H atoms in Table 4. A general view of the molecule with bond lengths is presented in Fig. 1, and the bond angles are given in Table 5.

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HYDROGENATION OF HETEROCYCLIC COMPOUNDS USING POLYMER-CONTAINING CATALYSTS

UDC 66.094.1:547.7

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The hydrogenation of a series of oxygen- and nitrogen-containing compounds: furan, sylvan, benzofuran, certain dioxa-compounds, and pyridine, was investigated under mild conditions in the presence of polymer-containing catalysts based on metals of group VIII. The catalysts used were soluble complexes of Pt, Pd, and Rh with various polymers and copolymers. The greatest activity was exhibited by rhodium complexes with carboxyl-containing polymers.

Despite the increased interest of researchers in metallocomplex catalysts, there are comparatively few studies devoted to the hydrogenation of heterocyclic compounds on the indicated catalysts. The hydrogenation of heterocyclic compounds on catalysts prepared using polymer macroligands has practically not been studied.

In this work we investigated the hydrogenation of a series of oxygen- and nitrogen-containing heterocyclic compounds in the presence of catalysts prepared on the basis of complexes of metals of group VIII (Rh, Pd, Pt, and Ni) with polymer macroligands: copolymers of styrene with maleic acid (I), a copolymer of maleic acid with methyl methacrylate (II), polyacrylic acid (III), and polyvinylpyrrolidone (IV). Hydrogenation was conducted at atmospheric pressure and a temperature of 20-60°C.

Rhodium and palladium catalysts exhibited high activity and selectivity in the hydrogenation of furan compounds (Table 1). At the same time, platinum and nickel catalysts were ineffective. A platinum catalyst showed low activity in the hydrogenation of benzofuran. It is interesting to note that the activity series in the hydrogenation of benzofuran with palladium,

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Item No.	Substance	Catalyst	Tem- pera- ture, °C	nŤ	Reactions products (yield, %)
1	Furan	l-Rh	30	52	Tetrahydrofuran (100)
2	2-Methylfuran	I-Rh	30	117	2-Methyltetrahydrofuran (100)
3	2-Methylfuran	I-Pd	30	19	2-Methyltetrahydrofuran (100)
4	2-Methylfuran	I-Pt(Ni)	30	0	2-Methylfuran (100)
5	2-Methylfuran	II-Rh	30	50	2-Methyltetrahydrofuran (100)
6	2-Methylfuran	III-Rh	30	20	2-Methýltetrahýdrofuran (100)
7	Benzofúran	I-Rh	30	18	2.3-Dihydrobenzofuran (77)
8	Benzofuran	I-Pd	30	53	2,3-Dihydrobenzofuran (100)
9	Benzofuran	I-Pt	50	7	2,3-Dihydrobenzofuran (38),
10	Benzofuran	III-Rh	30	48	phenols (5) 2,3-Dihydrobenzofuran (100)

*In No. 1, 2.19 mmoles of the starting material was used, in Nos. 2-6 2.27 mmoles was taken, and in Nos. 7-10 2.75 mmoles of the starting material was used; the catalyst contained 0.0391 mmole of the metal, 0.219 mmole of polymer I, 0.391 mmole of III (converted to the monomer unit). Solvent: 3 ml of distilled water, 3 ml of alcohol.

'Number of molecules of the substrate converted per metal atom per hour.

Item No.	Substance (mmoles)	Catalyst	Tem- pera- ture, °C -	n†	Reaction product (yield, %)
1	1,8-Dioxa 1,4,5,6,7,8,9,10- octahydronaphthalene (5,6)	III-Pd	30	11	1,8-Dioxadecahydronaphthal- ene (100)
2	1,7-Dioxa-4,7,8,9-tetrahy-	III-Pd	30	14	1,7-Dioxahexahydroindan
3	1,7-Dioxa-4-methy1-4,7,8,- 9-tetrahydroindan (5.6)	III-Pd	[`] 30	11	1,7-Dioxa-4-methylhexahy- droindan (100)
4	1,4-Benzodioxane (1.34)	I-Rh	30	1	Hexahydro-1,4-benzo-
5	1,4-Benzodioxane (2.68)	III-Rh	30	7	Hexahydro-1,4-benzodioxane
6	6-Nitro-1,3-benzodioxane (0.55)	III-Rh	20	4	6-Amino-1,3-benzodioxane (75)

TABLE 2. Hydrogenation of Dioxa-Compounds

*The catalyst contains metal: 0.1195 mmole in Nos. 1-3, 0.0284 mmole in Nos. 4 and 7, and 0.0391 mmole in No. 5; polymer 1.385 mmoles in Nos. 1-3, 0.391 mmoles in Nos. 5 and 7, and 0.184 mmole in No. 6. Solvent: 3 ml of distilled water, 3 ml of alcohol. [†]See the note to Table 1.

rhodium, and platinum catalysts coincides with the data that we obtained earlier on the hydrogenation of benzofuran on blacks of these metals [1]. In both cases the most active was a palladium catalyst, rhodium was less active, and platinum possessed the lowest activity and did not ensure 100% selectivity, leading to the formation of alkylphenols.

Table 2 presents the results of the hydrogenation of dioxa-compounds. The double bonds of the olefin ring in bicyclic 1,7- and 1.8-dioxa-compounds undergo rather rapid reduction. In the case of 1,4-benzodioxane, the benzene ring of the molecule is reduced, while in the case of 1,3-benzodioxane hydrogenation did not occur. This permitted us to conduct the selective hydrogenation of 6-nitro-1,3-benzodioxane to 6-amino-1,3-benzodioxane.

The investigated catalysts permit the hydrogenation of pyridine to piperidine (Table 3). Only rhodium complexes were catalytically active.

Attempts to hydrogenate sulfur-containing heterocycles did not give positive results.

Thus, we succeeded in producing catalysts of the hydrogenation of oxygen- and nitrogencontaining heterocyclic compounds based on complexes of metals of group VIII with carboxylcontaining polymers that are highly effective under mild conditions and selective. The catalysts were used in the form of aqueous alcohol solutions, which permits isolation of the re-

TABLE 3. Hydrogenation of Pyridine*

Item No.	Catalyst	Tempera- ture, °C	n†	Degree of conversion, %
1	I-Rh	30	13	73
2	III-Rh	30	9	64
3	III-Rh	45	49	100
4	I-Pt	20	0	0
5	IV-Pd	16	0	0

*In Nos. 1-5 there was 2.37 mmoles of the starting material, in No. 3, 3.72 mmoles. The reaction product was piperidine. The catalysts contained metal: 0.0284 mmole in Nos. 1, 2, 4, and 5 and 0.0196 mmole in No. 3; polymer: 0.227 mmole in Nos. 1 and 4, 0.391 mmole in No. 2, 0.386 mmole in No. 3, and 0.283 mmole in No. 5, converted to the monomer unit. The solvent was 3 ml of distilled water and 3 ml of isopropanol; in No. 3 isopropanol was replaced by methanol. [†]See the note to Table 1.

action products by extraction. Moreover, the catalyst was isolated from the reaction mixture by varying the pH of the medium.

EXPERIMENTAL

To prepare the catalyst, a weighed sample of the polymer was placed in a thermostatically controlled glass long-necked hydrogenation flask, and distilled water was added. After the polymer dissolved, a weighed sample of the metal salt ($RhCl_3 \cdot 4H_2O$ K₂PdCl₄ K₂PtCl₄ NiCl₂ \cdot $6H_2O$) and the alcohol component of the solvent were introduced. The solution obtained was treated with sodium borohydride in an amount equimolar to the amount of metal introduced. After the addition of the substrate, the reactor was connected to a thermostat and agitated (at a frequency of 400-500 oscillations/min). Hydrogen was delivered to the reactor from a gas burette. At the end of the reaction K₂CO₃ was added to the reactor, which led to coagulation of the catalyst. The reaction products were analyzed by the method of gas-liquid chromatography and chromato-mass spectrometry.

Analysis was conducted on a Tsvet-100 chromatograph, column 10% PEG-20M on chromosorb W, with a length of 3 m, diameter 3 mm, and on a Varian MAT-44 mass spectrometer, energy of ionization 70 eV, 180°C, using a capillary column with a length of 25 m, phase SE-54.

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