CATALYSIS ==

# Preparation of High-Performance Nanosized Palladium Hydrogenation Catalysts Using White Phosphorus and Phosphine

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Abstract—The nature and properties of nanosized palladium hydrogenation catalysts modified with elemental phosphorus and phosphine (PH<sub>3</sub>) were studied.

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Previously were studied the nature of particles active in hydrogenation that were formed by treatment with different reducing agents of palladium(II) complexes with organic phosphines [1-4]. Microheterogeneous nature of these catalysts was revealed, and the key steps of their formation was determined. In particular, the main reactions of palladium(II) phosphine complexes with hydrogen are reduction of Pd(II) to Pd(0) by hydrogenolysis of the Pd-X bonds (X is an acido ligand); degradation of phosphine ligands in the coordination sphere of Pd(0) by oxidative addition of organophosphorus ligands to Pd(0), followed by hydrogenolysis of the Pd-C bond with hydrogen and formation of polynuclear palladium phosphine and phosphinidene complexes (in the limiting case, palladium phosphides, Pd<sub>6</sub>P and Pd<sub>4.8</sub>P); and formation of Pd(0) clusters [2, 3]. Active in hydrogenation are Pd(0) clusters or cluster palladium hydrides  $[Pd_rH_v]$  immobilized on polynucliear palladium complexes with phosphide and posphinidene ligands or on palladium phosphides. Since formation of Pd(II) phosphine complexes involves stepwise degradation of organophosphorus ligands to form a heterophase system containing in the limiting case palladium phosphides of different composition and Pd(0) clusters, we suggested that phosphine (PH<sub>3</sub>) and white phosphorus  $(P_{4})$  can be used to modify the catalyst. This approach can simplify preparation of nanosized palladium hydrogenation catalysts. The aim of this study was to examine the nature and catalytic properties of the systems prepared by treatment with molecular hydrogen of mixtures of palladium bisacetylacetonate with white phosphorus or phosphine.

### **EXPERIMENTAL**

The solvents and chemicals were purified by standard procedures used in handling of organometallic compounds [5]. Benzene was additionally dried by distillation from  $\text{LiAlH}_4$  on a column and was stored in an argon atmosphere in sealed ampules over 4A molecular sieves.

To remove water and amine impurities, dimethylformamide was kept over anhydrous copper sulfate until a green solution was formed. Then the solvent was double-distilled in a vacuum (3 mm Hg) at temperature no higher than 42°C.

Palladium bisacetylacetonate was prepared by the procedure described in patent [6]. <sup>1</sup>H NMR:  $\delta$ (CH) = 5.04 ppm (s, 1H),  $\delta$ (CH<sub>3</sub>) = 1.76 ppm (s, 6H).

To prepare phosphine, a solution of 25 g of KOH in 25 ml of water was added dropwise to a suspension of 10 g of red phosphorus in 30 ml of toluene, preheated to ~110°C [7]. The liberating gas was successively passed through a Tishchenko bottle filled with a 50% solution of an alkali in an H<sub>2</sub>O + DMSO mixture to remove diphosphine impurities and then through columns packed with NaOH and P<sub>2</sub>O<sub>5</sub> to remove water traces. Phosphine was collected by dissolution in benzene placed in a finger-like vessel. The phosphine concentration in the benzene solution was determined by <sup>31</sup>P NMR spectroscopy using 85% H<sub>3</sub>PO<sub>4</sub> as external reference; <sup>31</sup>P NMR:  $\delta_P = -238$  ppm (q,  $J_{PH} = 188$  Hz).

To remove surface oxidation products of white phosphorus, it was washed with anhydrous benzene. A benzene solution of white phosphorus was prepared and stored under an inert atmosphere in a finger-like vessel. The design of this vessel allows evacuation and filling with argon. <sup>31</sup>P NMR:  $\delta_P = 523$  ppm.

Catalytic hydrogenation was performed in a duckshaped vessel thermostated at 30°C at the initial hydrogen pressure of 1 atm in the presence of the catalytic system formed in situ. To a solution of  $Pd(acac)_2$  (0.00304 g,  $1 \times 10^{-5}$  mol) in DMF (9 ml) placed in a duck-shaped vessel, a solution of phosphine  $(0.3 \times 10^{-5} \text{ mol})$  in benzene (1 ml) was added dropwise in a hydrogen stream. The mixture was stirred for 5 min at room temperature. Then the system was heated to 80°C with stirring in a hydrogen stream. The resulting black-brown "solution" was cooled to 30°C. A substrate was injected with a syringe. It was hydrogenated with vigorous stirring to exclude the diffusion control of the reaction. The reaction course was monitored by GLC. The experiments at other P/Pd ratios and preparation of the palladium catalyst modified with white phosphorus were performed similarly. The optimal time required for preparing  $Pd(acac)_2 - nP_4$  catalytic system at 80°C was 25–30 min.

The palladium catalysts modified with white phosphorus were prepared in a temperature-controlled duck-shaped glass vessel in hydrogen at 80°C. To a solution of Pd(acac)<sub>2</sub> (0.761 g,  $2.5 \times 10^{-3}$  mol) in DMF (90 ml), a solution of phosphine (0.75  $\times$  $10^{-5}$  mol) (P/Pd = 0.3) in benzene (25 ml) was added drop-wise in a hydrogen stream. The mixture was stirred at a hydrogen pressure of 1 atm and 80°C for 15 min. The solution color changed to dark brown in 2-5 min. After reaction completion, the black suspension was cooled to room temperature and was transferred under an inert atmosphere into a finger-like vessel. Then the solvent was removed in a vacuum (2/3 of the volume). Ether was added until a precipitate was formed. The precipitate was washed with ether in an argon atmosphere and was dried in a vacuum (50°C/1 mm Hg). Yield 0.235 g. Elemental analysis, %: Pd 87.88; P 3.59; C 0.99; H 0.25. IR: no absorption in the range 4000-400 cm<sup>-1</sup>.

Analysis for Pd and P was performed as follows. A weighed portion of the sample (about 0.01 g) was dissolved in 2 ml of boiling  $HNO_3$ . The resulting solution was diluted with water to 50 ml in a volumetric flask. The palladium concentration was determined by atomic absorption spectroscopy on a Perkin–Elmer 403 spectrometer in a propane–air flame. The phosphorus content was determined photocolorimetrically by the standard procedure [8].

The catalyst samples were studied by powder X-ray

diffraction on a DRON-3M diffractometer using  $CuK_{\alpha}$  radiation. The NMR spectra were recorded on a VXR-500S Varian pulse spectrometer. The <sup>31</sup>P chemical shifts are given relative to 85% phosphoric acid.

The samples were studied by transmission electron microscopy (TEM) on a BS-300 microscope (Czech Republic). A drop of the solution was applied onto a gauze coated with a carbon film and was dried in an argon atmosphere. The electron micrographs were taken under conditions excluding melting and degradation of the samples on exposure to an electron beam.

The procedure for determining Pd(0) is described in [9].

Previously we showed [1-4, 10] that palladium(II) β-diketonate-phosphine complexes became catalytically active in hydrogenation reactions only after their activation with a reducing agent, e.g., with molecular hydrogen. To compare the catalytic properties of the catalysts derived from palladium bisacetylacetonate [Pd(acac)<sub>2</sub>] modified with white phosphorus and phosphine with those of palladium(II) complexes with organic phosphines (PPh<sub>3</sub>, PHPh<sub>3</sub>, PH<sub>2</sub>Ph), these catalysts were prepared similarly in a hydrogen atmosphere at 80°C. It should be noted that at a lower temperature the rate of  $Pd(acac)_2$  reduction is lower (Table 1). The properties of palladium catalysts modified with phosphine or white phosphorus were studied in relation to different parameters. It was found that the dependences of the specific activity in styrene hydrogenation on the P/Pd ratio passed through maxima. The most active catalysts are formed at similar ratio P/Pd = 0.3 (Fig. 1). We observed the similar dependence for the Pd(acac)<sub>2</sub>-PH<sub>2</sub>Ph system [10]. The influence of organophosphorus compounds on the catalytic activity of Pd(acac)<sub>2</sub> decreases in the following order:  $P_4 \cong PH_2Ph$  [10] >  $PH_3$  >  $PHPh_2$  [11] >  $PPh_3$ [3].

The most active promoters are white phosphorus and phenylphosphine, all catalytic reaction conditions being the same; the phosphine is slightly less effective; the palladium bisacetylacetonate + triphenylphosphine system exhibits the lowest catalytic activity in alkene hydrogenation (Fig. 2).

It should be noted that the specific activity of the palladium catalysts modified with phosphine (PH<sub>3</sub>) increases with decreasing palladium concentration and reaches a maximum [330 (mol styrene) (g-at. Pd)<sup>-1</sup> min<sup>-1</sup>] at  $C_{Pd} = 5 \times 10^{-4}$  M. Nonlinear dependence of the reaction rate on the Pd(acac)<sub>2</sub> concentration in the case of the catalyst modification with both phosphine and phosphorus (Fig. 3) suggests associa-

Conditions of catalyst preparation in hydrogen			W, (mol H <sub>2</sub> ) (mol Pd) <sup>-1</sup> min <sup>-1</sup>	
<i>T</i> , °C	time, min		Dd(agag) DU	Dd(agag) D
	Pd(acac) <sub>2</sub> –PH <sub>3</sub>	Pd(acac) <sub>2</sub> –P <sub>4</sub>	$ru(acac)_2 - rn_3$	$ru(acac)_2 - r_4$
30	15	25	0	0
50	15	25	0	0
70	15	25	166	0
		40		181
80	15	25	190	280
90	15	25	56	137

**Table 1.** Hydrogenation of styrene in the presence of palladium catalysts modified with phosphine and white phosphorus.  $C_{Pd} = 1 \text{ mM}, \text{ P/Pd} = 0.3, \text{ [substrate]/Pd} = 870, \text{ solvent DMF}, T = 30^{\circ}\text{C}, P_{H_2} = 1 \text{ atm}$ 

**Table 2.** Specific hydrogenation activity of palladium catalysts modified with phosphorus and phosphine.  $C_{Pd} = 1 \text{ mM}$ , solvent DMF,  $V_{DMF} = 10 \text{ ml}$ , P/Pd = 0.3,  $T = 30^{\circ}\text{C}$ ,  $P_{H_2} = 1 \text{ atm}$ 

Substrate mal	W, (mol H <sub>2</sub> ) (mol Pd) <sup>-1</sup> min <sup>-1</sup>		Product yield, %	
Substrate, mor	Pd(acac) <sub>2</sub> –PH <sub>3</sub>	Pd(acac) <sub>2</sub> –P <sub>4</sub>	Pd(acac) <sub>2</sub> –PH <sub>3</sub>	Pd(acac) <sub>2</sub> –P <sub>4</sub>
Styrene, 8.7 Phenylacetylene, 9.1 Nitrobenzene:	190 59	280 157	Ethylbenzene, 100 Ethylbenzene, 100	Ethylbenzene, 100 Ethylbenzene, 100
4.9 2.4	21	64 128	Aniline, 100	Aniline, 100 Aniline, 100
Benzaldehyde, 9.8	1*	15*	Benzyl alcohol, 95; toluene, 5	Benzyl alcohol, 94; toluene (-)

\*  $c_{\rm Pd} = 5 \, {\rm mM}.$ 



**Fig. 1.** Hydrogenation of styrene in the presence of palladium catalysts modified with (*1*) white phosphorus and (2) phosphine.  $C_{Pd} = 1 \text{ mM}$ , [substrate]/Pd(acac)<sub>2</sub> = 870, solvent DMF,  $T = 30^{\circ}$ C,  $P_{H_2} = 1 \text{ atm.}$  (*W*) Specific activity; the same for Fig. 2.

tion of reactive palladium species in less active aggregates and microheterogeneity of the catalysts.

Palladium species modified with white phosphorus and phosphine are highly active and selective catalysts of hydrogenation of acetylene derivatives and nitroand carbonyl groups (Table 2). For example, phenylacetylene is successively hydrogenated to styrene and ethylbenzene without its side di- or oligomerization.



Fig. 2. Influence of the modifier on the specific activity of palladium hydrogenation catalysts.

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**Fig. 3.** Rate of styrene hydrogenation *R* in the presence of catalysts formed by reduction of (*1*)  $Pd(acac)_2-PH_3$  and (2)  $Pd(acac)_2-P_4$  systems as a function of palladium concentration. Solvent DMF, P/Pd = 0.3,  $T = 30^{\circ}C$ ,  $P_{H_2} = 1$  atm, [substrate] =  $8.7 \times 10^{-3}$  mol.

At 96% conversion of phenylacetylene, the selectivity with respect to styrene is 94–95%. Nitrobenzene is selectively reduced to aniline.

Thus, the activity of the palladium catalysts modified with white phosphorus and phosphine (PH<sub>3</sub>) is not only similar to, but in some cases even higher than that of the previously studied nanosized palladium catalysts prepared from palladium complexes with organic phosphines (PHPh<sub>2</sub>, PPh<sub>3</sub>).

The most active hydrogenation catalysts prepared by treatment of  $Pd(acac)_2 + 0.3PH_3$  (or P<sub>4</sub>) system with molecular hydrogen were studied by X-ray diffraction and TEM.

As determined by TEM, the reaction of the  $Pd(acac)_2 + 0.3PH_3$  system with hydrogen yields a microheterogeneous system containing mainly highcontrast particles 7.2-7.8 nm in diameter (Fig. 4a). When the time of hydrogen treatment increases from 15 to 30 min, the system becomes more structured (Fig. 4b). The loose and dendritic structure observed in the micrographs is typical for fractal clusters [12]. These clusters are formed by self-aggregation of nanoparticales of similar size in the absence of stabilizing factors. It should be noted that, in the course of formation of microheterogeneous hydrogenation catalysts in the presence of phosphine ligands, fractal clusters were observed for the first time. Palladium particles formed by reduction of palladium(II) complexes in the presence of tertiary [3], secondary [11], or primary phosphines [10] are more stable to aggregation.

The composition of the black precipitate (sample I) isolated from  $Pd(acac)_2-0.3PH_3$  system is described by the empirical formula  $Pd_{7.5}P_{1.07}H_{2.1}$ . As deter-

mined by X-ray diffraction, the precipitate is a heterophase mixture containing palladium phosphides of various compositions: Pd<sub>6</sub>P (d/n 2.696, 2.583, 2.368, 2.291, 2.256, 2.232, 2.093, 1.998 Å), Pd<sub>4.8</sub>P (d/n 2.439, 2.327, 2.256, 2.232, 2.122, 1.998 Å), Pd<sub>5</sub>P<sub>2</sub> (d/n 2.734, 2.696, 2.439, 2.291, 2.256, 2.232, 2.122, 1.993, 1.858, 1.432 Å) and crystalline palladium (d/n 2.256, 1.950, 1.375 Å) [13]. Palladium phosphides Pd<sub>6</sub>P and Pd<sub>4.8</sub>P prevail in the sample. The fraction of reduced palladium determined by the chemical method is 31%. Knowing the total content of palladium, and the composition of palladium phosphides, we can describe the composition of sample I by the empirical formula

 $[{Pd(0)}_{2,33}{Pd_6P}_{0,40}{Pd_{4,8}P}_{0,55}{Pd_5P_2}_{0,026}].$ 

The carbon and hydrogen in the sample most likely originate from the residual solvent (DMF). Hence, the composition will be described by the formula

 $[{Pd(0)}_{2.33}{Pd_6P}_{0.40}{Pd_{4.8}P}_{0.55}{Pd_5P_2}_{0.026}{DMF}_{0.3}].$ 

X-ray diffraction analysis of the catalyst prepared in the presence of white phosphorus  $[Pd(acac)_2-0.3P]$ shows that the sample consists of palladium phosphide Pd<sub>6</sub>P, crystalline palladium, and palladium hydride  $PdH_{0.7}$  [13]. The fraction of reduced palladium, determined by the chemical procedure, is 25%. It should be noted that reduction of Pd(acac)<sub>2</sub> with hydrogen is an autocatalytic reaction, with the induction period in the presence of white phosphorus increasing from 7 to 18 min. This fact can be explained as follows. Palladium atoms formed in the first steps of hydrogen reduction react with white phosphorus to form palladium phosphides which are not capable to activate molecular hydrogen. After the phosphorus is completely bound into palladium phosphides,  $Pd(acac)_2$  is autocatalytically reduced with hydrogen.

Thus, the general feature of formation of hydrogenation catalysts in the system in question is formation of palladium phosphides of different compositions and reduced palladium in the amount of about 25–30%. It should be noted that palladium phosphides as modifiers of organic phosphines, in particular phenyl- and triphenylphosphine, are formed after almost complete degradation of the organophosphorus ligand during treatment of the catalyst with molecular hydrogen at the molar ratio P/Pd  $\leq 0.5$  [3, 10, 14]. However, a long time required for reduction of Pd(acac)<sub>2</sub> with hydrogen in the presence of PH<sub>3</sub> and low stability of the resulting nanoparticles to aggrega-



Fig. 4. Electron micrograph of the  $Pd(acac)_2-0.3PH_3$  system treated with hydrogen at 80°C and particle size distribution. (d) Particle size. Treatment time, (a) 15 and (b) 30.

tion lead to a sharp decrease in the activity of the catalyst as compared to the catalysts prepared from  $Pd(acac)_2$  and  $P_4$ ,  $PH_3$ , and  $PH_2Ph$ .

To determine the mechanism of the promoting effect of the ogranophosphorus compounds on the catalytic properties of the palladium hydrogenation catalysts, we compared the fraction of the surface atoms for the Pd(acac)<sub>2</sub>–0.3PH<sub>3</sub> catalytic system and that of Pd black formed under the similar conditions from Pd(acac)<sub>2</sub>.

The size of Pd black particles determined by TEM is 25–30 nm, which is larger by a factor of almost 4 than that of particles formed in the  $Pd(acac)_2$ –0.3PH<sub>3</sub> system. It is known that the fraction of the surface atoms for metal particles 8–10 nm in diameter is 20–15%, and it decreases to 3–2% with increasing particle size to 25–30 nm [15]. The increase in the fraction of the surface atoms by a factor of 7 (on the average) correlates with the promoting effect of phos-

phine. Hence, formation of more finely dispersed system can be one of the reasons determining the promoting effect of phosphine. The assumption that the promoting effect of phosphine is due to an increase in the catalyst dispersity is well consistent with the experimental data for the case when Pd(0) atoms are located on the nanoparticle surface. Based on the results obtained, we suggest that microheterogeneous hydrogenation catalysts consist of nanoparticles whose cores are formed by palladium phosphides with Pd(0) clusters immobilized on the surface.

It should be noted that the high activity of nanosized palladium hydrogenation catalysts cannot be solely due to a small particle size. In particular, the particles of microheterogeneous palladium catalysts prepared from palladium complexes with organic phosphines are smaller (3–5 nm [3, 10]) than particles of the examined systems, but, as noted above, their catalytic activity is lower.

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This is due to the fact that transformation of palladium phosphine complexes under the action of molecular hydrogen is a complex multistep process. The general feature of formation of hydrogenation catalysts from Pd(acac)<sub>2</sub> and different phosphines in hydrogen is not only formation of microheterogeneous systems but also oxidation of palladium particles after degradation of the phosphorus-containing ligands or reaction of Pd(0) with elemental phosphorus. The ratio of oxidized and reduced palladium changes depending on the ratio of the reduction rates of Pd(II) complexes, aggregation of reduced palladium particles, and degradation of phosphorus-containing fragments in the coordination sphere of Pd(0). In addition, the electron density on Pd(0) clusters can change after their immobilization on palladium phosphides. The structure and catalytic properties of the palladium nanoparticles depend on all of these factors. The particles formed after hydrogen treatment of  $Pd(acac)_2$ modified with phosphine and elemental phosphorus have similar structure and a high content of reduced palladium, and hence their catalytic properties in hydrogenation are similar.

## CONCLUSIONS

(1) White phosphorus and phosphine  $(PH_3)$  were used for the first time as modifiers in synthesis of effective palladium hydrogenation catalysts whose catalytic activity is not only similar to, but in some cases higher than that of nanosized palladium hydrogenation catalysts prepared from palladium complexes with organic phosphines.

(2) Reaction of  $Pd(acac)_2$  with hydrogen in the presence of phosphine (PH<sub>3</sub>) and white phosphorus yields Pd(0) and palladium phosphides of various compositions.

(3) The promoting effect of phosphine is caused, in particular, by smaller particle size of the catalysts prepared from  $Pd(acac)_2$  as compared to Pd black.

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