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Modern approaches to the preparation of "palladium on charcoal" catalysts

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ABSTRACT. **The methods of preparation of deposited palladium catalysts on carbon carriers are discussed. The characteristics of the structures of porous carbon materials, the methods for the regulation of their structural and physicochemical characteristics, the methods for the deposition of palladium on a carbon carrier, and individual stages of a catalyst preparation process are examined.**

The bibliography includes 74 references.

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I. Introduction

The vigorous development of the industrial manufacture of products of organic synthesis, including monomers, dyes, medicinal preparations, biologically active substances, and various valuable semi-finished products has aroused during the last decade considerable interest among investigators in the creation of highly selective catalysts for fine organic synthesis. Pd/C catalysts have found extensive applications in the processes involved in fine organic synthesis. Such applications are based on the catalytic chemistry of palladium with its rich content, including virtually the entire range of hydrogenation, isomerisation, dehydrogenation, and hydrogenolysis processes,[1–3] as well as the wide assortment of activated charcoals with extensive porous structures and their ready availability.

The composition of these catalysts is very simple. They include only two components—metallic palladium and the carbon carrier. However, by varying the structural characteristics of the palladium (dispersity, particle shape, distribution within the carrier grain) and of the carbon carrier (grain size, porosity, specific surface), it is possible to create a large set of catalysts for a wide range of processes.[4]

Numerous patents describing the methods of preparation of Pd/C catalysts do not answer the question which physicochemical processes occur at each stage of their preparation and how these processes can be controlled.

Although the available reviews[5,6] and fundamental studies published recently[7–15] throw some light on the structure of the Pd/C catalysts, nevertheless there are as yet no reliable methods for their purposeful construction.

The development of the scientific principles governing the preparation of catalysts should help to elucidate the factors determining their properties and to devise procedures for controlling these factors. The most important characteristics of the Pd/C catalyst are as follows:

the texture of the carbon carrier;

the size and structure of the deposited palladium particles;

distribution of the palladium particles on the carrier surface.

The present review is devoted to the consideration of modern methods for the preparation of Pd/C catalysts and the analysis of processes occurring in individual stages of their preparation.

II. The structure of carbon carriers

The structure of carbon carriers and the principal procedures for their preparation have been described in monographs and reviews.[16–21] Porous carbon materials usually employed as catalyst carriers belong to the class of carbon-graphite materials consisting predominantly of sp^2-hybridised carbon atoms with a definite ordered arrangement in space (extended networks or microcrystallites).

The structure of carbon carriers is illustrated in Fig. 1. The dimensions of the graphite microcrystallites can vary in the range L_a = 0.7–10.0 nm and L_c = 0.9–6.0 nm depending on the nature of the raw material employed and the conditions in their carbonisation.[17,18] High-temperature heat treatment of carbon materials makes it possible to increase the degree of crystallinity of the carbon, i.e. to increase the parameters L_a and L_c and to diminish the interplanar spacing d_{002} to a value close to that for graphite (0.3354 nm).[18]

In the majority of carbon carriers, the carbon microcrystallites are oriented at random on the surface (Fig. 2*a*). At the same time, there exist procedures for the deliberate orientation of basal faces or end faces of microcrystallites. In particular, the deposition of pyrolytic carbon on a solid support promotes the preferential emergence onto the surface of the basal faces of the graphite microcrystallites[22–24] (Fiog. 2*b*). Pyrolysis of hydrocarbons on catalyst particles (Ni, Fe) leads to the formation of carbon fibres and in this case the end faces emerge preferentially onto the surface[25] (Fig. 2*c*).

The chemical nature of the surface groups exerts a considerable influence on the adsorption interaction of the active component with the carbon carrier. Surface oxygen groups are of greatest interest for the preparation of deposited catalysts.

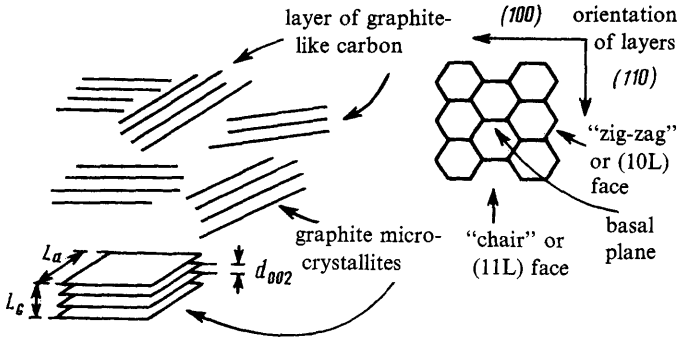


Figure 1. Schematic representation of the microstructures of carbon carriers (according to the data in Walker's book[17]).

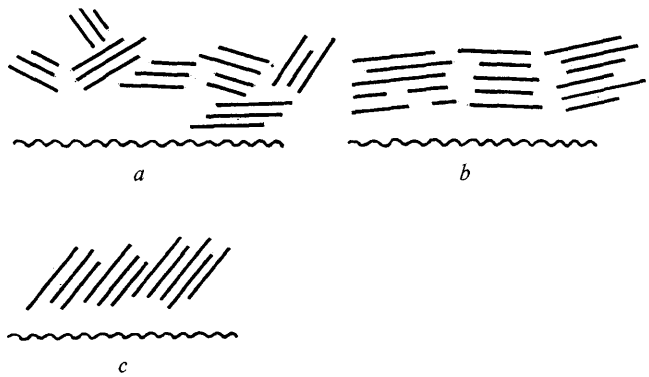


Figure 2. Orientation of graphite microcrystallites on the surfaces of carbon carriers obtained by carbonising cellulose (*a*), by the high-temperature gas-phase pyrolysis of hydrocarbons (*b*), and by the catalytic pyrolysis of hydrocarbons on transition metals (*c*),

Numerous data concerning the identification and study of the properties of such groups are available.[16,26–31] According to a classification,[28] mainly oxygen groups of four types, differing in acidity, are present on the surfaces of carbon carriers (Fig. 3).

The overall concentration of surface oxygen groups can be increased (or reduced) by heating the carbon carrier in an oxidising (or inert) atmosphere.[32] The proportions of groups of different types can be altered by selecting appropriate conditions for the treatment of the carrier and the nature of the oxidising agent.[19,33]

Basic surface oxygen groups can be formed as a result of the low-temperature chemisorption of oxygen on a carbon carrier subjected to a preliminary vacuum heat treatment.[28]

The porous structure of carbon carriers plays an important role in the transport processes involving the molecules of the reactants and reaction products.[31] According to the classification adopted by IUPAC, pores are divided into four types in terms of their dimensions:[34,35] micropores (r_{eq} < 0.6–0.7 nm); supermicropores (0.6–0.7 nm < r_{eq} < 1.5–1.6 nm); mesopores (1.5–1.6 nm < r_{eq} > 50–200 nm), and macropores (r_{eq} > 50–200 nm).

The traditional technological procedures for the preparation of porous carbon materials[18] involve the carbonisation of the initial raw materials and the activation of the carbon material. Pore-forming agents in the form of mineral additives or carbonised polymeric foam materials are used to increase the volume of the macropores.

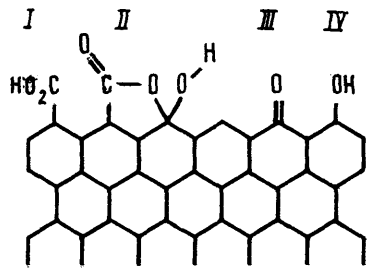


Figure 3. Types of surface oxygen groups: (I) carboxy-groups; (II) lactone groups; (III) carbonyl groups; (IV) phenolic groups.[28]

By using different kinds of carbonised raw material and by varying the parameters of its activation, it is possible to obtain a wide range of carbon carriers with an extensive system of micropores.[21,36]

Mesoporous carbon carriers, in which pores whose size is 2–10 nm predominate, can be obtained by carbonising mixtures of carbon black with a polymeric binder, for example, phenol–formaldehyde resin or furfuryl alcohol.[37]

A new class of porous materials called Sibunit has been developed for the preparation of deposited catalysts with a specified porous structure.[38,39] Sibunit is obtained by depositing a layer of pyrolytic carbon on the surface of technical carbon (Fig. 4). This results in the formation of a carbon–carbon composite material, in which the volume and size of the mesopores and macropores can be regulated by varying the dimensions of the primary globules of the technical carbon, their relative disposition, and the technical carbon/pyrolytic carbon ratio.[40,41] Activation of the composite carbon material with steam and oxygen makes it possible to increase the volume of the micropores and fine mesopores without altering significantly the size of the large pores.[42,43]

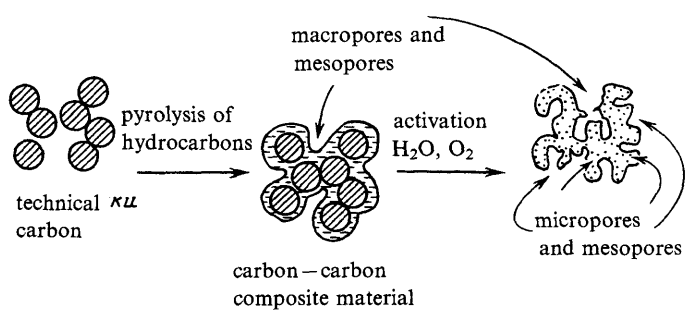


Figure 4. Schematic illustration of the formation of the porous structure of carbon carriers of the Sibunit type.

Thus there is a possibility of creating carbon carriers with specified structural and physicochemical characteristics.

III. Methods for the deposition of palladium on a carbon carrier

In the general case, the preparation of Pd/C catalysts includes two stages—the deposition of the active component and reduction, leading to the formation of metallic palladium on the surface.

It is possible to differentiate three main procedures for the deposition of the active component.

1. Deposition of palladium compounds in the molecularly disperse state

In the general form, this method can be described schematically as follows:



where the surface of the carbon carrier is shown shaded.

Palladium compounds are fixed on the surface of the carbon carrier under these conditions by means of adsorption or chemical interaction.

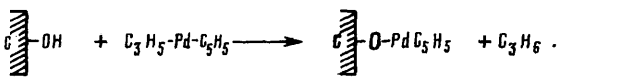
The complex PdL_x can be adsorbed as a result of the interaction of a palladium ion with the structural elements of the carrier surface. It has been shown in a number of studies[43–46] that palladium is adsorbed from solutions of its chloride complexes on the surface of the carbon carrier predominantly in the form of $PdCl_2$. On the surface of the carbon carrier, there are three types of adsorption centres: A_1, A_2, and A_3 which represent a set of surface structures containing unsaturated carbon–carbon bonds and differing in the strength of their interaction with $PdCl_2$. The centres for weak (A_1) and moderate (A_2) adsorption are located on the surfaces of mesopores and macropores, while the centres for strong adsorption (A_3) are in the micropores. The oxidation of the carrier surface by oxygen at 300 °C does not alter its adsorption properties, whilst the liquid-phase oxidation by powerful oxidants (H_2O_2, $KMnO_4$) diminishes appreciably the concentration of the above adsorption centres.[44]

The reduction with gaseous hydrogen of adsorbed palladium chloride complexes leads to the formation on the surface of the carbon carrier of metallic palladium particles, whose size ranges from 1–2 to 3.4–3.7 nm.[12] The reduced palladium particle size does not depend significantly on the volume of the micropores in the carbon carrier, but diminishes sharply after the treatment of the carrier with nitric acid,[15] which results in the formation of oxygen groups on the surface;[19,47,48] this should in turn tend to increase the palladium particle size by reducing the number of adsorption centres for palladium chloride.[44]

The increase in the dispersity of the metallic palladium as a result of the oxidation of the surface is apparently caused not by the adsorption of the chloride complexes but by the stabilisation of the metallic particles on the oxidised sections on reduction of the adsorbed compounds.

The adsorption of the palladium complexes PdL_x can proceed via the interaction of the ligands L with the surface of the carbon carrier. For example, the zerovalent palladium complex Pd_2DBA_3.DBA (where DBA = dibenzoylacetone) is adsorbed on the carbon carrier from a benzene solution. The thermal decomposition of the adsorbed complexes followed by reduction with hydrogen affords a catalyst in which the dominant metallic palladium particle size is approximately 2 nm.[49]

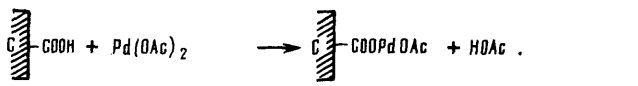
The chemical interaction of the active component with the carrier surface is widely used to obtain complexes fixed on the surface of oxide carriers in a molecularly disperse state.[50] This method has also been used in relation to carbon carriers.[51,52] Its essential feature is the interaction of the organopalladium compound with surface functional groups on the carrier, for example:



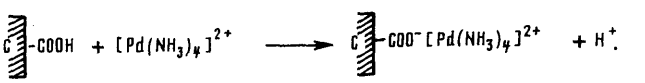
The subsequent reduction of the specimen in a stream of hydrogen leads to the formation of metallic particles on the surface having a particle size of 1–3 nm predominantly.

The chemical interaction of palladium compounds with a carbon carrier can also proceed as an oxidation-reduction process with participation of palladium(II) ions and surface groups having reducing properties (unsaturated carbon–carbon bonds, alcoholic groups, etc.).[53] This process has negative consequences, because palladium is deposited on the carrier surface in an uncontrolled fashion, giving rise to a bright film of metallic palladium. To prevent this process, palladium is deposited in the presence of oxidants: H_2O_2 [53] or Cl_2.[54]

Ion exchange on carbon carriers can also be used to prepare catalysts. The mechanism of the ion-exchange interaction between transition metal compounds and carbon adsorbents has been examined.[19,55] In the simplest case, such interaction takes place via the exchange of the acetate ligands in $Pd(OAc)_2$ for surface carboxylate groups:[56]



The reduction of surface compounds by hydrogen leads to the formation of highly disperse deposited palladium particles with an average size of ~2 nm. When this method is used, the surface concentration of carboxy-groups is important. A five-fold increase in the concentration of surface carboxy-groups after the oxidation of the initial carbon carriers with potassium permanganate diminishes the metallic palladium particle size to 1 nm. On the other hand, decarboxylation of the surface by vacuum heat treatment at 500 °C promotes the formation of large particles up to 10 nm.[56] The ion exchange method has been used most widely for the deposition of amminepalladium complexes:[12,15]

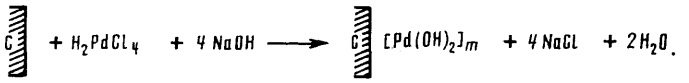


The subsequent reduction of the surface complexes in a stream of hydrogen leads to the formation of deposited palladium particles with an average size of 2.1–2.4 nm.[12] When this method is used, one should recall the significant role played by the texture and chemical composition of the carbon carrier. Thus, when palladium

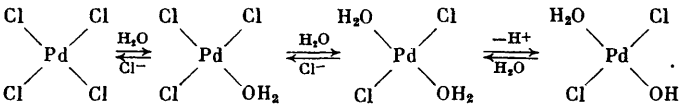
is deposited on the NORIT SXI GA 3/33 carbon carrier, the average particle size, determined from the adsorption of CO, is 48.3 nm. The activation of the initial carrier in a CO_2 atmosphere at 1200 K, involving the burning away of up to 23% of carbon which results in a decrease in the concentration of surface carboxy-groups, increases the palladium particle size to 120 nm.[14] The oxidation of the carrier surface with nitric acid (i.e. the formation of surface carboxy-groups) promotes a sharp decrease in the palladium particle size to 3 nm.[15]

2. Deposition of sparingly soluble palladium compounds

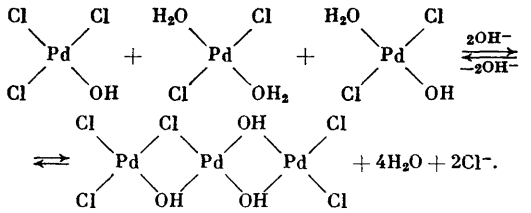
A traditional procedure for the preparation of a wide range of industrial catalysts involves the deposition of palladium hydroxide on the surface of a carbon carrier:



This method is based on the conversion of palladium chloride complexes in several stages. The first of these is the hydrolysis of H_2PdCl_4:

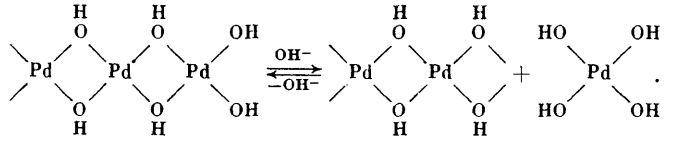


This stage is promoted by diluting the solution, by increasing the pH from 1 to 3, and by reducing the Cl^- concentration.[57-59] This is followed by the formation of a polymer:



The growth of the polymer is favoured by an increase in the concentration of palladium complexes, by an increase in pH from 3 to 8, and by a decrease in the Cl^- concentration.[59]

The polymer is degraded in a highly alkaline medium at pH > 12:



The size of the polymer molecules formed (a polynuclear hydroxo-palladium complex) can be regulated by selecting the pH, the Cl^- concentration, the temperature, and the duration of the "ageing" process.

Alkali metal hydroxides, carbonates, and bicarbonates are used for the deposition of polynuclear hydroxopalladium complexes on a carbon carrier. The Pd/C systems obtained using alkali metal carbonates and bicarbonates as the alkaline agent are the most active. Evidently this is due to the fact that pH 3–8, which is optimal for the formation of polynuclear hydroxo-complexes, is thereby established in the given instance.

When palladium is deposited on a carbon carrier, the order of the addition of the reactants can be various. When sodium carbonate is added to a suspension of activated charcoal in a chloropalladic acid solution,[60] a proportion of the palladium chloride complexes, corresponding to the adsorption capacity of the carbon carrier, is fixed on its surface via an adsorption mechanism, while the remaining palladium is deposited on the surface in the form of hydroxide particles (polynuclear hydroxo-complexes). This results in a multimodal size distribution of the palladium particles with a maximum at 2.0 nm and a plateau in the range from 6 to 16 nm.[47] When a solution of chloropalladic acid is added to a suspension of activated charcoal in a sodium bicarbonate solution,[61] the deposition takes place in a weakly alkaline buffer medium generated by sodium carbonate and the sodium form of the surface carboxylate groups of the carbon carrier.

When solutions of chloropalladic acid and the alkaline agent are added simultaneously to a suspension of the carbon carrier,[62] the deposition takes place at a constant pH 7.5–11.0, which ensures a more uniform size distribution of the palladium particles. Finally, preliminary mixing of solutions of chloropalladic acid and of the alkaline agent with subsequent deposition of the polynuclear hydroxopalladium complexes formed on the carbon carrier[15,63] makes it possible to attain a high dispersity of the palladium (2.0–3.0 nm) with a narrow size distribution of the particle.[63]

According to the mechanism of the hydrolysis of palladium chloride complexes,[59] an increase in the Cl^- concentration prevents an increase in the size of the particles of the polynuclear hydroxopalladium complexes. This may result in an increase in the dispersity of the palladium, which entails an increase in its activity. Indeed, an increase in the concentration of Cl^- during the deposition of palladium hydroxide on a carbon carrier makes it possible to increase by a factor of 1.5 the activity of the Pd/C catalyst in the hydrogenation of dinitrotoluene.[64]

3. Deposition of palladium in the form of colloidal particle sols

This method consists of two stages:

(1) the preparation of the colloidal solution (sol) of the palladium-containing compound $[Pd_c]L_x$, where L_x are ligands stabilising the colloidal palladium Pd_c particle in solution;

(2) deposition of the sol on the carbon carrier, which makes it possible to obtain catalysts with a uniform size distribution of the palladium particles and to regulate the particle size by selecting the conditions in the preparation of the colloidal solution and the palladium-containing compound:



Questions concerning the preparation of colloidal palladium solutions and the study of their properties have been surveyed in reviews.[65-68] It is possible to differentiate two main approaches to the preparation of these solutions. In one case, palladium vapour is

condensed in an inert solvent matrix. For this purpose, palladium is heated in a vacuum chamber and introduced to a stream of the inert solvent. The metal vapour formed is condensed together with the solvent on the walls of a trap cooled with liquid nitrogen. After heating the trap to the melting point of the solvent, a colloidal solution of palladium is obtained.

When methylcyclohexane is used as the solvent, the colloidal palladium solution thus obtained has an average particle size of 2.05 ± 0.5 nm and can be used to prepare deposited palladium catalysts.[65]

Another approach presupposes the reduction of palladium complexes in solution:

$$H_2PdCl_4 + xL \xrightarrow[-HCl]{Red} [Pd_c]L_x,$$

where Red is hydrogen, formaldehyde, sodium citrate, carbon monoxide, hydrazine, sodium formate, acrolein, titanium chloride, etc.[67]

The average size of the colloidal palladium particles formed in the chloropalladic acid–sodium formate–sodium hydroxide system can be regulated in the range from 47.0 to 12.5 nm by varying the pH in the range 2.1–11.2 and the duration of the reduction reaction from 1 to 180 h.

The use of sodium citrate as the reductant permits a decrease in the average palladium size to 7.5 nm.[67] Monodisperse palladium sols with an average metallic particle size from 0.9 to 7.5 nm have been obtained by reducing palladium chloride complexes with sodium citrate under an inert atmosphere at a controlled pH.[69] Pd/C catalysts in which the average metallic particle size is between 3.0 and 7.5 nm according to electron microscope data were prepared by this procedure.[70]

Table 1. The dispersity of palladium in the Pd/C catalysts prepared by different methods.

Method of deposition	Palladium compound	Average particle size, nm		References
		deposited	reduced	
Adsorption	H_2PdCl_4	Molecularly disperse state	3.4	[12]
			0.81–1.91	[15]
			1.0–2.0	[48]
	$Pd_2(DBA)_3.DBA$	Ditto	~2.0	[48]
Chemical interaction	C_5H_5–Pd–C_5H_5	»	1.0–3.0	[51]
Ion exchange	$Pd(OAc)_2$	»	~2.0	[56]
	$Pd(NH_3)_4^{2+}$	»	2.1–2.4	[12]
	$Pd(NH_3)_4^{2+}$	»	2.1–120	[15]
Deposition of sparingly soluble compounds	$Pd(OH)_2$	2.2	2.5	[71]
Deposition of palladium sol	Pd	2.5	3.0	[70]

When palladium is deposited both in the molecularly disperse state and in the form of the hydroxide or a sol, after the reduction of the catalyst the average particle size of the metallic palladium is in the range 1–3 nm (Table 1), which means that the process involving the migration of palladium during the reduction of the catalyst plays an important role in the formation of the deposited particles.

Indeed, the study of the characteristics of the reduction of deposited palladium compounds by hydrogen showed that the size and shape of the metallic particles formed depend on the concentration of palladium ions in the liquid phase.[71] The equilibrium concentration of Pd^{2+} ions in the solution over the palladium hydroxide deposited on the carbon carrier at pH ~ 7 is negligible and after reduction the size of the metallic particles corresponds to the size of the initial palladium hydroxide particles. In an acid or alkaline medium, the equilibrium Pd^{2+} concentration in the solution increases sharply by virtue of the formation of the $PdCl_4^{2-}$ or $Pd(OH)_4^{2-}$ complex. The reduction of the catalyst under these conditions leads to the formation of large palladium crystallites.[71]

The palladium reduction process can be represented in a general form by the scheme illustrated in Fig. 5, which makes it possible to explain the causes of the formation on the surface of the carbon carrier of particles of different size and with a wide variety of geometrical shapes. Thus the use of the procedures listed above leads to the possibility of the purposeful regulation of the dispersity of the deposited palladium particles.

The distribution of palladium with respect to the grain radii is one of the most important parameters determining the efficiency of granulated catalysts.[4] The traditional procedure for regulating the concentration profile of the active component are based on the diffusion of the deposited compound into the bulk of the carrier grain and its adsorption on the surface.[72,73]

The procedures for the regulation of the pore structure and chemical composition of the carbon carrier surface examined above can be used also for the selection of the optimum contributions of the processes involving the diffusion and adsorption of the deposited palladium compounds.

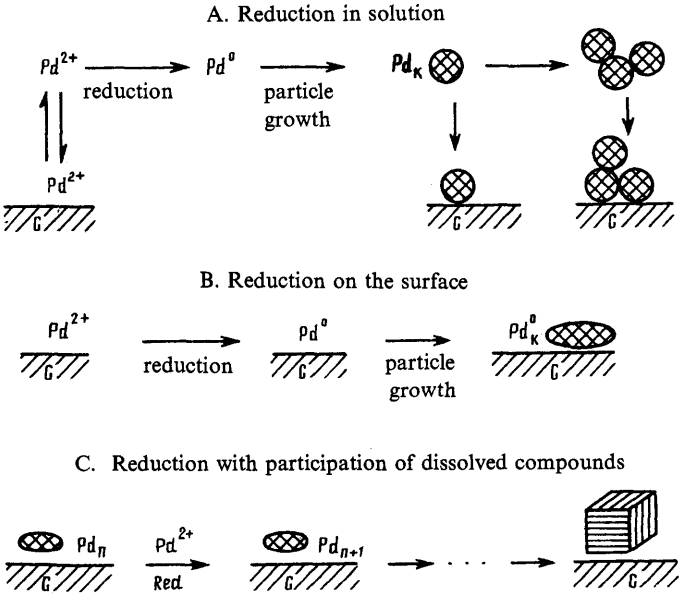


Figure 5. The formation of deposited metallic palladium particles during the reduction of the catalyst.

The preferential distribution of palladium in the outer layer of the catalyst grain can be achieved by the chemical reaction of the deposited component with the carbon carrier surface, for example, as a result of the reduction of palladium nitrate by the surface groups on the carbon carrier in an organic solvent.[74] A highly selective catalyst for the hydropurification of terephthalic acid was obtained in this way. It contained palladium particles, whose size was less than 3.5 nm and which were distributed in an outer layer of the grain up to 500 μm thick.

The deposition of palladium from colloidal solutions makes it possible to obtain crust type catalysts with a thickness of the active layer of ~50 μm.[63] Crust type catalysts can be prepared on carbon carriers with different microcrystalline structures, with pore volumes from 0.2 to 1.6 $cm^3\ g^{-1}$, mesopore and macropore sizes from 15 to 1000 nm, and specific surfaces from 10 to 1000 $m^2\ g^{-1}$.

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