# SYNTHESIS AND CATALYTIC PROPERTIES OF PALLADIUM COMPLEXES ON POLYMERIC SUPPORTS IN THE HYDROGENATION OF p-NITROCHLOROBENZENE

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Heterogenization of catalytically active complexes on macromolecular supports is one of the methods used to increase the activity and selectivity of these complexes [1-4]. In the work reported here, we investigated the anchoring of Pd(II), using the method of substitution of competing ligands, and the catalytic properties of the resulting products in p-nitrochlorobenzene hydrogenation.

## EXPERIMENTAL

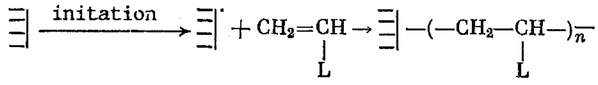
The polymeric supports were obtained by gas-phase graft polymerization (in the case of the polyethylene-graft-polyvinylcarbazole PE-gr-PVCz by liquid-phase graft polymerization) of the monomers 4-vinylpyridine 4-VP, allylamine AA, acrylonitrile AN, vinylpyrrolidone VPr), or vinylimidazole VIA on the surface of powdered PE ($s_{sp}$ = 4 $m^2/g$), following procedures given in [5]. The monomers used for the grafting were purified by standard procedures. The content of grafted fragments was determined by gravimetric and chemical methods. The $PdCl_2(C_6H_5CN)_2$ was prepared in accordance with [6]. The Pd(II) was deposited on the polymeric support from a benzene solution, using excess $PdCl_2(C_6H_5CN)_2$ and a suspension of the polymeric support, with vigorous stirring of the system for 30-60 min at 293-300°K. The product was separated by filtration and washed with benzene to remove unbonded Pd(II). The powders that were obtained, yellow to dark brown in color, were insoluble in organic solvents and unaffected by atmospheric oxygen or moisture. The content of Pd(II), which ranged from 0.71% to 2.4% by weight, was determined by nonflame atomic absorption spectrometry in a Saturn instrument. The IR spectra were recorded in a Perkin-Elmer 325 instrument, using samples in the form of tablets with CsI. The x-ray photoelectron spectra were recorded in a Varian IEE-15 spectrometer with a high-intensity magnesium anode [4].

Purified p-nitrochlorobenzene p-NCB was hydrogenated at 323°K in a glass reactor equipped with a temperature control jacket and a magnetic stirrer. The reactor was charged with the catalyst and 10 ml of a 2% $NaBH_4$ solution in isopropyl alcohol (activator); this mixture was stirred in a hydrogen atmosphere for 10 min, and then the p-NCB (1 mmole) was introduced, continuing the flow of $H_2$.

The quantity of $H_2$ adsorbed, as measured by means of a gas burette, was used to judge the completeness of hydrogenation of the p-NCB charge; the rate of $H_2$ absorption was used to judge the activity of the catalyst. The reaction mixture was analyzed by GLC [7].

## DISCUSSION OF RESULTS

The polymeric supports were prepared from PE with its surface activated by ionizing radiation, with subsequent grafting of the monomers



$$\equiv| \xrightarrow{\text{initation}} \equiv|^{\cdot} + CH_2{=}\underset{L}{\underset{|}{CH}} \rightarrow \equiv|{-}({-}CH_2{-}\underset{L}{\underset{|}{CH}}{-})_n{-} \qquad (1)$$

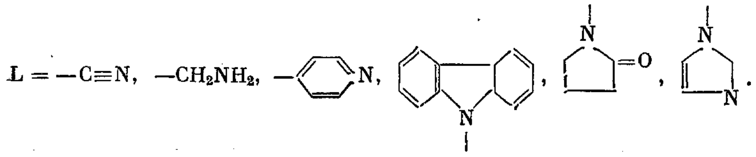


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TABLE 1. Characteristics of Immobilization of Pd(II) on Polymeric Supports by the Competing Ligand Method

| Catalyst | Polymeric support | Content, moles/g·$10^4$ | | $f$ | $\lg \overline{K}_0$ |
|---|---|---|---|---|---|
| | | grafted fragments | immobilized Pd(II) | | |
| Pd-1 | PE-gr-PVIA | 15,3 | 0,75 | 0,10 | 4,4 |
| Pd-2 | PE-gr-PAA | 3,6 | 0,70 | 0,40 | 6,8 |
| Pd-3 | PE-gr-PVP | 12,6 | 2,26 | 0,36 | 5,5 |
| Pd-4 | PE-gr-PVCz | 10,0 | 0,20 | 0,04 | 4,3 |
| Pd-5 | PE-gr-PVPr | 19,0 | 0,95 | 0,10 | 4,3 |
| Pd-6 | PE-gr-PAN | 1290 | 0,91 | 0,15 | 4,9 |
| Pd-7 | PE-gr-PAN* | 12,0 | 1,27 | 0,21 | 5,1 |

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*Original complex $PdCl_2(CH_3CN)_2$.

Nitrogen-containing groups differing in basicity were present in the grafted ligands. The calculated thickness of the grafted layer, depending on the degree of grafting, was 100-500 Å.

When Pd(II) is anchored from alcohol or water–alcohol solutions of $K_2PdCl_4$, the Pd(II) is partly reduced to Pd(0), with immobilization of the Pd(0) on the polymeric support [4]. To avoid this, the immobilization was performed in benzene by the competing ligand method

$$2\,\equiv\!|\!-L + PdCl_2(L')_2 \overset{\overline{K}_0}{\rightleftarrows} \equiv\!|\!-L)_2PdCl_2 + 2L' \qquad (2)$$

In principle, reaction (2) may proceed with the retention of one ligand L' on the anchored Pd(II), for example, in accordance with the scheme

$$\equiv\!|\!-L + PdCl_2(L')_2 \xrightarrow{\overline{K}_0'} \equiv\!|\!-LPdCl_2L' + L' \qquad (2')$$

However, IR spectroscopic data indicate that both $C_6H_5CN$ groups of the original Pd(II) complex are replaced by the ligand groups of the grafted fragments. The bands of the stretching vibrations of the nitrile group ($\nu C\equiv N$) $PdCl_2(C_6H_5CN)_2$ (2237 $cm^{-1}$) are not observed at all in the products from immobilization on PE-gr-PVIA, PE-gr-PAA, PE-gr-PVP, PE-gr-PVCz, and PE-gr-PVPr. In the spectrum of the $PdCl_2$·PE-gr-PAN, $\nu C\equiv N$ 2252 $cm^{-1}$ corresponds to stretching vibrations of the nitrile group of the grafted fragments.

On the basis of these facts, by using the balance ratio for the equilibrium concentrations, we can express the effective formation constant ($\overline{K}_0$) for the macromolecular complexes of Pd(II) as follows:

$$\overline{K}_0 = \frac{4([Pd(II)])^3}{(L_0 - 2[Pd(II)]^2)([PdCl_2(C_6H_5CN)_2]_0 - [Pd(II)])}, \qquad (3)$$

where [Pd(II)] is the concentration of bound Pd(II) on the support; $L_0$ and $[PdCl_2(C_6H_5CN)_2]_0$ are the initial concentrations of the grafted fragments and the Pd(II) complex.

From Table 1 it can be seen that the degree of utilization of the functional groups, which is equal to the ratio f of the number of coordinated functional groups to the total number, is close to 40% (mole) for the PE-gr-PAA and the PE-gr-PVP; for the other ligands, this ratio is considerably lower. This difference may be a consequence of steric hindrance due to the polymeric character of the grafted fragments and their limited solubility in the reaction medium. Therefore, only the sterically accessible functional groups are involved in the interaction. The degree of their accessibility decreases with increasing degree of grafting [8]. Apparently, from the standpoint of utilization of the functional groups, polymeric supports with a monolayer of functional groups would be optimal. The content of bound Pd(II) also depends on the strength of the original nitrile complex of palladium; in the case of $PdCl_2(CH_3CN)_2$, the content of immobilized Pd(II) is higher (complex Pd-7 in Table 1). It was not possible to establish any correlation between the basicity of the nitrogen atom in the grafted fragments and the effective formation constant for the complexes or the stability of the complexes (such as was established, for example, in the case of complexes of palladium anchored on modified silica gel [9]).

The products that were obtained are structurally homogeneous, and they contain four-coordinated Pd(II), $E_b$ = 338.1-338.5 eV (level $Pd_{3d^{5}/_{2}}$). In the low-frequency region of

TABLE 2. Hydrogenation of p-NCB in the Presence of Immobilized Complexes of Palladium*

| Catalyst | Initial rate, mmoles $H_2$/min | Activity, moles $H_2$/min per mole Pd | Composition of reaction products, % | | | | | S, % |
|---|---|---|---|---|---|---|---|---|
| | | | p-NCB | nitrobenzene | aniline | p-ACB | phenylhydroxylamine | |
| Pd-1 | 0,013 | 1,27 | 89,7 | 7,5 | 2,8 | 1,4 | – | 33 |
| Pd-2 | 0,067 | 6,41 | 35,2 | 4,3 | 49,8 | 11,1 | – | 18,3 |
| Pd-3 | 0,053 | 5,10 | 24,6 | 4,6 | 60,7 | 10,1 | – | 14 |
| Pd-4 | 0,022 | 2,09 | 60,3 | 4,4 | 26,9 | 8,5 | – | 24 |
| Pd-5 | 0,117 | 11,31 | 16,2 | 7,4 | 63,4 | 13,0 | – | 21 |
| Pd-6 | 0,042 | 4,01 | 24,0 | 2,0 | 53,0 | 18,0 | 3,0 | 25 |
| Pd-7 | 0,054 | 5,20 | 15,4 | 15,0 | 66,4 | 14,7 | 2,0 | 18 |
| Pd-3 † | 0,024 | 1,22 | 63,3 | 0,6 | 11,5 | 11,6 | 1,2 | 50 |

*Reaction conditions: $P_{H_2}$ = 1 atm, 50°, 10 ml 2% $NaBH_4$ solution in isopropyl alcohol, complex activation time 10 min, 0.158 g (1 mmole) p-NCB; Pd in catalysts 0.00104 g; reaction time 30 min.

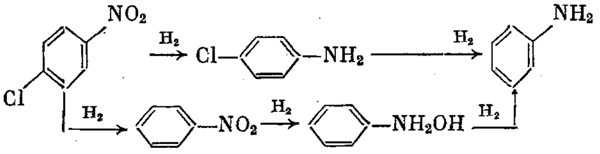
†Catalyst was obtained by the interaction of the macroligand with a solution of $PdCl_2$ in DMFA.

the spectrum, νPd-Cl is observed at 335-345 $cm^{-1}$. The complex of Pd(II) with PE-gr-PVPr is probably formed as a result of donation of an unshared pair of electrons of the N atom; and in the case of the PE-gr-PVIA, the complex is probably formed by donation of an unshared pair of electrons of the $N_3$ atom of the imidazole ring to the 3d orbital of the Pd atom. In the complex of Pd(II) with PE-gr-PVP, the band of stretching vibrations of the pyridine ring is observed at 1615 $cm^{-1}$, in contrast to 1595 $cm^{-1}$ in the original ligand. In the complexation of Pd(II) with PE-gr-PAA, the amino groups of the grafted fragments take part. Variation of the ligand environment in the polymeric complexes is manifested in the broadening of the $Pd_{3d^5/_2}$ lines.

After treatment with $NaBH_4$ and/or $H_2$, the color of the complexes becomes deeper, indicating conversion of the Pd(II) to the zero-valent state. $H_2$ treatment of the complex of palladium with PE-gr-PVP leads to reduction of the Pd(II) to PD(0) and immobilization of the latter by the polymeric support [4]. We can assume that analogous conversions occur with the other complexes that have been examined in this work.

It can be seen from Table 2* that the specific catalytic activity of the complexes depends on the type of polymeric support; in general, the activity increases with increasing values of log $\overline{K}_0$ (Fig. 1).

In the hydrogenation of p-NCB, p-aminochlorobenzene (p-ACB) is usually formed, along with the aniline that is formed as a result of the dehydrochlorination reaction that proceeds in parallel. The chemical processes can be represented by the scheme



(4)

All of the indicated compounds have been detected and identified. The side process (dehalogenation) proceeds even in the first stages of the reaction, as indicated by the presence of nitrobenzene in the reaction mixture. The process selectivity (S) was defined as the percentage content of p-ACB in the total products (p-ACB + aniline). The highest selectivity is shown by the complex obtained by the interaction of PE-gr-PVP with a solution of $PdCl_2$ in DMFA.

Table 3 shows that the selectivity of the process is the highest in the case of the immobilized catalyst; it is stable when used repeatedly. The activity of $Pd/Al_2O_3$ drops off by a factor of 2-3 in successive experiments, and the homogeneous analog of the immobilized systems is inactive even in its first reuse. This drop in activity is apparently related to aggregation of the reduced palladium Pd(0) and the formation of large particles that are not active in hydrogenation. In the immobilized systems, the formation of aggre-

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*T. B. Pogodina took part in the studies of p-NCB hydrogenation.

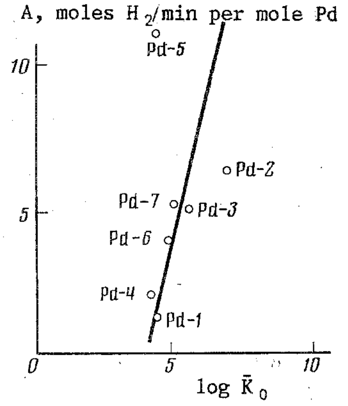

Fig. 1. Activity of immobilized palladium complexes as a funciton of log $\bar{K}_0$ (reaction conditions are given in Table 2).

TABLE 3. Comparison of Activity, Stability and Selectivity of Certain Palladium-Based Catalysts in the Hydrogenation of p-NCB*

| Catalyst | Initial rate, mmoles $H_2$/min | S, % |
|---|---|---|
| Pd-3 | 0,024 | 50 |
| Second use | 0,025 | 52 |
| Third use | 0,026 | 51 |
| $PdCl_2(C_6H_5CN)_2$ | 0,091 | 35 |
| Second use | Inactive | — |
| 5% $Pd/Al_2O_3$ | 0,127 | 18 |
| Second use | 0,077 | 25 |
| Third use | 0.046 | 26 |

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*Reaction conditions are given in Table 2.

gated particles of Pd(0) is prevented by the nitrogen-containing functional cover; therefore, the Pd(0) that is formed is stabilized by the functional groups of the polymeric support, and we may consider that complexes of Pd(0) are responsible for the catalysis, not particles of metallic Pd as is the case when $Pd/Al_2O_3$ is used. Similar facts were established in the hydrogenative amination of isobutanal by nitrobenzene, catalyzed by immobilized Pd(II) [4], in the polymerization of diene monomers catalyzed by Co(II) complexes anchored on polymeric supports [10], and in the dimerization of ethylene in the presence of Ni(II) complexes on supports of this type [11].

Thus, immobilization of Pd(II) complexes on polymeric supports by the competing ligand method offers significant possibilities for increasing the activity and selectivity of catalysts and also for improving the stability of catalyst operation.

## CONCLUSIONS

1. By the competing ligand method, starting with bis(benzonitrile)palladium dichloride, complexes of palladium(II) have been immobilized on polymeric supports, including functional covers of nitrile, vinylpyridyl, vinylimidazole, allylamine, vinylcarbazole, and vinylpyrrolidone groups. Both molecules of benzonitrile in the original complex are replaced by the functional groups of the polymeric support, thus leading to structural homogeneity of the products that are formed.

2. Experiments on the hydrogenation of p-nitrochlorobenzene in the presence of homogeneous, heterogeneous, and heterogenized palladium catalysts have shown that the immobilization of palladium on polymeric supports improves the activity, selectivity, and stability of the catalysts.

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# EVOLUTION OF HYDROGEN FROM ACIDIC AQUEOUS AND AQUEOUS-ALCOHOLIC SOLUTIONS BY REDUCED FORMS OF ISOPOLYTUNGSTATES

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It was established in [1] that reduced polytungstates (PTs) and polymolybdates that are formed by the association of $WO_4^{2-}$ and $MoO_4^{2-}$ in acidic aqueous solutions are capable of spontaneous reoxidation, accompanied by the evolution of $H_2$, the same as the reduced forms of heteropolyacids (HPAs) [2-4]. The work reported in this article was aimed at determining the specific nature of the hydrogen-releasing PT species and investigating the features of $H_2$ evolution by this species.

## EXPERIMENTAL

All experiments were performed in the pH interval 0-4. The acidity of the medium was adjusted by the addition of hydrochloric acid, Grade o.s.ch. ("ultrapure") or $H_2SO_4$, Grade kh.ch. ("chemically pure"). The PTs were prepared from normal Na tungstate. The concentration of the Na tungstate was varied from $10^{-4}$ to $10^{-2}$ M. The concentration of ethanol in the aqueous alcoholic solutions was 8.35 M.

In order to remove dissolved $O_2$, the samples were first purged with argon for 20 min. The PTs were reduced by Zn amalgam, after which the reduced forms were transferred to a reactor that did not contain amalgam; alternatively, the PTs were reduced by irradiation of aqueous-alcoholic solutions of the PT by soft UV light in the band corresponding to absorption of the PT (DRSh-1000 lamp with UFS-5 or UFS-6 filter).

The optical spectra and the kinetic curves were recorded at 22 ± 2° in a Shimadzu UV-300 spectrophotometer; the ESR spectra were recorded at liquid-nitrogen temperature in an RÉ-1306 spectrometer. The redox titrations for the determination of the degree of reduction of the PTs were performed with $(1\text{-}2)\cdot 10^{-3}$ N $KMnO_4$. The quantity of $H_2$ evolved was determined in an LKhM-8 MD chromatograph.

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