# Effect of the State of a Surface Layer on the Properties of Pd—P Catalysts in the Hydrogenation of Alkylanthraquinones

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Abstract—X-ray photoelectron spectroscopy (XPS) was used to study the state of the surface layer of a Pd–P catalyst, which exhibits high selectivity in the hydrogenation of 2-ethyl-9,10-anthraquinone. The preparation of the catalyst from Pd(acac)<sub>2</sub> and white phosphorus in hydrogen in a toluene–1-octanol solution led to the formation of Pd–P nanoparticles whose surface was enriched in electron-deficient palladium, apparently, as a constituent of an amorphized 2D layer based on a solid solution of Pd and P. Octyl esters of phosphoric acids, adsorbed on the surface, acted as stabilizers. A relationship between the properties of the Pd–P catalyst in the hydrogenation of 2-ethyl-9,10-anthraquinone and the state of the surface layer was considered.

*Keywords:* hydrogenation, 2-ethyl-9,10-anthraquinone, palladium–phosphorus catalysts, selectivity, XPS **DOI:** 10.1134/S0023158419060028

# INTRODUCTION

Chemoselective hydrogenation of alkylanthraquinones to alkylanthrahydroquinones and the subsequent oxidation of alkylanthraquinones with oxygen is the main industrial method for the production of hydrogen peroxide [1]



Alkilantraquinones

Alkilantrahydroquinones

In this case, the hydrogenation of alkylanthraquinones is invariably accompanied by side reactions, which decrease the yield of the target product. These side reactions primarily include the hydrogenation of aromatic rings and the hydrogenolysis of C–OH bonds in the resulting alkylanthrahydroquinone [2]. Various approaches are used to increase the yield of hydrogen peroxide. In order to reduce the contribution of side processes in industry, the catalytic hydrogenation of alkylanthraquinone is not carried out until its complete conversion, and the conversion of alkylanthraquinone usually does not exceed 60% [2]. In this regard, it is reasonable to develop new highly selective catalysts that reduce only the carbonyl groups of alkylanthraquinones without accelerating the hydrogenolysis of C–OH bonds in alkylanthrahydroquinones and without affecting the aromatic rings.

**Abbreviations:** CSR, coherent scattering region; HR TEM, high-resolution transmission electron microscopy; XRD, X-ray diffraction; FWHM, full width at half maximum of spectral lines; EDX, energy-dispersive X-ray spectroscopy.

Supported palladium catalysts are predominantly used as catalysts for the hydrogenation of alkylanthraquinones, and their selectivity is changed by adding promoters [3] or by modifying the support surface [4, 5]. Colloidal solutions of nanoparticles are the most convenient models for studying catalytic systems and optimizing their properties. Previously, Sterenchuk et al. [6] used the colloidal solutions of Pd as an example to found that the catalyst selectivity in the hydrogenation of 2-ethyl-9,10-anthraquinone cannot be increased only by changing the particle size of palladium. Along with the hydrogenation of C=O groups in 2-ethyl-9,10-anthraquinone, large star-like palladium crystallites ( $\sim d = 127$  nm) accelerated predominantly the hydrogenolysis of C-OH bonds, while small palladium nanoclusters (d = 1.5-2.5 nm) catalyzed the hydrogenation of aromatic rings in 2-ethyl-9,10-anthrahydroquinone. Modification of the palladium catalyst with phosphorus made it possible to increase the vield of hydrogen peroxide from 69 to 96-98% [6].

In this work, we studied the phase composition and the state of a surface layer of the Pd–P catalyst in order to determine the causes of the modifying effect of phosphorus on the properties of palladium catalysts for hydrogenation.

## **EXPERIMENTAL**

#### Materials

Solvents (benzene, toluene, and 1-octanol) were purified in accordance with standard procedures [7]. For deeper drying, benzene and toluene were additionally distilled from LiAlH<sub>4</sub> using a fractionating column. 1-Octanol was twice distilled (conventional distillation and distillation from sodium octylate) in a vacuum (2 Torr) at 59°C. All of the solvents were stored in an atmosphere of argon in sealed ampoules over 4A molecular sieves.

Bis(acetylacetonato)palladium(II)  $Pd(acac)_2$  was prepared according to a published procedure [8] with the subsequent recrystallization from acetone.

White phosphorus was mechanically cleaned of surface oxidation products and washed in anhydrous benzene immediately before use. A solution of white phosphorus in benzene was prepared and stored in an inert atmosphere in a Schlenk flask, which was pre-evacuated and filled with argon. <sup>31</sup>P NMR ( $\delta$ , ppm): -520 s.

#### Pd-P Catalyst Preparation Methods

**Method 1.** A Pd–P (in situ) catalyst for analysis by high-resolution transmission electron microscopy (HR TEM) was prepared by the same method as that used for studying its properties in the hydrogenation of 2-ethyl-9,10-anthraquinone. To a solution of Pd(acac)<sub>2</sub> (0.0152 g,  $5 \times 10^{-5}$  mol) in 7 mL of toluene placed in a thermostatically controlled thermostated 'duck' type glass vessel, 1 mL of a solution of phosphorus in benzene  $(1.5 \times 10^{-5} \text{ mol} \text{ in terms of the}$ atomic form of phosphorus) was added dropwise in a stream of hydrogen, and the contents were stirred at room temperature for 5 min. Then, 1-octanol (10 mL) was added; the temperature was raised to 90°C, and the catalyst was formed with vigorous stirring of the reaction mixture in hydrogen for 30–45 min until the quantitative conversion of Pd(acac)<sub>2</sub>. The conversion of Pd(acac)<sub>2</sub> was monitored by UV spectroscopy using an absorption band at 330 nm ( $\varepsilon_{330} = 10630 \text{ L cm}^{-1} \text{ mol}^{-1}$ ). The resulting black-brown colloidal solution was cooled to 30°C. A drop of the Pd–P catalyst solution was applied onto carbonized copper gauze (200 mesh) and dried at room temperature in a box with an inert atmosphere.

Method 2. A Pd–P catalyst for studying by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analysis was prepared as follows: To a solution of Pd(acac)<sub>2</sub> (0.4566 g,  $1.55 \times 10^{-3}$  mol) in 68 mL of toluene placed in a thermostatically controlled long-neck flask, 3.1 mL of a solution of phosphorus in benzene  $(4.5 \times 10^{-4} \text{ mol in terms of the})$ atomic form of phosphorus) was added dropwise in a stream of hydrogen, and the contents were stirred at room temperature for 5 min. Then, 1-octanol (44.5 mL) was added; the temperature was raised to 90°C, and the catalyst was formed with vigorous stirring of the reaction mixture in hydrogen for 30-45 min until the quantitative conversion of  $Pd(acac)_2$ . At the end of the reaction, the catalyst system formed was cooled to room temperature and transferred into a finger-type vessel in an inert atmosphere. Solvents (2/3 of the volume) were distilled off in a vacuum, and diethyl ether was added until the formation of a black precipitate. The precipitate was sequentially washed with benzene and diethyl ether in an atmosphere of argon and dried in a vacuum ( $50^{\circ}C/1$  Torr). The yield was 0.1090 g.

#### Research Methods

The UV spectra of the catalyst solutions were measured on an SF-2000 spectrophotometer (Russia) in quartz cells with an optical path length of 0.01 cm. The conversion of Pd(acac)<sub>2</sub> was monitored based on an absorption band at 330 nm ( $\epsilon_{330} = 10630 \text{ L cm}^{-1} \text{ mol}^{-1}$ ).

Additionally, the interaction products of Pd(acac)<sub>2</sub> with elemental phosphorus were analyzed on a GCMS-QP2010 Ultra Shimadzu chromatography– mass spectrometry instrument (Japan) equipped with a 30-m GsBP-5MS capillary column with a poly(5% diphenyl, 95% dimethylpolysilphenylene siloxane) phase. Electron impact ionization was used, and the ionization energy was 70 eV. The experimental mass spectra were compared with published data (Wiley, NIST, and NIST05 reference libraries). The XRD analysis of the Pd–P catalyst sample was performed on a Shimadzu XRD-7000 S diffractometer (Cu $K_{\alpha}$  radiation; Ni filter;  $\lambda = 1.5418$  Å).

The TEM images were obtained on a Tecnai  $G^2$  electron microscope (FEI, the United States) with an accelerating voltage of 200 kV. The images were recorded using a CCD camera (Soft Imaging System, Germany). The microscope was equipped with an energy-dispersive X-ray characteristic spectrometer (EDX, Phoenix) with a semiconductor Si(Li) detector. The parameters of particle images were measured using the iTEM 5.0 and DigitalMicrographs 1.94.1613 software. The fast Fourier transformation (FFT) and inverse fast Fourier transformation (IFFT) methods were used for analyzing periodic structures and filtering the images. An area containing at least 100 particles was treated to find the average size.

The XPS spectra were measured on a PHOIBOS 150 MCD 9 photoelectron spectrometer (SPECS, Germany) using monochromated Al $K_{\alpha}$  radiation from an X-ray tube (1486.74 eV). The survey spectrum was recorded with a step of 1 eV at an analyzer transmission energy of 20 eV, and high-resolution spectra (narrow scans), with a step of 0.1 eV and a transmission energy of 10 eV. The C1s line (285.0 eV) of carbon was used as a reference. Nonuniform charging was eliminated by irradiating the sample with slow electrons. The samples were etched with Ar<sup>+</sup> ions for 2 min using a PU-IQE 12/38 ion source (SPECS) at an accelerating voltage of 2.5 kV and an ion current of 20 µA, which ensured an etching rate of ~1 nm/min. The experimental data were processed using the CasaXPS program. The spin–orbital splitting of the  $Pd3d_{5/2-3/2}$  and  $P2p_{3/2-1/2}$  doublet lines was approximated by two Lorentz-Gaussian curves with doublet separations of 5.26 and 0.84 eV, respectively, at area ratios of 3/2 for  $Pd3d_{5/2-3/2}$  and 2/1 for  $P2p_{3/2-1/2}$ . The full width at half maximum (FWHM) of  $\leq 1.5$  eV of the spectral lines was taken according to published data for analogous substances and similar conditions used for measuring the spectra. We assumed that, if the FWHM exceeded 1.5 eV (1.2 eV for phosphorus), these lines should be approximated by several curves corresponding to different chemical species of the element. Because the oxygen 1s spectral line strongly overlaps with the palladium  $3p_{3/2}$  line, the number of chemical forms of palladium and the position of their lines were connected with the second  $Pd3p_{1/2}$  doublet line in the survey spectrum.

# **RESULTS AND DISCUSSION**

The introduction of phosphorus before the stage of  $Pd(acac)_2$  reduction with hydrogen affects the activity and selectivity of the palladium catalyst in the hydro-



**Fig. 1.** Effect of the phosphorus content on the properties of the Pd catalyst in the hydrogenation of 2-ethyl-9,10-anthraquinone: (*I*) the yield of  $H_2O_2$  and (*2*) the catalyst activity. [Pd] = 2.5 mmol/L; [2-ethyl-9,10-anthraquinone]/[Pd] = 42.3; solvent, 10 mL of 1-octanol + 10 mL of toluene; 50°C;  $P_{H_2} = 2$  atm.

genation of 2-ethyl-9,10-anthraquinone [6]. At P : Pd ratios of 0.3-1.0, phosphorus decreased the activity of the palladium catalyst in the hydrogenation of 2-ethyl-9,10-anthraquinone by almost an order of magnitude; in this case, the yield of hydrogen peroxide increased from 69% (Pd black) to 96-98% (Fig. 1). According to the TEM data, the average particle size of the Pd-P catalyst (P : Pd = 0.3) was almost 3.5 times smaller than that of the Pd black (Fig. 2); therefore, such a sharp drop in the activity of the Pd-P catalyst compared to that of the Pd black cannot be associated with a difference in dispersity. To experimentally substantiate the reasons for the modifying action of phosphorus, the state of a surface layer of the Pd-P catalyst formed in toluene-1-octanol solution was studied by XPS.

The surface composition of the palladium catalyst was represented by four elements: Pd, P, C, and O. Table 1 summarizes concentration ratios between the chemical forms of the elements. The initial spectrum of the Pd3d line consists of three  $3d_{5/2-3/2}$  spin-orbital doublets characterizing various chemical states of palladium (Fig. 3a). The binding energy of electrons of the high-intensity  $Pd3d_{5/2}$  component with a maximum at 335.5 eV corresponds to palladium similar to palladium in the reduced state Pd(0), conventionally designated as  $Pd^{\delta+}$  [9]. Shifts in the binding energies of the other two components (335.8 and 337.4 eV) relative to the binding energy of the  $Pd3d_{5/2}$  level of the bulk metal (335.2 eV [9]) indicate a positive charge on palladium. The  $Pd3d_{5/2}$  binding energy of 337.4 eV is characteristic of Pd<sup>2+</sup> in Pd(acac)<sub>2</sub> [10, 11]. The con-



Fig. 2. TEM images of (a) Pd black and (b) the Pd-P catalyst. The insets (a, b) show the electron diffraction spectra.

centration of the Pd(acac)<sub>2</sub> precursor among three different forms of palladium did not exceed 5.2%.

The main chemical state of palladium (72 at %) in the Pd–P catalyst is represented by a component with a Pd3 $d_{5/2}$  binding energy of 335.8 eV (Table 1). The electron-deficient form of palladium can result from the formation of a 2D surface palladium oxide  $(E_{\rm b}({\rm Pd}3d_{5/2}) = 335.5 \text{ eV}, E_{\rm b}({\rm O}1s) = 528.9 \text{ eV} [12]),$ small palladium clusters ( $E_{\rm b}({\rm Pd}3d_{5/2}) = 336.1$  eV for Pd<sub>10</sub> [13]), palladium phosphide, or a solid solution  $(E_{\rm b}({\rm Pd}3d_{5/2}) = 335.8 - 336.2 \text{ eV})$  [14, 15]. The absence of the O1s component with a maximum at 528.9 eV from the XPS spectrum (Table 1, Fig. 4c) excludes the formation of 2D surface palladium oxide. This con-

Table 1. Binding energies and concentrations of the elements in various states in the surface layers of the Pd-P catalyst isolated from the  $Pd(acac)_2 - 0.3P - H_2$  system after etching with argon

Spectral line	Binding energy, eV	FWHM, eV	Element concentration, at %		The most probable chemical species*
Pd3 <i>d</i> <sub>5/2</sub>	335.5	0.7	13.6	3.1	$Pd^{\delta^+}(0.23)^{**}$
	335.8	0.9		9.8	$Pd_{x}P(0.72)$
	337.4	1.5		0.7	$Pd(acac)_2 (0.05)$
P2p <sub>3/2</sub>	130	0.6	9.2	3.2	$Pd_{x}P(0.35)$
	131.1	1.2		1.2	$Pd^{\delta+}-P(0.13)$
	133.5	1.2		1.7	$R-O-PO_3^{2-}(0.18)$
	134.6	1.2		3.1	$PO_4^{3-}(0.34)$
O1s	532.4	2.80	16.5	_	$\mathrm{Pd}3p_{3/2}(\mathrm{Pd}^{\delta+},\mathrm{Pd}_{x}\mathrm{P})$
	533.1	1.70		16.5	O-C+O-P+O=C (1.0) (R-O-PO <sub>3</sub> <sup>2-</sup> , R-OH, Pd(acac) <sub>2</sub> )
	534.5	3.3		_	$Pd3p_{3/2} (Pd(acac)_2)$
C1s	285.0	1.4	60.7	50.6	$C-C + CH_2 + CH_3 (0.83)$
					$(R-O-PO_3^{2-}, R-OH, Pd(acac)_2)$
	286.8	1.2		7.2	С-О-Р (0.12)
					(R–O–PO <sub>3</sub> <sup>2–</sup> , R–OH)
	289.1	1.1		2.9	$C=O + CO_2 (0.05) (Pd(acac)_2)$

\* The atomic fraction of this chemical species is indicated in parentheses. \*\* The form  $Pd^{\delta^+}$  is similar to palladium in the reduced state Pd(0).



**Fig. 3.** (a, b) Pd3*d* and (c, d) P2*p* XPS spectra of the Pd–P catalyst (a, c) before and (b, d) after etching with argon. The broken line represents the experimental spectrum. The line enveloping the experimental spectrum corresponds to the sum of the decomposition components of the XPS line, and marked lines correspond to the components of XPS line decomposition into the chemical forms of (a, b) palladium (Pd<sup>0</sup>, Pd<sub>x</sub>P, and Pd(acac)<sub>2</sub>) or (c, d) phosphorus.

clusion was also confirmed by the quantitative analysis of the surface composition after etching with argon (Table 2).

At the same time, the phosphorus 2p XPS spectrum of the Pd–P catalyst consisted of four  $P2p_{3/2-1/2}$  spin–orbital doublets with the following positions of the maxima of the high-intensity component  $P2p_{3/2}$ : 130, 131.1, 133.5, and 134.6 (Fig. 3c). The  $P2p_{3/2}$  binding energies of 133.5 and 134.6 eV indicate the presence of the oxidized forms of tetracoordinated pentavalent phosphorus (R–O–PO<sub>3</sub><sup>2–</sup>, PO<sub>4</sub><sup>3–</sup>) on the surface [16], whereas the positions of maximums at 130 and 131.1 eV are characteristic of elemental phosphorus ( $E_b(P2p_{3/2}) = 129.9-130.4 \text{ eV}$ ) [17, 18], phosphorus in alloys ( $E_b(P2p_{3/2}) = 130.1 \text{ eV}$ ) and transition metal phosphides ( $E_b(P2p_{3/2}) = 128.5-130 \text{ eV}$ ) [17, 19], or a nanoscale (several monolayers) disordered (insufficiently coordinated amorphous) 2D surface

layer based on a solid solution of Pd and P. It is difficult to make a conclusion on the nature of surface compounds because the  $P2p_{3/2}$  binding energies in various metal phosphides and in solid solutions are similar. Based on the relative atomic concentrations of phosphorus and palladium (Table 1), the empirical formula of the main surface compound  $Pd_xP$ , characterized by binding energies of 335.8 eV (Pd3 $d_{5/2}$ ) and 130 eV (P2 $p_{3/2}$ ), can be represented as Pd<sub>3.06</sub>P. The empirical formula Pd<sub>3.06</sub>P of the surface compound corresponds to the composition of a palladium phosphide, Pd<sub>3</sub>P or Pd<sub>3</sub>P<sub>0.8</sub> [20], but the X-ray phase analysis data given below are inconsistent with the formation of the bulk phase of crystalline palladium phosphide.

The diffraction curve of the Pd–P catalyst exhibited two broad reflections at  $2\theta$  angles of  $39.59^{\circ}$  and  $71.21^{\circ}$  (Fig. 5). The interplanar distances of 2.2765



**Fig. 4.** (a, b) C1s and (c, d) O1s XPS spectra of the Pd–P catalyst (a, c) before and (b, d) after etching with argon. The broken line represents the experimental spectrum. The line enveloping the experimental spectrum corresponds to the sum of the decomposition components of the XPS line, and marked lines correspond to the components of XPS line decomposition into the chemical forms of (a, b) carbon or (c, d) oxygen.

and 1.3241 Å are closest to the interplanar distances of the planes (111) (d/n = 2.2458 Å) and (220) (d/n =1.37537 Å) of palladium crystallites (# 00-046-1043). The observed broadening of diffraction lines in the X-ray diffraction pattern can be due to a decrease in the particle size to less than 100 nm and microstresses caused by chemical inhomogeneity and defective structure. The size of the coherent scattering region (CSR) calculated from the half-width of the main reflection (at reflection angles  $2\theta = 39.59^{\circ}$ ) was no greater than 1.6 nm. However, according to the TEM data, the number average particle diameter of the Pd-P catalyst was  $34.4 \pm 13.7$  nm (Fig. 2b). Such a significant difference in the CSR size (as a rule, it is identified with the average crystallite size) and the TEM data indicates that the broadening of diffraction lines in the X-ray diffraction pattern is related to the defect structure of the sample and low structural ordering rather than a decrease in particle size to less than 100 nm. The difference by a factor of 1.8 between CSR sizes (1.6 and 0.9 nm) calculated from the half-widths of both reflections ( $2\theta = 39.59^{\circ}$  and 71.21°) clearly indicates the imperfection of the crystal lattice of the Pd–P catalyst. The electron diffraction data (Fig. 2b, inset) and the HR TEM images (Fig. 6b, inset) also indicate a low structural ordering of the sample. The size of ordering regions in the particles of the Pd–P catalyst does not exceed 0.6–1.0 nm (Fig. 6b, inset).

The distortion of the palladium crystal lattice is associated with the entry of phosphorus (a metalloid) into the composition of the particles. According to the EDX analysis data, the ratio between P and Pd for different sections of the Pd–P catalyst was 0.23 : 1(Fig. 6). Therefore, the empirical formula of the bulk phase was Pd<sub>4.3</sub>P. The interplanar distances in the diffraction curve, which are most characteristic of palladium, and the low structural ordering resulting from the incorporation of phosphorus into the palladium

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Spectral line	Binding energy, eV	FWHM, eV	Element concentration, at %		The most probable chemical species*
Pd3 <i>d</i> <sub>5/2</sub>	335.6	0.6	12.0	1.9	$Pd^{\delta^+}(0.16)^{**}$
	335.9	1.0		9.3	$\mathrm{Pd}_{x}\mathrm{P}\left(0.77\right)$
	337.7	1.5		0.8	$Pd(acac)_2 (0.07)$
P2p <sub>3/2</sub>	130.0	0.6	9.5	2.8	$\mathrm{Pd}_{x}\mathrm{P}\left(0.29\right)$
	131.1	1.2		1.1	$Pd^{\delta+}-P(0.11)$
	133.3	1.2		1.4	$R-O-PO_3^{2-}(0.15)$
	134.5	1.2		4.2	PO <sub>4</sub> <sup>3-</sup> (0.45)
Ols	532.2	2.5	19.6	_	$\mathrm{Pd}3p_{3/2}(\mathrm{Pd}^{\delta+},\mathrm{Pd}_{x}\mathrm{P})$
	533.3	1.7		19.6	O-C + P-O + O=C (1.0) (R-O-PO <sub>3</sub> <sup>2-</sup> , R-OH, Pd(acac) <sub>2</sub> )
	534.5	3.3		_	$Pd3p_{3/2} (Pd(acac)_2)$
C1s	285.0	1.4	58.9	49.9	$C-C + CH_2 + CH_3 (0.85)$ $(R-O-PO_3^{2-}, Pd(acac)_2)$
	286.9	1.2		7.0	C-O-P (0.12) (R-O-PO <sub>3</sub> <sup>2-</sup> , R-OH)
	289.0	1.5		2.1	$C=O + CO_2 (0.03) (Pd(acac)_2)$

**Table 2.** Binding energies and concentrations of the elements in various states in the surface layers of the Pd–P catalyst isolated from the  $Pd(acac)_2-0.3P-H_2$  system after etching with argon

\* The atomic fraction of this chemical species is indicated in parentheses.

\*\* The form  $Pd^{\delta^+}$  is similar to palladium in the reduced state Pd(0).

crystal lattice suggest the formation of a structurally disordered solid solution between palladium and phosphorus. The possibility of the formation of substitutional solid solutions was experimentally demonstrated by Moreau et al. [21] using nickel and phosphorus as an example despite differences in the atomic radii and electronegativities.

The quantitative analysis of the surface composition of the Pd–P catalyst showed that a total P : Pd ratio of 0.68 (Table 1) was higher by a factor of almost 2 than the initial ratio (P : Pd = 0.3). That is, the surface of the Pd–P catalyst was enriched in phosphorus compared to the bulk phase. In this case, more than a half of phosphorus (52%) occurred in an oxidized form (Table 1). The presence of the oxidized form of phosphorus was most often associated with the oxidation of surface transition metal phosphides with oxygen [22]. However, for the Pd–P catalyst obtained by the low-temperature method from Pd(acac)<sub>2</sub> and P<sub>4</sub> in hydrogen, other processes also contributed to the formation of oxidized phosphorus species. This conclusion is based on the data given below.

First, the surface compositions before and after argon etching differed only slightly (Tables 1 and 2). In this case, the fraction of phosphorus in the oxidized state after etching with argon did not decrease. Second, the C1s spectrum of the Pd–P catalyst contained three chemical forms of carbon (Fig. 4a) corresponding to the C–O–P ( $E_b(C1s) = 286.6 \text{ eV}$ ) and C=O ( $E_b(C1s) = 289.1 \text{ eV}$ ) fragments and C–C/C–H aliphatic radicals ( $E_b(C1s) = 285.0 \text{ eV}$ ) [23] (Table 1). The presence of the C–O–PO<sub>3</sub><sup>2–</sup> fragment indicated the presence of phosphoric acid alkyl esters on the surface of the Pd–P catalyst.

The formation of octyl phosphite in the reaction medium was confirmed by chromatography-mass spectrometry. Using UV spectroscopy, we found that ~15% Pd(acac)<sub>2</sub> in toluene-1-octanol solution in an inert atmosphere reacts with phosphorus at a P : Pd ratio of 0.3:



Fig. 5. X-ray diffraction pattern of the Pd–P catalyst. Vertical lines show the positions of the reflections of crystalline palladium.



Fig. 6. EDX spectrum of the Pd–P catalyst. The insets (a, b) show HR TEM images with different scales.

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

A third of the introduced phosphorus was spent in the redox process. The phosphoric acids formed in the redox process enter into an esterification reaction with 1-octanol used as a co-solvent. Octyl phosphites and/or octyl phosphates adsorbed on Pd–P catalyst particles act as stabilizers. A higher temperature (90°C) required for the reduction of Pd(acac)<sub>2</sub>, which contains O,O-chelate-bound acac ligands, with hydrogen in toluene–1-octanol solution, in contrast to dimethylformamide [24, 25], leads to the formation of particles of structurally disordered solid Pd–P solutions, the surface of which is enriched in electrondeficient palladium.

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The analysis of a surface layer of Pd–P particles (P : Pd = 0.3) formed in the toluene–1-octanol solution allowed us to formulate the following reasons for the modifying effect of phosphorus on the properties of palladium catalysts in the chemoselective hydrogenation of 2-ethyl-9,10-anthraquinone:

As noted above, a sharp drop in the activity and a significant increase in the selectivity of the Pd–P catalyst compared to Pd black cannot be explained by a change in the particle size (Figs. 1 and 2). First, the average particle size of the Pd–P catalyst was almost 3.5 times smaller than that of the Pd black (Fig. 2). If the geometrical factor played the main role, the activity in terms of total palladium should increase as a result of an increase in the dispersity of the Pd–P cat-

alyst. Second, both large (d = 127 nm) and small (d = 1.5-2.5 nm) palladium nanoclusters were characterized by a lower yield of hydrogen peroxide than that on Pd-P particles (Fig. 1), although they also accelerated various side processes [6].

In our opinion, the most important factor determining changes in the properties of the palladium catalyst upon phosphorus modification is the enrichment of its surface in electron-deficient palladium presumably in the form of a Pd-P solid solution and the presence of a stabilizer on the surface of the Pd-P catalyst particles. As a rule, Pd catalysts with a high electron density on palladium are more active in the hydrogenation of anthraquinone [3, 26]. Antibatic and symbatic effects of a decrease in the electron density of palladium on the catalytic activity and selectivity, respectively, were observed previously in the chemoselective hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes to unsaturated alcohols [27]. On the one hand, the appearance of a partial positive charge on palladium in Pd-P particles weakens the activation of molecular hydrogen and the H–H bond cleavage required for catalytic hydrogenation [28, 29]. On the other hand, the solubility of hydrogen, that is, the concentration of nonselective hydrogen, in solutions of palladium with phosphorus decreases in comparison with palladium crystallites [30]. In this case, the solutions of palladium with phosphorus contain more strongly bound hydrogen [31], which is not favorable for the hydrogenation of an aromatic ring [32]. A high yield of  $H_2O_2$ in the presence of amorphous Ni-Cr-B allovs, in contrast to crystalline nickel catalysts, was also noted by Liu et al. [32].

Thus, changes in the properties (activity and selectivity) of the palladium catalyst in the production of hydrogen peroxide by the anthraquinone method are associated with the enrichment of the surface of Pd–P particles in electron-deficient palladium during the formation of palladium catalysts in the presence of elemental phosphorus in hydrogen in toluene–1octanol solution and the stabilization of particles with the octyl esters of phosphoric acids.

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