Kinetics and Catalysis, Vol. 44, No. 5, 2003, pp. 623–630. Translated from Kinetika i Kataliz, Vol. 44, No. 5, 2003, pp. 683–691.
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CATALYTIC REACTION MECHANISMS

Formation of Nanosized Catalysts Based on Palladium Phosphine Complexes and the Nature of Their Activity

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Received October 9, 2002

Abstract—Findings on the formation and features of nanosized particles based on palladium complexes, which are active in hydrogenation catalysis, are summarized. Depending on the nature of a reducing agent, nanosized particles formed by the reduction of palladium(II) phosphine complexes are either metallic nuclei stabilized by organophosphorus ligands or associates of polynuclear phosphido or phosphinideno palladium complexes whose surface contains immobilized Pd(0) clusters. The ensembles of the Pd(0) atoms are active in hydrogenation.

INTRODUCTION

The nature of species active in catalysis is a topical problem of catalytic chemistry. Heterogeneous catalysts such as metals, metal oxides and sulfides, or supported catalysts were the most common by the mid-1950s. Then, the catalytic systems became more diverse due to the development of metal complex catalysis. The problem of the catalyst phase state appeared. The liquid-phase catalytic systems based on metal complexes are not necessarily homogeneous. For instance, among the Ziegler–Natta catalysts, only the titanium- and cobalt-based systems such as $(Cp)_2TiCl_2$ + $AlEt_3$, $Co(C_5H_7O_2)_2$ + PPh_3 + $AlEt_3$ are truly homogeneous. The Ziegler–Natta systems $M(C_5H_7O_2)_2$ + $AlEt_3$ containing no phosphine are microheterogeneous (nanosized) catalysts [1] in which the particles of the dispersed phase consist of metallic nuclei stabilized with the organoaluminum species AlR_x.

At the end of the 20th century, the nanosized catalysts and their syntheses and properties attracted increasing attention. From the viewpoint of the structure of matter, nanoparticles are intermediate between molecules and macroscopic materials. Because of a great fraction of the surface atoms, the physicochemical properties of nanoparticles differ from those of bulk substances and distinct molecules. Variations in the structure and electronic properties of nanoparticles are most important for catalysis because these parameters primarily determine the features of interaction between reactants and a catalytically active component, the nature and reactivity of intermediates, and the catalyst performance. The nature of nanoparticles and relations between their sizes and catalytic properties have received much attention [2–7].

The first catalytically active giant palladium clusters with a nuclei containing about 600 metal atoms were synthesized by I.I. Moiseev and co-workers by the successive treatment of a solution of the trinuclear palladium acetate $[Pd(OAc)_2]_3$ in acetic acid containing a small amount (≤1/2 mol/g-atom Pd) of 1,10-phenanthroline or 4,4'-dipyridine with gaseous H_2 and O_2 [5]. X-ray amorphous substances thus obtained were unique in their activity and selectivity as catalysts for both redox and acid–base reactions of organic substances: the oxidative acetoxylation of alkenes and alkylarenes; the oxidation of alcohols, aldehydes, and formic acid; the hydrogenation of multiple bonds (C=C, N=O, and C≡N) with formic acid; and the synthesis of acetals from carbonyl compounds and alcohols in neutral solutions [6, 7]. The ability of clusters to catalyze reactions typical of the acid catalysis allowed the authors to suggest that giant palladium clusters can operate not only as the electron transfer agents in redox processes but also as Lewis acids. Efficient catalysts for various transformations of organic substances were prepared, and the mechanisms of their formation were studied. Based on various indirect physical and chemical techniques, the idealized structure of the giant palladium cluster was formulated as $[Pd_{561}(phen)_{60}](OAc)_{180}$.

Most research in nanochemistry deals with the synthesis of nanoclusters with a narrow particle size distribution and their physical and chemical properties [2–4]. The problem of their formation is studied to a lesser extent.

In this work, our main findings are presented on the mechanism of formation and operation of microheterogeneous hydrogenation catalysts by palladium(II) phosphine complexes in the presence of various reducing agents.

EXPERIMENTAL

Palladium bis(acetylacetonate) and bis(acetylacetonato)-triphenylphosphine palladium were prepared according to the procedures described in [8]; and syntheses of triphenylphosphine and diphenylphosphine are described in [9, 10].

Interaction between the components of catalytic systems was studied by a combination of spectroscopic (NMR, IR, and UV) techniques, electron microscopy (EM), X-ray diffraction analysis (XRD), and GLC.

NMR spectra were obtained on a VXR-500S Varian pulse spectrometer. IR spectra were recorded in the range of 4000–400 cm^{-1} on a Specord IR-75 instrument in Vaseline oil and in a solution.

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

Transmission (TEM) and scanning (SEM) electron microscopic studies of the catalysts were performed on BS-300 and BS-540 electron microscopes (Czech Republic). The samples were preliminarily dispersed on a UZDN-A ultrasonic dispergator for 1 min in hexane (power input 100 W). A drop of the suspension was poured on a grid holder covered with the carbon film followed by drying in an argon atmosphere. The conditions of the TEM and SEM studies were chosen to prevent the melting and decomposition of the specimens under the electron beam.

Procedure of Pd(0) Analysis [11]

A solution containing 2×10^{-5} mol of Pd in 10 ml of DMF was placed in a preliminarily evacuated flask filled with argon and kept at a constant temperature and 0.148 g (0.4 mmol) of NBu_4I and 0.109 ml (1 mmol) of iodobenzene were added. The reaction mixture was stirred with a magnetic stirrer at 80°C until the constant concentration of the PdI_4^{2-} anion formed in the following reactions:

$$\mathrm{Pd(0) + PhI = PdPhI},$$

$$\mathrm{2PdPhI = Ph{-}Ph + PdI_2 + Pd(0)},$$

$$\mathrm{PdI_2 + 2(NBu_4)I = (NBu_4)_2[PdI_4]}.$$

The concentration of PdI_4^{2-} was measured by spectrophotometry on a VSU2-P spectrometer using an absorption band at 340 nm (ε_{340} = 23750 l cm^{-1} mol^{-1}) in an all-soldered quartz cell with a 0.1-cm thickness. Simultaneously, biphenyl was determined by chromatography.

RESULTS AND DISCUSSION

The Catalytic System Based on the $Pd(acac)_2PPh_3$ Complex and Sodium Hypophosphite

Sodium hypophosphite is widely used for preparing transition metal blacks or low-valent complexes [12, 13]. The reduction of transition metal compounds with sodium hypophosphite is described by the following general equation:

$$\mathrm{M}^{n+}\mathrm{X}_n + n/2\mathrm{NaH_2PO_2} + n/2\mathrm{H_2O}$$

$$\longrightarrow \mathrm{M}^0 + n/2\mathrm{NaH_2PO_3} + n\mathrm{HX}.$$

However, the interaction of the Pd(II) phosphine complexes with sodium hypophosphite is complicated by some side processes due to the easy occurrence of redox reactions in the palladium coordination sphere and the lability of the stabilizing ligands. Let us consider this process using the interaction of the $Pd(acac)_2PPh_3$ complex with sodium hypophosphite in a toluene–ethanol medium as an example.

The reaction of $Pd(acac)_2PPh_3$ with excess sodium hypophosphite produces acetylacetone, benzene (0.5 mol/mol PPh_3), molecular hydrogen, and sodium phosphite in practically 100% yield.

According to the ^{31}P and ^1H NMR data, the interaction of $Pd(acac)_2PPh_3$ with sodium hypophosphite occurs through a sequence of stages [14]:

$$\mathrm{Pd(acac)_2PPh_3 + NaH_2PO_2}$$

$$\xrightarrow[\mathrm{-Na(acac)}]{} \mathrm{Pd(acac)(H_2PO_2)(PPh_3)},$$

$$\mathrm{Pd(acac)(H_2PO_2)(PPh_3) + H_2O}$$

$$\xrightarrow[\mathrm{-H(acac)}]{} \mathrm{Pd(H_2PO_2)(OH)(PPh_3)},$$

$$\mathrm{Pd(H_2PO_2)(OH)(PPh_3)} \xrightarrow[\mathrm{-H_3PO_3}]{} \mathrm{[Pd(PPh_3)]}$$

$$\longrightarrow 1/n\mathrm{[Pd(PPh_3)]}_n,$$

$$\mathrm{H_3PO_3 + Na(acac)} \xrightarrow[\mathrm{-H(acac)}]{} \mathrm{NaH_2PO_3}.$$

It is known [12, 13] that the catalytic oxidation of sodium hypophosphite catalyzed in neutral media by the Ni, Pd, and Cu blacks or low-valent transition metal complexes produces molecular hydrogen:

$$\mathrm{NaH_2PO_2 + H_2O} \xrightarrow{\mathrm{Pd}} \mathrm{NaH_2PO_3 + H_2}.$$

Hydrogen evolution during the interaction of the starting components is indirect evidence for the occurrence of reduced palladium species or complexes.

The composition of final products of the initial complex transformation is rather complicated. Along with the trinuclear palladium complexes, $[Pd_3(PPh_2)_3(PPh_3)_3]^+acac^-$ and $[Pd_3(PPh_2)_2(acac)(PPh_3)_3]^+acac^-$, whose concentrations in the solution are at most 3–5% according to NMR data, a mixture of polynuclear palladium complexes with bridging diphenylphosphide and triphenylphosphine ligands is present in the reaction system. According to TEM data, a precipitate of the $[Pd_2(PPh_2)(PPh_3)]$ composition isolated from the reaction mixture is a low-contrast TEM substance (globules, ~0.25 μm in diameter) in which dark spherical particles with a typical diameter of 2.5–7.5 nm, predominantly 5 nm [15], are uniformly distributed. The concentration of Pd(0) in the sample determined by the chemical method is ~40%.

The above data suggest that the nanosized high-contrast TEM particles predominantly consist of Pd(0) and the low-contrast substances are polynuclear palladium complexes with diphenylphosphide ligands. The Pd(0) nanoparticles are stabilized by PPh_3. Their stabilization with oligomeric palladium complexes containing phosphide ligands is also possible.

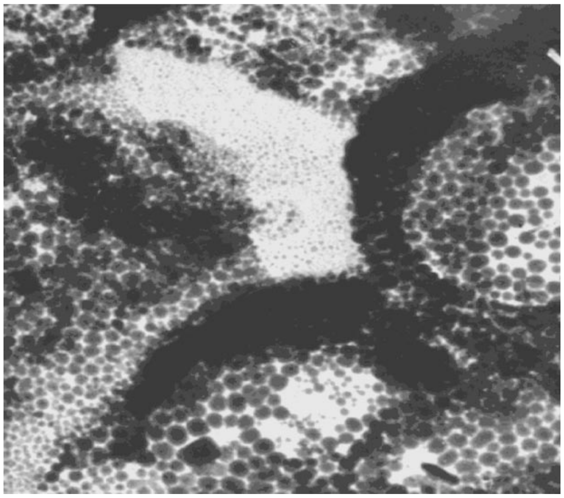
Thus, the conversion of the $Pd(acac)_2PPh_3$ complex by sodium hypophosphite results in Pd(II) reduction to Pd(0) and the formation of palladium nanoparticles. There are several reasons for this. First, the partial (10–15%) oxidation of triphenylphosphine with the residual oxygen and the redistribution of PPh_3 between the intermediates during the formation of trinuclear palladium complexes in which P/Pd = 2 results in the "denudation" of a fraction of Pd. Second, the well known reducing ability of triphenylphosphine toward palladium hydroxo complexes cannot be ruled out:

$$Pd(OH)(PPh_3)(H_2PO_2) \xrightarrow[-P(O)Ph_3,\ H_3PO_2]{} Pd(0).$$

Palladium(0) formed catalyzes the oxidation of sodium hypophosphite accompanied by hydrogen evolution. This leads to the destruction of organophosphorus ligands and the formation of various palladium complexes with the phosphide ligands.

The catalytic system $Pd(acac)_2PPh_3 + NaH_2PO_2$ formed in argon is highly active in hydrogenation of unsaturated hydrocarbons containing terminal double bonds (180 mol of substrate g-atom^{-1} Pd min^{-1}) and bisubstituted acetylene derivatives (170 mol of substrate g-atom^{-1} Pd min^{-1}) under mild conditions (T = 30°C, P_{H_2} = 1 atm). α-Acetylene derivatives were hydrogenated under the same conditions at a low rate (6 mol of substrate (g-atom Pd)$^{-1}$ min^{-1}) and a selectivity of 60%, and the reaction was accompanied by oligomerization. Furthermore, the effect of catalyst activation was found in the hydrogenation of α-acetylene derivatives. A sharp increase in the hydrogenation rate for α-acetylene derivatives and in the reaction selectivity from 60 to 95% was observed in the hydrogenation of the second portion of the substrate after the first portion hydrogenated to alkane [16].

For this system, we found for the first time that the organophosphorus ligands of the palladium complex catalysts are decomposed not only during the interaction of the $Pd(acac)_2PPh_3$ complex with sodium hypophosphite in argon but also during the operation of the catalytic system [15, 16], and the organophosphorus ligands are hydrogenated in parallel with the hydrogenation of unsaturated substrates. This process depends on the substrate nature. In the case of α-alkenes (styrene) or bisubstituted acetylene hydrocarbons (tolan), benzene was additionally formed during hydrogenation. Benzene was formed in the same amount (0.5 mol C_6H_6/mol PPh_3) in phenylacetylene hydrogenation only after phenylacetylene almost completely hydrogenated to styrene. The kinetic features of hydrogenation are due to different coordination abilities of the substrates. Phenylacetylene (PA) possesses high coordination ability and occupies vacant positions in the palladium coordination sphere preventing subsequent hydrogenation stages, namely, the activation of the hydrogen molecule and the destruction of PR_x ligands. After PA hydrogenation to styrene, palladium hydride can be formed, which is present during hydrogenation of both styrene and the second portion of PA.



1 cm = 0.07 μm

Fig. 1. TEM image of the product of the reaction $Pd(acac)_2PPh_3 + NaH_2PO_2 + H_2$.

Note that the estimated fraction of Pd(0) is different at various stages of the catalytic reaction. At first sight, contradictory data were obtained. The Pd(0) concentration was 37% after interaction of the starting components in argon, and it decreased to 21% after additional treatment with hydrogen. An increase in the benzene concentration in the solution was observed. During styrene hydrogenation, the Pd(0) concentration in the catalyst increased again to 43%.

According to TEM (Fig. 1), the number of large high-contrast spherical particles, 10–25 nm in diameter, in the $Pd(acac)_2PPh_3 + NaH_2PO_2$ catalytic system sharply increased after hydrogen treatment [15]. One can see at a magnification of 500 000 that the spherical particles with high electron density are not uniform but have a fine structure. Each microglobule looks as follows: darker particles, 2.5–3 nm in diameter, are embedded in a matrix of the less contrast substance. The number of dark particles within the microglobule ranges from a few to 20–30 particles. The phase of crystalline palladium is absent from the diffraction patterns of the $Pd(acac)_2PPh_3 + NaH_2PO_2 + H_2$ system.

The differences observed in the catalytic systems before and after hydrogen treatment indicate quantitative changes between Pd(0) and palladium polynuclear complexes because of permanent redox processes.

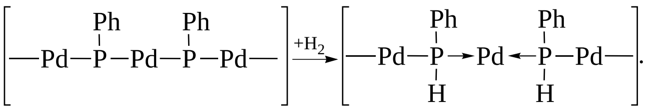
A decrease in the Pd(0) concentration after hydrogen treatment is due to the destruction of organophosphorus ligands, which can be presented as follows:

$$Pd(0) + PR_xL$$
$$\longrightarrow Pd(R)(PR_{x-1})L \xrightarrow{H_2} PdH(PR_{x-1})L + HR,$$

$$PdH(PR_{x-1})L + PR_xL \xrightarrow[-HR]{} Pd(PR_{x-1}L)_2,$$

where L is a fragment of the palladium complex.

An increase in the Pd(0) amount during hydrogenation can be due to the hydrogenolysis of the Pd–PPh bond:



$$\left[-Pd-\overset{Ph}{P}-Pd-\overset{Ph}{P}-Pd- \right] \xrightarrow{+H_2} \left[-Pd-\overset{Ph}{\underset{H}{P}} \rightarrow Pd \leftarrow \overset{Ph}{\underset{H}{P}}-Pd- \right].$$

The fraction of active sites in the $Pd(acac)_2PPh_3$ + NaH_2PO_2 system determined by poisoning with triphenylphosphite is at most 15% [16]. If one suggests that Pd(0) is the active component of this catalytic system, it is possible to show that only 40.5% of Pd(0) participates in hydrogenation. This value is comparable with the fraction of the surface metal atoms for nanosized particles 2.5–3.0 nm in diameter (39–45%). According to TEM data, the high-contrast particles of this size are present in the catalyst.

Thus, when sodium hypophosphite is used as a reducing agent, the nanosized Pd(0) particles that are active in hydrogenation are formed. The condensation methods are widely used to prepare metal sols, which are often stabilized by the quaternary alkylammonium salts or other nitrogen-containing compounds [17]. The feature of this system is related to the nature of both the metal and stabilizing ligand. A side process, the destruction of organophosphorus ligands in the palladium coordination sphere during both formation and operation of the catalyst, produces various polynuclear palladium complexes with phosphide and phosphinidene ligands, whose role will be considered below.

Catalytic System $Pd(acac)_2PPh_3 + H_2$

The interaction of the $Pd(acac)_2PPh_3$ complex (**I**) with hydrogen is an example of an autocatalytic reaction. According to the data of NMR and IR spectroscopies, the transformation of the starting complex **I** in hydrogen occurs through the stage of formation of the unstable intermediate $[Pd(acac)PPh_3]_2$ (**II**) and binuclear palladium complex $[Pd(acac)PPh_2]_2$ (**III**) containing the chelate $Acac^-$ and bridging PPh_2 ligands [18, 19]:

$$Pd(acac)_2PPh_3 + H_2$$

$$\xrightarrow[-H(acac)]{} [Pd(acac)(H)PPh_3] \xrightarrow[-H(acac)]{} [PdPPh_3],$$

$$[PdPPh_3] \longrightarrow Pd(Ph)(PPh_2)$$

$$\xrightarrow{+1/2H_2} [Pd(PPh_2)] + C_6H_6,$$

$$Pd(acac)_2PPh_3 + [Pd(PPh_2)]$$

$$\longrightarrow 1/2[Pd(acac)PPh_2]_2 + 1/2[Pd(acac)PPh_3]_2.$$

There may be two reasons for the autocatalytic nature of the reaction. On the one hand, in the transformation of **I** in hydrogen, the intermediate is formed, which is more active than **I** in the reaction with hydrogen and in the hydrogenolysis of the starting complex. This compound could be $Pd(acac)_2$. It is more readily reduced by hydrogen to Pd(0) compared to **I**,

$$Pd(acac)_2PPh_3 \rightleftharpoons Pd(acac)_2 + PPh_3,$$

$$Pd(acac)_2 + H_2 \xrightarrow[-2H(acac)]{} Pd(0),$$

and Pd(0) accelerates hydrogenolysis by the activation of hydrogen.

On the other hand, the reason for autocatalysis can be the formation of the trinuclear complex $[Pd_3(PPh_2)_3(PPh_3)_3]^+(acac)^-$ (**IV**) in the system. This complex was identified by ^{31}P NMR spectroscopy in the solution along with triphenylphosphine oxide. First, its formation should be accompanied with the redistribution of the organophosphorus ligands between the intermediates to form PPh_3-free palladium complexes, which accelerate **I** hydrogenolysis by the activation of molecular hydrogen. Second, its formation should be accompanied by the consumption of the starting complex **I** to form complex **IV**:

$$Pd(acac)_2PPh_3 + (Solv)PdPPh_2$$

$$\longrightarrow Pd(acac)PPh_3 + Pd(acac)PPh_2,$$

$$Pd(acac)PPh_3 \longrightarrow 1/2[Pd(acac)PPh_3]_2,$$

$$Pd(acac)PPh_2 + 2(Solv)PdPPh_2$$

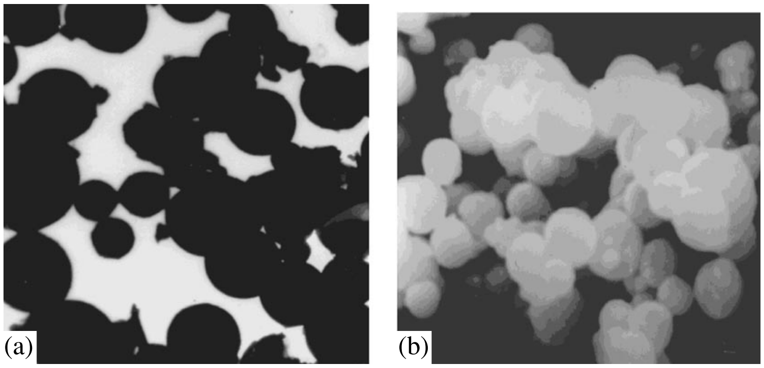
$$\xrightarrow{PPh_3} [Pd_3(PPh_2)_3(PPh_3)_3]^+(acac)^-.$$

Upon reaction completion, a black-brown, X-ray amorphous, and poorly soluble in DMF precipitate is formed (sample A). According to the elemental analysis, IR and NMR data, this is a mixture of palladium complexes substituted to various degrees by the organophosphorus ligands, which can be generally presented as $[Pd_5(PPh_2)_2(PPh)_2]$ or $[Pd_5(PPh)_3PPh_3]$. The electron microscopic study showed that the separated precipitate consists of regular spherical microglobules, 0.5–1 μm in diameter (Fig. 2) [19]. The formation of spherical particles on the 1 μm level is only possible under the conditions of phase separation. The regular spherical globule shape and growth mechanism (coalescence) give evidence for the formation of oligomers.

Experiments with the centrifugation of the solution of this sample showed that upon dissolution in DMF, the globules disintegrated to smaller particles with a size of at most 3 nm.

The sample also contained reduced palladium (Pd(0)), whose fraction estimated by the chemical method was 8%.

The above data suggest that sample A consists of the associates of polynuclear palladium complexes with the bridging diphenylphosphide and phenylphosphinidene ligands. The ability of the PPh ligand to form bonds with three and even four metal atoms is the reason for the nucleation of a new phase during the reduction of the phosphine palladium complexes. Apparently, polynuclear palladium complexes with PPh ligands mainly form the nuclei of the nanoparticles, and



1 cm = 1.4 μm

1 cm = 1.1 μm

Fig. 2. Microscopic images of the product of $Pd(acac)_2PPh_3$ reduction with hydrogen (sample A): (a) TEM, (b) SEM.

palladium complexes with the diphenylphosphide ligands are bound to them due to the donor–acceptor interaction. The ensembles of palladium atoms are immobilized on these supramolecular structures.

Note that palladium complexes with the phosphinidene ligands were prepared earlier by the reduction with hydrogen of the Pd(II) carboxylate complexes with tertiary phosphines [20–22]. In particular, Berenblyum *et al*. synthesized a polynuclear complex, $[Pd(OAc)_2PPh_3]_2$, which is highly active in hydrogenation of dienes, acetylenes, and olefins by hydrogenolysis of the binuclear complex $[Pd_5(PPh)_2]_4$ [20, 21]. Hence, the destruction of the organophosphorus ligands under reductive conditions resulting in various polynuclear palladium complexes with the diphenylphosphide and phenylphosphinidene ligands is a general feature of transformations of the palladium(II) phosphine complexes with oxygen-containing acido ligands in hydrogen.

The variation of the component ratio in the system $Pd(acac)_2 + nPPh_3 + H_2$ (n = 0.25, 0.50, and 0.75) results in a decrease in the induction period in the reaction with hydrogen, a deeper destruction of the organophosphorus ligands, and a change in the nature of the conversion products (Table 1). Palladium phosphides are formed as a result of the deeper destruction of the organophosphorus ligands in the $Pd(acac)_2 + nPPh_3 + H_2$ system along with the polynuclear palladium complexes with the PPh_2 and/or PPh ligands. At n = 0.5, palladium phosphides $Pd_{4.8}P$ and Pd_6P and crystalline palladium were found by the XPS method. According to published and experimental data, at the ratio $PPh_3/Pd(acac)_2$ = 0.25, a mixture of palladium phosphides, mainly Pd_3P, palladium compounds with phenylphosphinidene, and crystalline palladium is formed [19].

Among the products of the interaction of the $Pd(acac)_2 + nPPh_3$ system with hydrogen, the polynuclear palladium complexes on which Pd(0) clusters are immobilized are most active in the hydrogenation of unsaturated compounds (for example, 75 mol styrene (g-atom Pd)$^{-1}$ min^{-1}). When the P/Pd ratio is decreased (n = 0.5, 0.25), insoluble palladium phosphides are formed and, as a result, the hydrogenating catalytic activity decreases. When phosphines with branched groups are used, the association degree of the polynuclear palladium complexes should decrease and more loose structures are formed. This explains a sharp increase in the catalytic activity when PPh_3 is replaced by trioctylphosphine [23].

Table 1. Conversion products in the system $Pd(acac)_2 + nPPh_3$ in a hydrogen atmosphere

$\frac{PPh_3}{Pd(Acac)_2}$, mol/mol	$\frac{C_6H_6}{PPh_3}$, mol/mol		Pd(0), %	Data of XRD
	DMF	toluene		
0.25*	2.60	2.90	54	Pd cryst., X-ray amorphous
0.50*	1.68	2.16	30	Pd cryst., $Pd_{4.8}P$; Pd_6P, X-ray amorphous
0.75*	1.02	1.17	25	Crystalline phase, X-ray amorphous
1.00**	0.90	0.83	8	X-ray amorphous

Note: Solvent: toluene (*) or DMF (**).

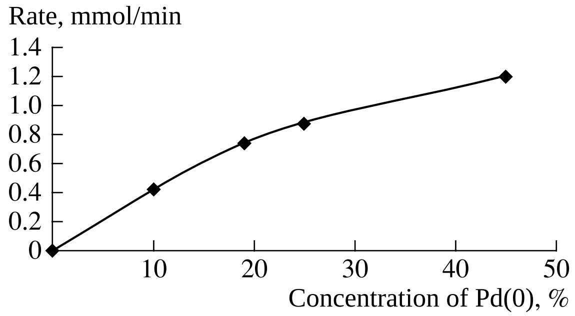


Fig. 3. A plot of styrene hydrogenation rate vs. Pd(0) concentration. $[Pd]_\Sigma$ = 1 mmol/l; T = 30°C, solvent, DMF.

Data on the interaction of $Pd(acac)_2$ + $nPPh_3$ with hydrogen suggest the following catalyst model: these are polynuclear palladium complexes or palladium phosphides with $P/Pd \leq 0.5$ on which the Pd(0)-containing clusters are immobilized. The ensembles of Pd(0) atoms and crystalline Pd are responsible for the hydrogenating catalytic activity.

The above examples of the formation of the hydrogenation catalysts based on palladium *bis*(acetylacetonato)triphenylphosphine and various reducing agents allow us to propose two models of microheterogeneous hydrogenation catalysts. When Pd(II) complexes are reduced with strong reducing agents such as sodium hypophosphite or organoaluminum compounds, the nanoparticles formed consist of the metal nuclei stabilized by organophosphorus ligands. When hydrogen is used as a reducing agent, the polynuclear palladium complexes with the phosphide and phosphinidene ligands are formed as a result of the destruction of the organophosphorus ligands. Associates of these complexes form the nucleus, and the Pd(0) clusters are grafted on its surface.

Based on the data obtained, we propose a new way for the synthesis of hydrogenation catalysts, viz. the preparation of the polynuclear palladium complexes with the organophosphorus ligands and the immobilization of Pd(0) clusters on these supramolecular structures. This methodology allows one to readily control the Pd(0) percentage avoiding insoluble palladium phosphides or crystalline palladium.

Hydrogenation Catalysts Based on Polynuclear Palladium Complexes with Organophosphorus Ligands

Polynuclear palladium complexes with diaryl- or dialkylphosphide ligands can be prepared by the interaction of the palladium(II) phosphine complexes $Pd(acac)_2PPh_3$ [24] or similar platinum complexes [25] with formic acid as well as through the reaction of the Pd(II) compounds with secondary phosphines or phosphides of alkali metals [26, 27].

In the operation with the palladium(II) phosphine or phosphite complexes, emphasis should be put on thorough solvent dehydration because tertiary phosphines and phosphates can exhibit reducing properties in the presence of water. In particular, we found that triphenylphosphine reduces palladium *bis*-acetylacetonate only in the presence of stoichiometric amounts of water with respect to palladium and at P/Pd > 1 [28]:

$$Pd(acac)_2 + 5PPh_3 + H_2O$$
$$= Pd(PPh_3)_4 + P(O)Ph_3 + 2H(acac).$$

The redox process between palladium acetate and triethyl- or triphenylphospite occurs in the presence of the corresponding amount of water at any P/Pd ratios [29]. A similar redox process between palladium acetate and triphenylphosphine was found more recently [30].

To prepare the polynuclear palladium complexes with bridging diphenylphosphide ligands and to elucidate their role in the hydrogenation catalysis, we studied the interaction of palladium *bis*-acetylacetonate with excess diphenylphosphine by NMR, IR, and UV spectroscopies.

Unlike tertiary phosphines, the reaction does not stop at the complexation stage but is accompanied by the exchange of the acetylacetonate ligands with the diphenylphosphide fragments and the redox process without water involvement [31]. The cyclic trinuclear palladium complex $[Pd_3(PPh_2)_4(HPPh_2)_2]$ (**V**) containing the bridging and terminal diphenylphosphide ligands, coordinated diphenylphosphine molecules, and free tetraphenyldiphosphile were identified in the reaction medium:

$$Pd(acac)_2 + 2.3HPPh_2$$
$$\xrightarrow[-H(acac),\ -(PPh_2-PPh_2)]{} 1/3[Pd_3(PPh_2)_4(HPPh_2)_2].$$

Table 2. Concentration of Pd(0) in the catalytic system **V** + $nPd(OAc)_2$ before and after styrene hydrogenation

No.	$Pd(OAc)_2$ **V**	Concentration of $Pd(OAc)_2$, %	Concentration of Pd(0) before hydrogenation, %	Concentration of Pd(0) after hydrogenation, %
1	0	0	0	0
2	0.1	9.1	2.5	19.7
3	0.2	16.6	3.7	24.9
4	0.7	41.2	38.8	44.2

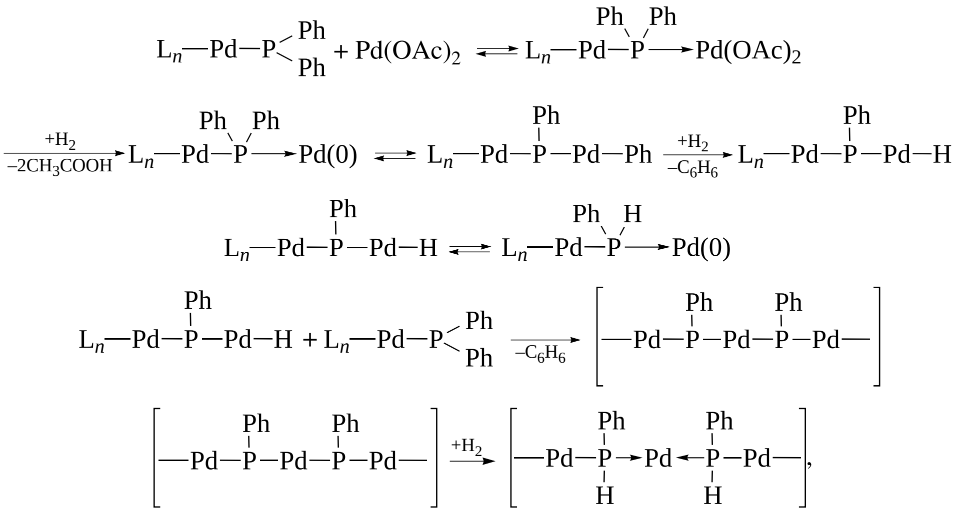
Complex **V** was inactive in hydrogenation at 80°C and P_{H_2} = 1 atm. The destruction of the PPh_2 fragments does not occur under these conditions. The introduction of palladium acetate in the reaction system followed by hydrogen treatment produces a catalytic system that is highly active not only in the hydrogenation of unsaturated bonds (140 mol nitrobenzene (g-atom Pd)$^{-1}$ min^{-1}, 30°C, P_{H_2} = 1 atm) but also in the reduction of a nitro group (85 mol styrene g-atom^{-1} Pd min^{-1}, 30°C, P_{H_2} = 1 atm). The specific activity of this system in nitro group reduction is 50 times greater than that of the nanosized palladium catalyst grafted on an ethylbenzene–divinyl copolymer [32].

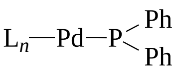
The synergistic effect found for this system depends on the ratio of the starting components and achieves a maximum at the $Pd(OAc)_2$/**V** ratios ranging from 0.2 to 0.5 [23]. Note that the formation of the catalytic system under hydrogen and the formation of the systems considered above was accompanied by the destruction of the organophosphorus ligands. However, the induction period in styrene hydrogenation is observed even after interaction with hydrogen and its duration decreases with increasing the $Pd(OAc)_2$/**V** ratio.

By estimating the Pd(0) concentration in the catalytic system **V** + $x$$Pd(OAc)_2$ at different stages of operation, we found a linear relation between the catalytic activity and the amount of Pd(0) in the range from 0 to 25% (Fig. 3). It was shown that the induction period is due to the absence of Pd(0) in the system [33].

The fraction of Pd(0) in the system increases in the course of hydrogenation (Table 2). Not only palladium introduced as Pd acetate but also a fraction of palladium in the trinuclear complex **V** is reduced. Note that even at a high concentration of palladium acetate in the starting system ($Pd(OAc)_2$/**V** = 0.7), crystalline palladium was not found by XPS in the catalyst after hydrogen treatment.

The data obtained provide evidence that the polynuclear palladium complexes serve not only as a carrier for the Pd(0) clusters but also actively participate in the formation, operation, and deactivation of the catalyst. On the one hand, the destruction of diphenylphosphide ligands results in the transition of Pd(0) to the oxidized state with catalyst poisoning. On the other hand, the newly formed palladium complexes with the phenylphosphinidene ligands regenerate Pd(0) likely by the hydrogenolysis of the Pd–P bond. The above data can be represented by the following scheme:



where  $L_n—Pd—P\begin{smallmatrix}Ph\\Ph\end{smallmatrix}$ is the fragment of the complex.

Thus, the performance of all the considered catalytic systems involves hydrogenation of both the substrates and organophosphorus ligands producing repeated redox processes. The deeper destruction of organophosphorus ligands can result in various palladium phosphides, and this process is accompanied by the formation of insoluble precipitates. In our opinion, this is the main reason for the deactivation of various palladium catalysts with phosphine ligands.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 01-03-32126) and the Ministry of Education of the Russian Federation (project no. UR 05.01.046).

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