Structure of polynuclear palladium(II) hydroxocomplexes and the mechanism of their adsorption by carbon materials

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Adsorption of polynuclear palladium(II) hydroxocomplexes (PHC) by carbon materials (CM) was studied. It was found that PHC are adsorbed from aqueous solutions without a change in their chemical composition and are composed of clusters (<10 Å) with metal—metal distances typical of the PdO chain structure. Three-dimensional ordered particles with the PdO structure were formed upon adsorption of PHC on carbon materials at room temperature or after the PHC suspension was dried in air at 400 °C (the size of the particles was 15 and 25 Å, respectively). Calculation of the electron-microscopic images of the adsorbed PHC with atomic resolution based on crystal structure modeling showed that PdO particles containing ~100 palladium atoms is the final product after drying of the adsorbed PHC.

Key words: palladium(II), hydrolysis, polynuclear hydroxocomplexes (PHC); carbon material, adsorption; radial atomic distribution method, X-ray phase analysis, electron microscopy; molecule structure modeling; synthesis of microscopic images.

The adsorption of polynuclear palladium(II) hydroxocomplexes (PHC) by carbon materials (CM) is used for the preparation of Pd/C catalysts. Earlier[1,2] we have studied hydrolysis of $[PdCl_4]^{2-}$ in aqueous NaOH solutions. The hydrolysis resulted in the formation of PHC of composition $[Pd(OH)_2]_n \cdot (NCl)_k$, where n ~100 and $k \le n$. The structure of PHC in solution is a filament, comprised of $[Pd(OH)_2]_n$ fragments, that is folded into a ball due to the tightening of some of its parts by N^+ cations. Hydrated Cl^- ions located on the periphery of the particles compensate the positive charge of Na^+ ions of the PHC and prevent coagulation of these particles. The adsorption of mononuclear Pd^{II} chlorocomplexes by different carbon materials has been studied[3,4] and it has been found that at least there types of adsorption centers exist on the surface of the porous carbon materials, differing in adsorption energy and composition of the surface palladium complexes formed.

The adsorption of PHC by the surface of CM and the structure of the adsorbed products are studied in this work.

Experimental

The initial compounds used were of "pure for analysis" grade. Base solutions of H_2PdCl_4 and Na_2PdCl_4 were prepared by co-dissolution of stoichiometric amounts of $PdCl_2$, NaCl, and HCl in water. For the studies of the PHC, solutions of Na_2PdCl_4 were prepared, and a NaOH solution was added until the necessary value of χ was achieved ($\chi = C_{NaOH}/C_{Pd}$, where C_{NaOH} and C_{Pd} are the concentrations of the alkali and

the starting Pd^{II} compound). For these solutions, the molar fraction of palladium in the PHC is $0.5 \cdot \chi$ at $0 \le \chi \le 2$. Sibunite[5] with specific surface 250 m^2 g^{-1} (according to BET) was used as a CM.

For the adsorption, a solution of PHC was added to an aqueous suspension of CM and the mixture was shaken for 15 min (as has been shown in the special experiment, the adsorption equilibrium is established in 3 min), and the CM was separated from the solution. The content of palladium in the CM was determined by the difference in the mass of palladium in the solution measured before and after the adsorption. Spectrophotometric analysis of solutions was carried out on a Specord UV-VIS spectrometer. Before the analysis, a 5 M solution of HCl was added to the PHC solutions, and palladium was completely transformed into H_2PdCl_4 complexes.

The content of Cl^- ions in the palladium compounds adsorbed was determined after the adsorption of PHC by CM in solutions. An excess of CM was used to ensure that palladium is not left in the solution (drop test with KI). The concentration of Cl^- ions in the solutions separated from the CM after adsorption of Pd^{II} was measured by potentiometric titration with a $AgNO_3$ solution using a platinum electrode (an EV-74 ionometer). The mass of the Cl^- ions adsorbed was calculated by the difference in their mass in the initial solutions and in the solutions obtained after adsorption.

X-Ray structural analysis was carried out on HZG-4C (copper irradiation) and HZG-4B (molybdenum irradiation) X-Ray diffractometers. The experimental procedure and the method for the calculation of radial atomic distribution curves were described previously.[6]

Preparation of samples. Three samples were prepared for the studies. Preliminary experiments showed that the rate of formation of the precipitate in PHC solutions depends on χ

and Pd concentration. For example, a solution with χ = 0.4 and C_{Pd} = 0.1 mol L^{-1} is stable for several tens of hours, whereas a solution with χ = 1.4—1.6 and C_{Pd} > 0.2 mol L^{-1} is transformed into an unstable gel, which fills all the reaction volume several minutes after preparation, and in solutions with χ > 1.6 and C_{Pd} > 0.01 mol L^{-1}, a precipitate is rapidly formed. Therefore, to prepare the first sample, the precipitate formed in a freshly prepared PHC solution (χ = 2, C_{Pd} = 0.2 mol L^{-1}) was washed with water, and the excess of water was removed by filtration on a porous filter for 10 min. To prepare the second sample, the PHC (χ = 1, C_{Pd} = 0.2 mol L^{-1}) was adsorbed on Sibunite and dried at room temperature for 24 h. Then the sample was again washed with a large amount of water and dried; the content of Pd was 20 %. The third PHC sample (χ = 2, C_{Pd} = 0.2 mol L^{-1}) was prepared by heating the sample 1 to constant weight in air for 10 h at 400 °C.

EM studies. The samples were prepared by ultrasonic sputtering of the CM with the adsorbed PHC, dried *in vacuo* at 20 °C for 1 h, on a perforated carbon support. For the detailed investigation of the PHC structure, samples adsorbed on a hydrophilized graphite were prepared. For hydrophilization, an aqueous suspension of graphite (99.9 %) ground in a mortar was additionally dispersed with ultrasound, the graphite was separated from the water and kept in a 5 *M* solution of acetic acid for 1 day, and the acetic acid was washed away by a large amount of water to pH 6—7. The adsorption of PHC on graphite and the preparation of the samples for EM studies were carried out by the same procedure as for Sibunite.

EM studies were carried out on JEM 100 CX (acceleration voltage 100 kV, point resolution 5 Å) and JEM 4000 EX (400 kV, resolution 1.7 Å) microscopes. Computer simulation of the PHC molecules was carried out using the Demo program. The EM images were simulated by processing of computer molecular models (taking into account the output parameters) using the authorized program package for IBM compatible computers.

Results and Discussion

Adsorption of PHC. Figure 1 shows the isotherms of adsorption of palladium from the PHC solutions with different χ. The surface concentration of palladium on the CM increases with increase in χ. Acidity of the solutions has practically no effect on the adsorption isotherms since the isotherms for the H_2PdCl_4 (pH ≈ 0.5) and Na_2PdCl_4 (pH ≈ 4) solutions coincide. It should be noted that the pH of the PHC solutions is a little higher than 4 and practically does not depend on χ since all the alkali added to a Na_2PdCl_4 solution is consumed for the PHC formation. The chemical composition of the PHC (see Ref. 2) does not change with increase in χ (at 0 < χ < 2), and only an increase in the fraction of Pd^{II} incorporated into the PHC is observed. The corresponding increase in the PHC concentration and decrease in the concentration of mononuclear complexes in the solutions are observed. Therefore, the divergence of the curves corresponding to the different χ values in Fig. 1 may only result from the increase in the PHC concentration in the solutions and on the CM surface.
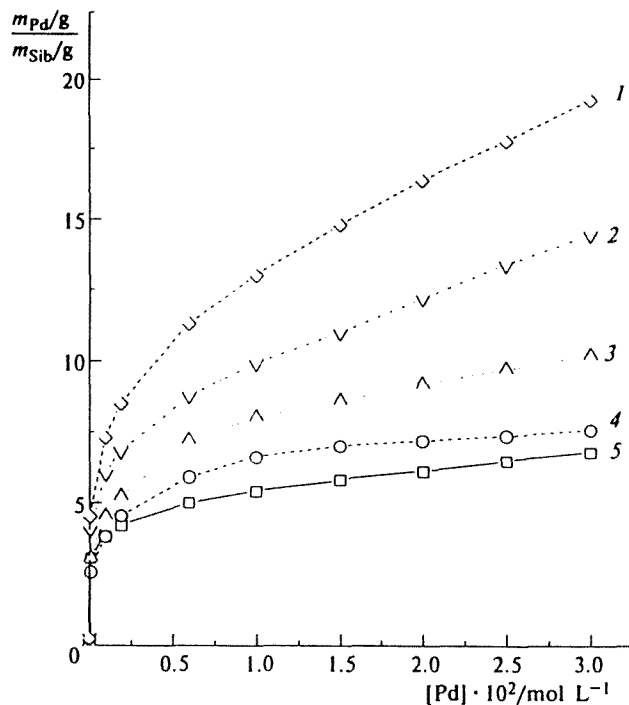

Fig. 1. Dependence of the change of the mass ratio of Pd^{II} adsorbed and Sibunite on the variation of the equilibrium concentration of Pd over the adsorbent. χ values of the initial PHC solutions: 1 (*1*); 0.8 (*2*); 0.5 (*3*); 0.2 (*4*); 0.0 (*5*).

If we assume that PHC particles on the CM surface occupy the same adsorption centers A^3 as mononuclear Pd^{II} complexes, the first member of the right part of the equation describing the adsorption equilibrium

$$Pd^{II}(\text{solution}) + PHC(\text{solution}) + A(CM) \rightleftharpoons$$

$$\rightleftharpoons [Pd^{II}\text{-}A](CM + [PHC\text{-}A](CM), \qquad (1)$$
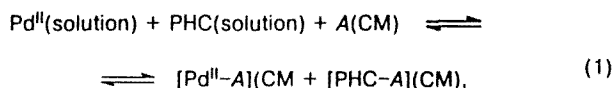
determines the concentration of the occupied surface adsorption centers. In fact, each PHC particle contains ~100 palladium atoms[1]; if it occupies one adsorption center, the contribution of the second member of the equation to the fraction of the occupied adsorption centers is ~1 %. Even in the case where an PHC particle occupies several adjacent adsorption centers, their fraction is not high as compared with the centers occupied by mononuclear complexes. Ignoring the fraction of the adsorption centers occupied by the PHC, we can plot on the axis of ordinates the concentration of the adsorbed mononuclear Pd^{II} complexes instead of the total concentration of Pd on the carrier. This concentration is calculated from the data[2] whereby all the alkali added to the Na_2PdCl_4 solution is consumed for the formation of $[Pd(OH)_2]_n$ and unreacted Pd^{II} is bound in $[PdCl_4]^{2-}$ complexes. Then the fraction of palladium in the mononuclear complexes is α = 1−0.5 χ, *i.e.*, for χ = 1, α = 0.5, for χ = 0.8, α = 0.6, for χ = 0.5, α = 0.75, and for
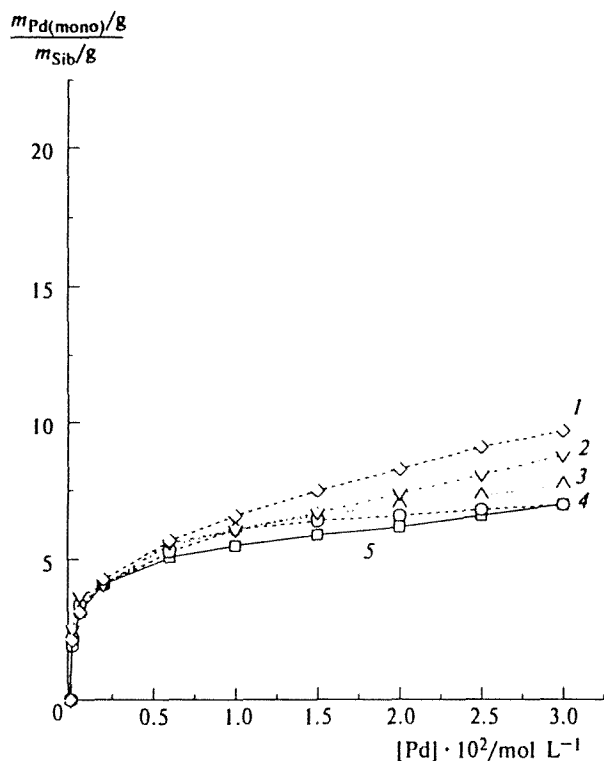
Fig. 2. Isotherms of the adsorption of palladium constructed on the assumption that the metal is adsorbed in the form of mononuclear complexes only, χ: 1 (*1*); 0.8 (*2*); 0.5 (*3*); 0.2 (*4*); 0.0 (*5*).

Fig. 3. Change in the relative mass of the Cl^- ions adsorbed with variation of χ; experimental (*1*) and calculated (*2* and *3*) data.

$\chi = 0.2$, $\alpha = 0.9$. The fraction of mononuclear complexes without the addition of the alkali is equal to 1.

The adsorption isotherms constructed taking into account the competition between mononuclear and polynuclear complexes are given in Fig. 2. The curves obtained for the solutions with different composition practically coincide in the region of low equilibrium concentrations of palladium in solutions. Some divergence of the curves in the region of high concentrations may be explained by the formation of PHC associates in the solutions. The probability of formation of such associates should increase with the increase in χ and Pd^{II} concentration. Macroscopic associates can be separated from the solutions together with the CM during filtration. The increase in the concentration of the adsorbed palladium is apparent since associates should remain unbound with CM. The EM study of the samples with the adsorbed PHC showed that such associates are absent. However, even if non-adsorbed associates were present in the samples prepared for the EM study, their concentration should be very small as compared with that of CM particles, and it is practically impossible to find them on examination under a microscope even at a high magnification.

Figure 3 shows the dependence of the concentration of Cl^- ions on χ in the Pd compounds adsorbed on the
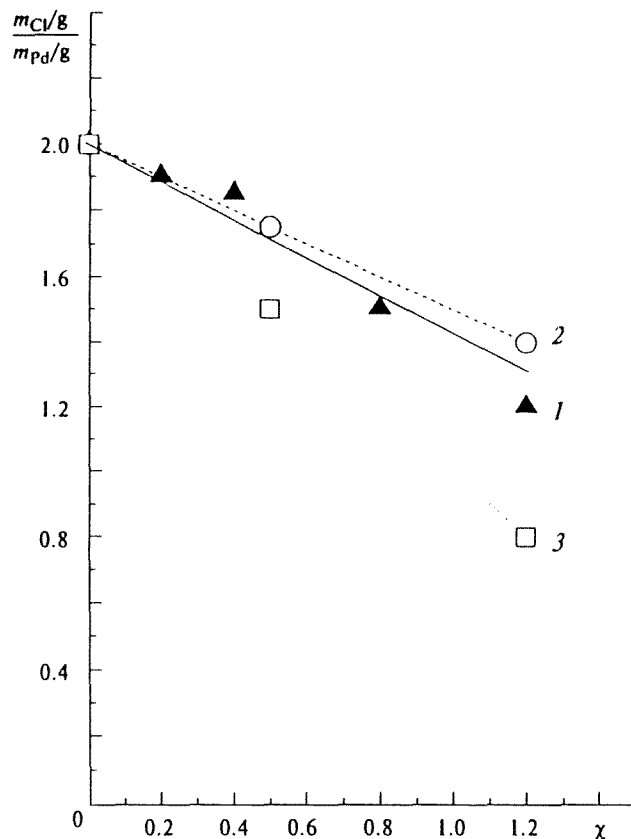
surface of the CM. In these experiments, the adsorption was carried out in such a way that the solutions over the CM do not contain palladium. It has been found in the preliminary experiments that CM practically does not adsorb Cl^- ions from solutions of HCl and NaCl. As can be seen from Fig. 3, the concentration of chlorine ions on the surface decreases linearly with increase in χ, *i.e.*, with increase in the PHC fraction. At the point $\chi = 0$ (Na_2PdCl_4 solution), two Cl^- ions per one Pd atom are liberated to the solution after the adsorption. This corresponds with the previously obtained data[3] that chloride complexes of Pd^{II} are adsorbed in the form of $PdCl_2$. In addition to the experimental data (line *1*), the calculated dependences (lines *2* and *3*) are also given in Fig. 3. Dependence *2* is constructed on the assumption that the composition of the PHC adsorbed does not differ from that in solution (one Cl^- ion per one Pd atom). Curve *3* is obtained on the assumption that the PHC are adsorbed as $Pd(OH)_2$ and do not contain chlorine ions. For both cases it was taken into account that mononuclear complexes are adsorbed in the form of $PdCl_2$. As can be seen from Fig. 3, curve *1* obtained from the experimental data is located near line *2*; therefore one may consider that the PHC maintain the ionic "coating" of hydrated Cl^- ions during the adsorption. The small divergence
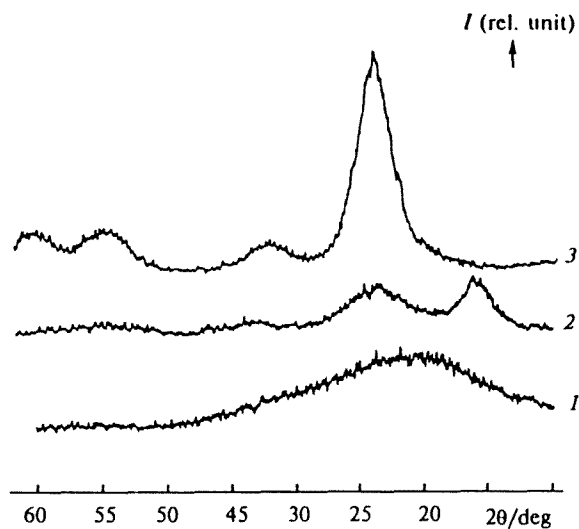
I (rel. unit)

60   55   50   45   30   25   20   2θ/deg

Fig. 4. Fragments of the diffraction patterns for the PHC samples: freshly prepared (*I*), precipitated on Sibunite (*2*), and dried in the air at 400 °C (*3*).

$4\pi r^2 \rho(r)/el^2$ Å^{-1}

Fig. 5. RAD curves for the PHC samples: freshly prepared (*I*), dried in the air at 400 °C (*2*), and for PdO structure (*3*).

between the lines in Fig. 3 may be associated with the desorption of Cl^- ions located between the PHC and the CM surface at the moment of adsorption.

Thus, it is established that the PHC composition remains practically unchanged during the adsorption.*

X-Ray diffraction studies. The diffraction patterns obtained on copper irradiation (Fig. 4) show different degrees of perfection of the structure of the samples studied: total disordering of the freshly prepared PHC (the coherent scattering region (CSR) < 10 Å), and formation of highly dispersed particles with PdO structure upon adsorption of the PHC on sibunite (CSR 15 Å) and drying at 400 °C (CSR 25 Å). The unit cell parameters determined for the sample with the most ordered structure, $a = 3.031$ Å, $c = 5.358$ Å, differ somewhat from those for PdO structure, $a = 3.043$ Å, $c = 5.337$ Å (*cf.* Ref. 7).

Analysis of the curves of radial atomic distribution (RAD) calculated from the experimental data on the intensity of X-Ray scattering at molybdenum irradiation gives useful information about the structural peculiarities of the samples. The curves (Fig. 5) are compared with the curve of interatomic distances (Pd—Pd, Pd—O) calculated for the PdO structure (space group $P4(2)/mmc$, atomic coordinates $Pd(1/2,0,0)$, $O(0,0,1/4)$). In the

tetragonal cell of palladium oxide, each metal atom is surrounded by four oxygen atoms at the tops of the plane tetragon; tetragons are connected by their sides in chains located at a 90° angle. The model of the fragment of the PdO crystal structure is given in Fig. 6. Table 1 presents the interatomic distances and coordination peak areas of an infinite crystal for PdO structure and a 25 Å particle.

Diffused coordination peaks (see Fig. 5) are typical of the RAD curve of the freshly prepared PHC, indicating a large disordering of the structure. Peaks corresponding to definite Pd—Pd distances in the PdO structure (see Table 1) appear mainly. The shortest Pd—Pd distances correspond to the two peaks, one of which ($r = 3.04$ Å) characterizes the distances inside one chain, and the other ($r = 3.43$ Å), the distances between metal atoms in the mutually perpendicular chains (see Fig. 6). The ratio of peak areas is 1 : 2 (see Table 1 and Fig. 5, curve *3*) for the perfect PdO structure and 1 : 1.18 for the freshly prepared PHC, which indicates the primarily formation of separate chains. A decrease in the peak area with $r = 5.50$ Å, which corresponds to the Pd—Pd distance for atoms from different chains, is also observed (see Fig. 6).

* If the samples for the X-Ray and EM studies were not thoroughly washed with water (in these cases, the mother liquor was quickly washed out from the samples), they contained NaCl. The NaCl maxima were recorded on a diffraction pattern ($d/n = 2.82$, 1.99 Å), and well-defined cubic crystals with size >100 Å were observed in the EM photographs.
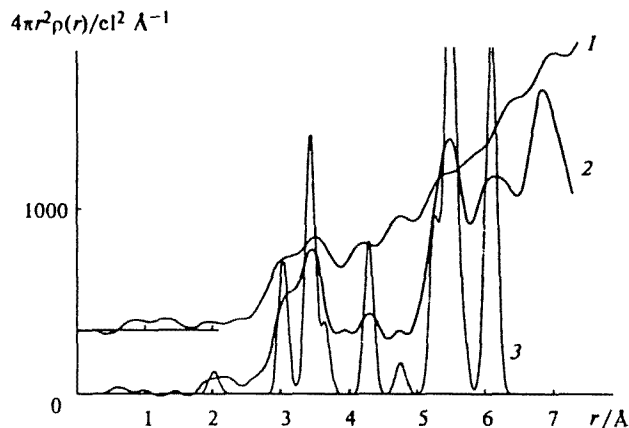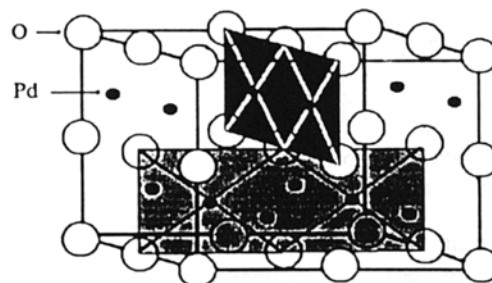

Fig. 6. Fragment of the PdO crystal structure. Perpendicular chains of the PdO_4 coordination squares are shown.

Table 1. Interatomic distances (r) and coordination peak areas (S)

Distance	Coordination number	Calculated			Experimental	
		$r/\text{Å}$	S/el^2		$r/\text{Å}$	S/el^2
			infinite crystal	$D = 25\ \text{Å}$		
Pd—O*	4	2.02	56	48.7	1.96 2.2	26 22 } 48
Pd—Pd*	4	3.04	249	199	3.04	202
Pd—Pd	8	3.43	498	388 } 474	3.46	314
Pd—O	8	3.65	113	86		
Pd—O	4	4.28	56	40 } 219	4.28	215
Pd—Pd	4	4.3	249	179		
Pd—O*	4	4.76	56	39	4.76	110
Pd—O	8	5.25	113	75		
Pd—Pd	2	5.33	124	82 } 876	5.46	889
Pd—Pd	16	5.5	996	647		
Pd—O	8	5.64	113	72		
Pd—O	4	6.07	56	34		
Pd—Pd	4	6.09	249	149 } 482	6.15	540
Pd—Pd	8	6.14	498	299		

Note. The calculated data are given for the PdO structure model, the experimental data for the RAD curves.
* Distance in one chain of plane rectangles.

The relative increase in the peak area with $r =$ 4.74 Å corresponding to the Pd—O distance inside one chain indicates the abundance of such distances in the PHC structure, which is explained by the polymer character of the structure and by the folding of chains.[1]

The RAD curve of the dried PHC (see Fig. 5, curve *2*) is better correlated with the PdO structure since the distance with $r = 2.02$ Å is less distorted, and the increased peak areas, which characterize the metal—metal distance in perpendicular chains ($r = 3.43$, 5.50 Å), make possible the formation of the bulky PdO structure.

If we compare the areas of the main coordination peaks calculated for a PdO particle with CSR 25 Å and those obtained from the experimental RAD curve, the values appeared to be close although the decrease in the area of the peak with $r = 4.76$ Å indicates a defective structure. For this sample, the ratio of the peak areas with $r = 3.04$ and 3.43 Å is 1 : 1.55.

Electron microscopy. Transmitting electron microscopy in combination with simulation of EM images involves construction of proposed computer models for a particle or a molecule, processing of models with the special program package for the calculation of EM images, choice of parameters of microscopic observation, and comparison of the photographs obtained with the simulated images.[8]

Figure 7 presents the photographs of the graphite and Sibunite samples with the adsorbed PHC (a JEM 100 microscope). The samples were prepared by saturation of the carriers with the Pd compounds. In the case of Sibunite, they correspond to the point in the adsorp-

tion isotherm with the coordinates $\chi = 1$, [Pd] = 0.03 mol L^{-1} (see Fig. 1). For graphite, a solution with $\chi = 1$ and equilibrium concentration [Pd] = 0.03 mol L^{-1} was used, the sample being saturated with palladium (4 mass. %). Figure 7 shows that spherical PHC particles are uniformly located on the surfaces of the carriers. The practically total absence of associates, the regular form of the particles, and their narrow size distribution indicate the absence of multilayer adsorption. The diameter of the particles in the photographs is ~25—30 Å, which exceeds the average diameter of particles in the samples with a low content of palladium (<0.5 % for Sibunite) by 5—10 Å. The similarity of the photographs of the Sibunite and graphite samples (see Fig. 7) indicates that the adsorption of the PHC proceeds on similar adsorption centers of these carriers. Since basal planes prevail in graphite, one may consider that the PHC are localized on the surface of both carriers primarily in the centers of the so-called weak adsorption.[3]

Using crystallographic data obtained with the RAD method we constructed the models of PdO particles, as well as the model of a disordered particle on the basis of the above-described[1] filament structure folded into a ball. The calculation of the EM images on the basis of the models allowed us to conclude that the crystal structure of the particle can be solved on a microscope with accelerating voltage 400 kV if graphite is used as a sorbent. These photographs were obtained on a JEM-4000 microscope. Figure 8 shows a photograph of the PHC particles adsorbed on graphite from the solution with $\chi = 1$ (the content of palladium in the sample was
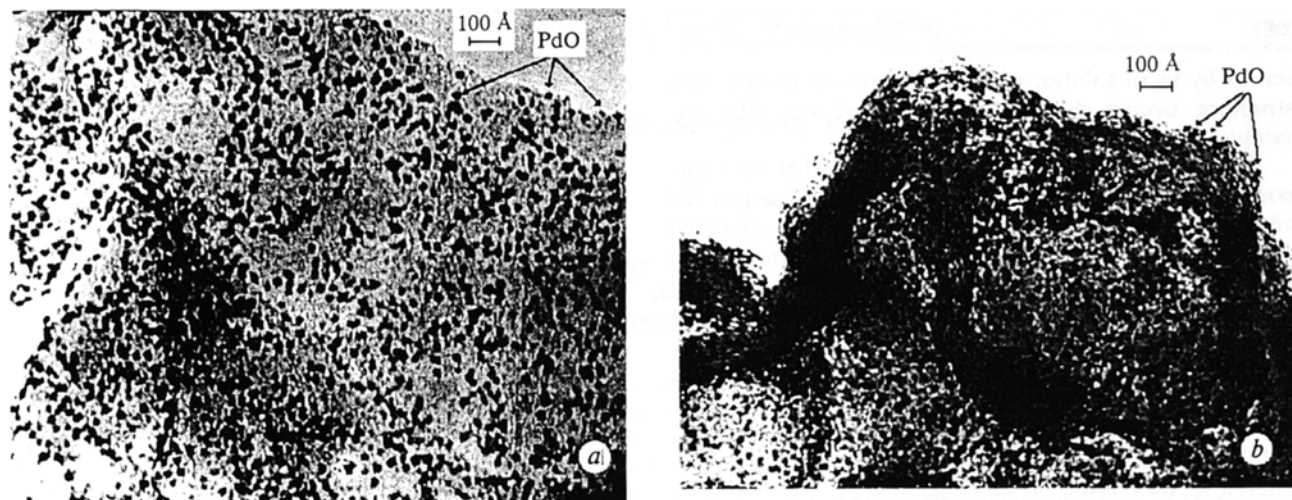
Fig. 7. Photographs of Sibunite (*a*) and graphite (*b*) samples saturated with Pd^{II} compounds from PHC solutions.

0.5 mass. %). The diameter of the PHC particles was 15—20 Å. The crystal lattice of the particles is clearly seen in the photograph. The model of the particle (circled in Fig. 8) was constructed for the accurate identification of the structure. The best agreement between the photograph of this particle and the EM image synthesized was obtained using the fragment of the PdO structure containing 100 Pd atoms as a model. This model is given in Fig. 9. It can be seen that the fragment of the PdO structure, whose outline coincides with the particle shown in Fig. 8, is located in the basal plane of the model of the graphite crystal. The good agreement between the EM photography and the calculated image shows that the rearrangement of the filament ball structure of the PHC, which has been ob-
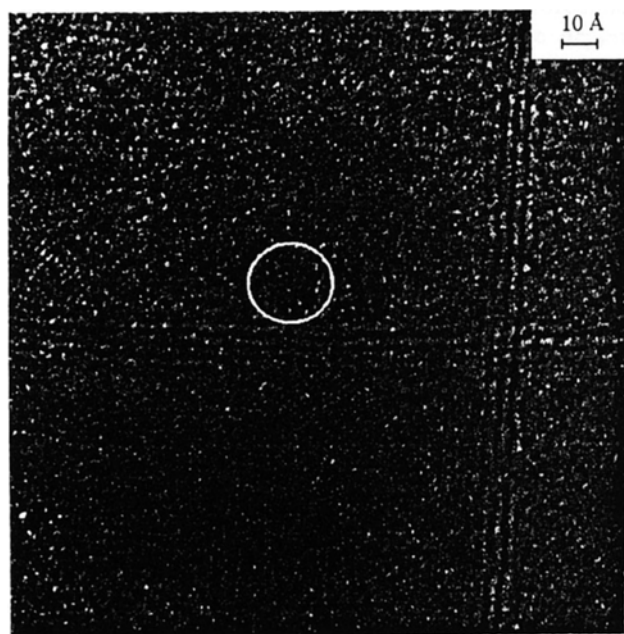

Fig. 8. Photograph of PHC particles on graphite. The particle-prototype of the model is circled.
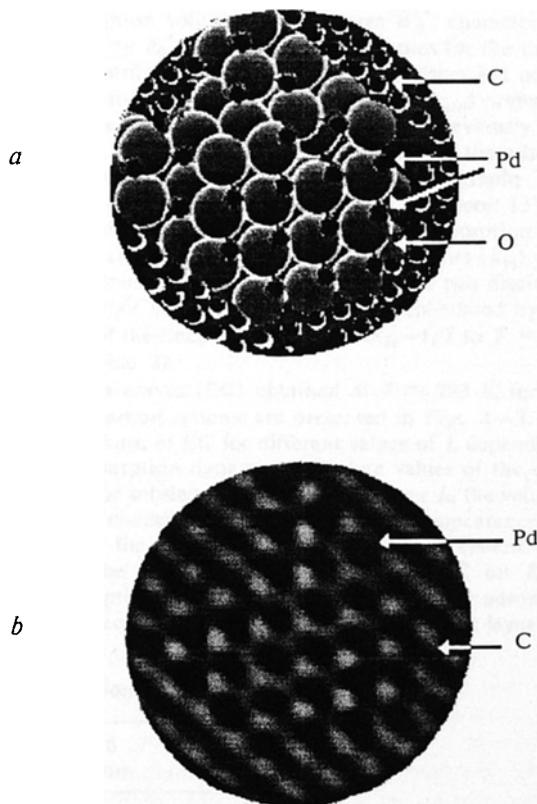

Fig. 9. Model of the PHC particle with PdO structure on basal plane of graphite crystal (*a*) and calculated EM image of this particle (*b*).

served by us in solutions,[1] into the ordered crystal PdO structure occurs during the drying of the PHC—C samples.

Thus, we establish in this investigation that the composition of the PHC is practically not changed on adsorption of the PHC by carbon carriers as compared with that in solutions. The consequent drying of the PdO—C samples results in the formation of particles with PdO structure. When the procedure is carried out under mild conditions and in samples with a low content of Pd, this rearrangement is not accompanied by a substantial change in the number of Pd atoms in a particle. The PdO—C system can be used for the preparation of PdO—C catalysts by reduction of Pd^{II} to metal. Therefore, by varying the conditions of the PHC synthesis we can regulate the size distribution of metal Pd particles in PdO—C catalysts.

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