Nanosized Hydrogenation Catalyst Based on Palladium Bisacetylacetonate and Phosphine: Formation, the Origin of Activity, and Properties

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Abstract—The nature and catalytic properties of a hydrogenation catalyst based on $Pd(acac)_2$ and PH_3 are considered. As demonstrated by a variety of physicochemical methods (IR and UV spectroscopy, ^{31}P and ^1H NMR, electron microscopy, and X-ray powder diffraction), nanoparticles consisting of various palladium phosphides (Pd_6P, $Pd_{4.8}P$, and Pd_5P_2) and $Pd(0)$ clusters form under the action of dihydrogen during catalyst preparation. The promoting effect of phosphine at low $PH_3 : Pd(acac)_2$ ratios is mainly due to the ability of phosphine to increase the extent of dispersion of the catalyst.

In recent years, researchers have expressed steady interest in the synthesis and characterization of nanosized particles, in particular, metal nanoparticles, whose application areas include catalysis [1–4]. In the absence of a stabilizer, metal nanoclusters are typical liophobic colloids with a low aggregation resistance. For this reason, nanosized particles of metals are usually synthesized in the presence of stabilizing ligands, among which are low-molecular-weight compounds (*ortho*-phenanthroline (phen) [5, 6], quarternary ammonium salts [7], and phosphines [4, 8, 9]), polyoxometallate ions (Mo(IV), W(VI), V(V), and Nb(V) [10, 11]), and macromolecular compounds [12, 13]. For example, palladium carboxylate reduction with hydrogen in the presence of *ortho*-phenanthroline followed by the oxidation of the intermediate product with oxygen yields catalytic palladium nanoclusters with the idealized formulas $[Pd_{561}(phen)_{60}](OAc)_{180}$ [1, 5, 6], $Pd_{147}(phen)_{32}O_{60}(OCOR)_{30}$ (R = Me, Et, CHMe, CMe$_3$) [14], and $Pd_{1215}(phen)_{60}O_{1100}$ [15].

The quarternary ammonium stabilizers turned out to be ineffective. The palladium nanoclusters obtained in the presence of these compounds aggregate within 5–6 min in a hydrogen atmosphere [7]. At the same time, by depositing these clusters onto a solid substrate, it is possible to prepare stable heterogeneous hydrogenation catalysts superior to the commercial Pt/C catalysts [7].

Catalytic systems active in hydrogenation can also be produced by reducing palladium(II) phosphine complexes [4, 9, 16–21]. As distinct from the other above-listed stabilizers, phosphine ligands undergo destruction via the stepped breaking of the P–R (R= Ar, Alk) bond during the formation and operation of hydrogenation catalysts in a hydrogen atmosphere or in the pres-

ence of other reducing agents, such as sodium hypophosphite [4]. Depending on the nature of the reducing agent and on the extent of destruction of the organophosphorus ligand, the resulting nanosized particles can be metal cores with a ligand shell, polynuclear palladium complexes with phosphide and phosphinidene ligands, or even palladium phosphides bearing immobilized Pd(0) clusters [4, 9, 18, 20, 21]. There have been reports on hydrogenation catalysts based on palladium complexes with various organic phosphines, including tertiary [4, 9, 16–19], secondary [20], and primary [21]. Unsubstituted phosphine, PH_3, has not been used in the synthesis of microheterogeneous hydrogenation catalysts.

In order to gain deeper insight into the modifying effect of phosphorus-containing compounds and to reduce the number of steps in the synthesis of efficient hydrogenation catalysts, we studied the formation and catalytic properties of the $Pd(acac)_2 – PH_3$ system.

EXPERIMENTAL

Chemicals

Solvents and substrates were purified by standard procedures used for organometallic compounds [22]. Benzene was additionally dried by distillation from $LiAlH_4$ in a distillation column. It was stored over molecular sieve 4 Å in an argon atmosphere in sealed tubes.

N,N-Dimethyl formamide was held over anhydrous copper sulfate until the formation of a green solution and was twice distilled in vacuo (3 Torr) at a temperature not exceeding 42°C for drying and amine removal.

Palladium bisacetylacetonate was obtained as described in [23]. ^{1}H NMR data for this complex: δ(CH) = 5.04 ppm (s, 1H); δ(CH$_3$) = 1.76 ppm (s, 6H).

Phosphine was synthesized by dropping an alkali solution to a toluene dispersion of red phosphorus heated to 80°C [24]. The resulting gas was purified of diphosphine by passing it through a Tishchenko bottle filled with a 50% alkali solution in DMSO; for removing the residual water, it was then passed through columns packed with NaOH and P$_2$O$_5$. Phosphine was condensed into benzene in an appendix-type reactor. The phosphine concentration in benzene was determined by ^{31}P NMR using H$_3$PO$_4$ as the external standard. NMR data for phosphine: δ = –238 ppm (q, J_{PH} = 188 Hz).

Reaction between Palladium Bisacetylacetonate and Phosphine

The reaction was carried out in dry, deoxygenized argon in a temperature-controlled vessel at various initial ratios of the reactants. The vessel was designed so that it could be pumped and filled with an inert gas before the reaction.

Phosphine (1.5 mmol) as a benzene solution (52 ml) was added to a stirred solution of Pd(acac)$_2$ (0.4566 g, 1.5 mmol) in benzene (55 ml) under flowing argon. Two to three minutes after the beginning of the reaction, the solution became turbid and turned into a brown dispersion. Thereafter, the reaction mixture was stirred for 24 h at room temperature. The filtrate was analyzed by UV spectroscopy at regular intervals. The palladium bisacetylacetonate concentration was derived from the intensity of the absorption band at 330 nm (ε_{330} = 10630 l mol^{-1} cm^{-1}); the acetylacetone concentration, from the intensity of the absorption band at 290 nm (ε_{290} = 5000 l mol^{-1} cm^{-1} for Hacac and 3090 l mol^{-1} cm^{-1} for Pd(acac)$_2$). After the reaction, the precipitate was collected on a Schott filter in an argon atmosphere, washed with benzene and diethyl ether, and dried at 30°C in vacuo (1 Torr). The product yield was 0.22 g. Elemental analysis data (%): Pd, 68.90; P, 24.66; C, 4.18; H, 2.25. The product was X-ray-amorphous. Its IR spectrum showed absorption bands at 2296, 1067, 977, 725, and 672 cm^{-1}.

The reaction was carried in this way for all initial reactant ratios.

Preparation of the Catalyst in a Hydrogen Atmosphere

The catalyst was prepared in a thermostated glass shaker. A benzene solution (25 ml) of phosphine (0.75 × 10^{-3} mol) was added in drops to a solution of Pd(acac)$_2$ (0.761 g, 2.5 × 10^{-3} mol) in DMF (90 ml) in a hydrogen atmosphere (1 atm). Thus, the PH$_3$: Pd(acac)$_2$ ratio (P/Pd) was 0.3. The reaction mixture was agitated at 80°C for 15 min. After 2–5 min, it turned blackish brown. After the reaction was complete, the resulting dispersion was cooled to room temperature and was

transferred in an inert atmosphere to an appendix-type reactor. Next, 2/3 of the solvent was removed in vacuo and diethyl ether was added until the formation of a precipitate. The precipitate was washed with diethyl ether in an argon atmosphere and was dried at 50°C in vacuo (1 Torr). The product yield was 0.235 g. Elemental analysis data (%): Pd, 87.88; P, 3.59; C, 0.99; H, 0.25. The IR spectrum of the product exhibited no bands between 4000 and 400 cm^{-1}.

Catalytic Hydrogenation

Hydrogenation was carried out in a temperature-controlled glass shaker at 30°C and an initial hydrogen pressure of 1 atm in the presence of the catalytic system Pd(acac)$_2$–PH$_3$ prepared in situ. A solution of phosphine (0.3 × 10^{-5} mol) in benzene (1 ml) was added in drops to a solution of Pd(acac)$_2$ (0.00304 g, 1 × 10^{-5} mol) in DMF (9 ml) contained in a temperature controlled shaker under flowing hydrogen. The reaction mixture was agitated for 5 min at room temperature. Next, the temperature was raised to 80°C and the catalyst was synthesized by agitating the mixture in a hydrogen atmosphere for another 15 min. The resulting blackish brown "solution" was cooled to 30°C, and the substrate was introduced. Hydrogenation was carried out under vigorous agitation to rule out the diffusion control of the reaction. The progress of the reaction was monitored volumetrically and by GLC. Hydrogenation at other P/Pd ratios was carried out in the same way.

Analytical Methods

IR spectra were recorded in the 4000–400 cm^{-1} range on an IFS25 spectrophotometer using KBr techniques. The samples to be characterized, which were either mulls in mineral oil thermally pretreated to remove the traces of water or KBr pellets, were prepared in a dry inert atmosphere in a glovebox.

NMR spectra were recorded on a VXR-500S Varian pulsed spectrometer. ^{1}H chemical shifts were determined relative to tetramethylsilane. ^{31}P shifts were determined relative to 85% H$_3$PO$_4$. Downfield shifts were assigned positive values. The solutions to be characterized by ^{31}P NMR were sealed in coaxial inserts prepumped and filled with argon.

X-ray powder diffraction patterns from catalysts were recorded on a DRON-3M diffractometer using CuK_α radiation.

TEM images were obtained with a BS-300 microscope (Czech Republic). A drop of a solution was placed onto a carbon-coated specimen grid and was dried in an argon atmosphere. The imaging conditions ruled out the melting or decomposition of the specimen under the action of the electron beam.

The Pd(0) determination procedure was described in an earlier publication [25].

Table 1. Styrene hydrogenation in the presence of the catalytic system Pd(acac)$_2$–0.3PH$_3$

Run no.	Catalyst formation conditions		Specific activity, (mol H$_2$) (mol Pd)$^{-1}$ min^{-1}
	time, min	temperature, °C	
1	15	50	0
2	15	70	166
3	15	80	190
4	15	90	56
5	5	80	156
6	10	80	163
7	30	80	116

Note: Palladium content, C_{Pd} = 1 mmol/l; styrene : Pd = 870; solvent, DMF; reaction temperature, T = 30°C; P_{H_2} = 1 atm.

RESULTS AND DISCUSSION

### Catalytic Properties of the Pd(acac)$_2$–PH$_3$ System

It was demonstrated earlier that palladium(II) β-diketonate phosphine complexes show their catalytic hydrogenation activity only after they are treated with a reducing agent [4, 9, 21, 26]. The activity and selectivity of these catalysts depend strongly not only on the reducing agent, the organophosphorus compound, and P/Pd, but also on the order in which the reactants are combined. Variations in the properties of the resulting microheterogeneous palladium catalysts arise from variations in the palladium nanocluster size, in the nature of the ligand shell, and in the extent of phosphine

Specific activity, (mol H$_2$) (mol Pd)$^{-1}$ (min)$^{-1}$

Fig. 1. Catalytic activity of the Pd(acac)$_2$–PH$_3$ system in styrene hydrogenation as a function of the P/Pd ratio (C_{Pd} = 1 mmol/l; substrate : Pd = 870; solvent, DMF; T = 30°C; P_{H_2} = 1 atm).

destruction under the reducing conditions, a process converting part of the palladium into the oxidized state.

The data presented in Table 1 illustrate how the catalytic properties of the Pd(acac)$_2$–PH$_3$ system in styrene hydrogenation depend on the catalyst formation conditions. The necessity of applying rather high temperatures in this reaction stems from the fact that, due to its chelate structure, Pd(acac)$_2$ requires more severe conditions to react with H$_2$ than does any other reported palladium(II) compound with oxygen-containing acido ligands [27].

The specific styrene hydrogenation activity of the Pd(acac)$_2$–PH$_3$ system as a function of P/Pd passes through an extremum (Fig. 1). The highest hydrogenation activity is observed at P/Pd = 0.3. As this ratio is further increased, the reaction rate falls dramatically. At P/Pd ≥ 1, phosphine acts as an inhibitor, as is clear from a comparison between the activity of this system and the activity of Pd black produced under the same conditions. A similar trend was observed earlier for a primary phosphine as the modifier [21]. With triphenylphosphine as the modifier, the alkene hydrogenation activity of the catalyst peaks at P/Pd = 0.75. In the family of palladium catalysts containing phosphine ligands, hydrogenation activity increases in the following order:
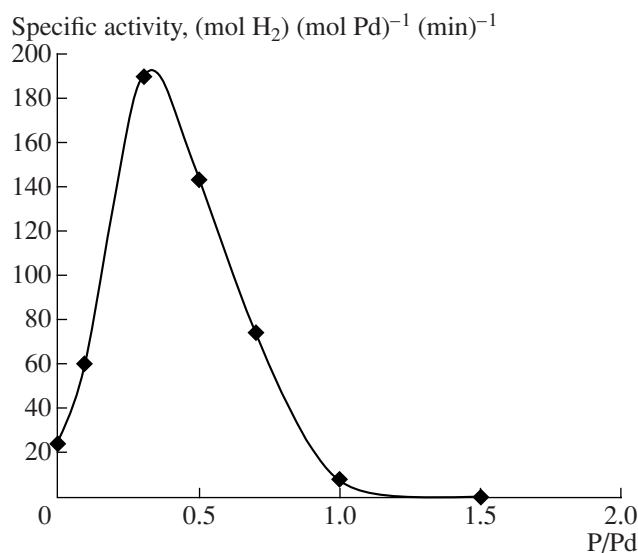
PPh$_3$ (40) [9] < PHPh$_2$ (140) [20]

< PH$_3$ (190) < PH$_2$Ph (280) [21].
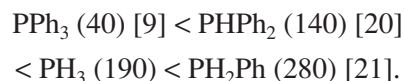
Here, the parenthesized numbers are the specific activities (in (mol styrene) (mol Pd)$^{-1}$ min^{-1}) of the catalysts with optimum P/Pd values produced in a hydrogen atmosphere under identical conditions.

The promoting effect of PH$_3$ on the palladium catalysts is 4.75 times stronger than the effect of triphenylphosphine and is 1.5 times weaker than the effect of phenylphosphine.

The specific hydrogenation activity of the Pd(acac)$_2$–PH$_3$ system can be increased by reducing the palladium concentration. The highest catalytic activity in the styrene hydrogenation reaction (330 mol (mol Pd)$^{-1}$ min^{-1}) is reached at a palladium concentration of 5×10^{-4} mol/l. The fact that the reaction rate as a function of the Pd(acac)$_2$ concentration passes through a maximum (Fig. 2) indicates that active palladium particles combine into less active aggregates and that the catalyst is microheterogeneous. Apparently, extending the duration of catalyst formation in a hydrogen atmosphere also impairs the aggregation resistance and, accordingly, reduces the specific catalytic activity (Table 1).

Some data characterizing the behavior of the Pd(acac)$_2$–0.3PH$_3$ system in the hydrogenation of a number of substrates are presented in Table 2. This system shows a rather high selectivity in the hydrogenation of the triple bond and the nitro and carbonyl groups. For example, phenylacetylene is successively hydrogenated to styrene and ethylbenzene and these reactions are not accompanied by dimerization or oligomeriza-

tion. At a phenylacetylene conversion of 96%, the styrene selectivity of the reaction is 94.4%. Nitrobenzene is selectively reduced to aniline.

Reaction between Pd(acac)$_2$ and Phosphine in an Inert Atmosphere

Investigation of the interaction between the initial components of the Pd(acac)$_2$–PH$_3$ system in hydrogen and in an inert atmosphere provided information concerning the nature and the formation of the catalytically active particles.

The interaction between a palladium β-diketonate complex and an organic phosphine in an inert atmosphere can proceed via the following three routes, depending on the nature of the phosphine and on reaction conditions: (1) phosphine coordination, which causes the acetylacetonate ligands to switch from the *O,O*-chelating mode to another binding mode [28, 29]; (2) redox reaction [20, 30, 31]; and (3) replacement of the β-diketonate ligands by phosphorus-containing groups, yielding polynuclear palladium complexes containing bridging phosphide or phosphinidene ligands [20, 21]. Since phosphine has the properties of both a Lewis base and a Brønsted acid and is a reducer, it is pertinent to consider the interaction between the initial components of the catalytic system in an inert atmosphere.

According to UV spectroscopic and ^{1}H NMR data, the reaction between Pd(acac)$_2$ and phosphine in benzene at P/Pd = 0.5–2.0 yields acetylacetone and a brown precipitate. At P/Pd = 0.5, the reaction yields 49% acetylacetone and 52% of the Pd(acac)$_2$ remains unreacted (Table 3). At P/Pd = 1 or 2, the resulting acetylacetone concentration is close to the theoretical value (89 and 100%, respectively). Therefore, Pd(acac)$_2$ and phosphine react in nearly equimolar proportions. According to ^{31}P NMR data, the solution resulting from the reaction at P/Pd = 2 contains free phosphine (δ = –238 ppm, J_{PH} = 188 Hz) and some of the phosphine hydrogen atoms are not involved in the exchange. If all of these atoms were replaced, then, at P/Pd = 0.5, the acetylacetone yield would be 75% on the Pd(acac)$_2$ basis.
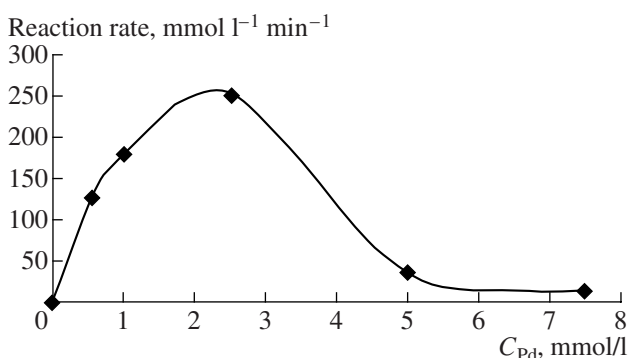
Fig. 2. Styrene hydrogenation rate in the presence of the catalytic system Pd(acac)$_2$–0.3PH$_3$ as a function of palladium concentration (solvent, DMF; T = 30°C; P_{H_2} = 1 atm; amount of styrene, 8.7×10^{-3} mol).

The brown precipitate that forms at P/Pd = 1 is unstable in air, and its composition can be described by the formula Pd$_1$P$_{1.2}$C$_{0.5}$H$_{3.3}$ (sample **I**). The IR spectrum of sample I shows an absorption band at 2296 cm^{-1}, which is characteristic of the stretching vibrations of the P–H bond ($v_{P–H}$) [32], and absorption bands at 1067, 978, 725, and 673 cm^{-1}, which are assignable to the bending vibrations of the same bond (Fig. 3). The absence of absorption bands characteristic of the C=O and C=C stretchings in the *O,O*-chelating acac ligand at the palladium atom (1560 and 1516 cm^{-1}) proves that the acetylacetonate ligands are replaced by phosphorus-containing groups. The presence of the P–H bending bands indicates that coordinated phosphine and/or phosphide (PH$_2$) fragments are present. The low solubility of sample I in both polar and nonpolar solvents did not allow us to record the ^{31}P NMR spectrum, so we cannot determine what particular phosphorus-containing groups (phosphide (PH$_2$) or phosphinidene (PH) fragments or palladium phosphides of various compositions (Pd$_x$P)) are present in sample I. The scarce information available on the outcomes of the reactions between phosphine and palladium(II) complexes suggests that these reactions can yield various products. For example, the reaction between PH$_3$ and the complex (PhCN)$_2$PdCl$_2$ in dry dioxane or chloroform yields

Table 2. Hydrogenation of various substrates in the presence of the catalytic system Pd(acac)$_2$–0.3PH$_3$

Substrate	C_{Pd}, mmol/l	Reaction rate, (mol H$_2$) (mol Pd)$^{-1}$ min^{-1}	Products	Yield, %
Styrene	1	190	Ethylbenzene	100
Phenylacetylene	1	59	Ethylbenzene	100
Nitrobenzene	5	21	Aniline	100
Benzaldehyde	5	1	Benzyl alcohol,	95
			toluene	5

Note: Substrate : Pd = 870; solvent, DMF; T = 30°C; catalyst preparation conditions: hydrogen atmosphere, 80°C, 15 min.

Table 3. Reaction between palladium bisacetylacetonate and phosphine in an inert atmosphere

P/Pd	Reaction time, min	Concentration, %			
		in benzene		in DMF	
		Pd(acac)$_2$	Hacac	Pd(acac)$_2$	Hacac
0.5	5	78	16	85	15
	30	59*	35*	75	26
	60	51**	46**	71	30
	1 day	52	49	62	42
1.0	5	65	34	66	34
	30	49	56	49	54
	60	38	66	40	65
	1 day	16	89	16	91
2.0	5	38	54	54	47
	30	13*	86*	38	64
	60	5**	98**	27	75
	1 day	2	104	0	98

Note: C_{Pd} = 4.2 mmol/l; T = 20°C; solvent, benzene or DMF; concentration determination error, ±10%.
    * The reaction time is 40 min.
    ** The reaction time is 80 min.

[Pd(PH$_2$)$_2$]$_n$, an insoluble amorphous compound [33]. At the same time, palladium(II) chloride dissolved in dioxane reacts with phosphine to yield the palladium(II) phosphide derivative (PdCl)$_3$P as a brown precipitate [34].

According to X-ray diffraction data, sample I is X-ray-amorphous. The amorphous halo observed at small reflection angles (diffuse peak at d/n = 13.556 Å (2θ = 6.52°)) is evidence that sample I has a low-order structure typical of polymer compounds [35]. Note that, in the diffraction patterns from palladium phosphides (Pd$_3$P, Pd$_6$P, Pd$_{4.8}$P, Pd$_5$P$_2$, etc.), the reflection 111 occurs in the 2θ = 35°–45° range [36]. The diffraction pattern from sample I shows neither reflections from a crystalline phase nor an amorphous halo in this region. Therefore, no palladium phosphides result from the reaction between Pd(acac)$_2$ and PH$_3$. Since Pd(acac)$_2$ and phosphine react in nearly equimolar proportions to yield ~2 mol of acetylacetone per mole of phosphine, the resulting oligomers are most likely polynuclear palladium complexes with bridging phosphinidene ligands (μ-PH). The formation of oligomer structures is possible owing to the ability of phosphinidene ligands to coordinate not only to two metal atoms, but even to three or four atoms [37–39]. According to IR spectroscopic and elemental analysis data, the polynuclear palladium complexes contain coordinated phosphine molecules along with μ-PH ligands.

Thus the reaction between Pd(acac)$_2$ and PH$_3$ in an argon atmosphere involves replacement of the acido ligands at the palladium atom and yields acetylacetone and randomly structured polynuclear palladium com-

plexes containing phosphinidene bridges (μ-PH) and a small proportion of coordinated phosphine ([Pd(μ-PH)]$_n$(PH$_3$)$_{0.2n}$). For P/Pd ≤ 1, unreacted Pd(acac)$_2$ remains in the reaction system.

The reaction between Pd(acac)$_2$ and phosphine in DMF, an inert medium, also involves the substitution of phosphinidene groups for acetylacetonate ligands (Table 3). The addition of phosphine to the carbonyl group, a process typical of aldehydes, was not observed [32].

A comparison between the above data and earlier data for the reactions of Pd(acac)$_2$ with phenylphosphine [21] and diphenylphosphine [20] demonstrates that a common feature of all of the reactions examined is the replacement of the acido ligands at the palladium atom by phosphorus-containing groups. However, these reactions yield different products. The reaction between palladium acetylacetonate and an equimolar amount of diphenylphosphine yields the dinuclear complex [Pd(acac)(μ-PPh$_2$)]$_2$; at P/Pd = 2, a redox reaction takes place, yielding tetraphenyldiphosphine and the trinuclear palladium cluster [Pd$_3$(μ-PPh$_2$)$_3$PPh$_2$(PHPh$_2$)$_2$]. Even in an inert atmosphere, the reaction between Pd(acac)$_2$ and phenylphosphine (P/Pd = 0.3–2) yields nanosized particles consisting of polynuclear palladium complexes with bridging phenylphosphinidene ligands and coordinated PH$_2$Ph molecules. In this reaction, as distinct from the reaction involving phosphine, the acetylacetonate ligands are completely replaced only at P/Pd ≥ 2 and the P/Pd ratio in the polynuclear palladium complexes is close to 2 (equals 1.7). As a consequence, at a given P/Pd molar ratio, the unreacted Pd(acac)$_2$ percent-
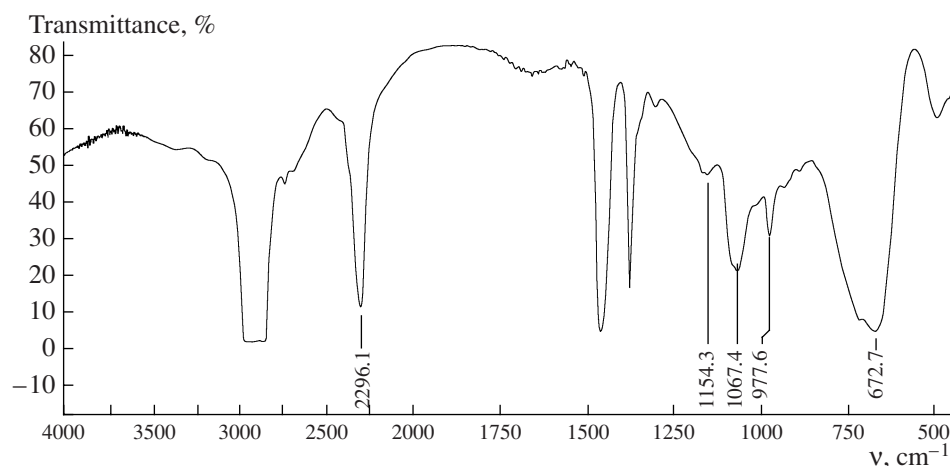
Fig. 3. IR spectrum of the product of the reaction between Pd(acac)$_2$ and phosphine (sample I as mineral-oil mulls).

age is higher for the reaction involving phenylphosphine than for the reaction involving phosphine. We believe that the difference between the behaviors of phenylphosphine and phosphine arises from the lower basicity of the latter.

Formation and Nature of the Hydrogenation Catalyst Based on Pd(acac)$_2$ and PH$_3$

The formation of the hydrogenation catalyst based on Pd(acac)$_2$ and PH$_3$ can arbitrarily be divided into two steps, namely, the reaction between these components in a hydrogen atmosphere at room temperature (5 min) and the reduction of the resulting system by hydrogen at 80°C (15 min).

Five minutes after addition of phosphine to a Pd(acac)$_2$ solution at room temperature in a hydrogen atmosphere, the ^{1}H NMR spectrum of the reaction system Pd(acac)$_2$–0.3PH$_3$ shows weak resonances at δ = 2.02 and 2.08 ppm along with the resonances due to the acac ligands coordinated to palladium (δ(CH) = 5.46 ppm, s; δ(CH$_3$) = 1.99 ppm, s). As will be demonstrated below, these weak resonances are due to the methyl protons of the enol and keto forms of acetylacetone. Since Pd(acac)$_2$ is irreducible by hydrogen under the above-specified mild conditions, the minor amounts of acetylacetone result from the side reaction between Pd(acac)$_2$ and phosphine.

Treating the catalytic system Pd(acac)$_2$–0.3PH$_3$ with hydrogen at 80°C yields a blackish brown solution. The ^{1}H NMR spectrum of this reaction system shows no signals from the acetylacetonate ligands of Pd(acac)$_2$ and exhibits signals from the keto and enol forms of acetylacetone: for the enol form, δ(CH) = 5.57 ppm (s), δ(CH$_3$) = 1.93 ppm (s), and δ(OH) = 16.24 ppm; for the keto form, δ(CH$_2$) = 3.65 ppm (s) and δ(CH$_3$) = 2.08 ppm (s). The stoichiometric formation of acetylacetone is confirmed by UV spectroscopic data. After the reaction is complete, the ^{31}P NMR spectrum of the

reaction system Pd(acac)$_2$–0.3PH$_3$–H$_2$ shows weak resonances at δ = 1.6 ppm (d, J_{PH} = 635 Hz) and δ = 0.6 ppm (s), with their intensity ratio equal to 1 : 0.3. These resonances are due to phosphorous and phosphoric acids, respectively. No other signals were detected between +500 and –500 ppm. A plausible explanation of the absence of any strong signals from reaction products is that the products form as a colloidal dispersion and can hardly be detected by NMR spectroscopy because of the very short relaxation time of the colloid particles [40].

Transmission electron microscopic examination of the reaction system demonstrated that the reaction of the components of the catalytic system with hydrogen yields a microheterogeneous system dominated by high-contrast particles 7.3–7.8 nm in diameter (Fig. 4). Extending the duration of catalyst formation in a hydrogen atmosphere from 15 to 30 min results in a better structured system (Fig. 5). The observed loose, branched structure is typical of fractal clusters [12, 41]. These clusters result from the self-organization (aggregation) of nanoparticles of similar sizes in the absence of stabilizing factors. The formation of these fractal clusters in the preparation of microheterogeneous palladium-based hydrogenation catalysts in the presence of phosphine ligands was observed for the first time. With a tertiary, secondary, or primary phosphine, the reduction of palladium(II) complexes yields nanoparticles with a higher aggregation resistance.

The composition of the black precipitate isolated from the reaction mixture (sample **II**) can be described by the formula Pd$_{7.5}$P$_{1.0}$C$_{0.7}$H$_{2.1}$. Its diffraction pattern shows peaks assignable to the phosphides Pd$_6$P (d/n 2.696, 2.583, 2.368, 2.291, 2.256, 2.232, 2.093, and 1.998 Å), Pd$_{4.8}$P (d/n 2.439, 2.327, 2.256, 2.232, 2.122, and 1.998 Å), and Pd$_5$P$_2$ (d/n 2.734, 2.696, 2.439, 2.291, 2.256, 2.232, 2.122, 2.093, 1.858, and 1.432 Å) and crystalline palladium (d/n 2.256, 1.950, and 1.375 Å) [36]. The dominant phases are Pd$_6$P and Pd$_{4.8}$P. As
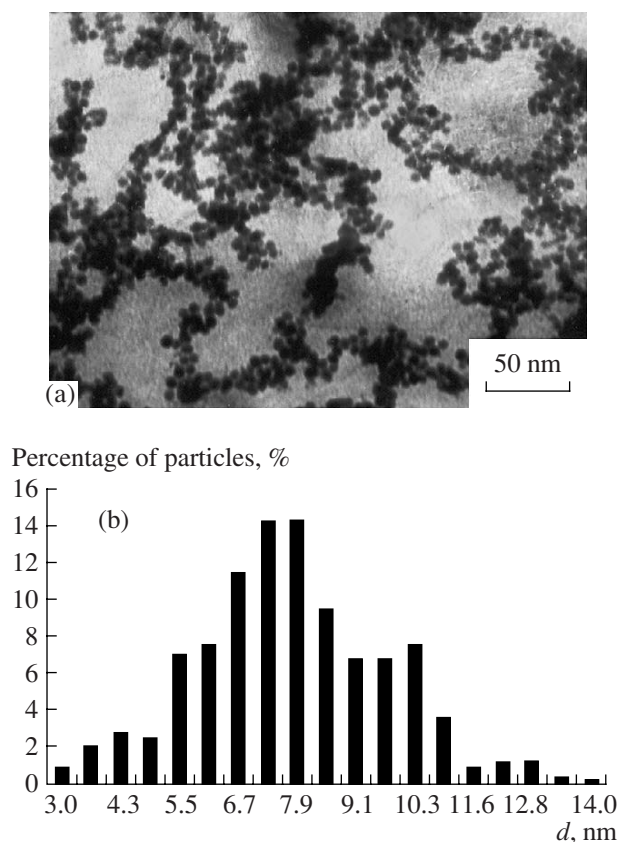
Fig. 4. (a) Electron micrograph of the Pd(acac)$_2$–0.3PH$_3$ system treated with hydrogen at 80°C for 15 min. (b) Particle size distribution.

determined by chemical analysis, the Pd(0) content of sample II is no higher than 31%. Knowing the total palladium and phosphorus contents, the proportion of reduced palladium, and the compositions of the palladium phosphides, one can express the composition of sample **II** as [{Pd(0)}$_{2.33}${Pd$_6$P}$_{0.40}${Pd$_{4.8}$P}$_{0.55}${Pd$_5$P$_2$}$_{0.026}$]. The source of carbon and hydrogen found in this sample is most likely dimethyl formamide, the solvent in which the synthesis was carried out. In view of this, the refined formula of sample **II** appears as [{Pd(0)}$_{2.33}${Pd$_6$P}$_{0.40}${Pd$_{4.8}$P}$_{0.55}${Pd$_5$P$_2$}$_{0.026}${DMF}$_{0.3}$].

Thus, the reduction of palladium bisacetylacetonate with hydrogen in the presence of phosphine yields palladium phosphides of various compositions, Pd(0), and phosphorous and phosphoric acids. These product composition data for the conversion of the Pd(acac)$_2$–0.3PH$_3$ catalytic system in hydrogen suggest the following product formation scheme.

The reaction between the components of this system can proceed at least via three routes:

(1) formation of a complex between palladium bisacetylacetonate and phosphine followed by the replacement of the bisacetylacetonate ligands by phosphorus-containing groups, yielding polynuclear complexes of the [Pd(μ-PH)]$_n$ type,

$$nPd(acac)_2 + nPH_3 = [Pd(\mu\text{-}PH)]_n + 2nHacac;$$

(2) reduction of part of the Pd(acac)$_2$ with hydrogen, yielding Pd(0) clusters,

$$Pd(acac)_2 + H_2 = Pd(0) + 2Hacac,$$

$$nPd(0) \longrightarrow Pd(0)_n;$$
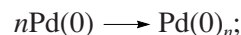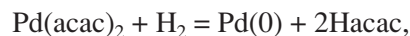
(3) reaction between Pd(acac)$_2$ and palladium complexes with phosphorus-containing ligands ([Pd(μ-PH)]$_n$) under reducing conditions, yielding various palladium phosphides,

$$[Pd(\mu\text{-}PH)]_n + 2nPd(acac)_2 + 1.5nH_2$$

$$= nPd_3P + 4nHacac,$$

$$Pd_3P + 3Pd = Pd_6P.$$
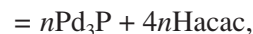
Note also that phosphine itself can reduce transition metal compounds [24]. The reducing action of phosphine in catalyst formation is confirmed by the formation of small amounts of phosphorous acid:

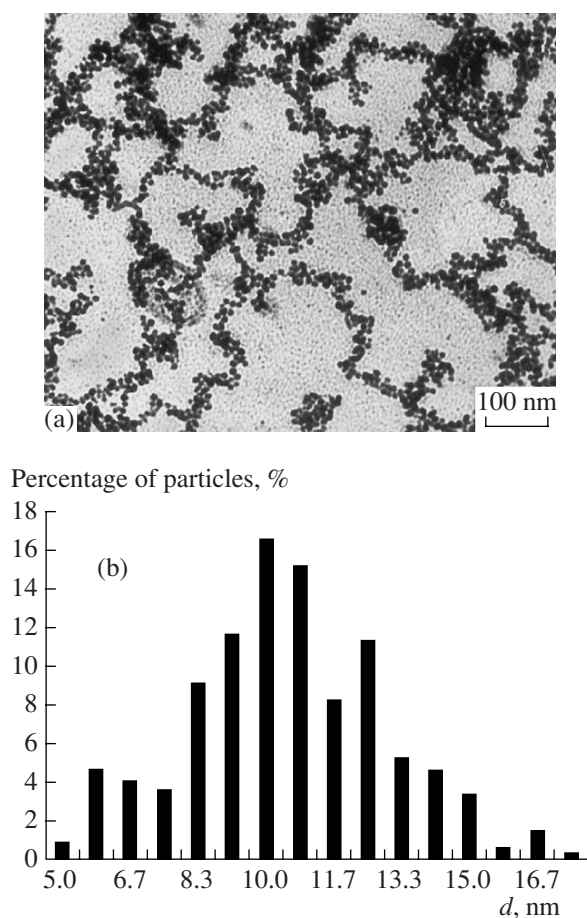$$3Pd(acac)_2 + PH_3 + 3H_2O = 3Pd(0) + H_3PO_3 + 6Hacac.$$
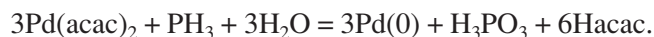
Water, which is necessary for this redox process, may be present as an impurity in the solvent, even though the solvent was dried. The resulting phosphorous acid is also a reducing agent, and it undergoes oxidation into phosphoric acid. Obviously, we cannot rule out the possibility that phosphorous and phosphoric acids result from the partial oxidation of phosphine into phosphorus(III) and phosphorus(V) oxides by traces of oxygen in the reaction system followed by the hydration of these oxides. However, in a special-purpose experiment, phosphine was heat-treated in a hydrogen atmosphere at 80°C and the ^{31}P NMR spectrum of the product showed only a signal from free phosphine ($\delta = -238$ ppm, q, $J_{PH} = 188$ Hz).

Transition metal phosphides are comparatively unreactive. Active hydrogenation catalysts are Pd(0) clusters or palladium hydride clusters resulting from the former during the hydrogenation process [9, 20, 21]. The following question arises here: If most of the palladium turns into palladium phosphides during the formation of the Pd(acac)$_2$–0.3PH$_3$ system, then what is the origin of the strong catalytic effect of this system in the hydrogenation of various substrates?

According to electron microscopic data, the particle size of the palladium black resulting from the reduction of palladium bisacetylacetonate with hydrogen in the absence of phosphine is 25–30 nm, almost four time as large as the particle size of the palladium catalyst examined. Therefore, one of the origins of the promoting effect of phosphine is that this compound favors the formation of a more finely dispersed system. The fraction of surface atoms is 20–15% for metal particles 8–10 nm in diameter and has a much smaller value of 3–2% for a particle diameter of 25–30 nm [42]. Thus, the percentage of surface atoms can increase by a factor of about 7, as does the reaction rate under the action of phosphine introduced into the catalytic system. The promot-

Fig. 5. (a) Electron micrograph of the Pd(acac)$_2$–0.3PH$_3$ system treated with hydrogen at 80°C for 30 min. (b) Particle size distribution.

However, the high extent of dispersion alone cannot be fully responsible for the high hydrogenation efficiency of the nanosized palladium catalysts prepared in the presence of phosphine. The conversion of the palladium phosphine complexes under the action of dihydrogen is a complicated multistep process. Common features of the formation, in a hydrogen atmosphere, of the Pd(acac)$_2$-based hydrogenation catalysts involving different phosphines are the formation of a microheterogeneous system and the oxidation of part of the palladium as a result of the decomposition of the phosphorus-containing ligands. The proportions of the oxidized and reduced palladium particles depend on the rate ratios between the reduction of the Pd(II) complexes, the aggregation of the resulting reduced palladium particles, and the decomposition of the phosphorus-containing groups in the coordination sphere of Pd(0). All these processes exert an effect on the nature and catalytic properties of the resulting nanoparticles.

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ing effect of phosphine that is associated with an increase in the extent of dispersion of the catalysts provides a satisfactory explanation for the observed experimental data under the assumption that the nanoparticle surface contains Pd(0) atoms. Therefore, the most likely model of a nanoparticle of the microheterogeneous hydrogenation catalyst is a palladium phosphide core on which Pd(0) clusters are immobilized.

Further studies are necessary to elucidate the role of the electron factor in the catalytic activity of the system.

Thus, the above experimental data suggest that the promoting effect of phosphine on palladium catalysts is not weaker and, in some cases, is even stronger than the effect of organic phosphines. The promoting effect of phosphine is in part due to the fact that phosphine ensures the formation of a microheterogeneous system that is dispersed more finely than Pd black obtained from Pd(acac)$_2$ under the same conditions. The resulting nanoparticles have a core consisting of various palladium phosphides, such as Pd$_6$P, Pd$_{4.8}$P, and Pd$_5$P$_2$, on which Pd(0) clusters are immobilized.

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