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Preparation of the Pd/C Catalysts: A Molecular-Level Study of Active Site Formation

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Abstract—This review summarizes the results of molecular-level studies on the mechanism of Pd/C catalyst formation from the $PdCl_2$ precursor. Two processes occur in acidic media during the contact of H_2PdCl_4 with carbon: (a) adsorption of palladium chloride to form surface complexes and (b) redox interaction between $PdCl_2$ and carbon with the formation of palladium metal particles. The ratio between these adsorbed palladium species depends on the conditions of adsorption and especially on the size of carbon support grains and the oxidative atmosphere. The observations are explained by the fact that carbon support exhibits electrochemical and ligand properties. X-ray diffraction, X-ray scattering, XPS, and high-resolution electron microscopy revealed that the nanostructure of carbon materials, in particular the extent of their three-dimensional ordering, is crucial for the ligand properties. The presence of two forms, metallic and ionic, of sorbed palladium determines the bimodal size distribution of the metal. After the reduction of ionic species, metal particles are "blocked" with support. The nature of the ionic forms of palladium (mostly $(PdCl_2)_n$) clusters chemically and epitaxially bound to the carbon surface suggests the mechanisms of the bimodal distribution of the supported metal particles on the surface and the methods for the control of the ratio between "blocked," low-dispersed, and highly-dispersed particles in the catalyst. One of these methods is the use of palladium polynuclear hydroxo complexes (PHCs) with low oxidation potentials as starting compounds for catalysts preparation. The data on the PHC structure in a solution and its change upon the adsorption of PHC on the surface of the carbon material obtained by the ^{17}O, ^{23}Na, ^{133}Cs, and ^{35}Cl NMR techniques are discussed. PHCs are shown to be a clew of the $[Pd(OH)_2]_n$ polymeric filament, whose fractions are bound with alkali metal ions. When PHC is adsorbed on the surface of the carbon support and then dried, palladium oxide is formed from which highly dispersed metal particles are formed during reduction. The nature of alkali metal ions in PHC affects the activity of the Pd/C catalyst. An important role of the ligand, electrochemical, and lyophilic properties of carbon material during the formation of the species of the active catalyst component is discussed.

INTRODUCTION

The adsorption of mono- and polynuclear Pd(II) complexes followed by the reduction of the adsorbed compounds to the metal is traditionally used for the preparation of palladium catalysts supported on porous carbon. The properties of these catalysts are known to depend on both the nature of a precursor and its interaction with the support. Therefore, the procedure of the deposition of palladium compounds on a carbon support is a sort of "know-how" [1, 2]. That is why the available data on the molecular aspects of this problem are scarce. In most cases, the authors trace only weak correlations between the properties of the catalysts and the nature of a support and a precursor, as well as the conditions for the deposition of palladium compounds. The data on the effect of such stages of the catalyst synthesis as drying, calcination, and reduction of the supported precursors to metal on the activity and physicochemical properties of the catalysts are even scarcer. These problems are rarely reported in detail or they are presented as hypotheses. As a result, the interpretation of the data obtained is ambiguous and the conclusions are based on guesses.

In this work, we attempted to summarize the available literature data and our findings on the molecular bases for the preparation of the Pd/C catalysts and on the formation of metal particles on the surface of porous carbon supports from the H_2PdCl_4 as a precursor.

I. FORMATION OF Pd/C CATALYSTS BY THE SORPTION OF PALLADIUM CHLORIDE COMPLEXES BY CARBON SUPPORTS

1. Impregnation of the Carbon Support with H_2PdCl_4 Solution

Mechanism of the sorption of H_2PdCl_4 by a carbon sorbent. When a H_2PdCl_4 solution contacts the carbon surface in the absence of air, two competing processes occur: (a) reduction of Pd(II) ions into metal by the "electron gas" of carbon crystallites accompanied by the adsorption of Cl^- ions [3]:

$$C + [PdCl_4]^{2-} \longrightarrow Pd^0/C + 2Cl^-/C^{\oplus} + 2Cl^-, \qquad \text{(I)}$$

where $C^{\oplus}$ is a positively charged "hole," which appears at the moment of Pd(II) reduction by the surface of the

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carbon matrix, and (b) $PdCl_2$ chemisorption on the surface fragments of the carbon framework, which can be treated as a three-dimensional polyfunctional macroligand [3, 4]:

$$C + [PdCl_4]^{2-} \rightleftharpoons PdCl_2/C + 2Cl^-. \qquad \text{(II)}$$

The following general features are typical of H_2PdCl_4 sorption by a carbon sorbent:

(1) The reduction of Pd(II) ions into metal occurs predominantly on the external surface of carbon particles (even when their sizes are smaller than 0.2 mm) [3, 5], because the rate of electron transfer from the bulk of the carbon crystallite to its surface is much higher than the rate of $[PdCl_4]^{2-}$ diffusion inside the pores of carbon particles, but $PdCl_2$ is uniformly distributed over the entire inner surface of the carbon support [3];

(2) During Pd(II) reduction into Pd^0 by a carbon support, the oxidation of the carbon surface into oxygen-containing surface species or gaseous oxides does not occur, and Cl^- anions are adsorbed from solutions in amounts corresponding to the number of electrons consumed from the porous carbon to reduce metal; that is, carbon is "chlorinated" [3];

(3) Independently of the ratio between the rates of reactions (I) and (II), the concentrations of hydrogen ions in a solution remain virtually unchanged, and the ratio Cl/Pd in the adsorbed products of the interaction of H_2PdCl_4 with carbon is close to 2 (usually it is 2.00–2.15) [3].

Numerous factors affect the extent of reactions (I) and (II): the chemical nature of the support surface, its textural characteristics and grain sizes, and the conditions for the deposition of palladium compounds, especially the pH of solutions and the composition of the gas phase [3–6]. Nevertheless, these effects can be completely explained in the framework of the electrochemical theory of adsorption of electrolyte ions reported by A. N. Frumkin and co-workers [7–14].

According to this theory, the surface of graphite-like carbon acquires an electrical charge because of the redox equilibration of the substances, which are present in a solution or adsorbed. When a component of the gas phase is involved in this process, carbon acts as an ordinary gas electrode whose potential depends in its value and sign on the composition of the atmosphere and the pH of the electrolyte solution [7–9]. Thus, when the carbon suspension contacts the air, it becomes an oxygen electrode. A double electrical layer (DEL) $C^{\oplus}\cdots OH^-$ appears on its surface:

$$2C + H_2O + 1/2O_2 \longrightarrow 2C^{\oplus}\cdots OH^-. \qquad \text{(III)}$$

The OH^- ions, which form the external layer of DEL, can exchange for the X^- anions of the electrolyte, and this results in alkalization of solutions:

$$C^{\oplus}\cdots OH^- + X^- \rightleftharpoons C^{\oplus}\cdots X^- + OH^-. \qquad \text{(IV)}$$

This is an electrochemical model for the appearance of the basic properties of carbons.

In an inert atmosphere, DEL appears when carbons participate in the redox transformations of various ions [11, 14]. For example, in the presence of transition metal cations (Fe^{3+}), DEL is formed as follows [14]:

$$C + Fe^{3+} + X^- \rightleftharpoons C^{\oplus}\cdots X^- + Fe^{2+}. \qquad \text{(V)}$$

We showed in [3] that the reduction of Pd(II) ions by reaction (I) and the reduction of Fe^{3+} ions by reaction (V) have the same nature. As a result of saturation by adsorbed compounds, the carbon surface acquires the potential that is close to that of a redox pair involved in the transformation independently of a carbon origin [15, 16]. This mechanism of the interaction between carbon and transition metal ions is operative when their solutions have a low oxidative ability [17] and the potential of carbon surface (φ) seems to be lower than 0.7 V. Under these conditions, thermodynamically favorable oxidation of the carbon surface into gaseous oxides, which was postulated in [5, 18] does not occur, probably because the oxidative corrosion of carbon is usually accompanied by a substantial overvoltage. Conversely, this electronic mechanism is not the only possible one when an electrolyte solution has a high oxidative ability [14, 17] and surface saturation with adsorbed compounds precedes the chemical corrosion of carbon that results in the formation of the surface oxygen-containing species, CO or CO_2 [17].

When the aqueous solution of H_2PdCl_4 contacts the carbon surface in *aerobic* conditions, DEL is formed simultaneously via several competitive pathways, which include the chemisorption of $PdCl_2$ and the electrochemical adsorption of Cl^- ions; the latter is the result of the reduction of both Pd^{2+} (reaction (I)) and other oxidants, for instance, O_2 (reactions (III) and (IV)).

Spontaneous reduction of H_2PdCl_4 and the state of chemisorbed chlorine. The reduction of Pd(II) ions according to reaction (I) begins with the contact of carbon with a solution of H_2PdCl_4 and, as the coverage of the surface with the adsorbed palladium compounds increases, rapidly reaches the constant level under the conditions chosen for adsorption. Reduction is especially efficient when (a) other processes capable of shifting the zero charge potential (φ_0) to the positive region or adding a free charge to the surface are either excluded or limited by diffusion and (b) the conditions of adsorption favor the maintenance of both a high oxidative potential of a Pd^{2+}/Pd pair and a high reducibility of carbon [3, 17] (Table 1).

We found that Cl^- ions coadsorbed with Pd^0 according to equation (I) are concentrated on the external surface of carbon grains (near Pd^0 particles), and the main fraction of chemisorbed chlorine is characterized by a high bond energy of 2*p* electrons ($E_{be}(Cl2p_{3/2}) \approx$ 199.5 eV) [3, 17]. This means that many $C^{\oplus}\cdots Cl^-$ ionic pairs in the potential-determining layer of DEL relax to the states in which the covalency of the Cl–C bond (of the ≡C–Cl type) is high. Relaxation is fast enough, so the "holes" $C^{\oplus}$ cannot "spread" along the whole surface of carbon (due to mutual electrostatic repulsion). As a result, they are fixed on the external surface of grains. Nevertheless, some fraction of chlorine in DEL remains ionic, and it is probably this fraction that is responsible for ion exchange in DEL:

$$2C^{\oplus}\cdots Cl^{-} + [PdCl_4]^{2-} \rightleftharpoons [PdCl_4]^{2-}\cdots 2C^{\oplus} + 2Cl^{-}. \qquad \text{(VI)}$$

The ion exchange intensifies with an increase in the overall amount of chlorine chemisorbed on the surface of carbon according to equation (I) or (IV) [17]. However, the amount of ion-exchanged palladium is very small in most cases.

The spontaneous reduction of H_2PdCl_4 according to the electrochemical mechanism (I) results in the appearance of very large Pd^0 particles (from 10 nm to several microns). The formation of these particles is determined by the regularities of electrolysis of solutions of metal salts, including the formation of particle nuclei and their subsequent growth [3]. At nearly the same Pd^0 content, metal particle sizes become larger with an increase in a carbon grain size or the partial pressure of O_2 in the atmosphere, as well as due to washing the support with an acid to decalcify it. In any case, this synthesis of Pd/C catalysts is of special interest because more dispersed catalysts are usually required.

Formation of the surface π-complexes of $PdCl_2$. The XPS study of H_2PdCl_4 adsorption on oxidized carbons [19, 20] and the chemical state of adsorbed $PdCl_2$ [4] revealed that Pd(II) complexes with oxygen-containing groups are not formed. The pH of a solution in the range of 1–2 and the presence of transition metal ions (Mn^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}) do not affect the H_2PdCl_4 adsorption according to equation (II). $PdCl_2$ is adsorbed on the oxidized regions on the carbon surface to form π-complexes with the >C=C< fragments of the carbon network. These complexes differ in their stability [4, 20]. The sites are characterized by at least three types of adsorption: weak (A_1), strong (A_2), and very strong or irreversible (A_3) (Fig. 1). A comparative study [4, 6, 19–21] of a series of carbon materials (graphite, active carbon, carbon black, Sibunit, and carbon filaments), including chemically modified carbon materials showed that the A_1-type site is a hexagon on the basal plane of quasigraphite carbon crystallite; the A_2-type site is likely a combination of the >C=C< fragments, which belong to both basal and side planes forming the surface step (a terrace), and the A_3-type sites are located in micropores (Fig. 2). In most cases, the concentrations of the A_1 and A_2 sites on the surface of nonoxidized carbons are proportional to their specific surface areas measured with the adsorption of phenol (S_{sp}):

$$[A_i] = a_i S_{sp} \quad (i = 1, 2), \qquad (1)$$

where $a_1 = 1.27$ μg-equiv/m² and $a_2 = 1.06$ μg-equiv/m².

The number of A_3 sites increases with the increasing micropore volume in carbon (V_m):

$$[A_3] = a_3 V_m, \qquad (2)$$

Table 1. Factors determining the $PdCl_2 : Pd^0$ ratio in adsorbed compounds

High ratio	Low ratio
1. Powder carbon support	1. Granulated support
2. Low temperature	2. High temperature
3. The presence of ligands that decrease the $E^0_{Pd^{2+}/Pd^0}$ value (for example, excess HCl)	3. Absence of ligands that decrease $E^0_{Pd^{2+}/Pd^0}$ in the solution of H_2PdCl_4
4. The presence of electrolytes with lyophilic anions (for example, SO_4^{2-}, etc.) (route *3*)	4. The presence of electrolytes with surface-active anions (for example, ClO_4^-)
5. The presence of additional oxidants, for example, O_2, H_2O_2, etc. (routes *1*, *4*)	5. The absence of other oxidants (inert atmosphere)
6. Fast penetration of Pd(II) ions into the pores of carbon: a high concentration of H_2PdCl_4, incipient wetness impregnation or adsorption from an excess solution under vigorous stirring	6. Slow penetration of Pd(II) ions into the carbon pores: low concentration of H_2PdCl_4 (an excess solvent)
7. High coverage of the carbon surface by palladium compounds	7. Low coverage of the carbon surface by adsorbate
8. Low electric capacity of the DEL of carbons:	8. High electrical capacity of carbon DEL:
low specific surface area of carbon supports;	large specific surface areas of carbon supports;
preliminary chlorination or oxidation of the surface of carbon supports (high content of acidic species) (route *4*);	no use of chlorination or oxidation of carbon supports (high content of basic sites);
preliminary chemisorption of acids in the presence of air (route *1*);	no preliminary treatment with acids;
high rate of chemisorption of $PdCl_2$ (Route *2*) (see p. 6 of this table).	diffusion limitation of the $PdCl_2$ chemisorption.

where a_3 = 0.23 μg-equiv/m^2. Expression (1) is not applicable to graphite, graphitized carbon blacks, and fullerene-like carbons (fullerenes and onion carbon [22]) on which the A_1 sites dominate or to filament carbon of some types [23] that are characterized by an enhanced concentration of A_2 sites. The contents of sites A_1, A_2, and A_3 decrease during modification (oxidation or hydrogenation) of the carbon surface, although the A_1 sites are more resistant to oxidants and H_2 than A_2 and A_3 [4, 6, 19].

At the stage of carbon impregnation with a H_2PdCl_4 solution during the synthesis of the Pd/C catalysts, most of $PdCl_2$ is usually sorbed on A_2. We have proposed a mathematical model for this adsorption equilibrium [20]. $PdCl_2$ was found to form mononuclear complexes with the A_2 sites. The formation constant (K_2) of the complex is determined by both substructural and surface chemical properties of carbon. K_2 increases as the carbon matrix becomes more disorderly (becomes more amorphous) [20, 21]. The dependence of K_2 on the chemical state of the carbon surface is described by the Hammett–Taft equation [6, 19]: electron-acceptor substituents (–COOH, >C=O, and –Cl) favor its increasing and electron donors substituents (–OH) result in a decrease in K_2. K_2 is an important characteristics of the state of a Pd/C catalyst precursor: it is widely known that dispersity and other properties of these catalysts essentially depend on the strength of the interaction between precursors and the surface of supports.

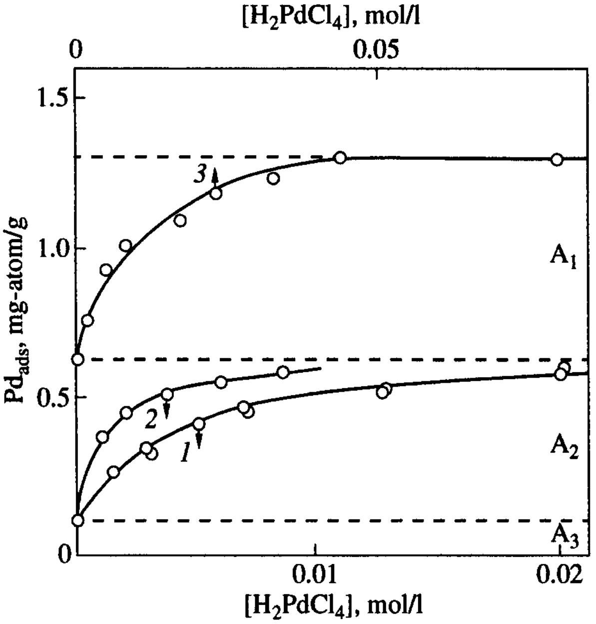

Fig. 1. Typical adsorption isotherms for H_2PdCl_4 on active carbon PS at 20°C from (*1*) 3.5 mol/l and (*2*) 1.0 mol/l solutions of HCl and (*3*) aqueous solutions. The regions of filling the sites of (A_3) irreversible, (A_2) strong, and (A_1) weak adsorption are designated by dotted lines.

2. *Drying*

Two general methods exist for the removal of a solvent after the contact of a carbon support and a H_2PdCl_4 solution: fast drying by heating under evacuation and slow drying by storing carbon impregnated by the mother liquor in air for a long time. In the first case, an insignificant increase in the amount of Pd^0 is observed, probably due to the thermal destruction of $PdCl_2$ π-complexes [3]. In the second case, a decrease in the amount of Pd^0 is possible because of the dissolution of metal particles under the action of O_2 and free HCl [18] followed by the interaction of $PdCl_2$ formed with carbon.

The clusters of $PdCl_2$ with a size of 1.8 × 0.2 nm were found in all dried samples by high-resolution electron microscopy (HREM). According to the data obtained by the atomic radial distribution function, these clusters have a structure of α-$PdCl_2$ [6, 24], but a fraction of deposited $PdCl_2$ still remains in a molecular-dispersed state. The size of clusters is virtually independent of the nature of carbon support and the mass concentration of Pd(II) in the sample over a wide range. For example, the concentration of Pd(II) in the active carbon can range from 1 to 20%. However, the ratio between the cluster and molecular species can change.

The fact that $PdCl_2$ particles are found in dried samples indicates an important role of the drying stage in the genesis of Pd/C catalysts. As a solvent is removed, the nature of the Pd(II) surface complex solvation changes. If a solvent enters its coordination sphere, the coordinatively unsaturated species are inevitably formed. Possible ways for the relaxation of these energetically unfavorable states are the migration of Pd(II) compounds along the carbon surface to regions with the highest adsorption potential (micropores or the regions where the structure of the support is most disordered) and their interaction with each other (agglomeration). The centers of agglomeration of $PdCl_2$ are the surface steps that interact with the $(PdCl_2)_n$ clusters both chemically with π-bonds preserved and epitaxially due to the presence of close interatomic distances in the structures of α-$PdCl_2$ and graphite (Fig. 3) [24].

Finally, the most important consequence of solvent removal is the blocking of the surface of some Pd^0 and Pd(II) particles by the fragments of the carbon framework. Analysis of our findings [6, 25] and the literature data [26, 27] suggests that this phenomenon is largely determined by the properties of the carbon matrix rather than by the method of metal compound deposition. The more disordered the crystal structure of carbon, the more it "swells" during the contact with various adsorbates [28–30]. It is known that, when porous carbon materials are impregnated with water, reconstruction and improvement of their pore structure take place [30]. The packing of the carbon networks becomes more even, and carbon crystallites become structurally similar to graphite [29, 30]. These facts suggest the following mechanism of blocking. In the samples of carbons impregnated with a solution of

H_2PdCl_4, the clearance between pores with a diameter of 2–10 nm located in the fragments of carbon particles in which the concentration of structural defects is relatively high should substantially increase due to a disjoining pressure[1], which can be 720–144 atm. The "intrapore" pressure can favor the ordering of the graphite-like elements of the support near the pore walls and the creation of the coherent packing of these elements and distinct carbon networks in the form of long-range graphite-like packets. When foreign particles are absent from the pores, the removal of a solvent may result in the complete relaxation of this state of carbon to the starting state. When small particles are present, almost complete relaxation of the carbon structure is also possible if the size of these particles is not greater than that of the pore in which the particle is located. The blocking of the surface of these particles (in the extreme case, their encapsulation) can occur when they are formed on the surface of those pores, which in the initial support are either close to or have a smaller size than these particles. In the latter case, carbon cannot completely recover its microstructure during drying, and we can assume that the foreign particles are incorporated inside the carbon matrix. When the Pd/C system is dried, Pd^0 crystallites incorporated inside the carbon matrix are closely covered by the graphite-like packets already at moderate temperatures. This "graphitization" of carbon around crystallites is likely due not only to the fact that they hamper the relaxation of the pore wall structure during drying but also to the ability of palladium to interact epitaxially with carbon networks [32, 33], which thereby favors the additional ordering of the crystalline structure of the nearest regions of carbon support.

3. *Reduction of the Adsorbed Precursors of Pd/C Catalysts*

It follows from the above data that the origin of metal particles in the Pd/C catalyst may be dual: some of them are formed at an initial stage, for example, during the impregnation of carbon with a H_2PdCl_4 solution, as a result of the spontaneous reduction of Pd(II) according to reaction (I), whereas other particles appear only at a final stage when the surface π-complexes and $(PdCl_2)_n$ clusters react with reducing agents. These components of supported Pd are designated below, according to their origin, as "primary" and "secondary" Pd^0; these names also reflect the order of their formation during the synthesis of the Pd/C catalysts.

The reduction of a sample by hydrogen at 250°C does not change the amount of "primary" Pd^0 or its size distribution despite the reduction of adsorbed palladium chloride. This is due to the fact that "primary" Pd^0 is concentrated at the periphery of carbon grains in the form of coarsely dispersed particles, whereas $PdCl_2$ is distributed more uniformly. Due to the reduction of the ionic species of adsorbed palladium, $[PdCl_4]^{2-}/2C^{\oplus}$, which appears via reactions (I) and (VI), the additional amount of relatively large (4.5–10 nm) Pd particles of Pd may appear [16]. Since these ionic precursors are likely concentrated near "primary" Pd^0 (because the concentration of $Cl^-/C^{\oplus}$ around these particles is high [3]), the reduction of precursors is accompanied by the fast sintering (agglomeration) of Pd^0 formed with the primary Pd^0.

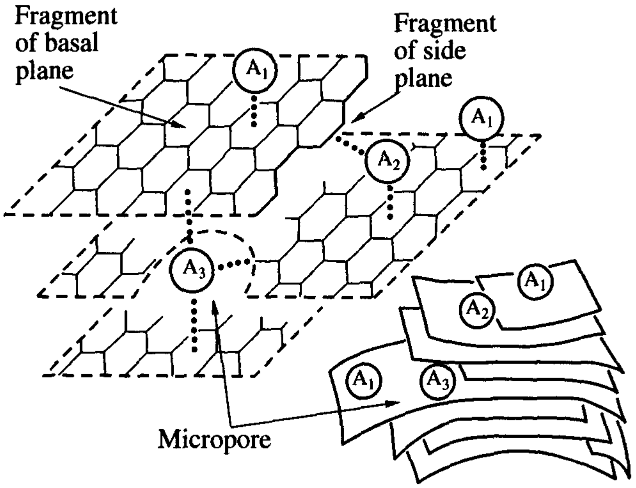

Fig. 2. Presumable positions of the sites of the (A_3) irreversible, (A_2) strong, and (A_1) weak adsorption of H_2PdCl_4 on the surface of carbon adsorbents and the nature of chemical binding of Pd(II) ions on these sites.

Highly dispersed (1–5 nm) particles of "secondary" Pd^0 are only formed during reduction of the surface π-complexes and clusters $(PdCl_2)_n$ (Table 2). The average size of these particles slightly depends on both the $PdCl_2$ content on the support (samples 2–6) and the concentration of the surface oxygen-containing groups (samples 10–13), which can vary in wide ranges [6]. The fact that oxygen-containing groups do not affect the ability of Pd^0 particles to sinter [34–36] is apparently due to the thermal destruction of these groups catalyzed by palladium under the conditions chosen (H_2, 250°C) [37]. Under these conditions, the average size of the "secondary" Pd^0 particles formed on nonoxidized supports strongly depends on the state of the main precursor: as can be seen in Table 2, this size decreases with increasing the concentration of the strong adsorption sites A_2 (samples 14–16) and the corresponding K_2 value (samples 1, 2, 7–9). A pronounced dependence of the catalyst dispersity on the state of precursor is undoubtedly due to the similarity in the chemical behavior of $PdCl_2$ and Pd^0 toward the compounds with unsaturated $>C=C<$ bonds [38]. As a result, the molecules and clusters $(PdCl_2)_n$, as well as the Pd^0 atoms and clusters formed from them, are influ-

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[1] Calculated according to equation $P = 4\sigma\cos\theta/d$, where σ is the surface tension of water equal to 72000 N/m, θ is the wetting angle (in most cases ~60° [31]), and d is a pore diameter.

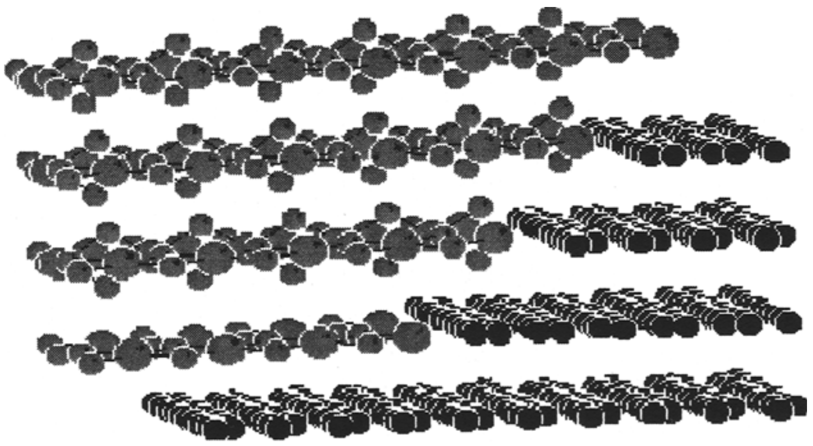

Fig. 3. The structure of α-$PdCl_2$ cluster formed from the surface π-complexes of $PdCl_2$ during drying and its possible orientation relatively the surface of a carbon matrix.

enced by the same surface factors in a similar way. The characteristics of the adsorption equilibrium of the precursor (K_2) are, in turn, determined by the nanostructural and subtextural properties of the support (see the above section on the surface π-complexes of $PdCl_2$). Consequently, the higher the contribution of the side faces of the carbon crystallites into the formation of the support surface and the higher the disordering of the structure of these crystallites, the smaller the sizes of the "secondary" Pd^0 particles [6, 39].

Nevertheless, nanostructural and microstructural properties of the support that favor the stabilization of highly dispersed metal particles can also be responsible for the blocking of the surface of these particles (see Section 2). As a result, the "secondary" Pd^0 particles on carbons with a strongly disordered crystalline structure or developed microporosity possess a lowered ability toward CO chemisorption and low activity in cyclohexene hydrogenation [6, 25].

4. *Effect of Adsorbed Precursors on the Properties of Pd/C Catalysts*

As mentioned above, the coexistence of two main routes for the formation of Pd^0 particles results in their bimodal size distribution of the Pd/C catalysts. Therefore, the formation of "primary" Pd^0 is another reason for the lowering in the extent of the metal use along with blocking.

The rate of the formation of "primary" Pd^0 is higher than the rate of $PdCl_2$ chemisorption, which is limited by H_2PdCl_4 diffusion inside carbon pores, and, other conditions being the same, the content of "primary" Pd^0 among the precursors of "secondary" Pd^0 decreases with an increase in the metal fraction in a solution. This is important for the rationalization of the features of Pd/C catalyst formation. Therefore, the volcano-shaped curve of palladium dispersity vs. its content on the support can be expected in the case of Pd/C catalysts prepared under the conditions favoring the formation of the substantial amount of "primary" Pd^0. This is due to the following reasons:

(1) When the reducibility of carbon is high, at the stage of the impregnation of carbon with a solution of H_2PdCl_4 at a low Pd concentration, nearly all palladium ions are reduced to comparatively large metal particles; that is, the dispersity of the catalyst is low;

(2) When the content of Pd on the support increases, as the "primary" Pd^0 appears, the adsorbed palladium chloride precursors are also formed, which then lead to highly dispersed metal particles, and the dispersity of palladium increases;

(3) When the amount of deposited Pd further increases, the adsorption of $PdCl_2$ according to reaction (II) starts to dominate; therefore, the dispersity of Pd in the Pd/C catalysts starts to depend slightly on the Pd content in some range of coverages and then decreases because of the fast agglomeration of "secondary" Pd^0 particles due to an increase in their surface concentration.

It follows from the above consideration that factors that determine the ratio between the rates of the formation of "primary" Pd^0 and π-complexes of $PdCl_2$ should manifest in the corresponding shift of the maximum of the Pd dispersity as a function of its content in the catalyst: a decrease in the ability of the support to reduce H_2PdCl_4 results in the shift of this maximum to lower surface concentrations of the metal, whereas an increase in this ability results in the opposite shift.

In the framework of this model, it is easily to explain the extremum relation observed in [35] between the palladium dispersity and the palladium content on the support in the Pd/C catalysts prepared by the reduction of adsorbed H_2PdCl_4. The effect of an increase in the palladium dispersity of the low-content (0.5–2%) Pd/C catalysts due to an increase in the extent of carbon surface oxidation [34–36, 40] can be newly explained as follows: this effect is due to a decrease in the reduction ability of carbon leading to the decrease in the amount of coarsely dispersed "primary" Pd^0 in the catalyst rather than the interaction between H_2PdCl_4 or Pd^0 clusters with the surface oxygen-containing species as it has was suggested in [36]. This is why the Pd dispersity in Pd/C catalysts increases in the presence of excess Cl^- ions (in the form of NaCl) [40] or H_2O_2 [41] introduced into the solution of H_2PdCl_4 at the stage of impregnation or by preliminary adsorption of chlorine on the support [42, 43] (see Table 1).

Thus, the use of H_2PdCl_4 for the synthesis of highly dispersed Pd/C catalysts imposes the strongest requirements to the physicochemical properties of carbons and the conditions for H_2PdCl_4 deposition to prevent undesirable processes, which can decrease the dispersity of the active phase. It follows from the above features of the formation of supported palladium particles that one of the approaches to the development of highly efficient Pd/C catalysts is to introduce into the H_2PdCl_4–carbon support system additional reagents that are able to (1) reduce the redox potential of the Pd^{2+}/Pd^0 pair and (2) result in the formation of Pd(II) cluster compounds, which are adsorbed on the support from a solution or formed on its surface where the blocking effect is minimum. Our studies revealed that the hydrolysis of Pd(II) chloride complexes adsorbed or present in a solution [25] is one of the methods to create the above conditions for the preparation of active Pd/C catalysts with high specific surface areas (Table 2, samples 17 and 18).

II. FORMATION OF ACTIVE SITES OF Pd/C CATALYSTS BY THE HYDROLYTIC PRECIPITATION OF Pd(II) COMPOUNDS

The introduction of alkali reagents in $PdCl_2$-containing solutions used for the impregnation of carbon support is a well-known procedure used in the commercial and laboratory synthesis of Pd/C catalysts.

The preparation of a catalyst can schematically be described by the following equations:

$$\text{a) } Pd(II) + OH^- \longrightarrow PHC,$$

$$\text{b) } PHC + C \longrightarrow PHC/C,$$

$$\text{c) } PHC/C + Red \longrightarrow Pd(0)/C,$$

where PHCs are palladium polynuclear hydroxy complexes, which are the products of the alkaline hydrolysis of $PdCl_2$, and Red is a reducing agent.

Stages (a) and (b) may be both successive and simultaneous during hydrolysis in the presence of the suspension of a carbon material. We do not consider the reduction of sorbed PHC, but we examine in detail the stages of their synthesis and adsorption on carbon materials.

1. Alkaline Hydrolysis of Pd(II) in Aqueous Solutions

The available literature data on the formation of polynuclear complexes shows that the findings substantially depend on the methods of studying and processing the experimental data.

Until recently, the methods based on potentiometric and spectrophotometric measurements of the concentrations of solution components (ligands, metal, and a starting complex or a reaction product) followed by the statistical processing of the results were most frequently used. The processing consisted in the choice of those values of the equilibrium constants of reactions possibly occurring in solutions, which enabled the best match between the experimental and calculated data [44]. In the case when polynuclear complexes are formed, this method of processing requires the (1) successive choice of a great number of equilibrium constants to take into account all possible reactions in solutions; (2) very high accuracy of measurement of physical parameters of equilibria; (3) taking into account secondary reactions, for example, the agglomeration of polynuclear complexes, which occur without a change in the concentration of mononuclear substrates.

The hydrolysis of palladium salts in aqueous solutions reported in a series of papers [45–53].

According to the results of pH-metric titration [45], polymeric products formed during alkaline hydrolysis of H_2PdCl_4 with the use of NaCl as a background electrolyte have the $[Pd(OH)]_n$ composition (without taking into account the components of the medium). The average number of PdOH units in a polymer (n) increases with an increase in the Pd concentration and a decrease in the NaCl concentration. The processing of the experimental data using the program Letagor allowed the authors [45] to conclude that the [PdOH] and $[PdOH]_4$ complexes prevail under these conditions.

It was found in [46] that, during hydrolysis of the Pd(II) salts in a solution of $HClO_4$ with pH < 2, the aqua complexes $[Pd(H_2O)]^{2+}$, $[Pd(OH)(H_2O)]^+$, and $[Pd(OH)_2(H_2O)]$ are formed. The formation of PHC was not mentioned.

The study of the products of Pd(II) hydroxide dissolution in water containing $HClO_4$ [47] with a combination of physicochemical methods (dialysis, solubility measurements, ion exchange) allowed the authors to conclude that the minimum number of Pd atoms in PHC that are stable under these conditions is six, and mononuclear complexes that are present in the solution have the $Pd(OH)_n$ composition, where $n = 1–4$. The question of the formation of higher compounds, as well as of their interaction with the materials of membranes and resins, remained open because of the insufficient accuracy of the measurements.

The existence of colloidal particles in the aqueous solutions of Pd(II) salts with pH 5 or 6 was shown in [48]; due to these particles, the Pd/C catalysts exhibiting a high catalytic activity can be prepared.

Table 2. Dependence of the dispersity and catalytic properties of supported palladium catalysts on the nature of carbon support, metal content, and conditions of preparation

No. of sample	Catalyst	Textural characteristics of a support and its adsorption properties toward H_2PdCl_4					Dispersion and specific catalytic activity[1] of palladium			
		S_{BET}, m^2/g	V_m, cm^3/g	S_{sp}, m^2/g	$[A_2]$, μg-equiv/m^2	K_2	HREM		CO chemisorption	
							D	SCA	D	SCA
1	1.1%Pd/PM-105[2]	112		106	0.925	240	0.30	1.9	0.24	2.4
2	1.05%Pd/C-1[2]	410	0.07	240	0.779	300	0.60	1.0	0.26	2.3
3	1.91%Pd/C-1[2]	–	–	–	–	–			0.25	2.4
4	3.08%Pd/C-1[2]	–	–	–	–	–			0.25	2.7
5	4.07%Pd/C-1[2]	–	–	–	–	–			0.26	2.6
6	6.0%Pd/C-1[2]	–	–	–	–	–	0.56	1.2	0.30	2.2
7	4.0%Pd/C-2[2]	550	0.15	270	1.03	310	0.68	1.6	0.41	2.7
8	7.5%Pd/PME-800[2]	770	0.09	440	1.04	400	0.74	0.9	0.32	2.1
9	3.0%Pd/PS[2]	950	0.38	490	1.09	1050	0.83	0.7	0.26	2.3
10	1.0%Pd/C-1 (initial)[3]	410	0.07	240	0.779	300	0.72	1.9	0.36	2.7
11	1.1%Pd/C-1 (12%H_2O_2, 2 cm^3/g C)[3]	380		210	0.619	390	0.76	1.8	0.38	3.6
13	1.0%Pd/C-1 ($KMnO_4$, 0.12 g/g C)[3]	360		189	0.434	570	0.71	2.1	0.45	3.3
14	1.0%Pd/Corax3 (graphitized)[4]	72	0.00	72	0.167	690	0.35			
15	1.0%Pd/PM-105[4]	112		106	0.925	240	0.62			
16	1.0%Pd/CFC-2[4]	85	0.028	80	1.67	210	0.96			
17	1.0%Pd/C-3[5]	500	0.154	305	0.895	550	0.23	4.8	0.34	3.2
18	1.0%Pd/C-3[6]	500	0.154	305	0.895	550	0.74	3.5	0.73	3.5

[1] Specific catalytic activity (SCA) of palladium was evaluated in cyclohexene hydrogenation (a static reactor with a volume of 100 cm^3, 0°C, suspension of 2–50 mg Pd/C in 3–4 cm^3 of a 5% solution of C_6H_{10} in ethanol; a stirring velocity of 800 min^{-1}). The catalyst was preliminarily ground in an agate mortar (in this case, the average size of carbon particles reaches ~5 μm and the extent of the use of the catalyst grain evaluated from the dependence of the reaction rate on the size of particles in a suspension is ~0.95).

[2] The sample was prepared by incipient wetness impregnation with an aqueous solution of H_2PdCl_4 in air (3–12 h) followed by drying under evacuation at 50–70 °C and reduction of $PdCl_2$/C by H_2 (1 atm, a flow reactor) at 250°C for 3 h.

[3] The same except for reduction during 2 h.

[4] The same except for reduction at 150°C for 1 h and then at 250°C for 1 h.

[5] The sample was prepared by the hydrolysis of Pd(II) complexes upon mixing the solutions of Na_2CO_3 and H_2PdCl_4, followed by the precipitation of colloidal $Pd(OH)_2$ on the support, washing with water, drying, and reduction by H_2 at 250°C (1 h).

[6] The sample was prepared by the hydrolysis of $PdCl_2$ preliminary adsorbed on the support from a solution of H_2PdCl_4 by the addition of a solution of Na_2CO_3, followed by washing with water, drying, and reduction by H_2 at 100°C (1 h).

It was found in the study of the alkaline hydrolysis of H_2PdCl_4 by measuring pH, pCl, and light scattering of solutions [49] that (1) at pH < 3, the Pd(II) complexes contain on the average 2.7 Cl ligands per one Pd atom; (2) at pH 3, PHCs appear that contain up to ten Pd atoms; and (3) at pH 3.5, the particles with more than 1000 Pd atoms are formed. At the end of titration, the precipitate has a $Pd(OH)_{1.6}Cl_{0.4} \cdot 0.1NaOH$ composition.

The data on the kinetics of alkaline hydrolysis of H_2PdCl_4 have been obtained in [50] by pH-metry. The pH of a solution rapidly decreases during the first minutes after the addition of an alkali. The storage of solutions for several days is accompanied by a gradual increase in their acidity. After storage of a solution with pH 3 for 20 h, the precipitate of Pd hydroxide appears (a solution becomes turbid). The addition of sodium chloride to a solution of Na_2PdCl_4 shifts the point of the precipitation to pH 6.

Many authors noted that, at a large excess of alkali, the complete substitution of chloride ligands occurs with the formation of $[Pd(OH)_4]$ complexes (see, for example, [51]). However, the authors disagree even regarding the composition of H_2PdCl_4 complexes in initial solutions. For instance, Kravchuk *et al.* [52] suggested on the basis of the spectrophotometric data that binuclear Pd complexes are present in these solutions. However, according to the spectrophotometric and potentiometric data and cryoscopic estimation of the molecular weight [53], only mononuclear Pd(II) complexes exist under the same conditions.

Thus, the data on the composition of the starting compounds and products of hydrolysis that formed upon alkalization of the solutions of Pd(II) complexes are contradictory and depend on the methods of investigation, data processing, and preparation of solutions [55]. Moreover, in most cases, the method of studying imposes stringent limitations on the concentration of the Pd(II) solutions.

We studied the alkaline hydrolysis of the Pd(II) compounds by a combination of modern physicochemical methods. These methods make it possible to analyze the composition of solutions by measuring directly the concentrations of different components and estimating their structural characteristics [56–60]. Most of these methods have not been previously used for this purpose. The concentrations of Pd that are often used in catalyst preparation are high, while reported concentrations are lower than 0.2 mol/l. Also, background electrolytes were used to stabilize the ionic strength of the solutions. Therefore, we varied, when possible, both the Pd concentration and the composition of the solutions over wide ranges.

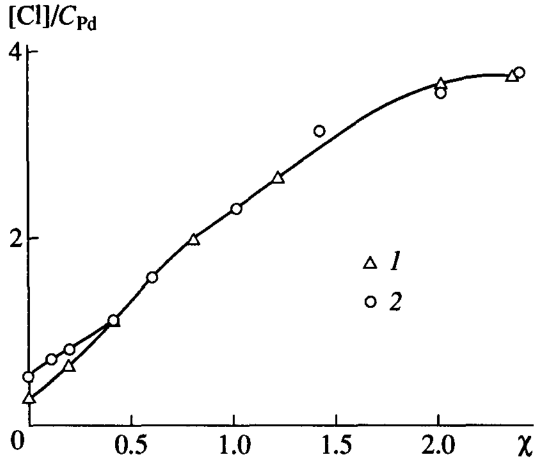

Fig. 4. Dependence of the relative concentration of Cl ions in solutions on the χ value at (*1*) [Pd] = 0.5 and (*2*) 0.25 mol/l.

2. Chemical Composition of the Compounds Formed upon the Alkalization of Na_2PdCl_4 Solutions

It was found by pH-metric titration [56] that PHC has the $[Pd(OH)]_n$ composition. This finding agrees with the data of [45]. However, the smoothness of the curve for potentiometric titration during the addition of NaOH to the solution of Na_2PdCl_4 in the range $0 < \chi < 2$ ($\chi = [Na_2PdCl_4]/[NaOH]$) allowed us to assume that in this case, the processing of the results within the framework of Sillen's theory "nuclei + monomeric units" [44] is incorrect.

The dependence of the concentration of free chloride ions calculated per one Pd(II) atom on the χ value was found by ^{35}Cl NMR spectroscopy [57] (Fig. 4). The curves for two different overall concentrations of Pd(II) in a solution deviate at the initial portions only. The middle portion of the plots are linear and can be used to determine the number of Cl^- ions evolved per one added OH^- group (in our case, two Cl^- ions) from the slope of these lines. The substitution of all chloride ligands for hydroxyls occurs at $\chi = 2$. At this χ value, the solution above the precipitate does not contain palladium, and the measurement of the equilibrium concentration of Cl^- ions showed that the precipitate contains 1 mole Cl^- per 1 mole Pd(II). The storage of the suspension of palladium hydroxide ($\chi = 2$) for 1 h does not change the Cl^- concentration. The variation of $[Cl^-]$ in time at $\chi = 1$ shows that during a period of 5 min to 2 h after the solution was prepared, the concentration of Cl^- ions remains constant despite the fact that the pH of a solution decreases by one during this period.

The deviation of the titration curves at their initial portions is due to autohydrolysis, which accompanies the alkaline hydrolysis of palladium compounds:

$$[PdCl_4]^{2-} + H_2O \rightleftharpoons [PdCl_3(H_2O)]^- + Cl^-. \quad (VII)$$

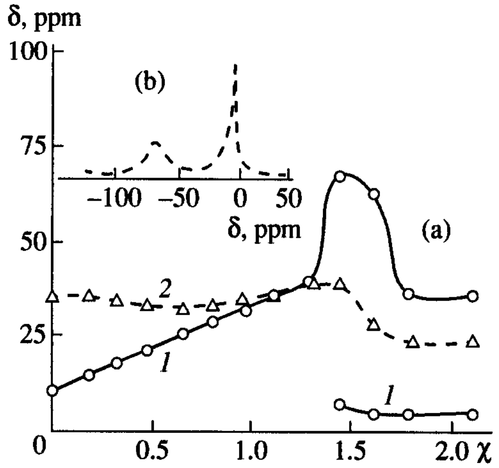

Fig. 5. (a) Dependence of the chemical shift on the χ value in solutions: (*1*) in the absence of a background electrolyte; (2) at the content of 2 mol/l NaCl. (b) The ^{133}Cs NMR spectrum of a solution without a background electrolyte at $\chi = 1.45$. $C_{Pd} = 0.2$ mol/l, and $C_{Cs} = 0.07$ mol/l.

After the formation of Cl^- ions (the products of alkaline hydrolysis) in a solution, this equilibrium shifts to the left, and its contribution becomes negligible.

The study of $[PdCl_4]^{2-}$ hydrolysis by UV spectroscopy [57] was carried out in the range of Pd(II) concentrations from 10^{-4} to 1 mol/l. The absorption bands at 45 000, 358 000, and 21 100 cm^{-1} typical of the $[PdCl_4]^{2-}$ ion [54] were observed for all solutions containing excessive NaCl. Mononuclear Pd(II) complexes containing OH^- and H_2O ligands were not found. A qualitative difference between the spectra of Pd(II) solutions with various χ values consists in an increase in the intensity of "background" absorption with an increase in χ in the short-wave region. A decrease in background absorption in the long-wave region suggests that the radiation (of the Rayleigh type) is scattered by the colloid particles of PHC, as has been observed in [49].

The variation in the concentration of $[PdCl_4]^{2-}$ ions in solutions with the χ change showed that the addition of one OH group per one Pd atom halves the concentration of tetrachloropalladate. Hence, two OH^- ions are necessary to bind one palladium atom to form PHC, and the composition of PHC can be expressed as $[Pd(OH)_2]_n$.

A similar picture was observed for solutions containing no background electrolyte, with two exceptions—at $C_{Pd} > 0.1$ mol/l, the $[PdCl_4]^{2-}$ complexes were present in solutions, and the absorption bands at 41800, 31800, and 23200 cm^{-1} typical of $[PdCl_3H_2O]^-$ [53] appeared in the UV spectra upon dilution with water.

At the same time, a weak band of water with the chemical shift of $\delta = -86$ ppm at the coordinate of Cl–Pd–H_2O was observed in the ^{17}O NMR spectrum of the starting solution of Na_2PdCl_4 ($C_{Pd} = 1$ mol/l) [56]. This indicates the presence of a $[PdCl_3H_2O]^-$ complex. The addition of alkali ($\chi = 0.1$) results in the broadening and weakening of this band, and at $\chi = 0.2$, it disappears.

Thus, the composition of reaction products suggests the following equation for the process:

$$n[PdCl_4]^{2-} + 2nOH^- \longrightarrow [Pd(OH)_2]_n + 4nCl^-. \qquad \text{(VIII)}$$

The coefficient n in equation (VIII) is so high that PHCs acquire the properties of colloidal particles.

The nuclei of the alkali metal cations respond to the anionic composition of solutions by a change in the position and intensity of the peaks in the NMR spectra [61]. Figure 5a shows the variation in the chemical shift in the ^{133}Cs NMR spectrum during the titration of the $Na_2[PdCl_4]$ solution containing the traces of CsCl by sodium hydroxide. A linear growth of the δ value in the region $0 < \chi < 1.2$ can be associated with the substitution of Cl^- ligands coordinated to palladium for OH^-, because $[Pd(OH)_4]^{2-}$ anions shift the line in the ^{133}Cs NMR spectrum stronger than $[PdCl_4]^{2-}$. However, δ changes are stronger than one might expect in the case of the formation of mononuclear $[Pd(OH)_4]^{2-}$ complexes. This disagreement is due to the interaction between Cs^+ and PHC.

A pronounced shift and line broadening occur at $\chi = 1.2$, and this is accompanied by the appearance of another, narrower line in the ^{133}Cs NMR spectrum (Fig. 5b). A position of the narrow line corresponds to the chemical shift of Cs in a solution containing $[PdCl_4]^{2-}$ and Cl^- (according to equation (VIII)). Therefore, cesium ions do not interact with PHC. A broad line in the spectrum is related to cesium ions that interact with PHC: because of the formation of PHC particles, some portion of the Cs^+ ions is located in closed cages formed by PHC chains, and these ions are separated from the solution bulk.

The effect of changing in the half-width of the line was also observed in the ^{23}Na NMR spectra, although the δ value remained constant during titration due to a low sensitivity of the Na nucleus to the chemical environment. The estimation of the concentration of Na^+ ions in a solution at $\chi = 2$ (a precipitate was filtered off) by ^{23}Na NMR showed that the precipitate contains ~1 Na^+ ion per 1 Pd atom. One can assume that alkali metal ions are the sites, linking the polymeric chains of the palladium hydroxide molecules, and thereby participate in the formation of the colloidal products of the alkaline hydrolysis of Pd(II) compounds.

Based on the data obtained and taking into account the material balance of cations and anions, the following scheme of the alkaline hydrolysis of $Na_2[PdCl_4]$ was proposed:

$$\begin{aligned} &\mathrm{a)Na_2PdCl_4} + 2\mathrm{NaOH} \\ &\longrightarrow \mathrm{Na_2[Pd(OH)_2Cl_2]} + 2\mathrm{NaCl}, \\ &\mathrm{b)}n\mathrm{Na[Pd(OH)_2Cl_2]} \\ &\longrightarrow \{\mathrm{Na[Pd(OH)_2]}\}_n \cdot n\mathrm{Cl} + n\mathrm{NaCl}. \end{aligned} \tag{IX}$$

Because step (b) is fast, the products formed in step (a) were unidentifiable.

3. Structure of Polynuclear Pd(II) Hydroxo Complexes

PHC particles sorbed from solutions on the surface of hydrophilized graphite were observed by high-resolution electron microscopy (HREM) [59]. The particles with diameters from 0.5 to 8 nm are seen on the micrographs of samples with $\chi = 0.2$ (Fig. 6). Large particles are the associates of the small particles. Generally, the particles have diameters of 0.8–1.2 and 2.0–2.4 nm. An increase in χ in solutions results in an increase in the number of particles per unit surface area of graphite (at a constant palladium content in the starting samples). The size distribution virtually does not change with an increase in χ in the samples prepared from solutions that were aged prior to adsorption.

The size distribution of PHC particles was studied by small-angle X-ray scattering (SAXS). The findings confirmed the HREM data that the distribution slightly depends on χ. Most particles fall into quite a narrow range of sizes, and particles with a diameter of 3.6 nm are the most abundant. In addition, the distribution maxima corresponding to the particles with the diameters of ~9.0 and ~13.0 nm are observed. The associates containing the central particle with a diameter of 3.6 nm surrounded by one (the first peak) or two (the second peak) layers of 3.6-nm particles should correspond to the sizes mentioned above.

Aging of solutions results in a decrease in PHC sizes. The diameter of small particles drops to ~2.8 nm, and the diameter of associates also decreases. The PHC formation processes can be divided into primary and secondary. The primary processes occur immediately after the addition of alkali to a solution of Pd(II) and result in the fast formation of particles according to equations (IX). The secondary processes consist in the formation of PHC associates and the oxide crystalline structure of particles, accompanied by a slow change in the acidity [50], as well as by the precipitation [49] and variation of other properties of the solutions.

Notably, the particle sizes determined by SAXS are somewhat larger than those found by HREM (1.8–2.0 and 2.8 nm, respectively). This is because HREM determines the particle sizes, taking into account only $\mathrm{Pd_2}$ ions of $[\mathrm{Pd(OH)_2}]_n$ clusters, whereas SAXS also takes into account ions in the solvate shell of clusters. A decrease in the particle sizes in the samples for HREM is due to the crystallization of PHCs adsorbed on graphite with the formation of the compact crystalline structure upon drying [60] (see below).

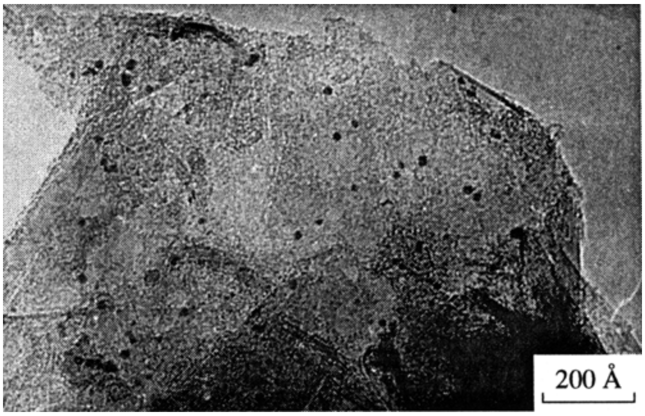

Fig. 6. A HREM pattern of the sample of Sibunit saturated by Pd(II) compounds from a solution of PHC.

The interatomic distances in the PHC structure were measured by the EXAFS technique [59]. The interatomic distances around Pd in the first coordination sphere of mononuclear Pd(II) complexes are as follows: Pd–Cl, 2.25 Å ($R - \delta' = 1.85$ Å), Pd–O – 2.0 Å ($R - \delta' = 1.5$ Å). The symbol R denotes the interatomic distance, and δ' is a correction equal to 0.5 Å for O and Cl atoms and 0.25 Å for Pd.

The EXAFS spectrum of a solution with $\chi = 1$ showed that Pd complexes are present in which the central atom is surrounded by both chloride and oxygen-containing ligands ($\mathrm{O^{2-}}$, $\mathrm{OH^-}$, and $\mathrm{H_2O}$). This method fails to distinguish between complexes in which the central Pd atom is surrounded by only $\mathrm{Cl^-}$ ligands, only oxygen-containing ligands, or mixed ligands. However, taking into account the above data [57] on the composition of PHC solutions, we attributed the signals of the ligands of the first coordination sphere to the Pd–Cl and Pd–O distances in $[\mathrm{PdCl_4}]^{2-}$ complexes and oxygen-containing ligands of PHC.

The spectrum of a solution with $\chi = 1$contains two additional intense peaks: with $R - \delta' = 2.4$ Å and $R - \delta' = 2.9$ Å. These interatomic distances were not found in crystallographic data on palladium compounds. Therefore, to assign these peaks, we built the PHC models with various arrangements of the plane coordination $\mathrm{PdO_4}$ squares. Figure 7 presents a fragment of the PHC structure that best agrees with the EXAFS data. Palladium atoms are coordinated to the oxygen atoms of two types. Oxygen atoms of bridging ligands (O3 and O4) that connect two neighboring Pd atoms by two oxygen bridges belong to the first type. In this case, the Pd1–O3—Pd2 angle is 90° and the Pd1–Pd2 distance is 2.65 Å ($R - \delta' = 2.4$ Å). The second-type oxygen atoms connect two Pd atoms via one bridge. The Pd2–O6–Pd3 angle is 106° (it is close to the H–O–H angle in a water molecule), and the Pd2–Pd3 distance is 3.2 Å ($R - \delta' = 2.95$ Å).

The EXAFS spectra of solutions with various χ values differ from that presented above only by the ratio of the peak intensities. The number of Cl^- ions bonded to Pd was calculated from the intensities of the peaks due to the ligands in the first coordination sphere of palladium. At $\chi = 0.25$, 0.5, and 1, the percentage of initial Cl^- ligands that are coordinated to Pd is ~90, ~30, and ~50%, respectively. At $\chi = 2$, the solution does not contain chloride ligands that are coordinated to Pd. These values are in good agreement with hydrolysis equations (IX).

The aging of the agar-stabilized PHC suspension (at $\chi = 2$) for 2 weeks results in an increase in the intensity of the peak at $R - \delta' = 2.95$ Å. This is associated with the gradual reconstruction of the filament structure of palladium hydroxide into the three-dimensional structure of its oxide [62] that can be represented as a stack of the coordination Pd_4 squares (Fig. 8). The reconstruction is accompanied by a decrease in the number of the double oxygen bridges. This process favors a more compact rolling of the filament structure of PHC and a decrease in the diameter of the particles. The reconstruction should also be accompanied by a decrease in the pH of the solutions mentioned above because, in this case, one bridge and one terminal hydroxyl are coordinated to two neighboring Pd atoms instead of two bridging OH^- ligands. Excess OH^- are provided by the dissociation of water with the evolution of H^+.

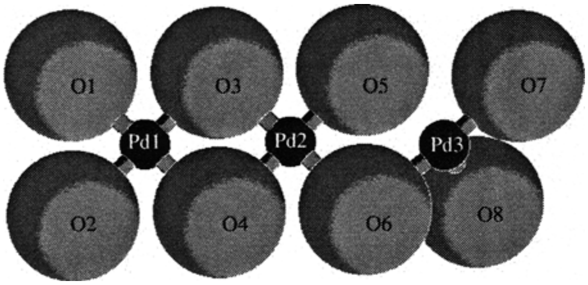

Fig. 7. A fragment of the PHC polymeric chain. Atom 09 (in *trans*-positions to 08) is omitted.

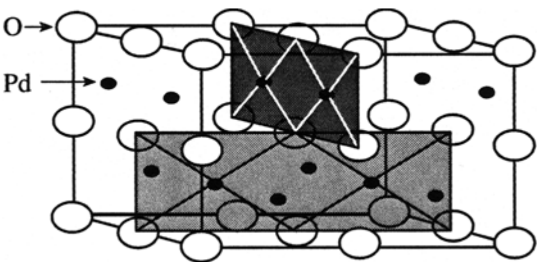

Fig. 8. A fragment of the crystalline structure of PdO. The perpendicular chains of coordination PdO_4 squares are shown.

To summarize the above data, we conclude that PHC is shaped as a filament consisting of planar PdO_4 squares that are rolled into a ball. The presence of single bridges makes the filament mobile, and it can roll into a compact particle. These branches also favor branching. A stable particle contains ~100 Pd atoms, and this value corresponds to the diameter of a compact globule found by HREM (2.0 nm).

4. Adsorption of Polynuclear Pd(II) Hydroxo Complexes on Carbon Materials

Adsorption isotherms for palladium from the PHC solutions with various χ values on Sibunit (S_{BET} = 250 m^2/g) give evidence [60] that the surface concentration of Pd increases with increasing χ. Acidity does not affect adsorption isotherms, and this is confirmed by the coincidence of the adsorption isotherms from solutions of H_2PdCl_4 with pH ~ 0.5 and Na_2PdCl_4 with pH ~ 4.

To find the reasons why adsorption intensifies with increasing χ, the experimental adsorption isotherms were processed assuming that PHC particles occupy the same sites (A) on the surface of the carbon material (CM) [20] as mononuclear Pd(II) complexes. Then the concentration of the occupied surface sites will be determined by the first member in the right-hand side of the equation that describes the adsorption equilibrium

$$\mathrm{Pd(II)(solution) + PHC(solution) + A(CM)}$$
$$\rightleftharpoons \mathrm{[Pd(II)\text{–}A](CM) + [PHC\text{–}A](CM)},$$

where the first member determines the concentration of the occupied adsorption sites, because every PHC particle contains ~100 Pd atoms. If we assume one-site adsorption, the contribution of the second member into the fraction of the occupied adsorption sites would be ~1%. Even if a PHC particle could occupy several neighboring adsorption sites, the fraction of these sites will be small as compared to that of the sites occupied by mononuclear complexes.

Consequently, the concentration of adsorbed mononuclear Pd(II) complexes calculated according to equation (IX) can be used instead of the overall concentration of Pd on the support. The fraction α of Pd in mononuclear complexes is $1–0.5\chi$; that is, at $\chi = 1$, $\alpha = 0.5$; at $\chi = 0.8$, $\alpha = 0.6$; at $\chi = 0.5$, $\alpha = 0.75$; and at $\chi = 0.2$, $\alpha = 0.9$. When adsorption is carried out from Na_2PdCl_4 solutions that do not contain added alkali, the fraction of mononuclear complexes is 1.0.

The adsorption isotherms of palladium from solutions of various compositions that were modified taking into account the competition between mononuclear and polynuclear complexes for the adsorption sites coincide in the region of low equilibrium concentrations in a solution [60]. Some deviation between the curves at high concentrations is due to the formation of PHC associates. It is reasonable to expect that the probability of the formation of these associates will increase with an increase in χ and the Pd(II) concentration.

The dependence of the concentration of Cl^- ions in the palladium compounds adsorbed by the surface of the carbon material on χ shows that adsorbed PHCs retain the ionic shell consisting of Cl^- ions solvated by water; their composition does not change as compared to that of PHCs in a solution [60]. It was found by XRD that the samples prepared by different methods are characterized by different degrees of structure perfection: complete disordering (a size of the region of coherent scattering is < 1.0 nm) is observed for the as-prepared suspension of PHC; highly dispersed particles with the PdO structure (the size of the coherent scattering region is 2.5 nm) form upon drying the suspension at 400°C; and the size of the coherent scattering region becomes 1.5 nm upon HPC adsorption on Sibunit followed by the drying of the sample for 24 h at room temperature.

Analysis of the intensity of X-ray scattering by the radial distribution of atoms (RDA) method for the bulk palladium oxide and PHC provides comprehensive information on the structural features of the samples. The metal atoms in the tetragonal cage of palladium oxide are surrounded by four oxygen atoms in the vertices of a planar tetragon, and the tetragons having common sides form chains which intersect at the angle of 90° (Fig. 8). Two peaks on the RDA curve correspond to the shortest Pd–Pd distance in this compound; one of them ($r = 3.04$ Å) relates to the distances within one chain, and the other ($r = 3.43$ Å) corresponds to the distances between the metal atoms of perpendicular chains. In the perfect PdO structure, the ratio between the areas of the above peaks is 1 : 2, whereas in the spectrum of as-prepared PHC it is 1 : 1.18, which indicates the predominant formation of separate chains. Similarly, the area of another peak corresponding to the distances between palladium atoms of different chains ($r = 5.50$ Å) significantly decreases. A relative increase in the area of the peak with $r = 4.74$ Å, corresponding to the Pd–O distance within one chain, provides evidence on a rather large number of these atoms in the PHC structure, that is, on its filament shape.

The curve describing the intensity of RDA for dried PHC corresponds to a greater extent to the PdO crystalline structure rather than to the structure of hydrated PHC: the areas of peaks that characterize metal–metal distances in perpendicular chains increase. This indicates the formation of the bulk PdO structure.

Thus, we were able to find that the composition of PHCs adsorbed on carbon supports does not change as compared to that in solution. The following drying of samples results in the reconstruction of an adsorbed PHC particle, namely, in the formation of the structure of PdO. This reconstruction performed under mild conditions and at a low Pd content is not accompanied by a substantial change in the number of Pd atoms in the particle.

Figure 9 presents the scheme for the formation of PHC particles adsorbed on the surface of carbon materials that are the precursors of the active sites of the Pd/C catalysts. Note that "the possibility" for hydrolysis according to this scheme was proposed in [63]. We determined the structure of the starting complexes A by UV, ^{35}Cl and ^{17}O NMR, and EXAFS spectroscopy. We failed to prepare chlorohydroxo complexes B due to their fast polymerization to form PHC (C). The composition of the latter complexes was studied by NMR and UV spectroscopy, chemical analysis, and potentiometry. The molecular-level study of the structure of PHC (D) was carried out by the EXAFS, RDA, and NMR techniques and on the macromolecular level (C), was

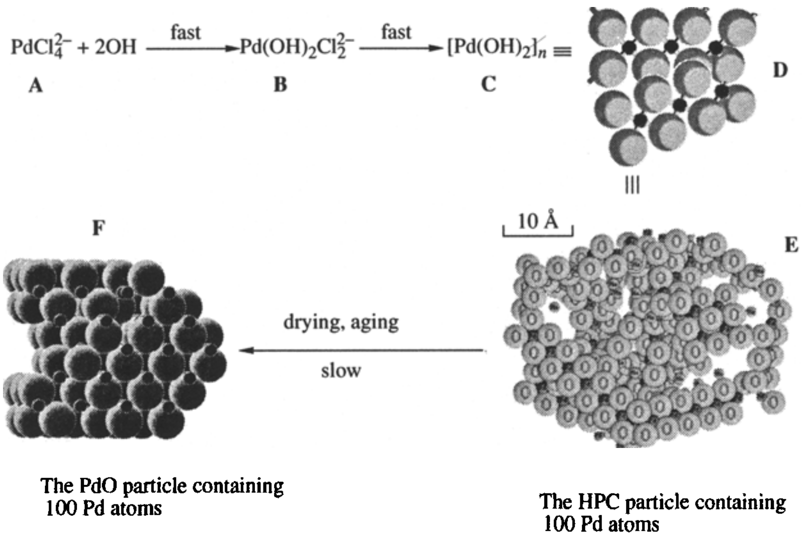

Fig. 9. A scheme of the formation of the precursor species of the catalytic sites.

Table 3. Activity of the 1% Pd/Sibunit catalysts in the hydrogenation of phenylacetylene and styrene at an atmospheric pressure and 50°C

χ	Activity, (ml H_2) (mg Cat)$^{-1}$ min^{-1}	
	Ph–C≡CH	Ph–CH=CH_2
0	0.03	0.07
0.2	0.04	0.012
0.4	0.09	0.025
1.2	0.012	0.032

examined by HREM, XRD, and SAXS. Upon drying or aging, the PHC molecules reconstruct into the dispersed particles of palladium oxide (F) as shown by HREM, EXAFS, SAXS, RDA, and XRD. After reduction, the highly dispersed particles of palladium metal are formed.

5. Some Features of Pd/C Catalysts Prepared Use PHC

A series of Pd/C catalysts was prepared by the synthesis of PHC followed by their adsorption from a solution on the surface of the carbon material (Sibunit) and reduction with sodium formate at 80°C.

Table 3 shows that the activity of the catalysts in hydrogenation of sterically “inconvenient” substrates (phenylacetylene and styrene) increases with increasing χ. We explain this by increasing the content of palladium metal particles accessible to reactants because PHC particles are only adsorbed in large (of a ~4.0 nm diameter) pores, whereas the metal particles blocked in narrow pores are formed from mononuclear complexes. Note that according to the HREM data, the monomodal distribution of Pd particles (the average size is 1.5–2.0 nm) is observed in the Pd/C catalyst already at $\chi = 0.1$.

As shown above, the alkali metal cations enter the composition of the PHC particles. Therefore, one could expect the effect of the nature of alkali metal on the composition and structure of oxide precursors formed upon PHC adsorption on the surface of carbon materials and, consequently, on the activity of Pd/C catalysts.

The rates of nitroethane hydrogenation (atmospheric pressure, 25°C) over the 1% Pd/Sibunit catalysts prepared using LiOH, NaOH, KOH, and CsOH at the stage of PHC synthesis and reduced with hydrogen at 200°C are equal to 15×10^{-3}, 10×10^{-3}, 5.5×10^{-3}, and 4×10^{-3} (ml H_2) (mg Cat)$^{-1}$ min^{-1}, respectively. As can be seen, the catalytic activity increases with the increasing atomic weight of the alkali metal. The reasons for this phenomenon are still unclear, but some hypotheses can be formulated:

(a) Alkali metal cations that remain in the composition of oxide precursors after destruction of adsorbed PHC are localized after reduction near palladium metal particles and modify them (this effect of alkali metal has been observed, for example, for the Ru/C catalysts for ammonia synthesis [64]);

(b) The nature of alkali metal in the composition of PHC affects its lyophilic properties and hence its position on the surface of the carbon support. Although alkali metal ions can be washed out during further transformation of PHC into a dispersed particle of palladium oxide, a palladium metal particle, which is formed from the palladium oxide cluster, is able to “recognize” its position, determined by the nature of the alkali metal.

The above data show how interesting and unexpected is the chemistry of the formation of active sites in the Pd/C systems that have long been known and reported in hundreds of articles and patents. To conclude, we would like to emphasize the role of the physicochemical properties of the surface of carbon material. The surface regions capable of adsorption can be treated as polyfunctional macroligands whose nature strongly affects both the structure of the precursors of palladium metal particles and their catalytic properties. Some technical “secrets” of Pd/C catalyst preparation have already received scientific explanation, although other problems are still to be solved.

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