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Synthesis, Properties, and Activity of Nanosized Palladium Catalysts Modified with Elemental Phosphorus for Hydrogenation

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Abstract—The applicability of elemental phosphorus as a modifier of palladium catalysts for hydrogenation was demonstrated, and the conditions for the synthesis of nanoparticles that are highly efficient in hydrogenation catalysis were optimized. The modifying effect of elemental phosphorus depends on the P/Pd ratio; it is associated with changes in the catalyst dispersity and the nature of the formed nanoparticles containing various palladium phosphides (PdP_2, Pd_5P_2, and Pd_6P) and Pd(0) clusters. The main stages of the formation of palladium catalysts for hydrogenation were determined, and a model of an active catalyst, in which the Pd_6P phosphide is the core of a nanoparticle and Pd(0) clusters form a shell, was proposed.

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INTRODUCTION

White phosphorus is the most reactive species of elemental phosphorus; it is a starting material for the synthesis of various organophosphorus compounds [1, 2]. Many studies devoted to the coordination chemistry of white phosphorus have been reported in the last few years [3–8]; the molecule of white phosphorus can serve as a η^1 or η^2 ligand [7]. The activation of the white phosphorus molecule in the coordination sphere of a transition metal can result in P–P bond cleavage followed by the recombination of small fragments into dinuclear complexes and polyatomic aggregates [3–6] or in hydrolytic oxidation in the presence of water [5, 8].

Interest in the use of elemental phosphorus as a promoter for palladium catalysts for hydrogenation is based on currently available data on the nature of nanosized catalysts. The formation of particles catalytically active in hydrogenation reactions based on palladium complexes with organic phosphines [9–11] or phosphine (PH_3) [12] in an atmosphere of hydrogen resulted in the formation of microheterogeneous systems because of the step-by-step degradation of phosphorus-containing ligands. Depending on the nature of phosphine and the P/Pd ratio, the resulting nanosized particles can consist of polynuclear palladium complexes with phosphide and phosphinidene ligands or palladium phosphides on which Pd(0) clusters are immobilized. We were the first to demonstrate [13] that not only organic phosphines or PH_3 but also elemental phosphorus can be used for the synthesis of highly efficient hydrogenation catalysts.

In this work, we report the results of a study of the formation, nature, and properties of palladium catalysts for hydrogenation modified with elemental phosphorus.

EXPERIMENTAL

Reagents

The solvents (benzene and *N*,*N*-dimethylformamide (DMF)) were purified by standard procedures used in operations with organometallic compounds [14]. For drying and removing amine impurities, DMF was 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. For deeply drying, benzene was additionally distilled from $LiAlH_4$ on a rectification column and kept in an atmosphere of argon in sealed ampoules over molecular sieve 4A. The concentrations of water in benzene and DMF were 1.1×10^{-3} and 0.8 mol/l, respectively, as measured by the Fischer method [15].

Bis(acetylacetonato)palladium was prepared in accordance with a published procedure [16]. Its ^{1}H NMR spectrum in benzene contained signals with the chemical shifts $\delta(CH) = 5.04$ ppm (s, 1H) and $\delta(CH_3) = 1.76$ ppm (s, 6H).

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).

Reaction between Bis(acetylacetonato)palladium and White Phosphorus

The reaction was performed in an inert atmosphere at various ratios between the initial components in a finger-type vessel.

For example, to obtain the ratio P/Pd = 3 (the ratios between the reagents are given in terms of the atomic form of phosphorus), 10 ml of a solution of white phosphorus (4.5 mmol) in benzene was added dropwise to a solution of 0.4566 g (1.5 mmol) of $Pd(acac)_2$ in 50 ml of DMF, and the contents were stirred at room temperature for 24 h. After 2–3 min upon the onset of reaction, the color of the solution changed from yellow to dark brown. Filtrate samples were analyzed at regular intervals using spectroscopic methods (NMR and UV spectroscopy). After completion of reaction, the solution was concentrated in a vacuum to 1/5 volume (40°C/1 Torr), and 10 ml of benzene was added. The resulting dark brown precipitate was filtered off, washed with benzene, and dried in a vacuum (30°C/1 Torr). The yield was 0.17 g. The sample was X-ray amorphous. The size of the coherent-scattering region was 1.4 nm, as calculated from the Selyakov–Scherrer formula. A diffuse halo appeared in the reflection angle range $2\theta = 35°–45°$, where the *hkl* (111) reflections of both crystalline palladium and palladium phosphides were observed. To convert it into a metal state, the sample was thermostated at 400°C in an inert atmosphere for 4 h. XRD data (*d*/*n*): 2.926, 2.884, 2.733, 2.491, 2.050, 1.993, 1.681, 1.466, 1.361 Å (PdP_2) [17]; 3.351, 2.733, 2.525, 2.491, 2.458, 2.289, 2.251, 2.123, 2.091, 2.050, 1.989, 1.930, 1.845, 1.720, 1.681, 1.488, 1.466, 1.434, 1.375, 1.361, 1.341 Å (Pd_5P_2) [18].

The experiments at other ratios between the reagents were performed in an analogous manner.

Synthesis of a Catalyst Based on $Pd(acac)_2$ and Elemental Phosphorus in a Hydrogen Atmosphere

The catalyst was prepared in a thermostated long-necked flask in an atmosphere of hydrogen at 80°C. A 2-ml portion of a solution of phosphorus (5.1×10^{-4} mol) in benzene was added dropwise to a solution of 0.51748 g (1.7×10^{-3} mol) of $Pd(acac)_2$ in 60 ml of DMF (P/Pd = 0.3). The reaction mixture was stirred at a hydrogen pressure of 1 atm and a temperature of 25°C for 5 min. After 1 min upon the addition of a white phosphorus solution, the color changed from yellow to dark brown. Then, the reaction mixture temperature was increased to 80°C, and stirring was continued for 15 min at an excess hydrogen pressure of 1 atm. According to UV-spectroscopic data, $Pd(acac)_2$ was completely converted in this time.

After completion of the reaction, the blackish brown solution was cooled to room temperature and transferred to a finger-type vessel in an inert atmosphere. Then, the solvent was distilled in a vacuum (2/3 volume), and benzene was added until the formation of a precipitate. The precipitate was washed three times with 10-ml portions of benzene in an atmosphere of argon and dried in a vacuum (50°C/1 Torr). The yield was 0.19 g. Elemental analysis data, %: Pd, 87.88; P, 3.59; C, 0.99; H, 0.25. In the region of 4000–400 cm^{-1}, absorption bands were absent from the IR spectrum. The sample was X-ray amorphous. A diffuse halo appeared in the reflection angle range $2\theta = 35°–45°$; the size of the coherent-scattering region was 3.13 nm. To convert the sample into a crystalline state, it was thermostated in an inert atmosphere at 400°C for 4 h. XRD data (*d*/*n*): 2.993, 2.570, 2.362, 2.259, 2.225, 2.210, 2.037, 1.926, 1.868, 1.852, 1.784, 1.573, 1.456, 1.419, 1.342, 1.284, 1.244 Å (Pd_6P) [18].

The catalyst with the ratio P/Pd = 1.2 was prepared in an analogous manner. The yield was 0.21 g. The sample was X-ray amorphous. A diffuse halo appeared in the reflection angle range $2\theta = 35°–45°$; the size of the coherent-scattering region was 1.96 nm. XRD data (*d*/*n*): 3.351, 2.733, 2.525, 2.491, 2.458, 2.289, 2.251, 2.123, 2.091, 2.050, 1.989, 1.930, 1.845, 1.720, 1.681, 1.488, 1.466, 1.434, 1.375, 1.361, 1.341 Å (Pd_5P_2) [18]; 2.926, 2.884, 2.491, 2.050, 1.993, 1.681, 1.466, 1.361 (PdP_2) [17]. The Pd_5P_2 palladium phosphide was predominant; the PdP_2 phosphide was present in small amounts.

Catalytic Hydrogenation

The reaction was performed in a thermostated glass long-necked flask at 30°C and an initial hydrogen pressure of 1 atm in the presence of an in situ formed catalytic system. A 1-ml portion of a solution of phosphorus in benzene (0.3×10^{-5} mol) was added dropwise to a solution of 0.00304 g (1×10^{-5} mol) of $Pd(acac)_2$ in 9 ml of DMF in the thermostated 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. Additional experiments showed that the optimum time of the formation of the $Pd(acac)_2$–*n*P catalytic system at 80°C was 25–30 min [13]. The resulting blackish brown "solution" was cooled to 30°C, and a substrate was injected into it with a syringe. Hydrogenation was performed under conditions of intense stirring to exclude the occurrence of reaction in the diffusion region. The course of the reaction was monitored using volumetry and GLC analysis.

In the experiments on catalyst poisoning with mercury, 0.03 ml of mercury (Hg/Pd = 200) was introduced into the reaction mixture with a syringe 2 min after the onset of the catalytic hydrogenation of styrene.

Spectroscopic and Electron Microscopic Studies

The UV spectra were measured on a Specord UV VIS spectrometer in a quartz cell. The concentrations of bis(acetylacetonato)palladium and acetylacetone were calculated from absorption at 330 nm (ε_{330} = 10630 l mol^{-1} cm^{-1}) and 290 nm (ε_{290} = 5000 l mol^{-1} cm^{-1} for Hacac or ε_{290} = 3090 l mol^{-1} cm^{-1} for $Pd(acac)_2$), respectively.

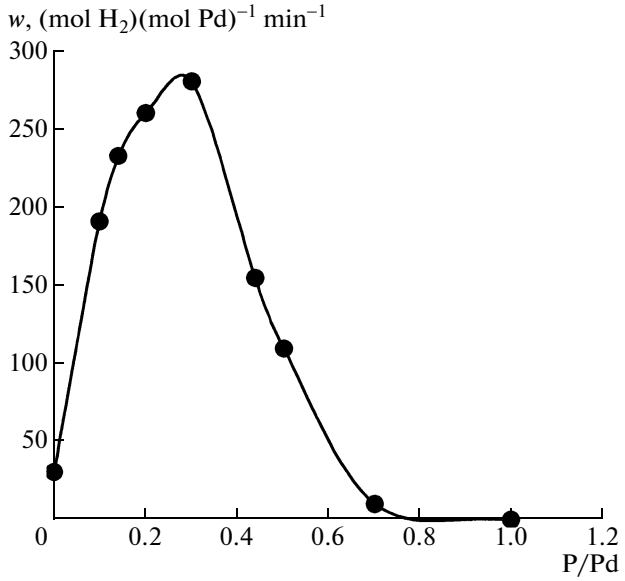


Fig. 1. Dependence of the activity of the $Pd(acac)_2$–P catalytic system in the reaction of styrene hydrogenation on the ratio between reagents. Pd content, 1 mmol/l; [substrate]/[Pd] = 870; solvent, DMF; $T = 30°C$; and P_{H_2} = 1 atm.

The ^1H and ^{31}P NMR spectra were obtained on a VXR-500S Varian pulse spectrometer. The chemical shifts of ^{31}P were measured with reference to 85% phosphoric acid. Positive values correspond to a downfield shift. In the analysis of the samples by NMR spectroscopy, the solution was sealed in a preevacuated insert ampoule filled with argon.

The XRD analysis of the catalyst samples was performed on a DRON-3M diffractometer (CuK_α radiation).

The samples were studied by transmission electron microscopy (TEM) on a Philips EM-410 microscope. A drop of an in situ formed catalyst solution was supported onto a support grid coated with a carbon film and dried in an atmosphere of argon. The analytical conditions excluded the melting and degradation of the test samples under the action of an electron beam.

The procedure for the determination of Pd(0) was described elsewhere [19].

RESULTS AND DISCUSSION

Catalytic Properties of Palladium Catalysts for Hydrogenation Modified with Elemental Phosphorus

The modifying effect of elemental phosphorus on the properties of hydrogenation catalysts based on $Pd(acac)_2$ formed in a hydrogen atmosphere at 80°C depends on the P/Pd ratio (Fig. 1).

The addition of small amounts of elemental phosphorus to bis(acetylacetonato)palladium (P/Pd = 0.3 in terms of phosphorus atoms) before the stage of the reduction of the latter with hydrogen dramatically (by a factor of >9) increased the catalyst activity in the reaction of styrene hydrogenation (Fig. 1). The promoting effect of elemental phosphorus on the palladium catalyst with the ratio P/Pd = 0.3 also manifested itself in the hydrogenation of other substrates: phenylacetylene, benzaldehyde, and nitrobenzene (Table 1). At the same time, at the ratios P/Pd > 0.75, the almost complete suppression of hydrogenation catalytic activity was observed (see Fig. 1).

A comparison between the modifying effects of elemental phosphorus and previously studied modifiers—phenylphosphine [11] and phosphine (PH_3) [12]—on the properties of palladium catalysts for hydrogenation allowed us to reveal the following regularities: the strongest promoting effect of phosphines

Table 1. Comparison between the catalytic properties of the $Pd(acac)_2$–0.3P system and Pd black in the hydrogenation reactions of various substrates

Substrate	Substrate content, mmol	Catalyst activity w, (mol H_2) (mol Pd)$^{-1}$ min^{-1}		Pd black		$Pd(acac)_2$–0.3P	
		Pd black*	$Pd(acac)_2$–0.3P	product	yield, %	product	yield, %
Styrene	8.7	30	280	Ethylbenzene	100	Ethylbenzene	100
Phenylacetylene	9.1	68	157	Ethylbenzene	100	Ethylbenzene	100
Nitrobenzene	4.9	–	64	–	–	Aniline	71
	2.4	36**	128	Aniline	40		100
Benzaldehyde	9.9	1	15	Benzyl alcohol	16	Benzyl alcohol	95
				Toluene	2	Toluene	5

Note: Concentration of Pd, 1 mmol/l; solvent, DMF; DMF volume, 10 ml; temperature, 30°C; and H_2 pressure, 1 atm.
* Prepared under analogous conditions by the reduction of $Pd(acac)_2$ with hydrogen.
** The concentration of Pd was 5 mmol/l.

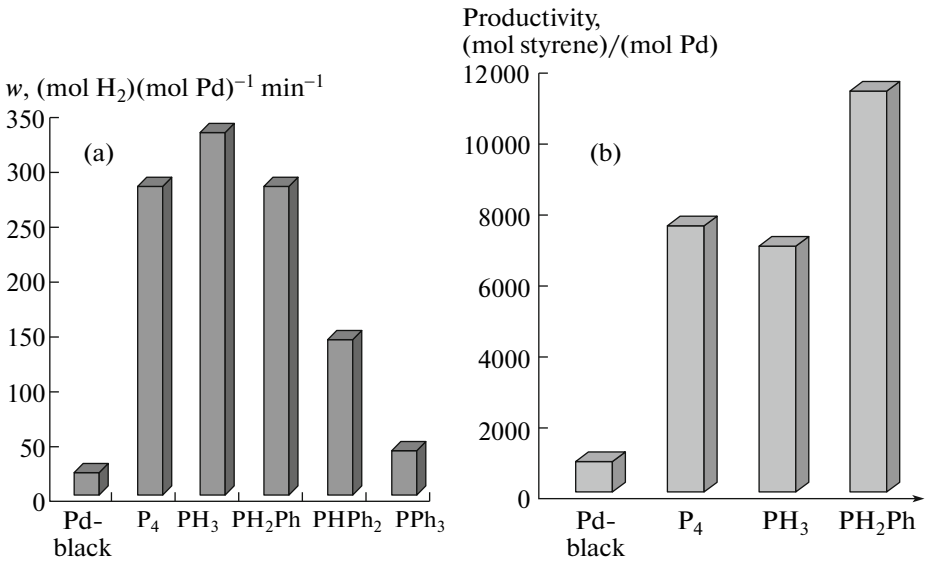


Fig. 2. Effect of the nature of the phosphorus-containing modifier on the (a) activity and (b) productivity of palladium catalysts in the reaction of styrene hydrogenation.

and phosphorus was reached at the same ratio P/Pd = 0.3. The test catalytic systems were close to each other in activity and selectivity (Fig. 2). The use of elemental phosphorus as a modifier simplified the formation of a highly active catalyst because the synthesis of phosphine ligands became not necessary. Triphenylphosphines and diphenylphosphines exhibited a much smaller promoting effect that of elemental phosphorus.

Palladium catalysts modified with elemental phosphorus and formed in an atmosphere of molecular hydrogen are much better in terms of activity than palladium nanoparticles prepared under the action of other stronger reducing agents: $AlEt_3$ [20], NaH_2PO_2 [21], and $LiAlH_4$ [22]. Thus, it is reasonable to study the nature of the catalytic test systems not only theoretically but also practically.

The Nature of Palladium Catalysts Modified with Elemental Phosphorus

The reduction of Pd(acac) with hydrogen in a DMF solution is an autocatalytic reaction, which occurs at a sufficiently high rate at 80°C. Modification with elemental phosphorus increased the induction period from 5 to 15–20 min (Fig. 3). This suggests that palladium atoms formed as a result of hydrogenolysis do not aggregate into Pd_x clusters, which are capable of activating molecular hydrogen, but react with white phosphorus or its conversion products.

It is well known that white phosphorus, which is a highly reactive elemental phosphorus species, readily reacts with transition metal compounds in both low and high oxidation states [2–8]. The interaction of white phosphorus with transition metal complexes in the lowest oxidation states results in the formation of new complexes, whereas redox processes accompanied by the release of metals [2] and metal phosphides [23] can occur on the interaction of P_4 with transition metal compounds in high oxidation states.

Analysis performed using ^{1}H NMR, ^{31}P NMR, and UV spectroscopy suggests that $Pd(acac)_2$ readily reacts with white phosphorus in an inert atmosphere at room temperature in a DMF solution to form acetylacetone. This is evident from the ^{1}H NMR spectra, which exhibited the following chemical shifts δ, ppm: enol form, 15.87 (s, 1H, OH), 5.74 (s, 1H, CH), 2.10 (s, 6H, CH_3); keto form, 3.82 (s, 1H, CH_2), 2.26 (s, 3H,

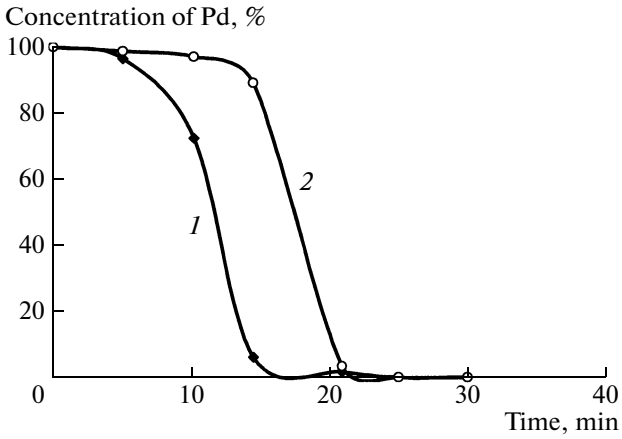


Fig. 3. Kinetic curves of the conversion of (*1*) $Pd(acac)_2$ and (*2*) the $Pd(acac)_2$–0.3P catalytic system in an atmosphere of hydrogen. Pd content, 1 mmol/l; solvent, DMF; $V_{DMF} = 10$ ml; $T = 80$°C; and $P_{H_2} = 1$ atm.

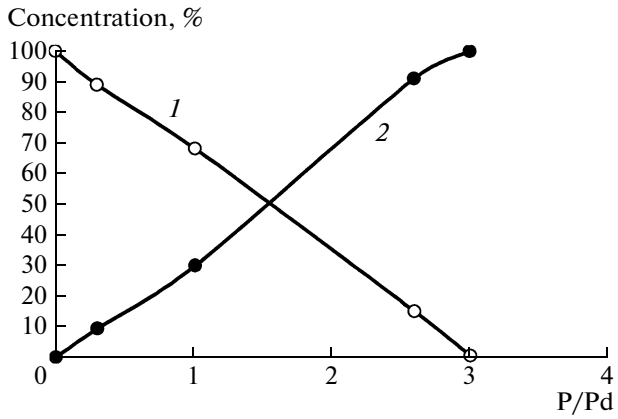


Fig. 4. Dependence of the concentrations of (*1*) $Pd(acac)_2$ and (*2*) acetylacetone on the ratio [P]/[$Pd(acac)_2$] in DMF (the initial concentration of $Pd(acac)_2$ was 5 mmol/l).

CH_3). Phosphorous acid (H_3PO_3) (^{31}P NMR: δ = 4.42 ppm, J_{P-H} = 531 Hz) and phosphoric acid (^{31}P NMR: δ = 3.35 ppm) were also formed. Special experiments with the use of D_2O showed that water occurring in solution served as a source of protons in the formation of acetylacetone; the concentration of water in DMF was as high as 0.8 mol/l.

The quantitative analysis of ^1H NMR and UV spectra suggests that the complete conversion of $Pd(acac)_2$ was reached at a threefold excess of white phosphorus (Fig. 4). At P/Pd < 3, unreacted $Pd(acac)_2$ remained in the reaction mixture.

The dark brown precipitate separated from the $Pd(acac)_2$–P reaction system (P/Pd = 3) consisted of the palladium phosphides PdP_2 and Pd_5P_2, and the former species was predominant. The ratio between PdP_2, Pd_5P_2, and unreacted $Pd(acac)_2$ increased as the concentration of white phosphorus was increased.

The set of the above data suggests that the reaction of $Pd(acac)_2$ with elemental phosphorus in an inert atmosphere is the redox process that can be described by the following reaction scheme:

$$3Pd(acac)_2 + 2P + 6H_2O = 3Pd(0) + 6Hacac + 2H_3PO_3.$$

The subsequent interaction of Pd(0) atoms with elemental phosphorus leads to the formation of the palladium phosphides PdP_2 and Pd_5P_2:

$$2Pd + P_4 = 2PdP_2;$$
$$PdP_2 + 4Pd = Pd_5P_2.$$

The reaction scheme proposed for the formation of palladium phosphides in an inert atmosphere is consistent with data published by Henkes et al. [24], who experimentally found that the synthesis of transition metal nanophosphides from $M(acac)_n$ and $P(C_8H_{17})_3$ at 300–360°C occurs through the step of the formation of metal nanoparticles.

The subsequent treatment of the $Pd(acac)_2$–nP catalytic system (P/Pd = 0.3–1) with hydrogen at 80°C resulted in the quantitative conversion of $Pd(acac)_2$ to form acetylacetone. According to TEM data, a disperse system was formed as a result of the hydrogenolysis of bis(acetylacetonato)palladium in the presence of elemental phosphorus, and the particle size of this system depended on the ratio P/Pd. At P/Pd = 0.3, highly contrast particles 5.2 nm in diameter were predominant in the system; at P/Pd = 1.0, a more highly dispersed system was formed (Figs. 5, 6). In both cases, the detected nanoparticles had a much smaller size than that of Pd black (d = 25–30 nm), which was formed under analogous conditions in the absence of elemental phosphorus [11]. The ratio P/Pd had no effect on the supramolecular structure: nanoparticles underwent aggregation to produce a loose branched structure characteristic of fractal clusters [25]. The formation of these clusters was related to the self-organization (aggregation) of nanoparticles with close sizes in the absence of stabilizing factors when the diffusion of nanoparticles was a rate-limiting step.

The nature of the nanoparticles formed depended on the ratio P/Pd. The black precipitate (sample I) separated from the $Pd(acac)_2$–0.3P–H_2 reaction system can be described by the empirical formula $Pd_{9.1}P_1C_{2.2}H_{6.7}$. The fraction of Pd(0) in the sample found by chemical analysis was ~27%. Diffraction maximums due to only the Pd_6P phosphide were detected in a study of sample I by XRD analysis. In our opinion, the apparent inconsistence between the results of elemental, chemical, and XRD analyses was due to the fact that Pd(0), which was present in sample I along with the palladium phosphide Pd_6P, occurred in a highly dispersed amorphous state. Knowing the total palladium and phosphorus concentrations, the fraction of palladium in a reduced state, and the composition of the palladium phosphide, we can express the averaged composition of sample I by the formula $\{Pd_6P\}_{1.0}\{Pd(0)\}_{3.1}$. It is most likely that carbon and hydrogen occurred in the sample resulted from the solvent in which the synthesis was performed, that is, DMF. Then, the composition of sample I can be better described by the empirical formula $\{Pd_6P\}_{1.0}\{Pd(0)\}_{3.1}\{DMF\}_{0.6}$. The following fact should be noted: PdP_2 and Pd_5P_2 were formed as a result of a redox process before treatment with hydrogen with the predominance of PdP_2, whereas the composition of palladium phosphides changed after the interaction of the components of the $Pd(acac)_2$–0.3P reaction system with hydrogen. Consequently, palladium atoms, which resulted from the hydrogenolysis of $Pd(acac)_2$, reacted with the PdP_2 and Pd_5P_2 phosphides present in solution to form the Pd_6P phosphide enriched in palladium:

$$Pd(acac)_2 + H_2 = Pd(0) + 2Hacac;$$
$$Pd_5P_2 + 7Pd = 2Pd_6P;$$
$$PdP_2 + 11Pd = 2Pd_6P.$$

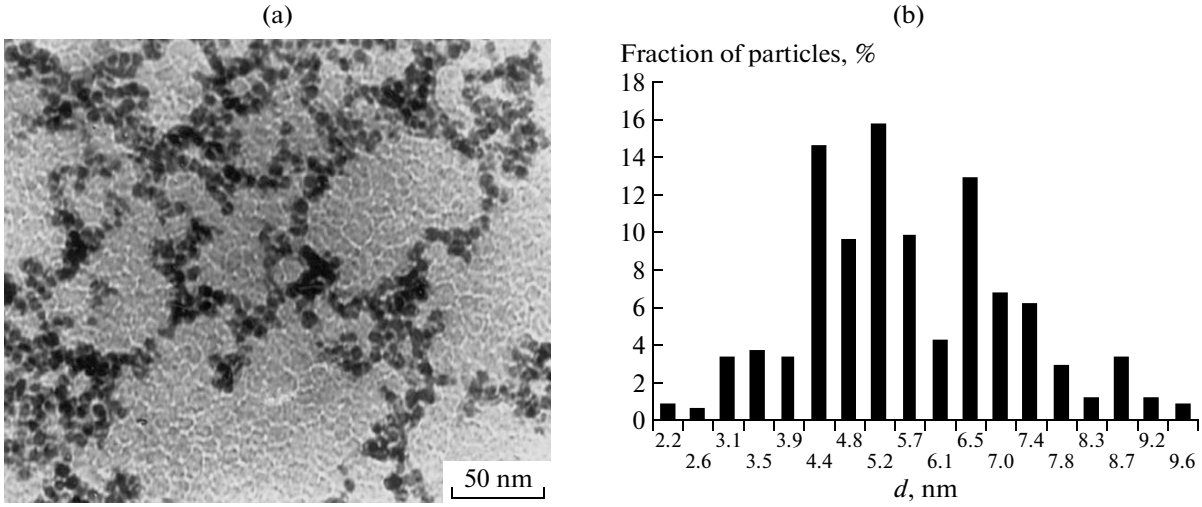


Fig. 5. (a) TEM image and (b) bar diagram of the $Pd(acac)_2$–0.3P–H_2 catalytic system.

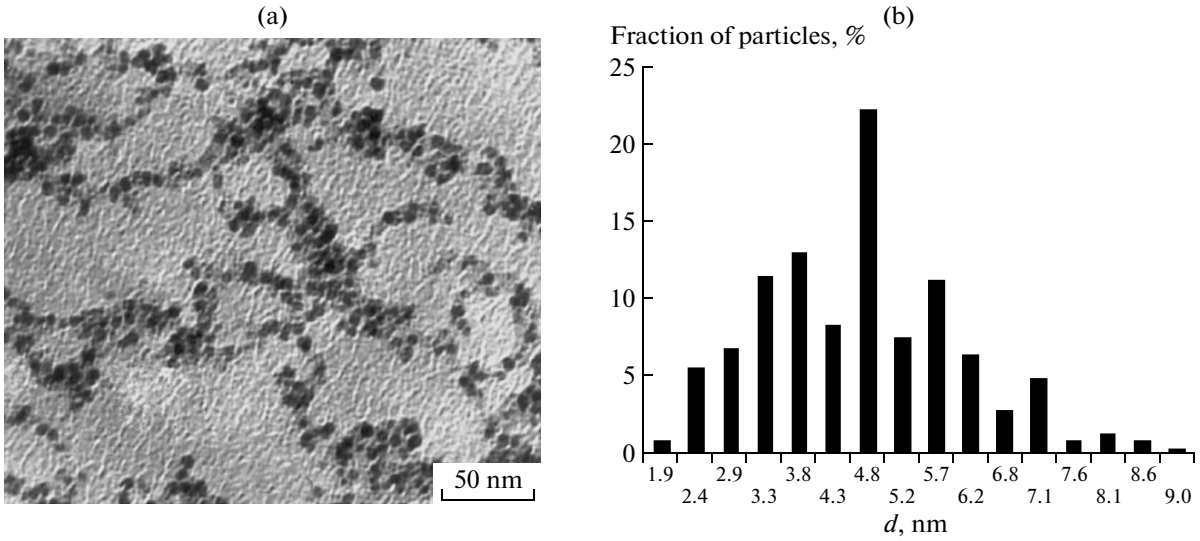
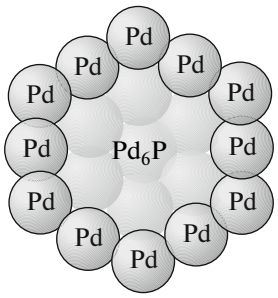


Fig. 6. (a) TEM image and (b) bar diagram of the $Pd(acac)_2$–1.0P–H_2 catalytic system.

This resulted in an experimentally observed increase in the induction period of $Pd(acac)_2$ reduction with hydrogen in the presence of elemental phosphorus. After the quantitative conversion of the Pd_5P_2 and Pd_2P phosphides into Pd_6P, palladium(0) atoms, which were formed from $Pd(acac)_2$ once again, formed Pd(0) clusters as a result of aggregation: $mPd \rightarrow Pd_m$.

Because insoluble palladium phosphide particles were present in the reaction system, the heterogeneous nucleation of palladium clusters should be considered the most likely mechanism in which nucleus–shell nanoparticles are formed, where the nucleus consists of the Pd_6P palladium phosphide and the shell consists of Pd(0):



The occurrence of particular species in the reaction system does not mean that these species are responsi-

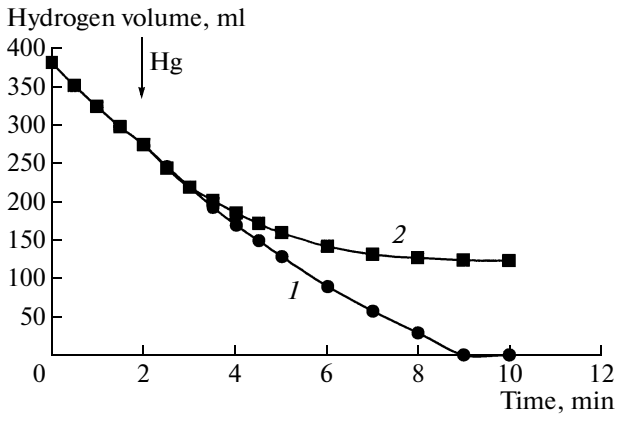


Fig. 7. Kinetic curves of styrene hydrogenation in the presence of the $Pd(acac)_2$–0.3P catalytic system: (*1*) with no mercury additive and (*2*) with a mercury additive. Pd content, 1 mmol/l; [substrate]/[Pd] = 1740; solvent, DMF; $T = 30°C$; and $P_{H_2} = 1$ atm.

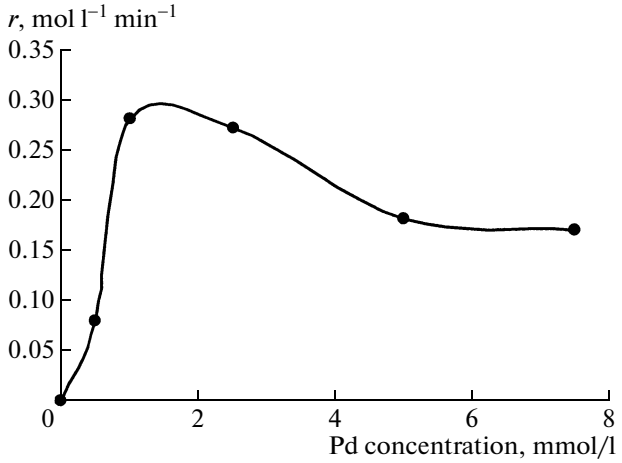


Fig. 8. Dependence of the rate of styrene hydrogenation (r) in the presence of the $Pd(acac)_2$–0.3P catalytic system on palladium concentration. Substrate content, 8.7 mmol; solvent, DMF; $T = 30°C$; and $P_{H_2} = 1$ atm.

ble for catalytic activity. Widegren and Finke [26] proposed seven tests for recognizing homogeneous and nanosized catalysis: the detection of the presence or absence of an induction period, the filtration and subsequent testing of the reaction solution, the evaluation of the addition of poisons that affect homogeneous or heterogeneous catalysts, the TEM identification of nanoparticles, etc.

The occurrence of an induction period in our experiments only suggests that the initial complex was a precursor of catalytically active species, but these species were not necessarily nanoparticles. Additional experiments were performed to discriminate hypotheses on the nature of the catalyst formed in the $Pd(acac)_2$–0.3P system. It is universally recognized that mercury is a poison for heterogeneous catalysts [27]. The introduction of an excess of mercury into the $Pd(acac)_2$–0.3P reaction system suppressed the catalytic activity (Fig. 7). However, it is our opinion that only this single test cannot be unambiguous evidence for the microheterogeneous nature of the catalyst because cases are known in which mercury also inhibited homogeneous catalytic processes [28]. At the same time, the nonlinear dependence of the reaction rate r on palladium concentration and a decrease in r at Pd(acac) concentrations higher than 3 mmol/l (Fig. 8) are consistent (together with the above facts) with the microheterogeneous nature of the catalyst.

Thus, the above results suggest that the palladium catalyst promoted with elemental phosphorus consisted of nanoparticles containing the palladium phosphide Pd_6P and Pd(0) clusters (see the above model). The formation of particles that were more highly dispersed than palladium black particles and the accessibility of Pd(0) clusters to the coordination and activation of substrates is a reason for the promoting action of elemental phosphorus.

The formation of nanoparticles also occurred at the ratio P/Pd = 1 (see Fig. 6); however, the $Pd(acac)_2$–1.0P–H_2 system did not exhibit catalytic activity in hydrogenation reactions. We experimentally found that an increase in the concentration of elemental phosphorus affected the composition of nanoparticles (Table 2). According to XRD data, the black precipitate separated from the reaction system (sample II) consisted of the Pd_5P_2 and PdP_2 palladium phosphides; however, unlike the sample prepared by the interaction of components in an inert atmosphere, the Pd_5P_2 phosphide was predominant in it. The fraction

Table 2. Characteristics of the products of $Pd(acac)_2$ conversion in the presence of elemental phosphorus in an atmosphere of hydrogen at 80°C

Sample	P/Pd	XRD data		Pd(0) fraction, %
		initial sample	sample after calcination	
I	0.3	X-ray amorphous (coherent-scattering region, 3.13 nm)	Pd_6P	27
II	1	X-ray amorphous (coherent-scattering region, 1.96 nm)	Pd_5P_2, PdP_2	8

of Pd(0), which was measured using a chemical method, was no higher than 8%; that is, in this case, Pd(0) atoms formed upon the hydrogenolysis of $Pd(acac)_2$, initially reacted with the PdP_2 phosphide present in the reaction system to form the Pd_5P_2 phosphide enriched in palladium. The PdP_2 content of this catalytic system was higher than that at the ratio $P/Pd = 0.3$; therefore, the major portion of Pd(0) atoms was consumed in the formation of palladium phosphides. Because of this, the fraction of Pd(0) also decreased. Since the hydrogenation of alkenes does not belong to structurally sensitive reactions [29], the detected small decrease in the catalyst particle size with increasing P/Pd ratio would only increase the rate of hydrogenation because of an increase in the fraction of surface atoms. However, an opposite effect was really observed. Consequently, the main reason for the inhibiting effect of phosphorus at $P/Pd > 0.75$ was a change in the catalyst composition and a decrease in the fraction of Pd(0) as a result of its conversion into palladium phosphides.

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