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Specific Features of the Catalytic Behavior of Supported Palladium Nanoparticles in Heterogeneous Catalytic Reactions

A. Yu. Stakheev, I. S. Mashkovskii, G. N. Baeva, and N. S. Telegina

Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences (IOC RAS),
Leninskii prosp. 47, Moscow, 119991 Russia
e-mail: st@ioc.ac.ru

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Abstract—Specific features of the catalytic behavior of supported palladium nanoparticles were analyzed in terms of both the size of the particles and their interaction with the support. The influence of these factors on the activity and selectivity of palladium nanoparticles in carbon–carbon bond hydrogenolysis, hydrogenation of aromatic compounds, olefins, and acetylenes, hydrodechlorination, as well as complete oxidation of organic compounds was discussed. It was shown that the optimal nanoparticle size depends on the type of the reaction and also such factors as the nature of interaction between the nanoparticles and support, absorptivity of the substrates and catalytic reaction products, and electronic and crystal structure of the nanoparticles.

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INTRODUCTION

Palladium enters into the composition of most supported catalysts containing noble metal nanoparticles as an active component [1–5]. This is explained both by the specific catalytic properties of palladium which exhibits versatile activity and by the high development of platinum-substitute catalytic technologies.

In the present review we made an attempt to analyze the specific catalytic properties that arise upon the transformation of bulk metal to nanoparticles.

Factors Affecting the Catalytic Properties of Supported Metal Nanoparticles

A change in the catalytic properties of metals, caused by the transformation from bulk metal to nanoparticles (1–100 nm), is one of the fundamental problems of heterogeneous catalysis [6, 7]. Supported metal particle size, too, can essentially affect the specific catalytic activity (reaction rate per one surface atom), the number of reaction cycles, as well as the rate of the catalytic reaction. As suggested [8–10], these changes are associated both with the electronic properties of nanoparticles and with features of their crystal structure (compared with bulk metal or coarse particles, the most part of surface atoms with low coordination numbers, residing at the angles and edges of fine particles). Furthermore, the support, too, changes the properties of supported nanoparticles by affecting their electronic and crystal structure. Thus, we can recognize electronic and geometric factors responsible for the specific catalytic properties of metal nanoparticles.

As particles size decreases, the number of particles surrounding a surface metal atom decreases, which, in its turn, affects the nature and strength of bonding with a molecule adsorbed on the particle. This is a so-called electronic (or ligand) effect. Moreover, the electronic properties of a metal nanoparticle are much varied, when the number of its constituting atoms gets below a certain value. Theoretical and experimental results show that as the number of atoms in a particle decreases to 20–30, the particle loses its collective properties characteristic of a bulk body, specifically electroconductivity and ferromagnetism [11, 12]. Fine metal particles smaller than 20–25 Å possess no band structure characteristic of bulk metals and are electron-deficient in this respect [3, 13]. As a result, 20–25-atomic particles have increased ionization energies reaching 1–1.5 eV [12]. As the ionization energy increases, the electron affinity decreases by 2–3 eV. Consequently, the absorption energies of such nucleophilic molecules as alkenes or alkynes can vary considerably with particle size. The result can be of two kinds. On the one hand, the substrate can be activated. On the other hand, the too strong adsorption can entail blocking the particle surface and thus decrease the catalytic activity of the particles.

Changing particle size much affects the coordination numbers of surface atoms. Thus, the surface of coarse atoms contains primarily crystallographic planes accommodating atoms with high coordination numbers, while small particles contain surface atoms residing on the edges of the crystallographic planes or on edge junctions. As a result, reactions involving surface metal atoms (en-sembles) strongly depend on the size of catalyst particles. This dependence is related to the geometric or ensemble effect. Furthermore, the absorption energy on low-coordinated atoms is much higher compared with that on a plane surface.

Both the electronic and crystal structure of metal nanoparticles are affected by their accommodating support surface [14]. The interaction with surface electron-acceptor centers (for example, Brønsted or Lewis acid centers) en-hances the electron-deficiency of nanoparticles. At the same time, the interaction with alkaline centers (for example, negatively charged oxygen atoms) imparts a negative charge to the particles. In addition, increasing metal–support interaction energy can affect the shape of metal nanoparticles. When the interaction energy is low, the particle shape is determined by the most favorable crystallographic configuration. For example, palladium, a metal having an edge-centered lattice, prefers a cube-octahedron shape. However, as the interaction energy increases, preference is given to a planar shape allowing a larger nanoparticle–support surface contact. Thus, the particle–support interaction much affects the area and relative shares of different crystallographic edges available for reaction.

Below we analyze the effect of the above factors on the catalytic properties of supported palladium nanoparticles in reactions of different types.

Hydrogenolysis of C–C Bond

Enhaced catalytic activity of metal nanoparticles applied on the acid form of zeolite Y in the hydrogenolysis of neopentane was first reported in late 1960s–early 1970s [15]. This reaction is still widely applied as a test reaction for correlation between the charge on a metal and its catalytic activity. Palladium exhibits a fairly low activity in hydrogenolysis compared with other Group VIII metals [16] and is rarely used in catalytic reactions involving C–C, C–N, and C–H bond cleavage. Nevertheless, since hydrogenolysis is quite sensitive to the charge and surface structure of the metal, it is of interest to find our how different factors affect the activity of palladium nanoparticles in this reaction.

Homeyer et al. [17] showed that the specific activity of palladium nanoparticles supported by the acid form of zeolite Y in the hydrogenolysis of ethane is 5–10 times higher compared with the Pd/NaY system and two orders of magnitude higher than with the Pd/SiO$_2$ system. Having excluded, not without grounds, certain possible explanations of this observation (such as adsorption and diffusion effects), the authors concluded that the catalytic activity is enhanced due to a change in the electronic structure of metal nanoparticles: An electron-deficient palladium compares with rhodium in electronic structure and catalytic activity in the hydrogenolysis reaction.

At the same time, it was established that the number of cycles of the neopentane hydrogenolysis reaction on metal nanoparticles applied on an alkaline support like zeolite KL decreases, as the alkalinity of the support is increased, say, by adding more potassium [18]. A similar effect was observed in the hydrogenolysis of propane and ethane, catalyzed by Pd/KL [19]. Consequently, the nature of the support much affects the catalytic activity of Pd nanoparticles: They become electron-deficient on acidic supports and electron-excessive on alkaline supports.

The above evidence shows that the change in the activity of metal nanoparticles in hydrogenolysis/isomerization reactions is associated with changes in their electronic properties rather than with the existence on their surface of some specific centers or edges [20]. It was established that the electron deficiency of nanoparticles is explained not by their small size but by the withdrawal of their electron density by acidic centers of the support [21]. Evidence for this conclusion comes from the fact that the most active catalyst contains larger particles, but they reside on the surface of an acidic support (Al$_2$O$_3$, H-LTL).

For quantitative differentiation between effects associated with nanoparticle size and effects associated with metal–support interaction, the catalytic activity of palladium nanoparticles of the same size and shape but with widely varied electronic propertis was studied in the neopentane hydrogenolysis reaction [22–24]. To obtain Pd nanoparticles of the same size, a special

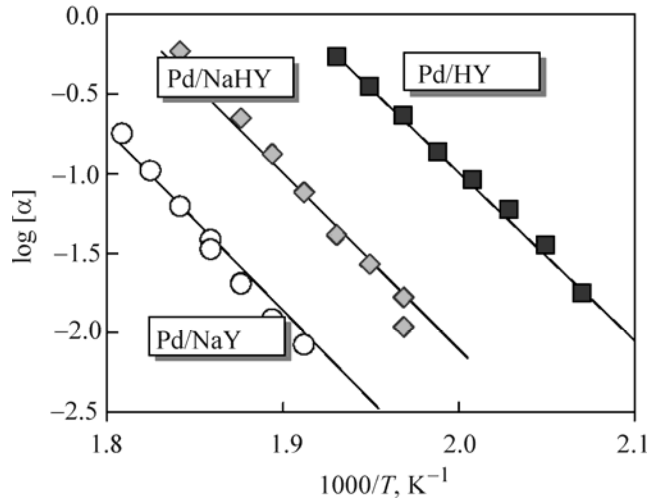

Fig. 1. Effect of the electron deficiency of supported palladium nanoparticles on their specific catalytic activity (α) in neopentane hydrogenolysis.

procedure was developed to synthesize Pd/Y catalysts by palladium encapsulation into the zeolite Y cavity. Thus, the size of palladium nanoparticles (~1.2 nm) was determined by the size of the zeolite cavity. The electronic state of supported palladium nanoparticles was varies by varying the local concentration of Brønsted acidic centers (BAC) in the vicinity of a nanoparticle. The highest concentration of acidic centers was attained with zeolite HY as a support (Pd/HY). To obtain a reference sample with a minimum electronic interaction of Pd nanoparticles with the support, BAC were neutralized either with gaseous ammonia (Pd/NH_4NaY) or with aquoeus NaOH (Pd/NaY).

A series of catalysts was synthesized in which the local BAC concentration in the vicinity of a Pd nanoparticle increased as follows: Pd/NaY ~ Pd/NH_4NaY << Pd/NaHY < Pd/MgHY < Pd/HY.

X-Ray photoelectron spectroscopy was used to establish that the higher the local concentration of Brønsted acidic centers, the higher the positive charge on palladium nanoparticles.

The specific catalytic activities of encapsulated nanoparticles in the neopentane hydrogenolysis reaction are compared in Fig. 1. The enhancement of the electron deficiency of supported palladium nanoparticles, induced by their interaction with the support, sharply enhances the catalytic activity in the C–C hydrogenolysis reaction. Thus, the neopentane hydrogenolysis rate increases two orders of magnitude in going from Pd/NaY to Pd/NaHY and Pd/HY. Therewith, the reaction temperature shifts by 50–60°C to the low-temperature range.

There are a number of suggestions advanced to explain such a strong effect the electronic structure of metal nanoparticles on their catalytic activity in hydrogenolysis. According to the suggestion in [25], the higher activity results from a strong adsorption of alkanes on electron-deficient nanoparticles. This hypothesis also readily explains the enhanced catalytic activity in isomerization (for example, of *n*-butane into isobutane). To explain the fact that both reactions follow the same compensation energy curve, a common intermediate product (dehydrogenated alkane) was suggested. The enhanced activity of electron-deficient metal nanoparticles in the cyclopropane hydrogenolysis reaction was explained in the same way [26], specifically by a strong cyclopropane adsorption on the positively charged nanoparticles due to the interaction of the π system of the strained hydrocarbon ring, which facilitates its activation.

An alternative explanation consists in that a changed electronic state of nanoparticles affects the character of hydrogen chemisorption due to the interaction of nanoparticles with acidic and alkaline centers of the support [27, 28]. As a result, the concentration of adsorbed hydrogen on electron-deficient nanoparticles increases, thus making the latter more active.

Hydrogenation of Aromatic Compounds

Aromatic hydrogenation is traditionally considered as an example of structurally insensitive reactions. Geometric factors only slightly affect the specific catalytic activity of metal nanoparticles in aromatic hydrogenation, except for ultrafine (3–6 atoms) nanoparticles which are virtually inactive in such reactions [29, 30].

The catalytic activity of larger particles (1–3 nm) is strongly affected the electronic interaction in the metal–support system. It was shown that the hydrogenation of aromatic compounds (in particular, benzene) on zeolite catalysts containing encapsulated metal nanoparticles depends on the acid–base properties of the zeolite support. Thus, the activity in benzene hydrogenation decreases with enhancing basicity of the support, i.e. as the electron density is transferred from the support to the metal, and the latter passes from the electron-deficient to electron-enriched state (platinum) [31]. Furthermore, a substituted aromatic ring, as, for example, in toluene, is more nucleophilic than benzene and, as a consequence, more sensitive to the electronic structure of metal particles. Thus, the rate of benzene hydrogenation, catalyzed by suppoted metal nanoparticles, increases 2–3 times in going from the acidic aluminum silicate to SiO_2 support, while the rate of toluene hydrogenation increases 5–6 times [32, 33]. By contrast, increased electron density decreases activity, as it was observed with Pd and Pt, supported by KL zeolite, when the latter had been additionally modified with KCl [34]. In the absence of expressed electronic metal–support interactions, the specific activity remains invariable, and the total activity of metal catalysts is controlled by their dispersity [14, 35].

Enhanced electron-deficiency of platinum and palladium nanoparticles also favors hydrogenation of condensed aromatic compounds. Corma et al. studied the catalytic activity of palladium on a mesoporous MSM-41 silica and Y zeolite [36] in naphtalene hydrogenation to show that Pd/HY exhibits a higher specific activity due to the interaction of Pd nanoparticles localized in large zelite cavities with strong Brønsted acidic centers. The same effect was observed in tetraline hydrogenation on Pd nanoparticles suported by the acid form of USY zeolite [37, 38]. Comparison of EXAFS data with the results of catalytic mesurements showed that the highest activity is characteristic of Pd nanoparticles encapsulated in Y zeolite cavities of about 1.2 nm in size. Along with enhanced activity in hydrogenation, these electron-deficient nanoparticles exhibit enhanced stability to sulfur compounds. These results are nicely consistent with the reported catalytic activity of palladium nanoparticles on an amorphous aluminum silicate in the hydrodesulfurization of 2,4-dimethyldibenzothiophene [39].

The high activity of electron-deficient nanoparticles in aromatic hydrogenation is associated with a change in the nature of hydrogen adsorption [40, 25]. A complex of methods, including direct chemisorption mesurements and XANES spectroscopy, as well as theoretical calculations were used to establish that enhanced electron deficiency of nanoparticles increases the bonding energy of chemisorbed hydrogen with nanoparticle surface and the surface concentration of atomic hydrogen, which, in its turn, favors faster hydrogenation.

Hydrogenation of Olefins and Acetylenes

The rate of palladium-catalyzed alkene and alkyne hydrogenation is much affected even if palladium nanoparticles are applied on an inert support, i.e. in the absence of a strong electronic palladium–support interaction. When the metal nanoparticle size gets below a certain limit, the specific activity drastically decreases [41–44], which is especially pronounced with 3–5-nm nanoparticles (dispersity 0.2–0.4) [45]. Larger nanoparticles are more active (even though the number of metal atoms available for reaction decreases). Thus, there is some optimal nanoparticle size, when the total catalyst activity is a maximum. Actually, the Pd/Al_2O_3 catalyst with a medium dispersity of metal particles shows the highest activity in alkyne hydrogenation reactions [46].

At the same time, according to [47–51], the reaction rate and specific catalyst activity not so strongly correlate with palladium dispersity if changes in the crystal structure of nanoparticle surface are taken into account. Of great importance here was shown to be a geometric factor, specifically the crystal structure of nanoparticles. For example, the specific activity of Pd nanoparticles in 2-methylbut-3-yn-1-ol hydrogenation doubles when the nanoparticle size increases from 6 to 13 nm. However, according to the calculations including the number of palladium atoms on the (111) crystal planes, the specific catalytic activity is constant over the entire size range [52].

Analogous data were obtained for buta-1,3-diene hydrogenation on a model $Pd/Al_2O_3/NiAl(110)$ catalyst [53]. In the case of ultrafine metal particles, a sharply reduced activity was observed [54–58].

Surely, the above estimates are arbitrary, since the reaction conditions in the cited works are quite different. Nevertheless, it can be concluded that the most general reason of a decrease in the specific catalytic activity of fine metal particles [10, 40, 41, 43, 59] consists in strong bonding of a nucleophilic alkene or alkyne molecule with low-coordinated surface metal atoms.

An even stronger decrease in catalytic activity is observed, as the electron deficiency of palladium nanoparticles is enhances either due to the size effect or due to their interaction with surface electron-acceptor centers of the support. Since the strength of alkene or alkyne bonding with electron-deficient palladium nanoparticles enhances, then, unlike what is observed in aromatic hydrogenation, the activity of the nanoparticles in alkyne hydrogenation decreases, in spite of their higher dispersity [60, 61]. Electron-deficient Pd and Pt nanoparticles were found to exhibit decreased activity in ethylene, buta-1,3-diene and but-2-yne hydrogenation [27]. This fact was explained by a very strong adsortion of double- and triple-bond hydrocarbons, which decreases the degree of hydrogen saturation of the support, thereby decelerating the reaction. Furthermore, increasing nanoparticle electron deficiency shifted the selectivity of buta-1,3-diene hydrogenation in favor of 1,4-addition. Based on the latter result, the authors of [27] suggested the but-2-ene formation reaction as a test for electron-deficient nanoparticle.

It should be noted that in olefin hydrogenation the specific catalytic activity is not as strongly correlated with Pd nanoparticle size as in alkyne hydrogenation, probably because of a lower nucleophilicity of the double bond. In most cases, the specific catalytic activity in olefin hydrogenation changes 2–3 times as the nanoparticle size changes from 1 to 10 nm [62, 63]. Quite reliable data on the influence of the size and geometry of Pd nanoparticles on their catalytic activity in olefin hydrogenation were obtained with model catalysts prepared by high-vacuum deposition of Pd nanoparticles on support surface. By varying deposition conditions, one can widely vary both the size and geometry of nanoparticles. With such model systems, it was establshed that, as the Pd nanoparticle size varies from 1 to 3 nm, the specific catalytic activity in ethylene hydrogenation increases 1.5–2 times. This finding implies that the reaction involving Pd nanoparticles above 1 nm in diameter is structurally insensitive [64]. Evidence for this conclusion was obtained by other researchers who found that the number of ethylene hydrogenation cycles remains invariable as the particle size varies from 1 to 5 nm [65, 66].

In the hydrogenation of olefins with a longer hydrocarbon chain (C > 4), a slightly stronger dependence of the specific catalytic activity of nanoparticles on their size is observed. Model Pd/Al_2O_3 systems were used to show that the specific catalytic activity in *n*-pentene hydrogenation increases 4–5 times as the nanoparticle size increases from 1 to 5 nm [67]. The slightly stronger structural sensitivity is associated with a different reaction mechanism of longer (> C_3) molecules, rather than with a stronger pentene adsorption. Ethylene hydrogenation primarily involves a π-adsorbed molecule linked to a single surface palladium atom, whereas propylene is hydrogenated via a di-σ-adsorbed state. Two-center adsorption requires an active center (ensemble) comprising more surface Pd atoms. The probability of formation of such a center increases with increasing nanoparticle size, which eventually leads to enhanced specific catalytic activity.

As to the influence of metal particle size on the selectivity of alkene hydrogenation, then, as shown in [40, 41, 46–48, 55, 68], catalysts containing larger (lower dispersity) nanoparticles exhibit a higher selectivity with respect to alkane formation. On the other hand, there is some evidence [42, 43, 47, 48, 51–54] showing that Pd nanoparticle size fairly slighly affects the selectivity of alkyne hydrogenation.

The selectivity of alkyne hydrogenation is probably associated with β-PdH phase formation [69, 70]. It is commonly accepted that the probability of formation of the β-PdH phase decreases with decreasing catalyst dispersity. In this connection, the high selectivity of alkene formation on finely dispersed palladium catalysts is explained by hindered formation of the β-hydride phase which is not involved in the hydrogenation process [71–73]. The β-PdH phase formation can be prevented by introducing a second metal (Ag, Zn) into the catalyst to form bimetallic nanoparticles. Thus, the use of heterobimetallic acetate complexes Pd–Zn(μ-OAc)$_4$(OH$_2$) as precursors makes it possible to obtain homegeneous Pd–Zn nanoparticles and highly selective supported catalysts for the hydrogenation of acetylene into ethylene on their basis [74].

Hydrogenation of Dienes

The interest in the catalytic properties of palladium nanoparticles in diene hydrogenation is first of all caused by the practical importance of selective buta-1,3-diene hydrogenation [75–77]. As a rule, the specific activity of Pd nanoparticles whose size is above a certain value remains invariable, but if the particle dispesity becomes higher of a certain threshold value (usually 25–35%, which corresponds to the particle size ~3–4 nm) the catalytic sharply decreases [74, 78, 79]. This interrelationship is complicated and depends on the nature of the support, reaction conditions, presence of absence of promoters, and other factors.

The observed dependence of specific catalytic activity on nanoparticle size is usually explained in terms of the electron deficiency of small palladium nanoparticles. The electron deficiency increases the absorption enegry of the nucleophilic diene molecules which block the nanoparticle surface, thereby decreasing hydrogen adsorption and slowing down hydrogenation [80, 76]. When the partial pressure of the diene is decreased and the partial pressure of hydrogen is increased, this effect is attenuated, and the reaction becomes less structure-sensitive [81].

As shown in [74, 75, 82], the nanoparticle size below which the catalytic activity starts to fall is largely dependent on the nature of the support. Thus, the specific activity of carbon-supported Pd nanoparticles remains invariable until their size reaches 1.5–2 nm, whereas the respective value for oxide supports is 4–5 nm [83]. Probably, this difference is associated with enhanced interaction of nanoparticles with oxide supports, electron transfer from palladium nanoparticles to electron-acceptor oxide surface centers, and the resulting electron deficiency enhancement of the nanoparticles.

Indirect evidence for this conclusion was provided by Sárkány [75] who found that the specific catalytic activity of Pd nanoparticles on a pumice support is preserved even if the particles are very fine. The author explained this result by the electron-donor character of the support surface containing alkali metal cations (K^+, Na^+). The decreased electron deficiency of palladium nanoparticles was confirmed by X-ray photoelectron spectroscopy.

Hydrogenation of Unsaturated Aldehydes and Ketones

Supported palladium nanoparticles are capable of catalyzing hydrogenation of compounds containing both a polar and a nonpolar double bond, which can be used to create highly selective catalysts for either C=C or C=O hydrogenation. Metallic palladium, unlike other Group VIII metals, exhibits a high selectivity in the hydrogenation of a nonpolar C=C bond [84]. This fact is related to a low width of palladium *d* band (it decreases in the order Os ~ Ir > Pt > Pd), due to which the asorption probability of unsaturated aldehydes and ketones is high [85, 86].

In going from bulk palladium to nanoparticles this effects enhances, since the *d* band gets even narrower due to decreasing number of interacting metal atoms and their electron deficiency. The selectivity of C=C hydrogenation increases, as the palladium nanoparticle size decreases. Lashdaf et al. [87] made use of palladium chemical vapor deposition to obtain finer Pd nanoparticles on Al_2O_3 and SiO_2 supports. The use of such catalysts allowed more selective hydrogenation of cinnamic aldehyde, even though the specifc activity of fine palladium nanoparticles much decreased. The same effect of C=C hydrogenation selectivity enhancement in unsaturated aldehydes was observed with an oxide-supported metal [82], since oxide supports provide a finer metal dispersion than carbon supports.

Apart from the electronic factor (electron deficiency of pallaium nanoparticles), the C=C hydrogenation selectivity enhancement is also contributed by the geometric factor. As the size of metal nanoparticles increases, the number of surface metal atoms with low coordination numbers decreases, and the area of the (111) edges on which, by steric reasons, adsorption involving the C=O bond is preferred may increase. Adsorption of unsaturated aldehydes on fine particles preferentially involves the C=C bond, which shifts the selectivity of saturated aldehydes. This regularity is suggested to be general and holds for different metal nanoparticles [88, 89].

Hydrodechlorination

Catalytic utilization of chlorinated hydrocarbons is a fairly new application field of catalalysts containing palladium nanoparticles as an active component [88, 90–97]. It was shown in a series of independent research that Pd particle size has a strong impact on the activity (total and specific) and selectivity of this process [98, 99]. Nanoparticles smaller than 5–10 nm exhibit a much higher catalytic activity. Moreover, catalysts of this size are more stable in operation.

The catalytic activity of the Pd/C system in CCl_2F_2 hydrodechlorination increases as the Pd nanoparticle size increases from 1.5 to ~5–7 nm. The number of reaction cycles at 100°C increases from 0.028 to 0.12 s^{-1} [95, 100]. The same effect was also observed in the reaction on Pd/Al_2O_3 [96], as well as on other supports [88]. In the hydrodechlorination of CF_3CCl_2F on Pd/Al_2O_3, a five-fold increase of specific catalytic activity was observed, when the size of Pd nanoparticles was increased from 11 to ~50 nm [101]. The specific catalytic activity in the hydrodechlrination of $CHCl_3$ on Pd/C increased jumpwise [97]: Pd nanoparticles less than 5 nm in size were almost inactive, while those with a mean diameter of up to ~15 nm were quite active.

The enhancement in the specific catalytic activity can be explained by different reasons. The prevailing explanation [102, 103] is that the limiting stage of the hydrodechlorination reaction is C–Cl hydrogenolysis in an adsorbed molecule, which is initiated by an ensemble of a fairly great large number of surface palladium atoms. The probability of formation of such an ensemble increases with increasing nanoparticle size; therewith, the specific catalytic activity is enhancing accordingly. According to a different hypothesis [96, 103], the reaction invoves carbide Pd_xC_y formation on nanoparticle surface; therewith, the process occurs much faster on extended planes of larger Pd nanoparticles, as a result of which the adsorption of halogen-containing reaction products becomes weaker and the regeneration of active centers occurs faster, thus favoring higher activity and stability of the catalyst.

Along with the geometric factors depending on the size and crystal structure of palladium nanoparticles, an important role in the hydrodechlorination reaction may belong to the electronic factor associated with nanoparticle interaction with electron-acceptor and electron-donor surface centers of the support [88, 104]. Thus, for example, the electron density on Pd nanoparticles supported by graphitized carbon increases due to donation of mobile graphite electrons, which favors hydrogenation of adsorbed carene-like fragments $=CHal_2$ and more selective formation of methane and other complete hydrogenation products. When electron-acceptor surface oxygen-containing groups are formed on the carbon support (mild support oxidation), the opposite situation occurs. In this case, electron-deficient palladium nanoparticles favor desorption of electrophilic intermediates $=CHal_2$ and =CHCl and shift the selectivity to incomplete hydrodechlorination products [99]. As the size of the nanoparticles increases, the effect of metal–support interaction gets weaker, and the selectivity of the reaction shifts to complete hydrodechlorination products (first of all, methane).

In connection with the use of palladium catalysts in hydrodechlorination reactions, quite an urgent question arises in regard to stability of their catalytic action. The case in point is that the surface of palladium nanoparticles strongly adsorbs halogen-containing compounds (first of all, HCl that forms), which entails blocking active centers and deactivation of catalysts. This process is more expressed with with small palladium nanoparticles (< 5 nm). With larger size particles, resistance to poisoning generally increases. Gopinath et al. [105] activated the Pd/Nb_2O_5 catalyst by micriwave irradiation. Therewith, the palladium nanoparticle size increased from 25 to ~40 nm, which not only enhanced activity, but also much enhanced the operational stability of the catalysts in chlorobenzene hydrodechlorination and its resistance to poisoning with HCl evolved dirung the reaction. Similar results were obtained with the Pd/Al_2O_3 catalyst [106, 107] which was used for gas-phase hydrodechlorination of CH_2F_2 and CCl_4. Resistance to HCl poisoning was also observed in a liquid-phase process [108]. It is suggested that the reason is in β-PdH formation which vigorously occurs on coarse palladium particles [105]. An alternative explanation consists in the formation of a surface Pd_xC_y carbide, which, too, adversely affects adsorption of HCl and other halogen-containing compounds [96, 103].

Complete Organic Oxidation Reactions

Supported palladium catalysts are widely used in the reactions of complete oxidation of organic compounds (solving environmental protection problems, flameless catalytic combustion for energy production, for example, for gas turbines, etc.). In this connection correlations between the structure of supported nanoparticles and their catalytic activity, as well as the effect of the support on the catalytic properties were studied. The question of whether the morphology of Pd nanoparticles on their behavior in complete oxidation reactions is quite controversial. This is explained by a number of reasons.

The structure of nanoparticles is much affected by reaction conditions, primarily temperature, oxygen partial pressure, as well as hydrocarbon/oxygen ratio, i.e. the redox properties of the reaction medium. Metallic pallaium is oxidized in air to form PdO at 300–400°C, anв this oxide remains stable up to 800°C. Above this temperature it undergoes thermolysis, and the catalytic function is fulfilled by metallic palladium. In general, these regularities are also characteristic of supported palladium nanoparticles [109], but the $Pd^0 \leftrightarrow PdO$ transition temperature sttongly depends both on the size of the nanoparticles and on the nature of the support. For example, Garbowski et al. [110, 111] in their research on correlation between the morphology of alumina-supported Pd nanoparticles and their activity in methane oxidation observed structural changes in the nano-particles directly during the reaction, specifically the Pd(200) edges enlarged by the expence of the (111) edges prevailing before the reaction initiation, which appreciably enhanced the catalytic activity.

There was active reserach on the size effect of Pd nanoparticles on their specific catalyric activity in complete methane oxidation. However, unambiguous resuts were not obtained. According to [112, 113], this reaction on supported Pd catalysts can be referred to as structurally insensitive. The number of reaction cycles, detemined at 335°C, increases from 0.02 to 1.3 s^{-1} as the nanoparticle size increases from 3 to 50 nm. Another group of researchers who studied a series of Pd/Al_2O_3 catalysts with the Pd nanoparticle size varied from 2 to 74 nm [114] revealed no correlation of specific catalytic

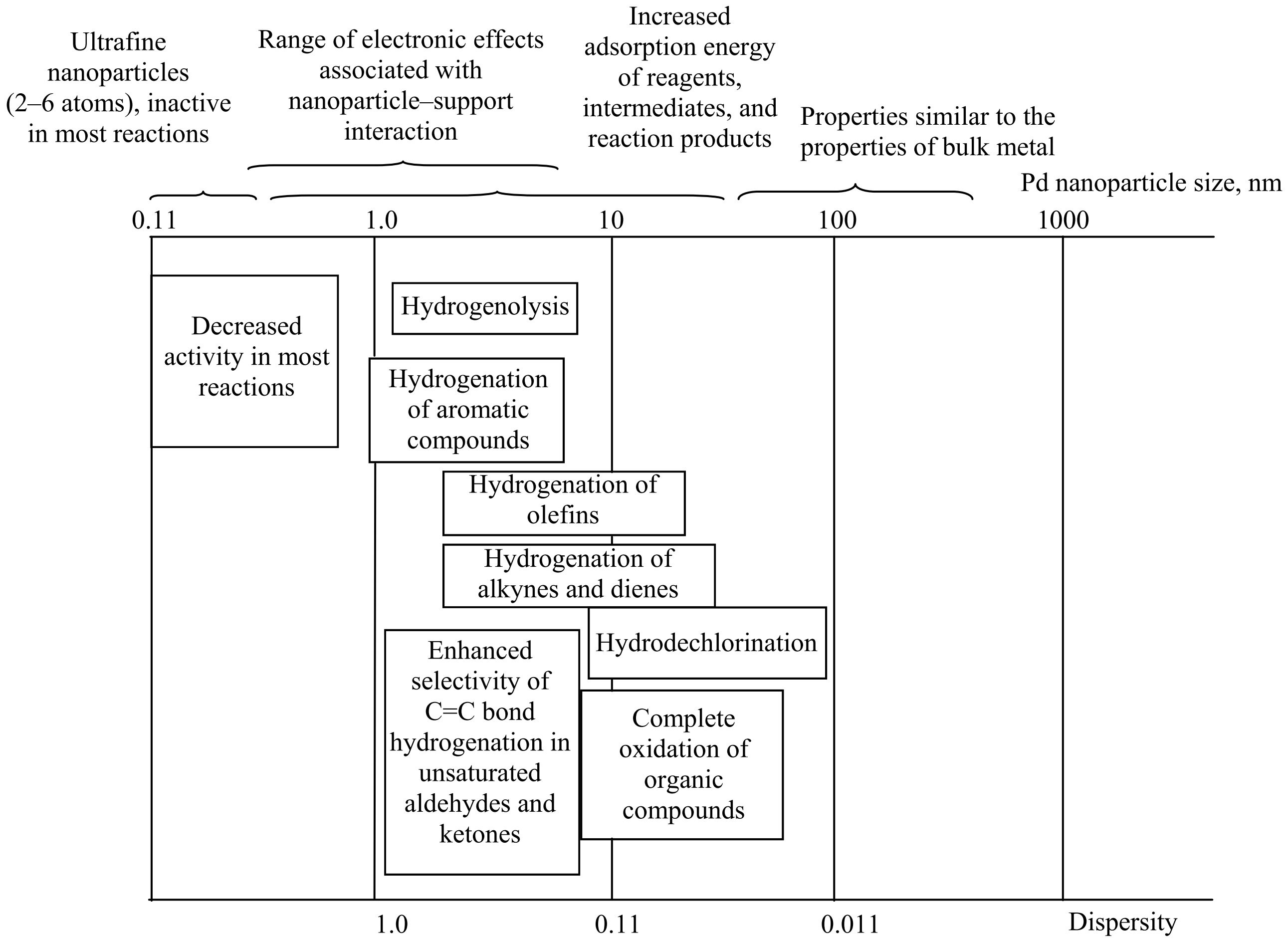

Fig. 2. Sizes of palladium nanoparticles, optimal for catalytic reactions of different types.

activity with Pd nanoparticle size. Similar reselts were obtained in [115].

Malinowski et al. [106] suggested that the principal reason for the above controversy was mistakes in the determination of the quantity of active centers by hydrogen chemisorption on preliminarily reduced catalysts. However, they left out of account that the quantity of active centers available for reaction may considerably vary over the reaction course in view of complete or partical transformation of Pd metal nanoparticles into its oxide nanoparicles.

The specific catalytic activity of palladium nonparticles in complete organic oxidation is not very size-dependent, but it generally tends to increse with particle size. Thus, for example, the activity of the Pd/SiO_2 catalyst slightly increases as the particle size increases from ~3 to ~7 nm [116]. Detailed specific catalytic activity measurements over the course of complete CH_4 oxidation with a series of palladium catalysts (ZrO_2, Al_2O_3, and SiO_2–Al_2O_3 supports) with the nanoparticle size varied from 2 to 130 nm [117] showed that the number of cycles vary in the range from 2×10^{-2} to 8×10^{-2} s^{-1}. Marceau et al. [118] established that the specific catalytic activity increases about two times as the size increases from 8 to ~19 nm.

The support nature essentially affects the specific catalytic activity of palladium nanoparticles. Thus, the low-temperature complete oxidation of various organic compounds (*n*-hexane, *n*-pentane, cyclohexane, benzene, toluene, acetone, and ethyl acetate) on Pd/SO_4^{2-}/ZrO_2 catalysts occurs more effectively than on Pt/Al_2O_3 [120]. It is suggested that the high acidity of the sulfated support enhances activity of supported nanoparticles, most likely due to modifying their electronic properties rather than increasing the surface area or dispersity of the supported metal. The superacidity of the sulfated catalyst on the basis of zirconium oxide enhances adsorption and facilitates activation of organic molecules on the supported metal, thereby driving the low-temperature combustion reaction.

However, some other researchers obtained evidence to show that the redox properties of the support affect the catalytic activity of palladium nanoparticles in oxidation reaction not by modifying their electronic properties, as is the case in hydrogenation and hydrogenolysis reactions.

The highest activity of palladium catalysts in C_3H_8 complete oxidation was observed on medium-acidity supports [121]. Furthermore, the acidity of the support defines the partial pressure of oxygen favoring the fastest reaction. It was found that on high-acidity supports ($Pd/SiO_2–Al_2O_3$) the maximum oxidation rate is attained at a high oxygen partial pressure. The catalyst on a low-acidity support (Pd/ZrO_2) proved to be the most active at low oxygen partial pressures.

The effect of the support is explained by the fact that it largely detemines the oxidation state of palladium under reaction conditions. The post-reaction structural study of the catalyst by X-ray photoelectron spectroscopy and X-ray phase analysis showed that the most active in the oxidation of propane is a mixed Pd^0–PdO phase. High-acidity supports enhance resistance of palladium nanoparticles to reduction and are the most suitable for preparing catalysts active at high oxygen partial pressures.

CONCLUSIONS

The specifics of the catalytic action of supported palladium nanoparticles is determined by a number of factors, including the size of the nanoparticles, their interaction with the support, as well as their crystal structure. There is an ample evidence showing that small nanoparticles (0.2–0.4 nm) comprising 3–6 metal atoms are virtually inactive in most reactions. This is probably associated with a too strong absorption of the starting materials and reaction products on highly imperfect nanoparticles. As the size of nanoparticles increases to 1–1.5 nm, their specific catalytic activity (calculated per one surface atom) increases, but the number of surface atoms therewith decreases, which all in all can negatively affect the total catalyst activity.

The degree and nature of the effect of the above-mentioned factors depend on the type of the catalytic reaction. Some catalytic reactions proceed with high efficiency on small nanoparticles (1–3 nm). For other reactions, larger nanoparticles (5–7 nm) are required. In this connection of interest is to find out what size of palladium nanoparticles is optimal for reactions of one or another type. The results of such analysis are systematized in Fig. 2 which lists the optimal nanoparicle size ranges for the reactions considered in the present review.

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