STRUCTURE AND CATALYTIC ACTIVITY OF SUPPORTED METAL COMPLEXES. COMMUNICATION 2. SYNTHESIS OF RHODIUM COMPLEXES ON SILICA GEL MODIFIED BY PHOSPHORUS- AND NITROGEN-CONTAINING LIGANDS

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In [1] a method is proposed for synthesizing palladium complexes on silica gels modified by Schiff bases of heterocyclic aldehydes, and it is shown that their catalytic activity and selectivity are determined by the nature of the bonded heterocyclic ligand. The complexes of Rh attached to the silica gels by bonded electron donor groups are very active in hydrogenation, the hydroformylation reaction, isomerism, and hydrosilylation [2-4].

In this work we synthesized Rh complexes immobilized on silica gels modified with aminophosphine groups. IR spectroscopy was used to investigate the structure of the modified support and the Rh complexes formed on them upon immobilization. The catalytic activity of the complexes was studied in a model reaction of the hydrogenation and isomerization of allylbenzene.

### EXPERIMENTAL

In the experiments a Silochrome  $\gamma$ -aminopropyl-containing silica gel ( $\gamma$ -AMPS) with a specific surface area  $S_{SP} = 120 \text{ m}^2/\text{g}$  and an NH<sub>2</sub> group content of  $7 \cdot 10^{-4} \text{ mole/g was used}$ . Diphenyl-chlorophosphine was obtained as described in [5]. The complexes [RhCl(COD)]<sub>2</sub> (COD-cycloocta-diene-1,5) and RhCl(PPh<sub>3</sub>)<sub>3</sub> were synthesized according to the methods used in [6, 7], respectively. The solvents used were dried and distilled in an Ar atmosphere. All operations involved in modifying the silica gel and immobilizing the complex were also carried out under Ar.

<u>Phosphination of  $\gamma$ -AMPS.</u> A sample of  $\gamma$ -AMPS was evacuated for 8 h at 10<sup>-5</sup> mm Hg and 110°C before being modified to remove adsorbed H<sub>2</sub>O, then placed in a three-neck flask equipped with a mixer, suspended in toluene, and a toluene solution of Ph<sub>2</sub>PCl introduced into it. To the reaction mixture was added Et<sub>3</sub>N to bind the HCl formed

$$\exists - 0 - \operatorname{Si}(OC_{2}H_{5})_{2} - (CH_{2})_{3} - NH_{2} + Ph_{2}PCl \frac{H_{4}N}{0-3^{2}} \\ \exists - 0 - \operatorname{Si}(OC_{2}H_{5})_{2} - (CH_{2})_{3} - NH - PPh_{2}$$

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The Ph<sub>2</sub>PCl:NH<sub>2</sub>:Et<sub>3</sub>N mole ratio was 1:1:1. The reaction was allowed to proceed at 0-3°C with continuous mixing for 3 h. The completeness of the phosphination of the surface amino groups was monitored by following the reaction of the NH<sub>2</sub> groups with sodium nitroprusside [8] and by an IR method. The  $\gamma$ -aminophosphinopropyl silica gel ( $\gamma$ -AMPPS) synthesized was rinsed with toluene, chloroform, and ether, and dried at 60°C. From the elemental analysis, the content of NHPPh<sub>2</sub> groups in the sample is 2.5·10<sup>-4</sup> mole/g.

Immobilization of the Complexes. The  $[RhCl(COD)]_2$  was immobilized on the modified silica gels in boiling  $CH_2Cl_2$  for 4 h with subsequent rinsing and evacuation of the sample. The RhCl<sub>3</sub> was bonded to the  $\gamma$ -AMPPS by a similar treatment in ethanol. RhCl(PPh<sub>3</sub>)<sub>3</sub> was bonded to the support by treating  $\gamma$ -AMPPS with a solution of the complex in benzene or toluene at 20°C for 7 days; the sample was rinsed with boiling solvent and evacuated. In all cases, the immobilization of the complexes was conducted at a bonded ligand:Rh mole ratio of 1:1. The Rh content in the samples was determined by an atomic-absorption method.

The IR spectra of the supports and the complexes were taken on a UR-20 instrument; the samples, pellets with a density of 5-10  $mg/cm^2$ , were prepared under pressure without a binder.

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Sample number	Modified support	Starting complex	Rh cont., (mole/g) <sup>•</sup> 10 <sup>5</sup>	L:Rh (molar)		
1 2 3 4	γ-AMPPS Y-AMPPS Y-AMPPS γ-AMPS	[RhC1(COD)] <sub>2</sub> RhC1(PPh <sub>3</sub> ) <sub>3</sub> RhCl <sub>3</sub> [RhC1(COD)] <sub>2</sub>	$ \begin{array}{c c} 6,2 \\ 4,5 \\ 6,4 \\ 6,3 \end{array} $	4,0 5,6 3,9 4,0		
	W <sub>0</sub> ,mol	e/min				

TABLE 1. Immobilization of the Rhodium Compound



Fig. 1. Effect of the amount of catalyst on the initial rate of conversion of allylbenzene in the presence of catalyst 1. Allylbenzene =  $3.2 \cdot 10^{-4}$  mole, T 50°C, P<sub>H<sub>2</sub></sub> = 1 atm, ethanol 20 ml.

Hydrogenation and Isomerization of Allylbenzene. The experiments were performed in a thermostatted long-necked reaction vessel fastened in a rocker. To the reaction vessel were added 0.05 g of a catalyst  $(2.3-3.2\cdot10^{-6} \text{ g-at Rh})$  and  $5\cdot10^{-3}$  g NaBH<sub>4</sub>. The system was evacuated and then filled with H<sub>2</sub> or Ar that had first been purified to remove trace O<sub>2</sub>; 10 ml of the solvent was introduced, and the rocker was turned on. After activation was complete (20°C, 20-30 min),  $6.9-9.6\cdot10^{-4}$  moles of allylbenzene in 10 ml of solvent was added to the reaction vessel. The reaction was allowed to proceed at 50°C. The reaction products were analyzed by GLC. The activities of the catalysts were characterized by the values of the initial specific rates (calculated per 1 g-at Rh) of conversion W<sub>tot</sub>, isomerization W<sub>i</sub>, and hydrogenation W<sub>h</sub> of allylbenzene.

# RESULTS AND DISCUSSION

In the spectrum of the original  $\gamma$ -AMPS, absorption bands are observed that are assigned to the deformational and stretching vibrations of NH<sub>2</sub> groups (1600-1630 and 3300-3370 cm<sup>-1</sup>) and of CH<sub>2</sub> and CH<sub>3</sub> groups (1380-1465 and 2850-2960 cm<sup>-1</sup>). The absence of absorption in the region of the stretching vibrations of free OH groups (3750 cm<sup>-1</sup>) points to the complete conversion of these groups in the modification by the  $\gamma$ -aminopropyltriethoxysilane. Following the phosphination of the  $\gamma$ -AMPS, a band is observed at 1540 cm<sup>-1</sup> that should be attributed to deformation vibrations of the NH in the P-NH group [9]. Absorption bands appear in the spectrum that are characteristic of the stretching vibrations of the CH groups of phenyl at >3000 cm<sup>-1</sup> and the vibrations of the phenyl ring (1440 cm<sup>-1</sup>) bonded to P [10]. There is a simultaneous reduction in the intensity of the band at 1600 cm<sup>-1</sup>, a reduction in the intensity and a shift to lower frequencies of the bands at 3300-3370 cm<sup>-1</sup> to 3200 and 3280 cm<sup>-1</sup>, which is evidence of the appearance of NH groups and the partial disappearance of NH<sub>2</sub> groups [11, 12]. The last observation is in agreement with the results of the elemental analysis that indicate that approximately a third of the amino groups of the support are involved in the phosphination reaction. The bulky phenyl rings of the phosphine groups apparently screen the nearby amino groups of the support, thereby preventing their phosphination.

A study of the formation of Rh metal complexes on the supports obtained showed that the structure of the bonded Rh complexes depends on the nature of the functional group bonded and the nature of the immobilized complex. Bonding of [RhCl(COD)]<sub>2</sub> can occur only by breaking

bridging bonds or by replacing the cyclooctadiene ligand with a ligand of the support. Chromatographic analysis showed that after the  $[RhCl(COD)]_2$  was immobilized on the  $\gamma$ -AMPS, there was no COD in solution. In the spectrum of the bonded complex, absorption bands are observed at 1470 cm<sup>-1</sup> and at 2850-2950 cm<sup>-1</sup> which are characteristic of COD bound to Rh [13]. Both olefin bonds participate in the coordination with the Rh, which leads to a lowering in the frequency of the vibrations from 1650 to 1470 cm<sup>-1</sup>. Thus, in the heterogenization of [RhCl-(COD)]<sub>2</sub> on  $\gamma$ -AMPS, COD is not displaced from the complex's coordination sphere. Based on the results obtained and the data in [6], where the interaction of amines and diamines with [Rh-Cl(COD)]<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> solution was studied, it can be hypothesized that structures (I) and (II) below form on the surface



Structure (I), where Rh is coordinated like a chelate, is realized primarily when there is a high concentration of surface amine groups. If chelation is hindered, structure (II) forms.

A different picture is observed when  $[RhC1(COD)]_2$  bonds to  $\gamma$ -AMPPS. GLC shows that 2 moles of COD are liberated per mole of coordinated compound in the process of immobilization. In the IR spectrum of the supported complex, absorption bands corresponding to COD vibrations are absent.

The difference in the nature of the complex formation on  $\gamma$ -AMPS and  $\gamma$ -AMPPS that occurs with and without replacement of the COD, respectively, and the high density of the  $-Si(OC_2H_5)_2$ -(CH<sub>2</sub>)<sub>3</sub>-NH-PPh<sub>2</sub> allows us to assume that in the case of the aminophosphinated support, Rh is coordinated primarily via the P atom with ligand exchange and the formation of structures (III) and (IV).



Attachment of the RhCl(PPh<sub>3</sub>)<sub>3</sub> to the  $\gamma$ -AMPPS results in the formation of structures (IV) and (V). When the surface triphenylphosphine ligand in (V) or in the aminophosphine ligand in (IV) dissociates, structure (III) is obtained. Since elemental analysis reveals that the P:Rh mole ratio in an immobilized complex is 3.9-5.6 (Table 1), it is clear that for these Rh complexes, the formation of chelate-type structures (III)-(IV) is characteristic, and only some fraction of the surface functional groups are coordinated with the Rh.

The IR spectroscopic data allow us to consider the question of the degree to which heteroatoms of the ligand bonded to the surface participate in the formation of immobilized Rh complexes. In the spectrum of sample 1 (Table 1), the band at 1540 cm<sup>-1</sup> is observed to shift to 1517 cm<sup>-1</sup> (NH-P) and that at 1440 cm<sup>-1</sup> to 1435 cm<sup>-1</sup> (P-Ar), with a simultaneous decrease in the intensity and broadening of the latter band. For sample 2, the shift of the 1540 cm<sup>-1</sup> band to lower frequencies is smaller (%5 cm<sup>-1</sup>), and the 1440 cm<sup>-1</sup> band does not shift at all.

TABLE 2. Hydrogenation and Isomerization of Allylbenzene

Samp.	Solvent	W. Ľ	w <sub>h</sub>	Wtot	Samp.	Solvent	wi	w <sub>h</sub>	Wtot
No.	i	mole/g-at Rh•min		No.		mole/g-at Rh•min			
1	1 Methanol Ethanol Propanol Butanol Isopropanol tert-Butanol		6,4 12,8 9,4 13,0 9,9 7,0	13,7 24,8 17,4 21,5 17,0 11,4	2 3 3*	Methanol Ethanol Methanol Ethanol ''	$\begin{array}{c} 1,1\\ 10,9\\ 5,0\\ 4,8\\ 10,9\end{array}$	$0,9 \\ 11,3 \\ 5,1 \\ 7,4 \\ 14,6$	2,0 22,2 10,1 12,2 25,5

This can be explained by the fact that in the complexation of  $[RhCl(COD)]_2$  on  $\gamma$ -AMPPS (cf. structures (III) and (IV)), the P, N, and Ph participate in the redistribution of the electron density. When RhCl(PPh<sub>3</sub>)<sub>3</sub> (sample 2) bonds to the surface it is apparently primarily structure (V) that forms, and the extent to which the N and Ph of the surface ligand are involved decreases due to the presence of the PPh<sub>3</sub> ligand.

It is of great importance to elucidate how the activity of the immobilized Rh complexes is affected by their structure and by the conditions under which the reaction occurs. None of the metal complexes except sample 4, which is unstable in H<sub>2</sub>, displayed any perceptible activity in the hydrogenation and isomerization of allylbenzene without lengthy prior activation. After being exposed to  $H_2$  for 6-8 h at 20°C, the color of the complexes was little changed, and they displayed only slight catalytic activity. Only after being treated with a solution of NaBH4 did the color of the samples change from yellow to dark brown, and their activity increased sharply. Apparently, under these conditions hydrides of the Rh phosphine complexes form which, according to [7], are responsible for the catalytic activity in the hydrogenation and isomerization reactions of the olefins. As the amount of NaBH, increases from 13 to 40 mole/g-at Rh, the activity of catalyst 1 in converting allylbenzene increases linearly from 0.4 to 25.1 mole/g-at Rh.min. At higher NaBH, concentrations the activity decreases somewhat. Raising the activation temperature to 50°C leads to a reduction in the rate of conversion of the allylbenzene. Special tests showed (Fig. 1) that for a constant concentration of the support, its rate of conversion rises linearly from 0.1 to 2.7 mole/min as the amount of catalyst 1 increases from 0.01 to 0.1 g  $(6.2 \cdot 10^{-7} - 6.2 \cdot 10^{-6} \text{ g-at Rh})$ .

The course of the process is substantially affected by the choice of solvent (Table 2). For example, in the case of sample 1 the specific activity of the complex varies as follows: in the hydrogenation of allylbenzene: ethanol  $\sim$  butanol > propanol  $\sim$  isopropanol > methanol  $\sim$  tert-butanol; in the isomerization of allylbenzene: ethanol > butanol  $\sim$  propanol > methanol  $\sim$  isopropanol > tert-butanol; in the overall conversion of allylbenzene: butanol  $\sim$  ethanol > isopropanol > tert-butanol  $\sim$  methanol. The highest values of Wtot, W<sub>i</sub>, and W<sub>h</sub> are observed for ethanol and butanol, and the lowest, for tert-butanol. It should be pointed out that replacing ethanol by methanol affects the activity of the Rh complex immobilized on the  $\gamma$ -AMPPS in different ways: for [RhCl(COD)]<sub>2</sub>, the rate of reaction is halved, for [RhCl(PPh<sub>3</sub>)]<sub>3</sub> it falls to a tenth of its original value, while for RhCl<sub>3</sub> it is practically unaffected (Table 2). For 25% H<sub>2</sub>O in ethanol, W<sub>tot</sub> for sample 1 is halved. We note that when the homogeneous complex RhCl(PPh<sub>3</sub>)<sub>3</sub> is used, adding the same amount of water to ethanol inhibits the reaction completely.

Interesting patterns emerge when we compare the activities of complexes with the value of the solvent conductivities. According to [14], the conductivities of alcohols ( $\kappa$ ,  $\Omega^{-1}$ ) increase in the order:  $C_2$  (1.35·10<sup>-9</sup>) <  $C_4$  (9·12·10<sup>-9</sup>)  $\approx C_3$  (9·17·10<sup>-9</sup>) < i- $C_3$ (0.51·10<sup>-6</sup>)  $\approx$  t- $C_4$  (0·29·10<sup>-6</sup>). This order is the reverse of that for  $W_1$  (Table 2).

It is of particular interest to consider the effect of the nature of the immobilized complex on the activity and selectivity in the conversion of allylbenzene. For samples 1 and 2, identical values of  $W_h$  and  $W_i$  are characteristic, while for sample 3, the activity in these processes is lower, with  $W_i/W_h = 0.6$  (Table 2).

These data are in good agreement with the structures of the immobilized complexes proposed above. The similar catalytic properties of samples 1 and 2 can be explained by the fact that in both cases surface structures (III)-(V) form, which are capable of interconverting. The difference in the behavior of sample 3 is apparently related to the formation of different surface structures.

To explain the possibility of allylbenzene hydrogenating in the presence of sulfur compounds, we studied the effect of thiophene additives on the activity of the immobilized complexes. The experiments showed that thiophene affects neither the activity nor the selectivity of the catalysts even at a thiophene:rhodium mole ratio of 20:1, in contrast to its effect on Group VIII metal complexes.

The conditions under which the immobilized catalysts are prepared affect their catalytic properties considerably (Table 2). The RhCl<sub>3</sub> was bonded to the  $\gamma$ -AMPPS in ethanol at 20°C and then rinsed with either cold or boiling solvent. When the catalyst was rinsed with cold ethanol, sample 3<sup>\*</sup> was obtained, which is twice as active as the sample rinsed with boiling ethanol (sample 3). It is interesting that when thiophene was added, the activity of sample 3<sup>\*</sup> fell, while that of sample 3 remained practically the same. The increased activity of sample 3<sup>\*</sup> and its partial deactivation in the presence of thiophene is apparently related to the formation of a metallic Rh phase resulting from the incomplete removal of weakly bound RhCl<sub>3</sub> by rinsing.

It should be noted in particular that the immobilized Rh complexes, after being activated by NaBH<sub>4</sub>, were active in the isomerization of allylbenzene when this was conducted in an atmosphere of Ar with no H<sub>2</sub> present. (Under these conditions, hydrogenation did not occur.) The rates of conversion of the double bond in samples 1-3 (in ethanol) under these conditions were 7.9, 11.3, and 2.5 mole/g-at Rh·min, respectively. The major reaction product is trans-propylbenzene. It is interesting to note that RhCl(PPh<sub>3</sub>)<sub>3</sub> heterogenized on  $\gamma$ -AMPPS displays the same isomerization activity in both Ar and H<sub>2</sub>. These findings suggest that Rh hydrides on the surface during activation.

### CONCLUSIONS

1. Silica gel has been modified by aminophosphine groups and rhodium complexes immobilized on it:  $[RhCl(COD)]_2$ ,  $RhCl(PPh_3)_3$ , and  $RhCl_3$ . IR spectroscopy was used to follow the formation of aminophosphine groups on the surface of the silica gel as the  $\gamma$ -aminopropyl silica reacted with the  $Ph_2PCl$ .

2. Using IR spectroscopy and GLC it has been shown that bonding of  $[RhCl(COD)]_2$  on a  $\gamma$ -aminopropyl-containing silica gel proceeds without replacement, while on the  $\gamma$ -aminophosphino-propyl-containing silica gel, the cyclooctadiene ligand is replaced. When complexes become bound to the latter support, the rhodium atom coordinates through the phosphorus atom of the aminophosphine group; the extent to which the nitrogen participates depends on the identity of the type of compounds immobilized.

3. The activity and selectivity exhibited by the catalysts obtained in the conversion of the allylbenzene depends on the nature of the bonded ligand and the starting complex, the degree of ligand exchange, and the properties of the solvent.

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EFFECT OF MODIFYING ADDITIVES ON THE SELECTIVITY OF TRANSFORMATION OF METHANOL INTO AROMATIC HYDROCARBONS OR LOWER OLEFINS IN THE PRESENCE OF PENTASILS

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The development of new catalytic systems based on high-silicon zeolites (HS) for preparation of lower olefins and aromatic hydrocarbons (AH) from nonpetroleum raw material is currently an urgent problem. Pentasils ZHS, ZHM, Ultrasil, and ZSM in the decationized form exhibit relatively high activity in transformations of methanol into hydrocarbons [1-3]. However, zeolites in the H form are not very stable and are insufficiently selective. Modification with different additives is one of the methods of increasing the activity and stability and regulating the selectivity of catalysts of conversion of methanol [4-7]. It was previously shown [6] that the nature and amount of the matrix ( $Al_2O_3$ ,  $SiO_2$ , MgO) has a significant effect on the catalytic properties of HS zeolites in transformations of methanol. In particular, it was found that the 70% HZHM + 30%  $Al_2O_3$  composite is optimum for conversion of methanol into hydrocarbons.

The effect of the nature and amount of modifying additives and the conditions of preliminary treatment and conducting the experiments on the activity and selectivity of action of catalysts prepared from the 70% HZHM + 30%  $Al_2O_3$  zeolite-containing composite was investigated in the present study. Metal oxides (cobalt oxide, mixture of chromium and zinc oxides) which promote the formation of AH from CO and H<sub>2</sub> [1] and phosphoric acid, which increases the selectivity of formation of C<sub>2</sub>-C<sub>4</sub> olefins from methanol, were selected as the modifying additives.

### EXPERIMENTAL

A composite consisting of 70% HZHM and  $30\% \gamma - Al_2O_3$  (base) was used for preparing the modified zeolite-containing systems. Modification was conducted by impregnating the base with solutions of Co, Zn, and Cr nitrates and phosphoric acid as in [6]. The following samples of catalysts were thus prepared and tested in conversion of methanol: CT-1-base, CT-2-TC-4, corresponding to 0.5, 5.0, 10.0 Co<sub>2</sub>O<sub>3</sub>/base, Ct-5-Cf-9 contain zinc and chromium oxides applied to the base: Ct-5 (2% ZnO and 2% Cr<sub>2</sub>O<sub>3</sub>), subsequently Ct-6 (2 and 10), Ct-7 (5 and 2), Ct-8 (5 and 5), Ct-9 (5 and 10). Samples Ct-10-Ct-12 with 5, 10, and 20% P<sub>2</sub>O<sub>5</sub>/base.

The studies were conducted in a flow-type setup and in a pulsed microreactor [7]. The catalyst load was 2.5 and 5.0 cm<sup>3</sup> (flow reactor) and 500 mg (pulsed reactor); the volume flow rate of CH<sub>3</sub>OH varied from 1.4 to 8.4 h<sup>-1</sup>; the size of the sample in the pulsed mode was  $10 \,\mu$ l. The experiments were conducted at 250-500°C and atmospheric pressure. The products of the reaction were analyzed by GLC.

To determine the optimum conditions of activation of the modified zeolite catalysts, the effect of the conditions of preliminary heat treatment was studied on the example of Ct-2, 3, and 6: in a reducing medium ( $H_2$ , 500°C, 5 h: method I), in a redox medium (successively air, 520°C, 5 h, then  $H_2$ , 500°C, 3 h: method II), and in an oxidizing medium (air, 520°C, 5 h: method III) on the activity and selectivity of their effect in transformations of methanol.

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