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Differential Selectivity of Palladium–Phosphorus Catalysts in the Competitive Hydrogenation of Isomeric Chloronitrobenzenes

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Abstract—The competitive hydrogenation of chloronitrobenzene isomers in the presence of different palladium-containing catalysts was studied. The nature of catalytic activity carriers for the Pd–P nanoparticles containing both Pd(0) clusters and palladium phosphides was determined by the method of phase trajectories. It was found that the hydrogenation of chloronitrobenzene isomers under mild conditions occurred on the clusters of Pd(0), and the dependence of the differential selectivity of Pd–P clusters in the hydrogenation of *o*- and *m*-chloronitrobenzene on the P/Pd ratio was related to the dispersity of the Pd(0) clusters.

Keywords: hydrogenation of chloronitrobenzene isomers, palladium–phosphorus catalysts, differential selectivity

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INTRODUCTION

Present-day international conventions for environmental protection and ecological safety impose new requirements that are ever more stringent on catalysts, catalytic reactions, and their operational feasibility. For a number of fine organic synthesis processes, the development of not only highly selective catalysts but also catalysts that make it possible to regulate the composition of products with atomic accuracy is a problem of primary importance [1]. This scientific problem does not have trivial solutions because the majority of catalysts accelerate several thermodynamically allowed reactions rather than a single reaction. The selectivity of catalytic action is determined by a number of factors: the nature of a catalyst and a substrate, process parameters and conditions, etc. In the case of heterogeneous catalytic systems, additional conditions responsible for activity and selectivity are their correlations with the particle size and shape of an active constituent of the catalyst and with its electronic state [2–5]. A reasonable strategy of the development of catalytic systems and the selection of reaction conditions is impossible without the knowledge of the mechanisms of formation and functioning of catalytically active centers (complexes).

A study of the nature of catalytic activity carriers in Pd–P nanoparticles formed by a low-temperature method, which contain both Pd(0) clusters and palladium phosphides, is of considerable current interest [6]. The Pd–P catalysts are characterized by high activity, selectivity, and productivity in the hydrogenation of alkenes [7], aldehydes [7], and nitroarenes [8] and by chemoselectivity in the reduction of chloronitrobenzene with the formation of the practically important products—chloroanilines [9]. The phosphides of transition metals, in particular, nickel, and other M–P-containing X-ray amorphous materials (M = Fe, Co, Ni, Ru, Mo, W, Rh, Pd, and Pt) obtained with the use of PH_3 were tested for the first time in different processes (the hydrogenation, isomerization, and dimerization of alkenes) [10]. However, the phosphides of transition metals were not considered as hydrogenation catalysts because of the very low catalytic activity even under severe conditions. The increased stability of *d*-metal phosphides to deactivation in the reactions of hydrodesulfurization [11–13], chloronitrobenzene [13, 14], and hydrodechlorination [15] in comparison with metals and metal sulfides, carbides, and borides; the synthesis of phase-pure *d*-metal phosphides in a highly dispersed state [16, 17]; and the development of methods for their supporting [17] facilitated the expansion of the fields of research into the catalytic properties of the M–P particles [18–21].

The simultaneous presence of two potentially active forms (Pd(0) clusters and palladium phosphides) in the highly dispersed Pd–P catalysts hampers the development of approaches to the goal-oriented regulation of their properties in different catalytic processes. The results obtained earlier on the phase composition and the state of a surface layer of Pd–P catalysts did not make it possible to unambiguously discriminate hypotheses on the true nature of activity carriers [6, 22]. This problem is difficult to solve because both a ratio between palladium phosphides and palladium(0) clusters and the size and electronic state of the Pd(0) clusters change on varying the P/Pd ratio and the nature of acidoligand in the precursor [6, 7]. Moreover, the phase composition of phosphides can change not only at the stage of formation [7, 12] but also in the course of catalytic reaction [12].

For the discrimination of the nature of catalytic activity carriers in the Pd–P nanoparticles under mild conditions, we used a kinetic approach to study differential selectivity in the competitive hydrogenation of chloronitrobenzene isomers, which exclusively depends on the active constituent of the catalyst.

EXPERIMENTAL

Materials

The benzene and *N*,*N*-dimethylformamide (DMF) solvents were purified in accordance with standard procedures [23]. For deeper drying, benzene was additionally distilled from $LiAlH_4$ on a rectification column and stored in an atmosphere of argon in sealed ampoules over molecular sieves 4 Å. For drying and removing amine impurities, DMF was additionally kept over anhydrous copper sulfate until the formation of a green solution and twice subjected to vacuum distillation (8 Torr) at a temperature of no higher than 42°C. The DMF prepared was stored in an atmosphere of argon in sealed ampoules over molecular sieves 4 Å.

Bis(acetylacetonato)palladium ($Pd(acac)_2$) was prepared in accordance with a published procedure [24] and recrystallized from acetone.

Palladium dichloride ($PdCl_2$) of chemically pure grade was used without additional purification.

White phosphorus was mechanically cleaned to remove surface oxidation products and washed with anhydrous benzene immediately before use. The solution of white phosphorus in benzene was prepared and kept in an inert atmosphere in a finger-type vessel, whose design allowed us to evacuate it and fill with argon. ^{31}P NMR spectrum: $\delta = -522$ ppm (s).

o-Chloronitrobenzene and *m*-chloronitrobenzene (Acros Organics, >98% purity) were preliminarily recrystallized from 95% ethanol and then distilled at a reduced pressure (*o*-chloronitrobenzene: 120°C/10 Torr; *m*-chloronitrobenzene: 111°C/10 Torr).

Examples of Hydrogenation Experiments

Hydrogenation in the presence of a Pd–P catalyst. The hydrogenation of chloronitrobenzene isomers was performed in a thermostatically controlled glass long-necked flask at 30°C and an initial hydrogen pressure of 2 atm in the presence of an in situ formed Pd–P catalyst.

A 1-mL portion of a solution of phosphorus (1.5×10^{-5}–3.5×10^{-5} mol in terms of the atomic form of phosphorus) in benzene was added dropwise to a solution of $Pd(acac)_2$ (0.0152 g, 5×10^{-5} mol) in 9 mL of DMF placed in the thermostatically controlled long-necked flask in a flow of hydrogen, and the contents were stirred at room temperature for 5 min. Then, the temperature was increased to 80°C, and the reaction mixture was stirred in an atmosphere of hydrogen for 10–15 min until the quantitative conversion of $Pd(acac)_2$. The resulting blackish brown “solution” was cooled to 50°C; a hydrogen pressure of 2 atm was derived, and an equimolar mixture of the substrates—*o*-chloronitrobenzene (2.0838 mmol) and *m*-chloronitrobenzene (2.0838 mmol)—was injected with a syringe. Hydrogenation was performed with intense stirring to exclude the occurrence of reaction in the diffusion region; the aliquot portions of reaction mixture for GLC analysis were taken at regular intervals.

Hydrogenation experiments with the use of other palladium precursors were carried out in an analogous manner. Differences consisted in the temperature and time of catalyst formation. In the case of $PdCl_2$, the catalytic system was stirred in hydrogen at 30°C for 5 min and then at 50°C for 5 min.

Hydrogenation of chloronitrobenzenes in the presence of the Pd/C catalyst. A solution of $Pd(acac)_2$ (0.0152 g, 5×10^{-5} mol) in 9 mL of DMF was added to a weighed portion of Sibunit coal (0.2607 g, a fraction of 0.2–0.4 mm) placed in a long-necked flask in a flow of hydrogen. The reaction mixture was stirred at room temperature for 60 min; the temperature was increased to 80°C, and the catalyst was formed for 2 h at a hydrogen pressure of 2 atm. Then, the temperature of the reaction mixture was reduced to 50°C, and an equimolar mixture of the substrates—*o*-chloronitrobenzene (2.0838 mmol) and *m*-chloronitrobenzene (2.0838 mmol)—was injected.

Reaction monitoring of the competitive hydrogenation of *o*- and *m*-chloronitrobenzenes. The course of the reaction was monitored by measuring a pressure drop with a manometer and by gas–liquid chromatography (GLC) analysis on a Chromatec-Crystal 5000 chromatograph (Chromatec, Russia) equipped with a capillary column BPX5 with a length of 30 m (5% phenyl, 95% polysilphenylene-siloxane stationary phase) and a flame-ionization detector under the following temperature programming conditions: 180°C (5 min) and 270°C (5 min) at a heating rate of 30 K/min. The intermediates and reaction products were additionally identified on a GCMS-QP2010 Ultra gas chromatography–mass spectrometry instrument (Shimadzu, Japan) with a capillary column GsBP×5MS with a length of 30 m (5% diphenyl, 95% dimethyl polysiloxane stationary phase). Electron-impact ionization (70 eV) was used.

The dispersity of Pd black and the Pd/C catalyst was calculated based on the average particle size from the formula

$$D_{\mathrm{TEM}} = \frac{6M_{\mathrm{Pd}}}{\rho_{\mathrm{Pd}} d_{\mathrm{TEM}} A_{\mathrm{Pd}} N_{\mathrm{A}}},$$

where M_{Pd} is the atomic mass of Pd (g/mol), A_{Pd} is the surface area of a Pd atom ($m^2_{\text{surface Pd}}/\text{atom}_{\text{surface Pd}}$), ρ is the density of palladium (g/m^3), d_{TEM} is the surface weight-average diameter of particles (m), and N_{A} is Avogadro's number.

The sizes of particles were determined using transmission electron microscopy (TEM) by applying a drop of a suspension or colloidal solution (in the case of Pd–P catalysts) to carbonized copper grid (200 mesh) and drying in a box at room temperature in an inert atmosphere. The TEM images were obtained on a Tecnai G^2 electron microscope (FEI, the United States; accelerating voltage, 200 kV) equipped with an energy-dispersive X-ray spectrometer (EDX) (Phoenix, Germany) with a semiconductor Si(Li) detector. The images were recorded with the aid of a CCD camera (Soft Imaging System, Germany).

RESULTS AND DISCUSSION

As noted above, the Pd–P catalysts contain two species potentially active in hydrogenation: palladium(0) nanoclusters and palladium phosphides. Chemical reaction serves as the most reliable information source, which makes it possible to determine the nature of catalytically active particles. Therefore, for the determination of contributions from the two potentially active forms of Pd–P catalysts, we applied a kinetic approach, which uses the differential selectivity of catalytic systems under the conditions of the competition of several substrates as the main parameter to be measured [25, 26]. Differential selectivity depends on the nature of a catalyst; however, in contrast to catalytic activity, it does not depend on the concentration of a precursor used. The application of two uniform substrates makes it possible to substantiate more reliably a hypothesis on the transformations of competing substrates at the same active center of a catalyst by identical mechanisms [25].

The hydrogenation of chloronitrobenzene is a complex reaction accompanied by a number of side reactions. A formal kinetic study of the hydrogenation of *o*-chloronitrobenzene in the presence of a Pd–P catalyst (P/Pd = 0.3) showed that the partial order of reaction with respect to the catalyst was close to 1 ($n_{\text{Pd}} = 1.12$) in a Pd(acac)$_2$ concentration range of 0.001–0.005 mol/L. According to TEM data, the appearance of a plateau in the region of high catalyst concentrations (Fig. 1a) is a consequence of a decrease in the surface area as a result of the aggregation of nanoparticles. The dependence of the rate of hydrogenation of *o*-chloronitrobenzene on its concentration passed through a maximum (Fig. 1b). An extremal shape of the concentration dependence of the rate of *o*-chloronitrobenzene hydrogenation in a concentration range of 0.12–1.18 mol/L is indicative of the competitive adsorption of the molecules of hydrogen and *o*-chloronitrobenzene at the active centers of the Pd–P catalyst. The nearly zero concentration order of reaction with respect to *o*-chloronitrobenzene in a concentration range of 0.45–0.78 mol/L and the first order with respect to hydrogen ($n_{\text{H}_2} = 1.1$) under mild reaction conditions (1–2 atm) (Fig. 1c) are indicative of the saturation of the catalyst surface with the substrate and the participation of hydrogen in the rate-limiting stage of the reaction. Formal kinetic data indicate that the hydrogenation reaction of *o*-chloronitrobenzene in the presence of the Pd–P catalyst proceeds by the Langmuir–Hinshelwood mechanism [27].

The hydrogenation of *o*-chloronitrobenzene in a DMF solution is accompanied by two side reactions: the condensation of intermediates (chloronitrobenzene and chlorophenylhydroxylamine) with the formation of adducts (azo- and azoxychlorobenzenes) and the hydrodechlorination of *o*-chloroaniline [8, 9]. Taking into account the fact that the fraction of aniline in the course of *o*-chloronitrobenzene hydrogenation in the presence of the Pd–P catalyst usually did not exceed 2–5% and it sharply increased after the complete conversion of the initial substrate [8, 28], we can state that the adsorption of *o*-chloronitrobenzene and *o*-chloroaniline also occurs at the same active centers, and it is competitive. The formation of condensation products (azo- and azoxychlorobenzenes) occurs in solution rather than on the catalyst surface [29]. A basic solvent is favorable for the reaction of condensation. Indeed, to 40% *o*-chloronitrobenzene was converted into adducts in the course of its hydrogenation in DMF [8], whereas the hydrogenation of *o*-chloronitrobenzene under the action of the Pd–P catalyst in toluene was almost not accompanied by the formation of azo- and azoxychlorobenzenes [19].

The reactions of *o*-chloronitrobenzene hydrogenation and hydrodechlorination carried out in the presence of the Pd–P catalyst at the same active centers facilitate the analysis of the phase trajectories of reaction, which refer to the dependence of the concentration of a reaction product (or substrate) on that of the other. Because the slope to any point of a phase trajectory is equal to differential selectivity [25], the coincidence of phase trajectories obtained with the use of different palladium catalysts is indicative of the identical nature of active centers with a high probability. The noncoincidence of phase trajectories will make it possible to make a conclusion on the different nature of active centers in the hydrogenation reactions of chloronitrobenzene isomers.

Previously, Schmidt et al. [25] used the method of phase trajectories for the substantiation the type of catalysis (homogeneous or heterogeneous) in C–C coupling reactions. In this case, the phase trajectories of competitive C–C coupling reactions in the presence of heterogeneous palladium catalysts frequently did not coincide, and they depended on the nature of the precursor of a heterogeneous palladium catalyst

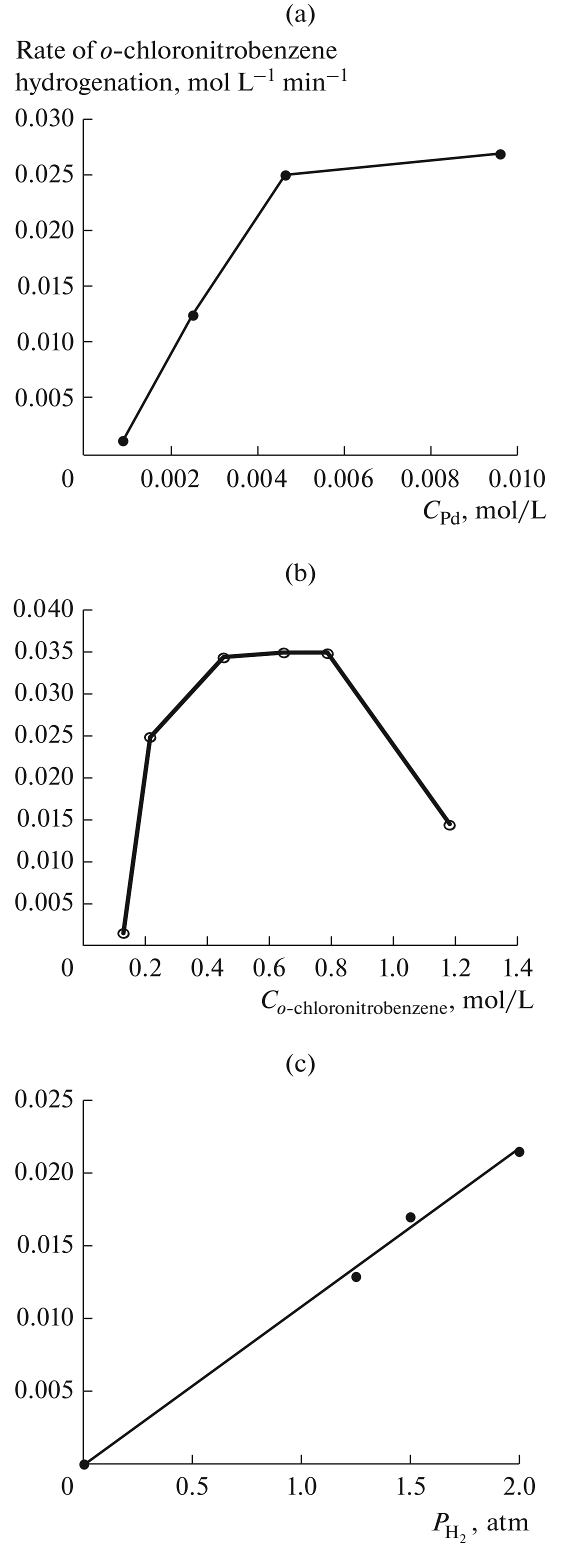

Fig. 1. Dependence of the rate of *o*-chloronitrobenzene hydrogenation in the presence of a Pd–P catalyst (P/Pd = 0.3) on the concentrations of (a) the catalyst and (b) the substrate and (c) on the pressure of hydrogen at $T = 50°C$. Reaction conditions: (a) $C_{o\text{-chloronitrobenzene}} = 0.4$ mol/L, $P_{H_2} = 2$ atm; (b) $C_{Pd} = 4.78$ mmol/L, $P_{H_2} = 2$ atm; and (c) $C_{Pd} = 4.78$ mmol/L, $C_{o\text{-chloronitrobenzene}} = 0.4$ mol/L.

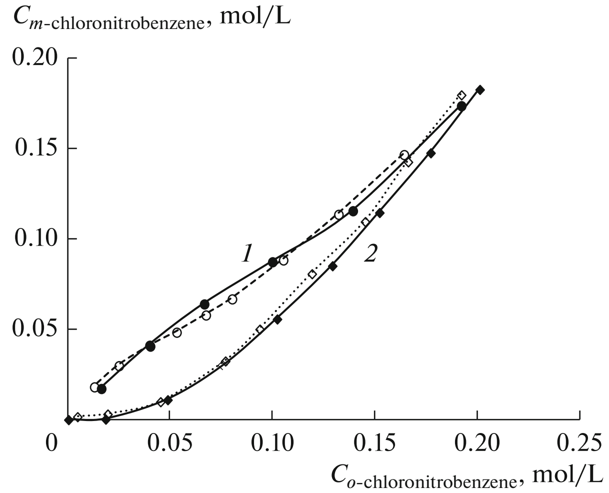

Fig. 2. Phase trajectories of the competitive hydrogenation of *o*- and *m*-chloronitrobenzenes in the presence of (*1*) Pd black and (*2*) the Pd/C catalyst: $C_{Pd} = 4.78$ mmol/L, $T = 50°C$, and $P_{H_2} = 2$ atm.

and a support. Schmidt et al. [25] related this fact to the effect of the nature of the precursor, a reducing agent, and a support on the size of the resulting palladium nanoclusters and their environment and reactivity. Because we used in situ formed nanosized (Pd–P) and supported heterogeneous palladium-containing catalysts, the question arose as to whether the noncoincidence of phase trajectories is related to the nature of active centers (palladium clusters and/or palladium phosphides) and different dispersity of catalysts or it is caused by the low reproducibility of experiments.

The coincidence of phase trajectories for parallel experiments on the competitive hydrogenation of *o*- and *m*-chloronitrobenzenes in the presence of different heterogeneous catalysts (Pd black and Pd/C) (Fig. 2) and Pd–P nanoparticles (P/Pd = 0.3) (Fig. 3) made it possible to exclude the factor of reproducibility from the consideration and to analyze phase trajectories for different palladium catalysts.

The phase trajectories of the competitive hydrogenation of *o*- and *m*-chloronitrobenzenes and the phase trajectories of the formation of the target products (*o*- and *m*-chloroanilines) do not coincide for similar catalysts (Pd black and a Pd/C catalyst), which were obtained from the same precursor ($Pd(acac)_2$) in hydrogen and were different from one another in terms of dispersity (Fig. 2). Figure 4 shows the TEM images of different palladium catalysts. The average particle sizes of Pd black, Pd/C, and Pd–P catalysts (with P/Pd = 0.3 and 1.0) were 34, 3.4, 5.6, and 5.3 nm, respectively. The dispersity of Pd black ($D_{\text{Pd black}} = 0.024$), which was calculated from the weight-average diameter of particles, was smaller by a factor of 6.6 than the dispersity of the Pd/C catalyst ($D_{\text{Pd/C}} = 0.16$).

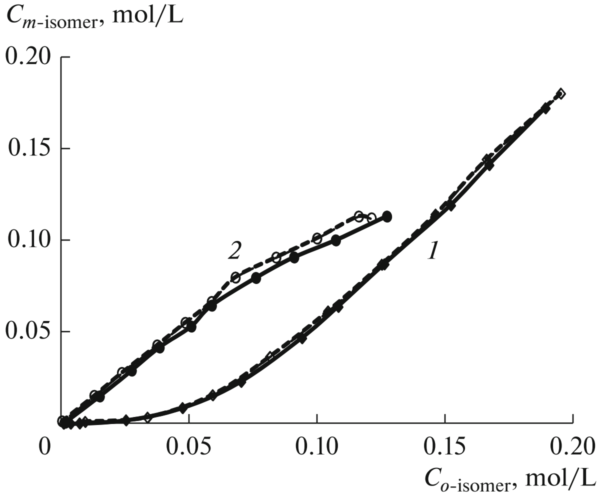

Fig. 3. Phase trajectories of (*1*) the competitive hydrogenation of *o*- and *m*-chloronitrobenzenes and (*2*) the formation of *o*- and *m*-chloroanilines in the presence of the Pd–P catalyst (P/Pd = 0.3): C_{Pd} = 4.78 mmol/L, T = 50°C, and P_{H_2} = 2 atm.

Thus, the differential selectivity of the palladium-containing catalysts in the hydrogenation of chloronitrobenzenes depends on the dispersity of the catalyst. This conclusion is consistent with available published data on the structural sensitivity of a hydrodechlorination reaction [30].

A symbatic relationship between the integral selectivity of Pd–P catalysts for *o*-chloroaniline and the P/Pd ratio was found in the studies of the modifying action of phosphorus on the properties of palladium catalysts in the hydrogenation of *o*-chloronitrobenzene [8, 9, 28]. However, integral selectivity depends not only on the nature but also on the quantity of a catalyst. Its value could be influenced by catalyst deactivation in the course of the catalytic process. The noncoincidence of phase trajectories (i.e., differential selectivities) of Pd–P (P/Pd = 0.3) and Pd–P (P/Pd = 0.7 and 1.0) catalysts (Fig. 5) in the competitive hydrogenation of *o*- and *m*-chloronitrobenzenes confirms differences between these catalysts in the nature of active centers and/or dispersity. An analysis of the phase trajectories of the competitive hydrogenation of chloronitrobenzenes in the presence of different palladium catalysts makes it possible to note the following regularity: In the competitive hydrogenation of *o*- and *m*-chloronitrobenzenes, phase trajectories almost coincided for the following pairs of catalysts: Pd–P (P/Pd = 0.7) and Pd–P (P/Pd = 1.0) on the one hand, and Pd–P (P/Pd = 0.3) and Pd/C on the other hand (Fig. 5).

The coincidence of phase trajectories for the Pd–P (P/Pd = 0.3) and Pd/C catalysts indicates with a great probability that the nature of particles active in hydrogenation is the same. In our opinion, a situation when different active centers exhibit the same selectivity is improbable. Earlier, it was shown that the introduction of phosphorus before the stage of Pd(acac)$_2$ reduction with hydrogen increases the dispersity of palladium catalyst and changes the nature of nanoparticles [6, 7]. According to XPS data [22], palladium in the Pd–P catalyst (P/Pd = 0.3) occurs in two states: palladium(0) clusters (E_b(Pd3$d_{5/2}$) = 334.5 eV) and palladium phosphides (E_b(Pd3$d_{5/2}$) = 336.2 eV and E_b(P2$p_{3/2}$) = 129.5 eV). The empirical formula of phosphide ($Pd_{9.8}P$) indicates the enrichment of the surface in palladium. The nanoclusters of palladium(0) exhibited a smaller binding energy in comparison with that of the bulk metal (E_b(Pd3$d_{5/2}$) = 335.2 eV). According to Tsirul’nikov et al. [31], this is

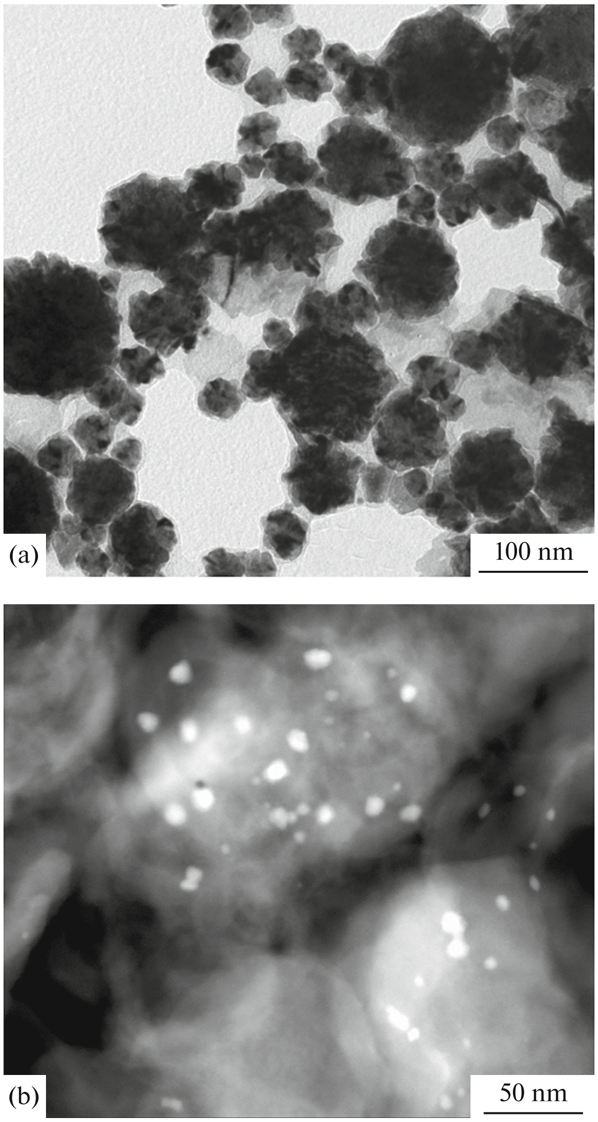

Fig. 4. (a) TEM micrograph of Pd black and (b) STEM (Z-contrast) image of the Pd/C catalyst obtained from Pd(acac)$_2$ in hydrogen in a DMF solution at 80°C and a hydrogen pressure of 2 atm.

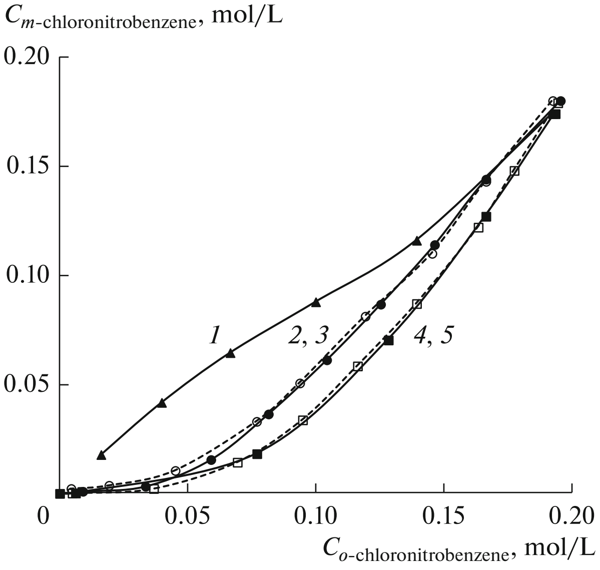

Fig. 5. Phase trajectories of the competitive hydrogenation of *o*- and *m*-chloronitrobenzenes in the presence of (*1*) Pd black, (*2*, ●) Pd/C, and Pd–P catalysts formed from $Pd(acac)_2$ at the following P/Pd ratios: (*3*, ○) 0.3, (*4*, □) 0.7, and (*5*, ◆) 1.0. Reaction conditions: C_{Pd} = 4.78 mmol/L, T = 50°C, and P_{H_2} = 2 atm.

characteristic of zerovalent palladium Pd^0 in a dispersed state, whose coordination number is lower than 12. The atomic ratio between these two forms of palladium is Pd(0) : $Pd_xP \approx 0.55 : 0.45$. The same nature of the active centers of Pd–P (P/Pd = 0.3) and Pd/C catalysts in the competitive hydrogenation of *o*- and *m*-chloronitrobenzenes is consistent with a core–shell model proposed earlier for Pd–P nanoparticles (the core consists of palladium phosphides (or of substitutional solid solutions), and the palladium(0) clusters are located on the surface). According to XRD analysis data, the size of palladium crystallites in the Pd–P catalyst was ~2 nm [6]. Thus, in the case of the Pd–P (P/Pd = 0.3) catalyst, the nanoclusters of Pd(0) with a diameter of ~2 nm, on which the activation of hydrogen and substrates occurs, are active in the hydrogenation of chloronitrobenzenes.

Another situation is characteristic of the Pd–P catalysts formed at the P/Pd ratios of 0.7 and 1.0. As noted above, phase trajectories in the competitive hydrogenation of *o*- and *m*-chloronitrobenzenes on these catalysts almost coincided with each other, but their differential selectivities were different in comparison with those of the Pd/C, Pd black, and Pd–P (P/Pd = 0.3) catalysts (Fig. 5).

It should be noted that the following changes in the Pd–P catalysts were observed as the P/Pd ratio was increased: the fraction and size of Pd(0) clusters decreased from 2 nm (P/Pd = 0.3) to ~1 nm (P/Pd = 0.7 and 1.0), and the phase composition of palladium phosphides changed [6]. The Pd_5P_2 phosphide was the prevailing species of the Pd–P catalysts (P/Pd = 0.7 and 1.0). The following two chemical forms of palladium were mainly present in the surface layer of the Pd–P catalyst (P/Pd = 0.7): small clusters of size ~1 nm ($E_b(Pd3d_{5/2})$ = 335.6 eV) and the Pd_5P_2 palladium phosphide ($E_b(Pd3d_{5/2})$ = 336.0 eV; $E_b(P2p_{3/2})$ = 130.0 eV) in a ratio of 2.17 : 1 [6]. The small clusters of palladium are electron-deficient [32]. The appearance of a positive charge in the small clusters of metals is caused by a decrease in the efficiency of hole screening by valence electrons with decreasing particle size, that is, by the effect of a final state. In the surface layer of the Pd–P catalyst (P/Pd = 1.0), two chemical forms of palladium were also predominant: small clusters ($E_b(Pd3d_{5/2})$ = 335.7 eV) and a mixture of palladium phosphides (Pd_5P_2 and PdP_2 ($E_b(Pd3d_{5/2})$ = 336.2 eV; $E_b(P2p_{3/2})$ = 129.9 eV) in a ratio of 0.4 : 0.6).

Thus, a distinction between the Pd–P catalysts (P/Pd = 0.7 and 1.0) and the Pd–P nanoparticles obtained at the ratio P/Pd = 0.3 consists in the presence of small electron-deficient palladium clusters of size ~1 nm, the formation of which was demonstrated by XPS ($E_b(Pd3d_{5/2})$ = 335.7 eV)) and STEM (Z-contrast) methods [6, 9]. A simultaneous change in two factors (the size of palladium clusters and the phase composition of palladium phosphides) does not make it possible to unambiguously formulate the reason for differences in the differential selectivity of Pd–P catalysts as the P/Pd ratio is increased from 0.3 to 0.7 and 1.0. Therefore, we carried out additional studies.

Based on the assumption that the electronic state of surface palladium atoms exerts a determining effect on their properties in catalysis, we carried out the competitive hydrogenation of *o*- and *m*-chloronitrobenzenes in the presence of three palladium catalysts, which have similar characteristics of the states of surface layers according to XPS data [6, 9]. They included the Pd–P catalysts obtained from $Pd(acac)_2$ and white phosphorus in hydrogen at the ratios P/Pd = 0.7 and 1.0 and the Pd–P catalyst obtained from $PdCl_2$ at P/Pd = 0.3. The presence of the small clusters of palladium on the surface is a common feature of these three catalysts. The basic difference consists in the composition of phosphides. The following three chemical forms of palladium were present on the surface of a Pd–P catalyst sample formed from $PdCl_2$ and white phosphorus in hydrogen (P/Pd = 0.3) [9]: the small clusters of palladium ($E_b(Pd3d_{5/2})$ = 335.7 eV), palladium phosphide ($E_b(Pd3d_{5/2})$ = 336.2 eV; $E_b(P2p_{3/2})$ = 129.9 eV), and Pd–Cl surface fragments $E_b(Pd3d_{5/2})$ = 337.2 eV; $E_b(Cl2p_{3/2})$ = 198.2 eV). The phase composition of the phosphides of the Pd–P catalyst (precursor, $PdCl_2$; P/Pd = 0.3) included the $Pd_{4.8}P$ and Pd_6P phosphides, whereas the empirical formula of the surface palladium phosphide corresponded to $Pd_{1.2}P$.

Figure 6 shows the phase trajectories of the competitive hydrogenation of *o*- and *m*-chloronitrobenzenes. The coincident differential selectivity of the three Pd–P catalysts in the competitive hydrogenation of chloronitrobenzenes is indicative of the same nature of the active centers that participate in the hydrogenation and the similar dispersity of the catalysts. Because the small clusters of palladium were present in these three catalysts, but they were different from each other in terms of the composition of phosphides, we can confidently hypothesize that the small clusters of palladium are the carriers of catalytic activity in the Pd–P catalysts (P/Pd = 0.7 and 1.0) under mild conditions.

Thus, the application of a kinetic approach based on the analysis of differential selectivity made it possible to unambiguously relate the activity of Pd–P catalysts in the hydrogenation of chloronitrobenzenes to Pd(0) clusters present in these catalysts. This conclusion is valid for operations under mild conditions. Of course, in the presence of chemically different active centers, the reaction occurs predominantly on those characterized by the smallest activation energy. The phosphides of *d* metals are usually less active in hydrogenation catalysis than metallic catalysts, but they are more resistant to deactivation [12]. For example, the Pd–P catalyst (P/Pd = 0.3) containing Pd(0) clusters and palladium phosphides (activity, 170 min^{-1}; T = 30°C; P_{H_2} = 2 atm; and d = 5.6 nm) was superior to the phase-pure (according to published data [21]) palladium phosphide $Pd_3P_{0.95}$ (activity, 16 min^{-1}; T = 25°C; P_{H_2} = 1 atm; and d = 4–4.8 nm) [21] and the nickel phosphide Ni_2P (activity, 0.16 min^{-1}; T = 85°C; P_{H_2} = 6 bar; and d = 25 nm) [33] in terms of activity in the hydrogenation of phenylacetylene. Therefore, the problem of the activity of phase-pure palladium phosphides in the hydrogenation of unsaturated compounds under mild conditions calls for further investigation. In our opinion, changes in the electronic state of a metal are primarily responsible for the lower activity of transition metal phosphides, as compared with that of metallic catalysts (with the same dispersity). On the one hand, electron transition from palladium to phosphorus and a high degree of electron deficiency in the Pd of palladium phosphides decreases reactivity toward the activation of molecular hydrogen and suppresses the formation of palladium hydride [33, 34]. The behavior of phosphorus in the phosphides resembles the action of carbide phases, which limit the formation of palladium hydrides [33]. On the other hand, the electron density deficiency in Pd changes sorption affinity for nucleophilic and electrophilic substrate molecules [35]. In contrast to the phase-pure *d*-metal phosphides, the presence of Pd(0) clusters in the Pd–P catalysts imparts high activity in the hydrogenation of different unsaturated compounds under mild conditions to these catalysts.

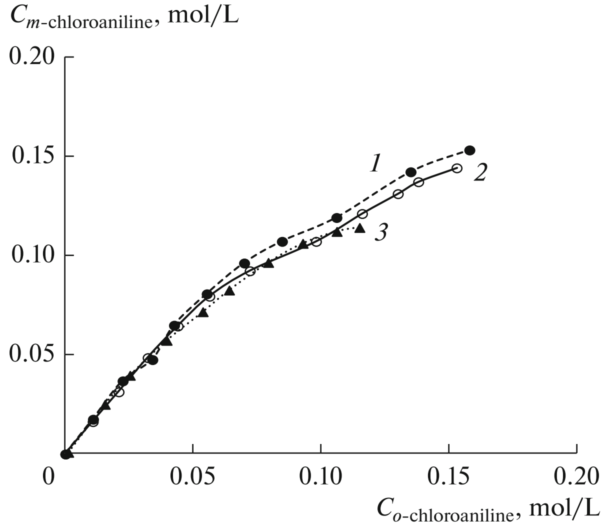

Fig. 6. Phase trajectories of the formation of *o*- and *m*-chloroanilines resulting from the competitive hydrogenation of *o*- and *m*-chloronitrobenzenes in the presence of Pd–P nanoparticles obtained from $Pd(acac)_2$ at the following P/Pd ratios: (*1*, ●) 1.0, (*2*, ○) 0.7, and (*3*, ▲, $PdCl_2$ precursor) 0.3. Reaction conditions: C_{Pd} = 4.78 mmol/L, T = 50°C, and P_{H_2} = 2 atm.

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