversions of isooctane were studied under similar conditions. It was found that 2,2,4-trimethylpentane in the presence of Rh-1 likewise forms appreciable quantities of the product of C_5-DHC; the selectivity of the process with respect to 1,1,3-trimethylcyclopentane is approximately 17%.

The Rh-1 catalyst differs from Rh-2 in having a more clearly expressed capability for structural isomerization. The selectivity of isomerization on Rh-1 at 400°C is 30-35%, depending on the structure of the original hexane, and the selectivity drops off with increasing temperature, evidently because of a reinforcement of cracking and aromatization processes.

The capabilities of the Rh-1 that we have noted for performance the C_5-DHC process and for structural isomerization of alkanes are combined with an activity in methane formation that considerably is suppressed in comparison with the Rh-2. Even at 400°C, the content of the total $C_1 + C_2$ hydrocarbons in the product obtained on the Rh-1 is no greater than 14% at 17% conversion of the original hydrocarbon. In comparison, the Rh-2 catalyst, even at 250°C, converts the n-C_6 almost completely to low-molecular-weight products of hydrogenolysis (C_1-C_4), to a considerably greater degree than the Rh-1 at 400°C. The main products from conversion of hexanes on Rh-2, other than the C_1-C_4 hydrocarbons, are coke and benzene; the yields of isomeric hexanes are insignificant, and, the same as in [3], no formation of MCP is observed (see Table 1).

The differences in catalytic activity of the alumina—rhodium catalysts differing in genesis show up very clearly in the minimal temperature at which appreciable conversion of hexanes is observed. On the Rh-1, these processes are significant only above 375°C; on the Rh-2 or Rh-3, they are appreciable even at 200°C (Table 1). The activities of the Rh-3 and Rh-2 catalysts, which differ in rhodium content (3.5% and 0.6%, respectively), in the conversion of n-C_6, 2-MP, and 3-MP at 200°C are almost identical; when the temperature is increased to 250°C, the catalytic properties of the Rh-3 and Rh-2 are also very similar.

It appears that the differences we have found between the catalytic activity and selectivity of the Rh-1 and that of the Rh-2 and Rh-3 are related primarily to differences in their physicochemical properties. For example, the method of catalyst preparation has a substantial influence on the Rh dispersity (the ratio of fractions of the metal on the surface and in the bulk of the crystallites Rh_s/Rh_t is 0.35 for the Rh-1 and 0.74 for the Rh-2), and the differences are also related to the adsorption properties of the catalyst (Table 3 and Fig. 3). According to the data on chemisorption of O_2, within the limits of accuracy allowed by the method [8], the specific surface area S_{sp} for the Rh-1 is little more than half that for the Rh-2. It is noteworthy that changes in the catalyst dispersity by a factor of 2 are observed in the "mitohedric" region (8-40 Å), where, according to [9], we can expect a considerable

TABLE 3. Influence of Rh/Al_2O_3 Preparation Method on Dispersity

Catalyst	Dispersity, Rh_s/Rh_t	S_{sp}, m^2/g
Rh-1	0,35	160
Rh-2	0,74	340

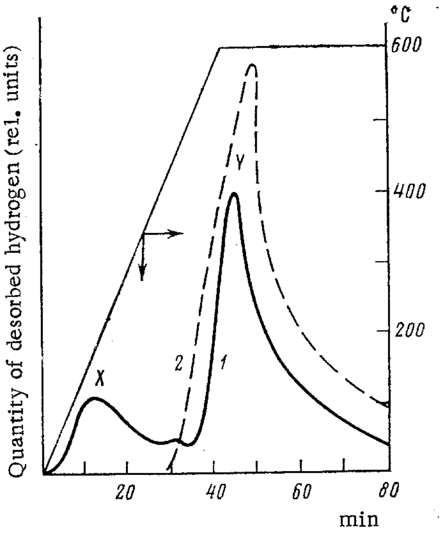

Fig. 3. Thermal desorption of hydrogen from alumina–rhodium catalysts of different genesis: 1) from $RhCl_3$ (Rh-2); 2) from $[(CH_3)_2S]_3RhBr_3$ (Rh-1).

dependence of the catalytic activity on the dispersity of the metal. Anderson et at. [6] similarly found a very definite increase in the yield of MCP from n-C_6 when the size of the crystallites in an Rh—Co alloy was increased from 13 to 28 Å; they attributed this solely to the decrease in the fraction of the Rh on the surface of the Co—Rh alloy. According to [10, 11], monometallic Rh and Co catalysts do not perform the C_5-DHC reaction on alkanes.

A characteristic feature of the Rh-1 catalyst is a perturbation of the Al_2O_3 structure that can be registered by x-ray diffraction; apparently this is caused by implantation of the metal in the lattice of the support. The above-noted structural features of the Rh-1 and Rh-2 have appreciable effects on the adsorption properties of these catalysts. Thus, for the Rh-1 and Rh-2, the respective values of H/Rh are 1.86 and 1.38; and the ratios of the X and Y forms of hydrogen, the desorption of which takes place below 80°C and in the interval 80-600°C, is approximately 35/65 for the Rh-2 and approximately 0/100 for the Rh-1 (Fig. 3).

We believe that the higher activity of the Rh-2 in methane formation in comparison with the Rh-1 is related to catalytic centers, which in the Rh-1 are either completely absent or present in considerably smaller quantities. This view is consistent with the data we have presented on the thermal desorption of hydrogen, which is different for the Rh-1 and Rh-2 catalysts. The absence of any products of the C_5-DHC reaction of alkanes with the Rh-2 catalyst reflects the fact that the hydrogenolysis rate is considerably greater than the C_5-DHC rate.

Thus, the conversions of alkanes that are typical for platinum-group catalysts (C_5-dehydrocyclization, skeletal isomerization, and dehydroisomerization of MCP to benzene, along with a reduced activity in methane formation) also take place on alumina–rhodium catalysts obtained by decomposition of the complex $[(CH_3)_2S]_3RhBr_3$. Such a catalyst is substantially different from the traditional Rh/Al_2O_3 catalyst obtained by impregnating the support with $RhCl_3$. The differences show up in the catalytic activity and selectivity in alkane reactions and also in the physicochemical properties (dispersity of metal, thermal desorption characteristics, and x-ray diffraction characteristics).

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CONCLUSIONS

1. On the alumina–rhodium catalyst obtained by decomposition of $[(CH_3)_2S]_3RhBr_3$, heterogenized on Al_2O_3, reactions that are typical for platinum-group metals take place: C_5-dehydrocyclization, skeletal isomerization, dehydroisomerization, and others.

2. The catalytic, structural, and adsorption properties of the alumina–rhodium catalysts that we have investigated are determined by their genesis.

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CONVERSIONS OF ETHERS ON DEHYDRATING CATALYSTS.

4.[†] KINETICS OF DISPROPORTIONATION REACTION

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In the present work, for an elucidation of the possible mechanism of disproportionation of ethers, we carried out a study of the kinetic relationships of this reaction in the presence of Al_2O_3 alone and Al_2O_3 treated with HCl (9.3%). We investigated the conversion of a mixture of diethyl and dipropyl ethers to ethyl propyl ether,

$$\mathrm{Et_2O + Pr_2O \rightleftarrows 2EtOPr}$$

The kinetic experiments were performed at 200°C on Al_2O_3, and at 175°C, 185°C, and 200°C on Al_2O_3–HCl.

EXPERIMENTAL

The reaction was carried out in a completely sealed flow-circulating unit at atmospheric pressure; the original mixture was diluted with nitrogen. Cylinder nitrogen was purified by passing successively through a column with nickel–chromium catalyst and a trap with zeolite, chilled by a mixture of dry ice and acetone. The catalyst was regenerated in a stream of air at 450°C. In all experiments, the catalyst charge was 4 cm^3 (2.4 g), and the catalyst particle size was 1-2 mm. The original mixture of ethers, from thermostated saturators, was passed through the reactor, and the products were analyzed chromatographically every 10-15 min. After establishing steady-state operation, the experiment was continued for 45-120 min, with the activity remaining unchanged. The constancy of catalyst activity was checked in control

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[†] For communication 3, see [1].

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