CATALYSIS

Effect of the Nature of a Solvent on Properties of Pd–P Catalysts in Hydrogenation of *ortho*-Chloronitrobenzene

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Abstract—Fundamental aspects of the influence of solvent nature on the activity and selectivity of palladium catalysts modified with white phosphorus in hydrogenation of *ortho*-chloronitrobenzene were determined. The conditions are suggested in which the chemoselectivity of palladium catalysts modified with white phosphorus can be raised to 93–95% with respect to *ortho*-chloroaniline in the temperature range 30–80°C without accumulation in the reaction system of undesirable products, *ortho*-chlorophenylhydroxylamine and azo- and azoxychlorobenzene.

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The unique ability of transition metals and their complexes to catalyze the hydrogenation of unsaturated organic molecules with hydrogen gas has been known since the early XX century and is used in numerous industrial processes among which the following can be noted: chemoselective hydrogenation of alkynes and dienes to monoenes, hydrogenation of benzene to cyclohexane and phenol to cyclohexanone [1], hydrogenation of polymers with aryl radicals and, in particular polystyrene to poly(cyclohexaethylene) [2]. The hydrogenation reaction belongs to processes on which theoretical problems of catalysis in chemistry are studied.

In recent years, a steadily increasing attention has been given to issues related to the ecological safety, and, therefore, a search is being continued for new catalysts and new approaches to synthesis of effective catalysts for hydrogen-involving processes: hydrogenation of nitrohaloarenes [3, 4], hydrodechlorination of aryl and alkyl halides [5], hydrodenitrogenation, and hydrodesulfurization [6].

The best studied catalysts for hydrogenation of nitrohaloarenes are metals (Pt, Pd, Ni, Ru) and sulfides of Group-VIII metals [3, 4]. However, the catalytic reduction of a nitro group in nitrohaloarenes by molecular hydrogen may be accompanied by a number of side processes leading to a decrease in the yield of the target product, haloaniline. One of the main problems in the reduction of nitrohaloarenes by molecular hydrogen is the hydrogenolysis of the C-Hal bond. This process most frequently cannot be suppressed without application of S-, P-, or N-containing modifiers [3]. According to the commonly accepted opinion, these modifiers are preferably absorbed on the most active centers and thereby hinder the adsorption of haloanilines and nonselective hydrogenation [7]. However, the selectivity with respect to haloanilines in the reduction of the corresponding nitro derivatives via application of S-, P-, or N-containing modifiers is achieved at the expense of the catalytic activity, with hydroxylamines accumulating in the reaction system. The decomposition of hydroxylamines is an exothermic reaction, and, therefore, raising their concentration in the reaction system may be explosionhazardous [8]. The concentration of hydroxylamines in the course of hydrogenation of nitrohaloarenes can be avoided via addition of activators, vanadium compounds. A set of highly selective Pt/C activators modified with hypophosphorous acid (Pt/C-H₃PO₂) and activated with vanadium compounds has been suggested on the basis of this approach [9].

Another approach to improving the chemoselectivity of metallic catalysts in the hydrogenation of nitrohaloarenes is based on the structural sensitivity of the reaction of hydrogenolysis of the C–Hal bond [4, 10]. It has been shown in this way that nonselective platinum, nickel, and gold-containing catalysts can be made chemoselective by varying the size and shape of particles [11].

A new class of hydroprocessing catalysts is constituted by phosphides of transition metals [6, 12–15], which proved to be the most efficient in hydrodesulfurization and hydrodenitrogenation processes, compared with aluminum-cobalt-molybdenum catalysts [6], and more stable in hydrodehalogenization processes [12]. In addition, it has been shown previously that introduction of phosphorus into a reaction system makes it possible to raise by an order of magnitude the activity and output capacity of palladium catalysts in alkene hydrogenation [16] and to increase chemoselectivity in hydrogenation of ortho-chloronitrobenzene (o-CNB) [17, 18]. However, performing the hydrogenation of o-CNB in N,N-dimethylformamide (DMF) resulted in the formation of azo- and azoxychlorobenzenes, products of condensation of ortho-chlorophenylhydroxylamine and chloronitrosobenzene. Because the condensation process occurring in the volume phase, rather than on the catalyst surface, is favored by a basic medium, replacement of the solvent (DMF) may lead to an increase in the yield of ortho-chloroaniline.

The goal of our study was to examine the effect of the nature of a solvent on the properties of palladium catalysts modified with white phosphorus and supported on a carbon carrier (Pd–P/C) in the hydrogenation of *ortho*-chloronitrobenzene.

EXPERIMENTAL

Solvents (DMF, ethanol, toluene) were purified by the standard procedures [19]. For deeper drying, toluene was subjected to an additional distillation over LiAlH₄ in rectification column and stored in the atmosphere of argon in sealed ampules over 4A molecular sieves. To dehydrate DMF and remove amine impurities, it was kept over anhydrous copper sulfate until a green solution was formed and twice subjected to a vacuum distillation (8 mmHg) at a temperature not higher than 42°C.

Palladium bis(acetylacetonate) [Pd(acac)₂] was produced by the procedure described in [20] and recrystallized from acetone. ¹H NMR spectrum in benzene: δ (CH) = 5.04 ppm (s, 1H), δ (CH₃) = 1.76 ppm (s, 6H). *ortho*-Chloronitrobenzene was recrystallized from 95% ethanol. Immediately prior to being used, white phosphorus was mechanically cleaned to remove surface oxidation products and washed with anhydrous benzene. A solution of white phosphorus in benzene was prepared and stored in an inert atmosphere in a vessel of the "finger" type, whose design envisages evacuation and filling with argon. ³¹P NMR spectrum: $\delta = -522$ ppm (s).

To prepare a hydrogenation catalyst, a solution of $Pd(acac)_2$ (5 × 10⁻⁵ mol, 0.0152 g) in 9 mL of DMF was poured into a reaction vessel of the "duck" type with a weighed portion of a carbon (0.2607 g, Sibunit brand, 0.2-0.4 mm fraction). The reaction mixture was agitated at room temperature for 20 min and then 1 mL of a white phosphorus solution $(3.5 \times 10^{-5} \text{ in terms})$ of the atomic form of phosphorus) was added and the mixture was additionally agitated for 10 min more. After the Pd-P/C catalyst was formed during 15-20 min at 80°C in the atmosphere of hydrogen (hydrogen pressure 1 excess atmosphere), the temperature of the reaction mixture was lowered to 50°C and the substrate, orthochloronitrobenzene, was introduced. The reduction with hydrogen was performed under vigorous agitation, which ruled out the occurrence of the reaction under the diffusion control. The hydrogenation process was monitored by the pressure drop indicated by a gage and by analyzing samples by the GLC method on a chromatograph equipped with a 30-m-long capillary column (stationary phase 5% diphenyl + 95% dimethylpolysilylphenylene siloxane) and a flame-ionization detector (FID). The composition of intermediates and reduction products of orthochloronitrobenzene was identified by chromatographymass spectrometry on a Shimadzu GCMS-QP-2010 mass spectrometer (Japan).

To perform the process in other solvents, the catalyst was formed in a similar way, but, after the Pd-P/C catalyst was formed in DMF, the solvent was evaporated and a 10-mL portion of a solvent (ethanol or toluene) was added, the internal standard (diphenyl, 9.9481×10^{-4} mol, 0.1534 g) and the substrate (*ortho*-chloronitrobenzene, 0.5 mL) were introduced and the hydrogenation was performed at a certain temperature.

RESULTS AND DISCUSSION

To determine how the medium affects the properties of phosphorus-modified palladium catalysts (Pd-P/C), we performed the liquid-phase hydrogenation of o-CNB in three solvent of varied nature: ethanol (polar protic), DMF (polar aprotic), and toluene (nonpolar solvent). Nanoparticles of the Pd-P catalyst were formed in the presence of the carbon support (Sibunit) to preclude formation of a palladium mirror because of the different solvating capacities of the solvents and, in particular, toluene at P/Pd = 0.7. It has been shown previously that, at this component ratio of the Pd–P system, the catalyst is characterized by the highest chemoselectivity with respect to *ortho*-chloroaniline in the hydrogenation of *o*-CNB [18]. The experimental results are listed in Table 1.

As follows from the data in Table 1, the hydrogenation of o-CNB in DMF in the presence of a Pd/C catalyst (without a modifier) is characterized, as also that in the case of Pd-black, by a substantial accumulation of ortho-chlorophenylhydroxylamine and condensation products, azoxy- and azochlorobenzenes, in the reaction mixture. The rate of hydrogenolysis is rather high, up to 2.02 mM min⁻¹. The hydrogenolysis rate is only three times lower than the rate of ortho-chloroaniline formation. At a 99% conversion of o-CNB, the selectivity of the Pd/C catalyst with respect to ortho-chloroaniline does not exceed 59% (Fig. 1). A catalytic process additionally performed to hydrogenate the resulting intermediates, ortho-chlorophenylhydroxylamine, and biproducts, azoxy- and azochlorobenzenes to ortho-chloroaniline failed to provide perceptible results. The chromatographic yield of ortho-chloroaniline was 61%, but the share of aniline increased in this case to 34.5% (Table 1).

Modification of the palladium catalyst with phosphorus changes its catalytic properties. Introduction of phosphorus diminishes the catalytic activity of Pd-P/C in the reduction of the nitro group by a factor of 5.4, compared with the Pd/C catalyst, from 40 to 7.4 mM min⁻¹ (Table 1). According to the GLC and chromatographic–mass-spectrometric data, the low yield of *ortho*-chloroaniline at a nearly full conversion of *o*-CNB is due to the formation and accumulation of *ortho*-chlorophenylhydroxylamine and condensation products (azoxy- and azochlorobenzenes) in the reaction system. At a nearly 100% conversion of *o*-CNB, the conversion products of the starting substrate contain nearly 28% undesirable compounds, *ortho*-chlorophenylhydroxylamine and azoxy- and azochlorobenzenes.

Further reduction of *ortho*-chlorophenylhydroxylamine and azoxy-and azochlorobenzenes makes it possible to raise the selectivity to *ortho*-chloroaniline to 89.9%. In this case, the fraction of aniline grows only slightly, from 1.9 to 4.4%. A close value of the selectivity with respect to *ortho*-chloroaniline (92–94%) is characteristic of the catalytic system Pd(acac)₂–0.7P in DMF in the absence of a carbon support [18].

Replacement of the solvent with ethanol changes the catalytic properties of Pd–P/C in the hydrogenation of *o*-CNB (Table 1). The rate of *ortho*-chloroaniline formation is nearly comparable with the rate of this



Fig. 1. Yield of (1) ortho-chloroaniline and (2) aniline vs. the conversion K of o-CNB in DMF in the presence of the Pd/C catalyst. $c_{Pd} = 5 \text{ mM}$, P/Pd = 0.7, [o-CNB]/[Pd] = 87, T = 50°C, $P(H_2) = 2 \text{ atm.}$ (C) Selectivity; the same for Figs. 2–4.

process in DMF (5.69 mM min⁻¹). The rate of *ortho*chloroaniline formation is 0.85 of the rate at which *o*-CNB is hydrogenated (6.64 mM min⁻¹). This indicates that the contribution of the condensation pathway is small when the process is performed in ethanol. The solvent mainly affects the change in the ratio of formation rates for *ortho*chloroaniline and aniline. These rates differ in ethanol by a factor of 9.6, whereas in DMF, the corresponding ratio is close to 50. Despite the high rate of hydrogenolysis of the C–Cl bond in ethanol (0.537 mM min⁻¹) as compared with that in DMF, the chromatographic yield of *ortho*-chloroaniline at a 99% conversion substantially



Fig. 2. Yield of (1) ortho-chloroaniline and (2) aniline vs. the conversion K of o-CNB in DMF in the presence of the Pd–P/C catalyst. $c_{Pd} = 5 \text{ mM}$, P/Pd = 0.7, [o-CNB]/[Pd] = 87, T = 50°C, $P(H_2) = 2$ atm; the same for Figs. 3 and 4.

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Fig. 3. Yield of (1) *ortho*-chloroaniline and (2) aniline vs. the conversion K of *o*-CNB in ethanol in the presence of the Pd–P/C catalyst.

exceeds, reaching a value of 81.3%, that in DMF (Fig. 3). The increase in the yield of *ortho*-chloroaniline at a nearly 100% conversion of *o*-CNB is due to the smaller contribution of the condensation process. When the process was performed until not only *o*-CNB, but also all the intermediates (*ortho*-chlorophenylhydroxylamine and azoxy- and azochlorobenzenes), were fully reduced, the yield of *ortho*-chloroaniline remained nearly unchanged (82.9%) due to the high rate of hydrogenolysis. In this case, the fraction of aniline increased to 20%.

Another behavior was observed when *o*-CNB was reduced in toluene in the presence of a Pd–P/C catalyst. The following points can be considered positive. First, the reaction system did not contain azo- and azoxychlorobenzenes in the course of *o*-CNB



Fig. 4. Yield of (1) *ortho*-chloroaniline and (2) aniline vs. the conversion K of *o*-CNB in toluene in the presence of the Pd–P/C catalyst.

hydrogenation, but also chlorophenylhydroxylamine was recorded in trace amounts. Second, the difference between the rates of *ortho*-chloroaniline formation and hydrogenolysis of the C–Cl bond was as large as a factor 149 (Table 1). This kinetic pattern resulted in that the selectivity of the Pd-P/C catalyst with respect to *ortho*-chloroaniline was high (94–97%) during the whole time of *o*-CNB hydrogenation, with the fraction of aniline not exceeding 1% (Fig. 4). At 99% conversion of *o*-CNB chromatographic yield of *ortho*-chloroaniline was significantly higher (94.8%) than when carrying out the process in DMF and ethanol. It should be noted that the high chemoselectivity of Pd–P/C catalysts with respect to *ortho*-chloroaniline and the above aspects of the process in toluene were observed at various temperatures

Table 1. Quantitative characteristics of the Pd–P/C catalyst in hydrogenation of *ortho*-chloronitrobenzene $c_{Pd} = 5 \text{ mM}$, P/Pd = 0.7, [o-CNB]/[Pd] = 87, $T = 50^{\circ}C$, $P(H_2) = 2 \text{ atm}$

Parameter	DMF	Ethanol	Toluene	DMFa
Catalytic activity a, mol H ₂ (mol Pd min) ⁻¹	4.4	4.0	2.2	24
<i>o</i> -CNB hydrogenation rate r_1 , mM min ⁻¹	7.40	6.64	3.09	40
<i>ortho</i> -Chloroaniline formation rate r_2 , mM min ⁻¹	5.40	5.69	2.98	9.6
Hydrogenolysis rate r_3 of the C–Cl bond, mM min ⁻¹	0.11	0.54	0.02	2.1
r_2/r_3	49.0	10	149	4.6
Conversion of <i>o</i> -CNB, %	99.8	99.0	99.1	99.2
Yield of <i>ortho</i> -chloroaniline, %	70.6 89.9 ^ь	81.3 82.9 ^b	94.8 93.8 ^b	59.2 61.4 ^b
Yield of aniline, %	1.9 4.4 ^b	9.3 20.0 ^b	1.0 1.5 ^b	21.9 34.4 ^b

^a Pd/C catalyst.

^b Upon 100% conversion of o-CNB and hydrogenation of intermediate compounds.

Table 2. Effect of temperature on the chemoselectivity of the Pd–P/C catalyst with respect to *ortho*-chloroaniline and on the turnover frequency (TOF) in the reduction of *ortho*-chloronitrobenzene with hydrogen. $c_{Pd} = 5 \times 10^{-3}$ mM, P/Pd = 0.7, [o-CNB]/[Pd] = 87, solvent toluene, $P(H_2) = 2$ atm

<i>T</i> , °C <i>o</i> -Cl	o CND conversion 9/	Composition of products, mol %			TOF a min-1
	0-CINB conversion, 78	o-CAN ^b	aniline	othersc	TOF," IIIII '
30	100	94.9	0.5	4.6	1.5
50	100	95.8	0.6	3.6	2.2
80	100	94.0	1.0	5.0	3.6

^a The turnover frequency is calculated from the initial rates of o-CNB reduction.

^b The molar percent for ortho-chloroaniline (o-CAN) correspond to the selectivity of the palladium catalyst with respect to o-CAN.

^c ortho-Chlorophenylhydroxylamine, 2,2'-dichloroazoxybenzene, 2,2'-dichloroazobenzene.

(Table 2) and P/Pd ratios (Table 3). Therefore, the observed decrease in the rate of *o*-CNB hydrogenation in the presence of Pd–P/C in toluene (by a factor of \sim 2), compared with polar solvents, can be compensated by raising the temperature. It should be noted that the Pd–P/C catalyst retained a constant activity in hydrogenation of eight portions of *o*-CNB in toluene in the recycling mode.

The solvent can solvate the reactants and active surface centers of the catalyst, change the solubility of reactants and reagents, diffusion rate, and other kinetic and thermodynamic parameters of the reaction [21]. In view of this fact, it is reasonable to relate the effect of the solvents under consideration on the catalytic properties of palladium catalysts to their physical properties: density, viscosity, dielectric constant, and solubility of hydrogen.

Sibunit belongs to mesoporous adsorbents, and, therefore, the internal diffusion is one of stages of the heterogeneous-catalytic reaction. If the hydrogenation of *o*-CNB were limited by the internal diffusion of the

reactants to the catalyst surface, an increase in the solvent viscosity would make the reaction rate lower [22]. The increase in the density and viscosity of the solvent hinders the transfer of the fluid into the catalyst pores. In this case, the highest rate would be observed in liquid-phase hydrogenation of o-CNB in the presence of a Pd-P/C catalyst in toluene ($\eta = 0.584$ mPa s), and the lowest, in ethanol ($\eta = 1.17$ mPa s). This contradicts the experimental data (Table 1). Consequently, the viscosity of solvents is not the main factor determining the catalytic properties of Pd-P/C catalysts. The effect of the nature of a solvent on the properties of Pd–P/C cannot be attributed to hydrogen solubility, either, because the hydrogen solubility in toluene is 1.59 times (mL L⁻¹) that in DMF [23]. A high rate of o-CNB hydrogenation is observed in polar solvents having a high dielectric constant of the medium (ε_{DMF} = 36.77, $\varepsilon_{ethanol} = 24.30$, $\varepsilon_{toluene} = 2.3$) (Table 1). Therefore, it is reasonable to assume that the change in reactivity as a result of an additional polarization of o-CNB and

Table 3. Effect of the P/Pd ratio on the chemoselectivity of the Pd–P/C catalyst with respect to ortho-chloroaniline and on
the turnover frequency (TOF) in the reduction of <i>ortho</i> -chloronitrobenzene with hydrogen. $c_{Pd} = 5 \times 10^{-3}$ mM, P/Pd = 0.7,
$[o-CNB]/[Pd] = 87$, solvent toluene, $P(H_2) = 2$ atm, $T = 50^{\circ}C$

P/Pd <i>o</i> -CNB conversion	a CND conversion 9/	Composition of products, mol %			TOE a min-1
	0-CINB conversion, 76	o-CAN ^b	aniline	othersc	IOF,ª min ⁻¹
0	100	86.7	1.6	11.7	4.8
0.3	100	91.3	1.3	7.4	2.5
0.7	100	94.0	1.0	5.0	2.4
1.2	100	94.4	0.8	4.8	2.3

^a The turnover frequency is calculated from the initial rates of o-CNB reduction.

^b The molar percent for o-CAN correspond to the selectivity of the palladium catalyst with respect to o-CAN.

c ortho-Chlorophenylhydroxylamine, 2,2'-dichloroazoxybenzene, 2,2'-dichloroazobenzene.

intermediates in a polar solvent [24] is the main factor affecting the properties of the Pd–P/C catalyst. The basic solvent (DMF) also favors the occurrence of the reaction by the condensation pathway, whereas the protic polar solvent enhances the hydrogenolysis of the C–Cl bond.

CONCLUSIONS

(1) Modification of palladium catalysts (Pd–P/C) with white phosphorus makes it possible to raise their chemoselectivity with respect to *ortho*-chloroaniline in hydrogenation of *ortho*-chloronitrobenzene to 94.4%, compared with the Pd/C catalyst (61%).

(2) The catalytic characteristics of the Pd–P/C catalyst depend not only on the P/Pd ratio and on the temperature at which the catalytic process is performed, but also on the nature of a solvent. In the case of reduction of *ortho*-chloronitrobenzene in toluene, it is possible to nearly fully avoid accumulation in the reaction system of undesirable compounds, *ortho*-chlorophenylhydroxylamine and its condensation products. In this case the rate of *ortho*-chloroaniline formation is 149 times that of *ortho*-chloroaniline hydrogenolysis, and the fraction of aniline at the 100% conversion of *ortho*-chloronitrobenzene does not exceed 1%. The high chemoselectivity of the Pd–P/C catalyst with respect to *ortho*-chloroaniline is preserved in the temperature range 30–80°C.

(3) Polar protic and aprotic solvents differently affect the chemoselectivity of the Pd–P/C catalyst. In the basic aprotic solvent (dimethylformamide), the rate of hydrogenolysis is low, but the basic solvent accelerates the formation and accumulation of azoxy- and azochlorobenzenes in the reaction medium. In the protic solvent, ethanol, the rate of hydrogenolysis of the C–Cl bond sharply grows. Despite the higher selectivity of the Pd–P/C catalyst with respect to ortho-chloroaniline in ethanol at a 99% conversion of *ortho*-chloronitrobenzene, because of the smaller contribution of the condensation pathway, the selectivity of Pd–P/C with respect to *ortho*-chloroaniline in ethanol is lower than that in dimethylformamide at full conversion of not only *ortho*-chloronitrobenzene, but also the intermediates.

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