PALLADIUM ON POLY{BENZO[BIS(BENZIMIDAZOLO)PHENANTHROLINE]DIONE} AS A CATALYST FOR THE HYDROGENATION OF UNSATURATED COMPOUNDS

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Polynaphthoylenebenzimidazoles have a number of properties that could make them useful as supports for heterogeneous catalysts. Such polymers are high in thermal stability and mechanical strength, they have little solubility in organic solvents, and they are resistant to acids and alkalis [1]. Because of the presence of donor atoms and a system of conjugated bonds, such polymers can act as macroligands and can have a modifying effect on the catalytic properties of transition-metal atoms. Thus far, however, the only information published in this area has been in patents [2, 3].

Here we are presenting results on the preparation of catalytic systems based on poly-{benzo[bis(benzimidazolo)phenanthroline]dione}* (PBI) and PdCl₂, and data on the catalytic properties of these systems in hydrogenation reactions.



The catalyst PBI•PdCl₂, containing $4 \pm 0.25\%$ Pd, was prepared by impregnating the PBI with an aqueous solution of Na₂PdCl₄.

An investigation of the PBI•PdCl₂ by x-ray photoelectron spectroscopy (XPS) showed that $E_b Pd3d_{5/2} = 338.2 \text{ eV}$ corresponds to the value characteristic for PdCl₂. Treatment of a suspension of PBI•PdCl₂ in DMF with hydrogen at ~20° leads to the formation of a catalyst PBI•Pd in which, according to the XPS data, the palladium is present in the form of Pd° ($E_b Pd3d_{5/2} = 335.7 \text{ eV}$). An x-ray diffraction study of the PBI•Pd showed that the palladium forms clusters with a dimension of 35 ± 10 Å. Similar results are obtained on samples of PBI•Pd prepared by reducing PBI•PdCl₂ by sodium borohydride in DMF. Since the PBI•PdCl₂ is reduced by hydrogen to PBI•Pd, in the catalytic experiments we introduced the substrate into the reactor after a 30-min period of shaking the suspension of PBI•PdCl₂ in DMF under H₂.

The experiment showed that the PBI•PdCl₂ in DMF medium catalyzes the hydrogenation and isomerization of various unsaturated compounds at 20°C and 0.1 MPa H₂ (Table 1). The dienes are hydrogenated at the highest initial rate. Olefins with an inner double bond react more slowly than olefins with a terminal double bond. For such substrates as cyclohexene, cis-2-octene, and trans-2-octene, the reaction is pseudo-first-order, with respective rate constants of $8.1 \cdot 10^{-2}$, $6.6 \cdot 10^{-2}$, and $5.3 \cdot 10^{-2}$ min⁻¹. For benzene derivatives, the functional groups are hydrogenated, the aromatic ring not being involved. Thus, only aniline is formed from nitrobenzene. Phenylacetylene is converted to styrene and then to ethylbenzene, the hydrogenation of the triple bond and the absorption of the first mole of H₂ proceeding at a lower rate than the absorption of the second mole of H₂ (Fig. 1).

In the hydrogenation of allyl alcohol, propanol and propanal are formed in a ratio varying from 1:1 to 1:2. The high relative content of propanal indicates that the rate of iso-*The method of PBI synthesis developed by one of the authors gives a polymer with a large surface area $(30-100 \text{ m}^2/\text{g})$ [4].

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TABLE 1. Initial Rates of Hydrogenation of Unsaturated Compounds in the Presence of PBI•PdCl₂ (catalyst 0.05 g, DMF 10 ml, substrate concentration 0.17 M, 20° C, $p_{\mu} = 0.1$ MPa)

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Substrate	Rate of H ₂ ab- sorption, ml/	Substrate	Rate of H ₂ ab- sorption, ml/
	min	<u> </u>	111 1. 11
1-Octene	20	Phenylacetylene	8
Cyclohexene	9	Benzene	0
Isoprene	60	Naphthalene	0
Piperylene	30	Cyclohexanone	0
Cyclohexadiene	16	Octanal	0
Allyl alcohol	25	Propargyl alcohol	0
Nitrobenzene	3	1	



Fig. 1. H_2 absorption rate as a function of time in hydrogenation of phenylacetylene. 0.05 g PBI•PdCl₂, 10 ml DMF, 0.17 M phenylacetylene, 20°C, $p_{H_2} = 0.1$ MPa.

merization of allyl alcohol, leading to the formation of propanal, is equal to or even higher than the hydrogenation rate. However, in the absence of H_2 , neither PBI•PdCl₂ nor PBI•Pd will isomerize allyl alcohol.

The hydrogenation of terminal olefins is also accompanied by isomerization. In the case of 1-octene, for example, the initial rate of H₂ absorption is high (~20 ml H₂/min), but it drops off appreciably even in the first minute (Fig. 2), and the reaction proceeds in accordance with a pseudo-first-order equation with k = $5.9 \cdot 10^{-2} \text{ min}^{-1}$, which is very close to the rate constant in the hydrogenation of 2-octenes. As indicated by GLC analysis of the reaction mixture taken immediately after the change in reaction rate (~1.5 min, vH₂ \approx 0.36 mole H₂ per mole of 1-octene), the original 1-octene has completely disappeared, and the mixture contains cis-2-octene, trans-2-octene, and octane in an approximate ratio of 1:4.8:5.5.

The 2-octenes, in turn are subject to cis, trans-isomerization. Thus, in the hydrogenation of trans-2-octene, cis-2-octene appears in the reaction mixture.

In the hydrogenation of branched olefins, the drop in the H₂ absorption rate after the initial period of high activity is even more pronounced than in the case of the 1-octene. When using 3-methyl-1-butene, the H₂ absorption curve shows a break (Fig. 2). The reaction mixture corresponding to the break contains ~45% 2-methyl-2-butene and ~55% isopentane; i.e., in the hydrogenation process, there is also isomerization of 3-methyl-1-butene to 2-methyl-2-butene. The sharp retardation of the H₂ absorption after the point of the break is related to the low hydrogenation rate of 2-methyl-2-butene (k = $0.53 \cdot 10^{-2} \text{ min}^{-1}$). Attention is drawn to the very marked drop of the reaction rate (by a factor of approximately 10) when the change is made from 2-octenes to 2-methyl-2-butene. By way of comparison, let us note that for Pd black, the rate of hydrogenation of 2-methyl-2-butene is only some 2.5 times lower than the rate of hydrogenation of an unbranched β -olefin [5]. These data indicate that the catalytic palladium centers on the PBI are more sensitive to the structure of the olefin substrate.

H₂, moles/mole substrate



Fig. 2. H_2 absorption curves in hydrogenation: 1) 1-octene; 2) 3-methyl-1-butene. 0.05 g PBI•PdCl₂, 10 ml DMF, 0.17 M olefin, 20°C, $p_{H_2} = 0.1$ MPa.

Fig. 3. H_2 absorption curves in the hydrogenation of dienes: 1) piperylene; 2) isoprene. 0.05 g PBI•PdCl₂, 10 ml DMF, 0.17 M olefin, 20°C, $P_{H_2} = 0.1$ MPa.

Isomerization reactions also play a substantial role in the hydrogenation of dienes. In the case of isoprene, the reaction is strongly retarded when ~1 mole of H₂ per mole of diene has been absorbed (Fig. 3). The reaction products at this moment contain 82% 2-methyl-2-butene and small amounts of 2-methyl-1-butene (6%) and isopentane (12%). The subsequent absorption of H₂ (after the break) corresponds to the hydrogenation of 2-methyl-2-butene.

The preferential formation of 2-methyl-2-butene might be explained by predominant 1,4addition of H_2 to the isoprene. However, this explanation is invalidated by the following data. The reaction rate can be reduced substantially by diluting the H_2 with N_2 . Under these conditions, after the absorption of ~0.6 mole H_2 per mole of diene, the mixture, apart from the isoprene content (44.8%), contains 2-methyl-2-butene (28.4%), 3-methyl-1-butene (18.7%), and 2-methyl-1-butene (18.1%). The change in the ratio of monoolefins in comparison with the experiment with undiluted H_2 indicates that the observed high selectivity of 2-methyl-2-butene formation is not related to preferential 1,4-addition of H_2 to the isoprene, but rather to the high rate of isomerization of the initially formed terminal olefins to give the 2-alkene. The absence of isopentane in the experiment with the H_2-N_2 mixture indicates that the hydrogenation of the monoolefins formed from isoprene begins only at a rather high level of conversion. In this respect, the behavior of PBI•PdCl₂ is similar to that of other heterogeneous palladium catalysts [6].

An analogous picture is observed in the case of piperylene (see Fig. 3). At the instant of the bend in the absorption curve (~0.9 mole H_2), the mixture consists of 2-pentenes and 1-pentene. Then the 1-pentene disappears, and pentane appears.

These features that we have noted in the reactions of hydrogenation and isomerization of monoolefins can be explained on the basis that both reactions proceed through an associative mechanism with a common key intermediate, containing a σ -bond between the palladium and the sec-alkyl [7, 8]. The ease of formation of such an intermediate will depend on the number and character of substituents on the carbon atom at the double bond and also on the steric effects of the ligand environment of the Pd atom. We can assume that the high sensitivity of the catalytic centers to the structure of the olefin substrate that is observed in our case can be explained on the basis that the polymer, acting as a macroligand with respect to the palladium, increases the steric hindrance to the formation of the key σ -alkyl complex and influences the direction of its decomposition.

The modifying influence of the polymeric ligand is also one of the probable factors responsible for the dependence of the catalyst activity on the character of the solvent. Thus, in the hydrogenation of 1-octene and cyclohexene in the presence of PBI•Pd that has been prepared previously, the reaction rate drops off by a factor of approximately 4 when the change is made from alcohol to hexane. For comparison, let us note that for Pd black, the rate of hydrogenation of the terminal olefin 1-hexene increases when alcohol is replaced by hexane, and the rate of hydrogen of the inner olefin 2-pentene drops off by a factor of only ~ 1.8 when alcohol is replaced by hexane [5].

Interesting features are observed when using cyclohexadiene as the substrate; the reaction products contain cyclohexane (62%) and benzene (38%). The formation of benzene indicates a catalytic redistribution of hydrogen between cyclohexadiene molecules during the course of hydrogenation. And in fact, when using PBI•Pd in the absence of H_2 , with cyclohexadiene in DMF for 1 h at 20°C, a mixture of benzene and cyclohexene is formed (1:1). The initial catalyst PBI•PdCl₂ without H_2 is not active in this reaction. The observed disproportionation of cyclohexadiene is established in the stage of cyclohexene formation. In this respect, PBI•Pd differs from the "classical" catalysts of irreversible catalysis of N. D. Zelinskii, of the Pd/C type, which carry this reaction to benzene and cyclohexane [9]. Analogous results were obtained in [10], where PdCl₂ in polyethyleneimine was used as the catalyst.

EXPERIMENTAL

<u>Preparation of PBI•PdCl₂</u>. A mixture of 0.0316 g PdCl₂ and 0.0207 g NaCl in 100 ml water was stirred at 70°C until a brown solution was formed (above the insoluble material). To the filtered solution, 0.45 g PBI was added, and the mixture was stirred at ~20°C until the solution above the polymer was decolorized (~18 h). The residue was separated out, washed on the filter with water and acetone, and dried in air.

<u>Preparation of PBI•Pd(0).</u> a) 0.05 g PBI•PdCl₂, 10 ml DMF, and 0.003 g NaBH₄ were stirred for 15 min. The insoluble material was separated, washed with water and acetone, and dried in air.

b) A reactor with a magnetic stirrer was charged with 0.1 g PBI•PdCl₂ (4.1% Pd) and 5 ml DMF; the reactor was then evacuated and filled with hydrogen. In 4 min, $2.47 \cdot 10^{-4}$ mole of H₂ was absorbed (6.4 moles H₂/g-at Pd*). The initial colorless solution took on a perceptible green tint. The solution did not give any ESR signal. In air, the green color changed to raspberry, and a strong singlet signal appeared in the ESR spectrum, with g = 2.0032. The completely oxidized light-brown solution was diamagnetic. These data can be explained by partial transfer of electrons from the H₂ to the polymer.

Experiments on Hydrogenation of Unsaturated Compounds. The hydrogenation was performed in a long-necked flask charged with 0.05 g catalyst and 10 ml of DMF, and filled with H_2 . The mixture was shaken for 30 min, the substrate was introduced while purging with H_2 , and the rate of H_2 absorption was measured. Preliminary experiments were performed to select shaking conditions at which the rate of H_2 absorption would be independent of the shaking rate.

In reactions with the participation of PBI•PdCl₂, the use of other solvents to replace DMF resulted in lower rates of hydrogenation of the organic substrates. For example, the rate of nitrobenzene hydrogenation dropped off in the order DMF > DMSO > EtOH >> THF ~ ben-zene. In the last two solvents, no H₂ whatever was absorbed; this is explained by the difficulty of reducing PBI•PdCl₂ to PBI•Pd by hydrogen in these solvents. This hypothesis is consistent with the fact that the hydrogenation of nitrobenzene in THF on prereduced PBI•Pd catalyst proceeds at almost the same rate as in DMF.

CONCLUSIONS

1. Palladium chloride supported on poly{benzo[bis(benzimidazolo)phenanthroline]dione} (PBI) is reduced by hydrogen to PBI•Pd, which is an active catalyst of the hydrogenation of unsaturated compounds and also the isomerization of olefins and ally1 alcohol.

2. The PBI•Pd catalyzes the disproportionation of cyclohexadiene to benzene and cyclohexene.

LITERATURE CITED

- 1. A. L. Rusanov, S. N. Leont'eva, and Ts. G. Preshashvili, Usp. Khim., 46, 151 (1977).
- 2. O. R. Hughes, U.S. Pat. 4,077,906 (1978).
- 3. R. D. Taylor, U. S. Pat. 3,985,679 (1976).

^{*}With allowance for solubility of H₂ in DMF.

- 4. V. V. Korshak, A. L. Rusanov, A. M. Berlin, S. Kh. Fidler, and F. I. Adyrkhaeva, Vysokomol. Soedin. A, 21, 68 (1979).
- 5. I. B. Dobroserdova, V. Yu. Fishbein, A. I. Leonova, and I. V. Gostunskaya, Vestn. Mosk. Univ., Ser. Khim., 22, 192 (1981).
- 6. L. Kh. Freidlin and E. F. Litvin, in: Problems in Kinetics and Catalysis. XI. Scientific Principles of Catalyst Selection for Heterogeneous Catalytic Reactions [in Russian], Nauka, Moscow (1966), p. 162.
- 7. M. Orchin, in: Catalysis. Stereochemistry and Mechanisms of Organic Reactions [Russian translation], Mir, Moscow (1968), p. 7.
- 8. S. Zigel', in: Catalysis. Stereochemistry and Mechanisms of Organic Reactions [Russian translation], Mir, Moscow (1968), p. 127.
- 9. N. D. Zelinskii and G. S. Pavlov, Chem. Ber., 66, 1420 (1933).
- 10. V. N. Perchenko, I. S. Mirskova, and N. S. Nametkin, Neftekhimiya, 20, 518 (1980).

SURFACE COMPOSITION OF DEALUMINIZED MORDENITES AND THEIR CATALYTIC ACTIVITY IN XYLENE CONVERSIONS

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The changes in catalytic activity and acidity of zeolites as a result of removal of aluminum from the skeleton have been investigated many times [1]. In analyzing the relationships among the activity, acidity, and composition of dealuminized zeolites, these investigators have started with the premise that the concentrations of aluminum and acidic centers on the surface are identical to those in the depth of the crystallites. However, this assumption has not yet been verified experimentally. It was shown quite recently that a decrease in the particle size and an increase in the external surface area of mordenite during the synthesis will accelerate the dealuminization quite substantially [2]. Such an effect is most readily explained if we assume that the aluminum is removed primarily from the surface layers.

Therefore, it is a matter of considerable interest to determine how much the surface and bulk compositions of dealuminized mordenites actually differ.

In the work reported here, we have analyzed the surface of dealuminized mordenites by x-ray photoelectron spectroscopy (XPS) and have determined the catalytic activities of these samples in xylene conversions.

EXPERIMENTAL

A series of mordenites with degrees of dealuminization up to 70% was obtained by treating the original Na form $(SiO_2/AI_2O_3 = 10)$ with HCl solutions (0.25-4 N). Four samples of mordenite with $SiO_2/AI_2O_3 = 12$, 15, 18, and 23 were synthesized by direct crystallization [3].

The x-ray photoelectron spectra were recorded in a Kratos ES-200B spectrometer at $\sim 20^{\circ}$ C. The values of (Si/Al)_{surf} were determined from the ratio of integral intensities of the Si 2p and Al 2p lines, with allowance for the photoionization cross sections and the depths of free dissipation of photoelectrons. The accuracy of determination was 10-20% (rel.). When the Al content was reduced to 3%, the intensity of the Al 2p signals was lower, and the error increased to 30%. The values reported here are the mean values from two or three measurements.

The catalytic activity in the isomerization and disproportionation of xylenes was determined in a micropulse unit at 230°C. Before making the measurements, the catalyst specimen (20 mg) was activated in a stream of helium for 1 h at 500°C. The tests were run with a

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