Formation of palladium nanoparticles in olefin oxidation with iron(III) aqua ions in the presence of the $Pd/ZrO_2/SO_4$ metallic catalyst

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The reactions of the $Pd/ZrO_2/SO_4$-catalyzed oxidation of ethylene, propene, and but-1-ene in a 0.1—1.5 *M* solution of perchloric acid with iron(III) aqua ions to carbonyl compounds, *viz.*, acetaldehyde, acetone, and methyl ethyl ketone, respectively, were studied. The formation of palladium nanoparticles (5 nm) in solution on contact of the initial heterogeneous $Pd/ZrO_2/SO_4$ catalyst with perchloric acid was proved by transmission electron microscopy. The palladium nanoparticles are assumed to play the key role in olefin oxidation with the iron(III) aqua ions.

Key words: Wacker process, Pd^{II} tetraaquacomplex, palladium nanoparticles, iron(III).

The discovery of the Wacker process provoked the formation of certain concepts on the catalytic oxidation of organic compounds in the presence of the palladium(II) compounds.[1—5] It has been found that for the regeneration of the oxidized palladium form with a cooxidant the latter should be characterized by the redox potential not lower than the potential of the Pd^{II}/Pd^{0}_{metal} pair.[5,6] For instance, in a chloride-containing system the potential of the Pd^{II}/Pd^{0}_{metal} pair, namely, $[PdCl_4]^{2-}/Pd^0$, is equal to 0.623 V (*vs.* hydrogen electrode).[7] Therefore, the Cu^{II} and V^{V} compounds and *p*-benzoquinone traditionally make a redox pair to palladium in catalytic processes of olefin oxidation in a medium of hydrochloric or acetic acid.

However, the Wacker process in the absence of chloride ions is more preferential, because the formation of ecologically hazardous chlorine-containing by-products is excluded in this case. In this connection, the Pd-catalyzed reactions based on the palladium(II) tetraaquacomplex are of special interest.

The redox potential of the $[Pd(H_2O)_4]^{2+}/Pd^{0}_{metal}$ pair for the Pd^{II} tetraaquacomplex is 0.987 V (*vs.* hydrogen electrode).[7] In this case, an oxidant of palladium(0) should manifest stronger oxidation properties than Cu^{II} in the halide system. Among possible cooxidants, we can indicate only the vanadium(V) compounds, which compose a redox pair to the Pd^{II} tetraaquacomplex in olefin oxidation.[6,8,9] In other cases (for instance, Ce^{IV}, Tl^{III}, CrO_4^{2-}), both olefin and target products are oxidized due to strong oxidation properties of the cooxidant.

In recent years, researchers manifested increased interest in studying the physicochemical properties of metal nanoparticles,[10—18] in particular, palladium particles,[17,19—21] due to their possible participation in catalytic processes.[22—24] One of the unique properties of nanoparticles is their decreased redox potential compared to the metal in the "bulk metal" state[13—15,17] and the smaller is the metal particle size, the lower is its redox potential.[13]

Thus, by generating *in situ* palladium nanoparticles during the catalytic process, one can perform the Wacker process with the cooxidant, whose potential is lower than the standard redox potential (SRP) of the $[Pd(H_2O)_4]^{2+}/Pd^{0}_{black}$ pair (Pd_{black} is palladium black), for instance, using Fe^{III} aqua ions (SRP of Fe^{III}/Fe^{II} = 0.77 V).

We have earlier reported the selective catalytic oxidation of lower aliphatic alcohols of the series C_1—C_4 (see Ref. 25) and some tertiary alcohols[26,27] to the corresponding carbonyl compounds in the Pd^{II} tetraaquacomplex—Fe^{III} aqua ions system. It was assumed that low-valent palladium particles, whose oxidation with the Fe^{III} aqua ions results in the regeneration of Pd^{II}, were formed during the reaction.

It can be assumed that reasons for catalysis in alcohol oxidation involving the Pd^{II} tetraaquacomplex can appear to some extent during olefin oxidation.

The present work is devoted to the experimental proof of the efficient oxidation ability of the iron(III) aqua ions during the catalytic oxidation of olefins to carbonyl compounds in the chloride-free system in the presence of both the Pd^{II} tetraaquacomplex and the palladium-containing metallic catalyst $Pd/ZrO_2/SO_4$ and to the elucidation of the key role of palladium nanoparticles in this process.

Experimental

Ethylene, propene, and but-1-ene (Aldrich, purity >99%), sulfated zirconium oxide (MEZRO52OEI MEL Chemicals),

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alumina (specific BET surface area 155 $m^2 g^{-1}$), and silica (specific BET surface area 550 $m^2 g^{-1}$) (Aldrich) were used. A solution of the Pd^{II} tetraaquacomplex was prepared according to a previously described procedure.**[28]** The source of Fe^{III} aqua ions was a solution of the $Fe_2(SO_4)_3 \cdot 9H_2O$ salt in perchloric acid.

The concentration of palladium(II) was determined spectrophotometrically in a green-colored solution of the complex, which was obtained by the addition of excess tin(II) chloride to the analyzed sample.**[29]** The concentration of iron(III) as a complex with sulfosalicylic acid was determined spectrophotometrically.**[30]**

The preparation of the Pd-supported metallic catalyst $Pd/ZrO_2/SO_4$ was based on the reduction of the Pd^{II} tetraaquacomplex with the Fe^{II} aquacomplex.**[31]**

$$2\,[Fe(H_2O)_6]^{2+} + [Pd(H_2O)_4]^{2+} \longrightarrow 2\,[Fe(H_2O)_6]^{3+} + Pd^0. \qquad (1)$$

The calculated amount of sulfated zirconium oxide ZrO_2/SO_4 (0.45 g) was introduced into a temperature-controlled reactor, and a solution (25 mL) of the Pd^{II} tetraaquacomplex (concentration 2 mmol L^{-1}) in 0.5 *M* perchloric acid was added. Then the calculated amount of Mohr´s salt (0.2 g) corresponding to an iron(II) concentration in the resulting solution of 0.02 mol L^{-1} was added. The mixture was vigorously stirred magnetically for 1 h under argon at 60 °C. Then the solution was filtered, and the precipitate was multiply washed with water and dried above P_2O_5. The prepared $Pd/ZrO_2/SO_4$ catalyst (dark gray powder) contained 1 wt.% Pd. A similar procedure was used for the preparation of Pd/Al_2O_3 and Pd/SiO_2.

The kinetic experiment was carried out as follows. A weighed sample of $Pd/ZrO_2/SO_4$ (40 mg) or a solution of the Pd^{II} tetraaquacomplex was added to a solution of iron(III) in perchloric acid with a specified concentration. In all experiments, the volume of the reaction solution was 10 mL. The reaction was carried out in an volumetric setup in a temperature-controlled shaken reactor of the "catalytic duck" type in the 40—80 °C temperature interval, and the amount of consumed olefin was directly determined. The frequency of shaking, above which the reaction rate remained unchanged, *i.e.*, when the kinetic regime was established, was determined in preliminary experiments. Testing reactions were carried out for comparison, where a magnetic stirrer with a rotation rate of 1200 ppm was used as a stirring device, and adequate values of the reaction rate were obtained.

The products of olefin oxidation were extracted from aqueous solutions with chlorobenzene and analyzed by chromatography coupled with mass spectrometry (HP 5890 GCD, column HP-5 Crosslinked 5% PH Siloxane, column length 30 m). The concentration of a carbonyl compound was determined by the gravimetric method by measuring the amount of hydrazone, which is formed by the interaction with a solution of 2,4-dinitrophenylhydrazine.

Studies by transmission electron microscopy (TEM) were carried out with a JEOL 1200 EXII microscope (100 kV). The solvent was removed *in vacuo* from 1 mL of the analyzed solution (sulfuric acid was used instead of perchloric acid), and ethanol (5 mL) was added. The resulting solution was ultrasonicated, filtered, and supported on copper. The particle size distribution was determined using an amplified (by 100 times) TEM image. Three conforming diagrams (at least with two hundreds of nanoparticles) were analyzed to attain good statistics.

X-ray diffraction (XRD) studies were carried out with a Bruker D5000 instrument equipped with a rotating anode. The specific surface area of samples was determined by the Brunauer—Emmett—Teller (BET) method with a Micromeritics Gemenie surface analyzer.

Results and Discussion

It has been reported previously**[6,32,33]** that lower olefins are rapidly oxidized with the Pd^{II} tetraaquacomplex to form the corresponding carbonyl compounds and palladium black. The introduction of Fe^{III}, regardless of its excess over Pd^{II}, does not result in the catalytic reaction with respect to palladium. However, in the present work we found the catalytic oxidation of ethylene, propene, and but-1-ene in the presence of the Pd^{II} tetraaquacomplex and Fe^{III} aqua ions in an aqueous medium to the corresponding carbonyl compounds.

On contact of ethylene, propene, or but-1-ene with the catalytic solution, palladium black precipitates rapidly within several minutes. At the same time, Fe^{III} is quantitatively reduced to Fe^{II}, and the corresponding carbonyl compound (acetaldehyde, acetone, or methyl ethyl ketone) is formed according to the reaction

$$H_2C{=}CHR + 2\,Fe^{III} + H_2O \xrightarrow{[Pd]} MeC(O)R + 2\,Fe^{II} + 2\,H^+, \qquad (2)$$

R = H, Me, Et.

The material balance of reaction (2) is presented in Table 1. The data in Table 1 show that the amount of the formed carbonyl compound exceeds the initial concentration of Pd^{II} by several times. This indicates the catalytic character of reaction (2) in which the turnover number reached 250 under certain conditions.

The conversion of Fe^{III} in reaction (2) is close to 100%. As can be seen from the data in Table 1, the change in the initial palladium concentration ($[Pd^{2+}{}_{aq}]_0$) by more than order of magnitude changes insignificantly the reaction rate and depth. It was found that the solution retains catalytic activity after palladium black was separated. It is most likely that during the reaction the palladium particles responsible for catalysis are reversibly transferred to solution from the palladium black surface under the action of the medium.

$$[Pd^0{}_n]_{black} \xrightleftharpoons{+\,x\,H_3O^+} [Pd^0{}_{n-m}(H_3O)_x{}^+)]_{aq} + [Pd^0{}_m]_{black}$$

It can be assumed that the concentration of these particles in solution is characterized by the limiting value in all cases.

Table 1. Oxidation of olefins in the Pd^{II}_{aq}—Fe^{III}_{aq} system ($[HClO_4] = 0.7$ mol L^{-1}, $T = 65$ °C, $P = 0.1$ MPa)

Olefin	$[Pd^{II}_{aq}]_0$	$[Fe^{III}_{aq}]_0$	Reaction duration/min	N^a	$[Fe^{III}_{aq}]_\tau^b$	$[CH_3C(O)R]/[Pd^{II}]$
	mmol L^{-1}			mmol L^{-1}		
Ethylene	0.1	60	90	25	10	250
	1	60	90	29	4	29
	5	60	90	33	4	6
	5	30	90	20	0	4
	5	120	90	40	50	8
	5^c	120	25	65	0	13
Propene	0.1	60	90	25	10	250
But-1-ene	0.1	60	90	25	10	250
	5^d	120	60	65	0	13

[a] Amount of unreacted olefin.

[b] Concentration of Fe^{III} at the end of the reaction.

[c] Ethylene pressure 0.3 MPa.

[d] But-1-ene pressure 0.25 MPa.

An analysis made after reaction (2) and separation of palladium black showed that the palladium concentration in solution was $(1—5) \cdot 10^{-5}$ mol L^{-1} (concentrated nitric acid was added to the solution during the analysis). This value is comparable with that presented in Ref. 19, whose data also evidenced for the key role of dissolved palladium nanoparticles in catalysis during hydrogen oxidation with oxygen in the presence of the heterogeneous palladium-containing catalyst in an aqueous medium.

The presence of palladium nanoparticles is clearly seen in the TEM photograph of the solution obtained after ethylene oxidation and decantation of palladium black (Fig. 1).

Thus, it can be assumed that the palladium nanoparticles formed in olefin oxidation and heterogeneous oxidation of hydrogen are responsible for catalysis in reaction (2).

The use of homogeneous catalysts in industry is restricted because of difficulties in the separation of the reaction products from the catalyst solution. In the present work, we attempted to heterogenize the palladium nanoparticles formed by the reduction of the Pd^{II} tetraaquacomplex. Sulfated zirconium oxide, whose acid sites should facilitate the immobilization of palladium nanoparticles, being weak Lewis bases, as well as Al_2O_3 and SiO_2, were chosen as supports.

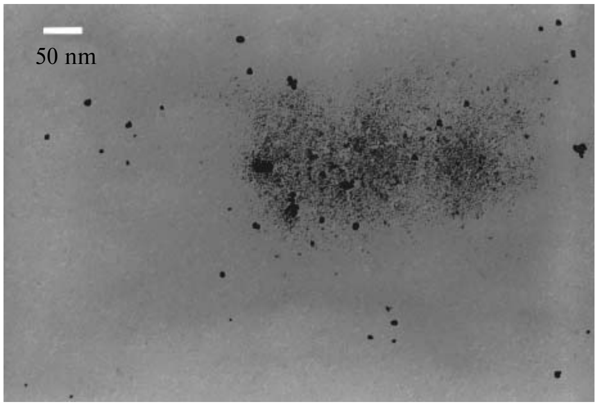

Fig. 1. TEM photograph of the solution after ethylene oxidation; $[Pd^{II}_{aq}] = 5$ mmol L^{-1}, $[Fe^{III}_{aq}] = 30$ mmol L^{-1}, $[HClO_4] = 0.5$ mol L^{-1}.

The specific surface area of the Pd-supported metallic catalyst $Pd/ZrO_2/SO_4$ measured by the BET method is larger (316 $m^2 g^{-1}$) than that for the initial support (209 $m^2 g^{-1}$). In the case of Pd/Al_2O_3 and Pd/SiO_2, the specific surface area also increased, being 165 and 602 $m^2 g^{-1}$, respectively.

The increase in the specific surface area is caused, most likely, by a change in the morphology of the support surface under the conditions of catalyst preparation. For instance, when the catalyst was prepared on sulfated zirconium oxide, the weight of the initial support could decrease due to the transition of the "heavy" SO_4^{2-} anions to the solution.

The temperature treatment (to 300 °C) of the prepared Pd-supported catalysts did not change the specific surface area.

An XRD analysis in the range $2\theta = 10—60°$ showed that any palladium states differing from the metallic palladium phase are absent in the prepared catalysts.

The catalytic activity of $Pd(1\%)/ZrO_2/SO_4$ was tested in the oxidation of ethylene, propene, and but-1-ene with the Fe^{III} aqua ions in an aqueous perchloric solution. No transformations of the olefins under study in a perchloric solution of iron(III) in the presence of the initial sulfated zirconium oxide were preliminarily found. For the oxidation of ethylene, propene, and but-1-ene in a perchloric solution, the catalytic activity of palladium changes, depending on the olefin nature (Fig. 2).

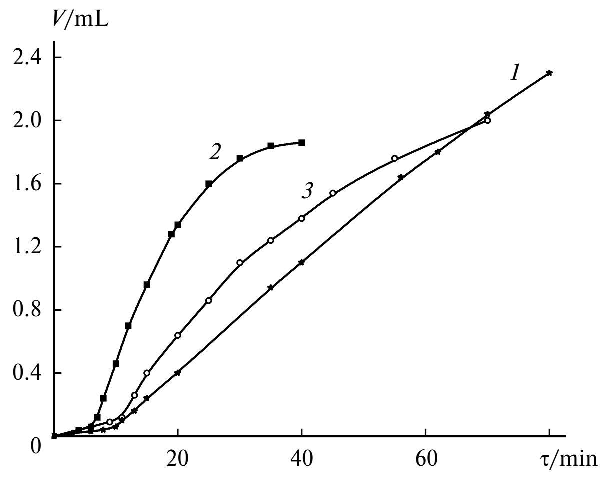

Fig. 2. Kinetic curves of the oxidation of ethylene (*1*), propene (*2*), and but-1-ene (*3*) with Fe^{III} in the presence of Pd(1%)/ZrO_2/SO_4 (40 mg); $[HClO_4] = 0.5$ mol L^{-1}, $[Fe^{III}{}_{aq}]_0 = 0.03$ mol L^{-1}, 65 °C, $P = 0.1$ MPa; V is the volume of absorbed gas.

Iron(III) is reduced to iron(II) due to olefin oxidation. In the case of ethylene, the conversion of iron at 65 °C and 90-min duration of oxidation is equal to 80%, and the turnover number with respect to palladium exceeds 26. The molar ratio of oxidized olefin to reduced iron is 2, regardless of the olefin nature and reaction depth. Ethylene is selectively oxidized to acetaldehyde, propene is oxidized to acetone, and but-1-ene oxidation gives methyl ethyl ketone. Thus, catalytic reaction (2) occurs in the presence of $Pd/ZrO_2/SO_4$.

Under the same initial conditions, the rate of olefin oxidation increases in the following order: $C_2H_4 < C_4H_8 < C_3H_6$.

The observed sequence of the change in the rate of olefin oxidation indicates the homogeneous character of the processes under study during which an electrophilic Pd^{II} particle is formed. If the oxidation would be caused by olefin chemisorption on the Pd^0 particles, *i.e.*, heterogeneous process, then the rate would be maximum for ethylene as a weaker nucleophile in the olefin series.

As can be seen from the data in Fig. 2, the kinetics of oxidation of the olefins under study is characterized by an induction period, which is caused by the interaction of the medium of a reaction solution with palladium in the initial $Pd/ZrO_2/SO_4$ catalyst. A portion of palladium from the heterogeneous phase of the catalyst is transferred into solution under the action of the medium. In our opinion, olefin is oxidized on the homogeneous palladium catalyst. This conclusion is confirmed by the results of the following experiments.

A weighed sample (40 mg) of the initial Pd(1%)/ZrO_2/SO_4 catalyst was stored for 1 h in a 0.5 *M* solution of perchloric acid under argon at 65 °C. Then the mixture was filtered, and Fe^{III} (0.03 mol L^{-1}) was added to both the filtrate and precipitate. Both systems, being homogeneous and heterogeneous solutions, respectively, were treated with ethylene. Ethylene oxidation in a homogeneous solution proceeded without an induction period. In the case of ethylene oxidation with iron(III) in a heterogeneous solution, the reaction occurred with a lower rate than in the system before storage of $Pd/ZrO_2/SO_4$ in perchloric acid (Fig. 3, curve *2*).

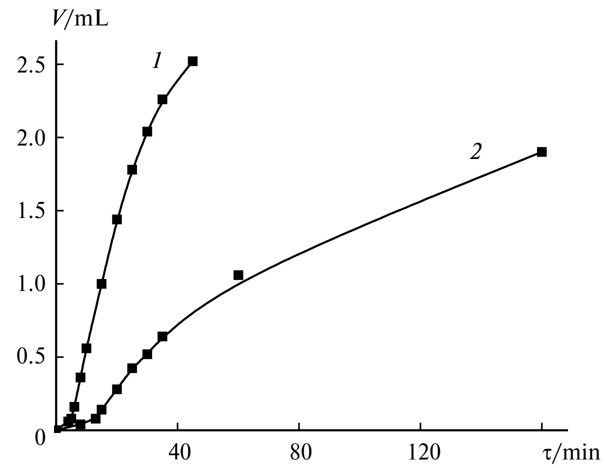

Fig. 3. Kinetic curves of the oxidation of ethylene with Fe^{III} in the presence of $Pd/ZrO_2/SO_4$ at 65 °C: freshly prepared $Pd/ZrO_2/SO_4$ (40 mg) (*1*) and after storage in 0.5 *M* $HClO_4$ (*2*).

An absolutely opposite tendency was observed after Pd(1%)/ZrO_2/SO_4 was stored in water at pH 7: in the case of a homogeneous solution, ethylene was not oxidized with the iron(III) aqua ions, and the reaction rate in a heterogeneous solution corresponded to the rate of ethylene oxidation with Fe^{III} on the freshly prepared Pd(1%)/ZrO_2/SO_4 catalyst.

The obtained results indicate convincingly that palladium from the solid phase of the initial catalyst is transferred into solution under the action of perchloric acid. This is also confirmed by the TEM data.

The results of TEM analysis of the solution obtained after storage of Pd(1%)/ZrO_2/SO_4 in a 0.25 *M* solution of sulfuric acid (sulfuric acid was used instead of perchloric acid) under argon prove the formation of palladium particles in the solution with an average diameter of 5 nm (Fig. 4).

The substantial role of acid in the formation of the palladium nanoparticles in solution follows from the fact that the rate of catalytic olefin oxidation increases with an increase in the concentration of perchloric acid (Fig. 5).

All the data obtained suggest that palladium is washed into solution in the form of nanoparticles, which are characterized by enhanced reduction properties compared to those of palladium black, under the action of perchloric acid on the supported metallic $Pd/ZrO_2/SO_4$ catalyst.

We found that 75% of palladium in the oxidized form are transferred into solution for 12 h at 60 °C when 40 mg

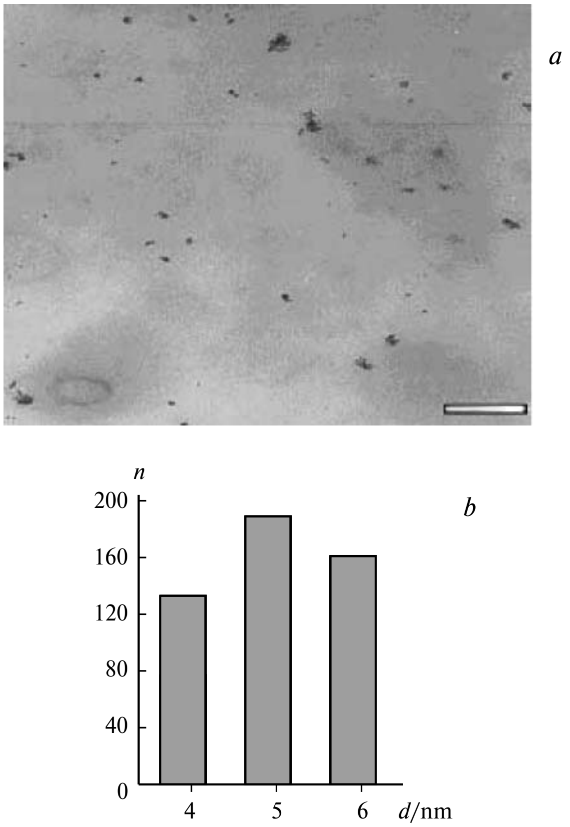

Fig. 4. TEM photograph of the Pd nanoparticles in a solution after storage of $Pd/ZrO_2/SO_4$ in 0.5 *M* acid (*a*) and the histogram of the particle size distribution (*b*). The scale is 100 nm; *n* is the number of nanoparticles.

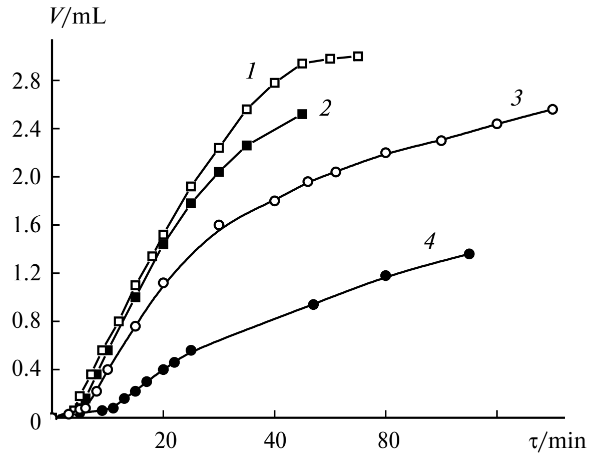

Fig. 5. Influence of the perchloric acid concentration on ethylene oxidation with Fe^{III} at $[HClO_4]$ = 1.5 (*1*), 0.5 (*2*), 0.2 (*3*), 0.05 (*4*); $[Pd/ZrO_2/SO_4]$ = 40 mg, $[Fe^{III}{}_{aq}]_0$ = 0.03 mol L^{-1}, 65 °C.

of $Pd(1\%)/ZrO_2/SO_4$ interact with the Fe^{III} aqua ions (concentration 0.03 mol L^{-1}) in a solution of 0.5 *M* perchloric acid. The replacement of the Fe^{III} aqua ions by *p*-benzoquinone or Cu^{II} and $[Fe(CN)_6]^{3-}$ aqua ions does not result in the formation of Pd^{II}. Therefore, no olefin oxidation occurs in the presence of these oxidants on the $Pd(1\%)/ZrO_2/SO_4$ catalyst.

Thus, on contact of the heterogeneous Pd-containing catalyst with an aqueous solution of a strong mineral acid, palladium is transferred into solution as nanoparticles. Since the palladium nanoparticles have strong reduction properties, they are easily oxidized with the iron(III) aqua ions to form palladium(II), which then oxidizes olefin under homogeneous conditions.

When olefins are oxidized with iron(III) in the presence of the Pd^{II} tetraaquacomplex, the reaction also results in the formation of the palladium nanoparticles, which finally cause catalysis during olefin oxidation with iron(II), *i.e.*, the Pd^{II} tetraaquacomplex acts as the catalyst precursor.

In our opinion, the driving force of transport of the palladium particles from the solid phase of the initial catalyst to the liquid phase is the acid-base interaction between the Lewis basic sites of palladium and protons of the medium.

References

1. P. M. Henry, *Palladium Catalyzed Oxidation of Hydrocarbons*, Eds R. Ugo and B. R. James, Reidel, Dordrecht, 1980, p. 41.
2. P. M. Maitlis, *The Organic Chemistry of Palladium*, Academic Press, New York—London, 1971, 190 pp.
3. J. Tsuji, *Palladium Reagents and Catalysts*, John Wiley and Sons, Chichester, 1995, p. 560.
4. A. Heumann, K.-J. Jens, and M. Reglier, *Progress in Inorganic Chemistry*, 1994, **42**, 483.
5. I. I. Moiseev, *π-Kompleksy v zhidkofaznom okislenii olefinov* [*π-Complexes in Liquid-Phase Oxidation of Olefins*], Nauka, Moscow, 1970, 240 pp. (in Russian).
6. K. I. Matveev, *Kinet. Katal.*, 1977, **18**, 862 [*Kinet. Catal.*, 1977, **18**, 862 (Engl. Transl.)].
7. *Spravochnik khimika* [*Chemist´s Handbook*], Khimiya, Moscow—Leningrad, 1964, Vol. **3**, 1005 pp. (in Russian).
8. I. V. Kozhevnikov, *Chem. Rev.*, 1998, **98**, 171.
9. A. Lambert, E. G. Derouane, and I. V. Kozhevnikov, *J. Catal.*, 2002, **211**, 445.
10. I. I. Moiseev and M. N. Vargaftik, *Catalysis with Palladium Clusters*, Eds R. A. Adams and F. A. Cotton, Wiley-VCH, New York, 1998, Ch. 12, p. 395.
11. G. Schmidt, *Chem. Rev.*, 1992, **92**, 1709.
12. L. N. Lewis, *Chem. Rev.*, 1993, **93**, 2693.
13. A. J. Henglein, *Chem. Rev.*, 1989, **89**, 1861.
14. A. J. Henglein, *J. Phys. Chem.*, 1993, **97**, 5457.
15. K. A. Gingerich, D. L. Cocke, and F. Miller, *J. Chem. Phys.*, 1976, **64**, 4027.
16. G. Schmidt, *Clusters and Colloids*, VCH, Weinheim, 1994, 186 pp.
17. B. G. Ershov, *Usp. Khim.*, 2004, **73**, 107 [*Russ. Chem. Rev.*, 2004, **73** (Engl. Transl.)].
18. H. Shi, H. Bi, B. Yao, and L. Zhang, *Appl. Sur. Science*, 2000, **161**, 276.

19. D. P. Dissanayake and J. H. Lunsford, *J. Catal.*, 2002, **206**, 173.
20. N. R. Jana and T. Pal, *Langmuir.*, 1999, **15**, 3458.
21. N. R. Jana, Z. L. Wang, and T. Pal, *Langmuir.*, 2000, **16**, 2457.
22. V. V. Potekhin, V. A. Matsura, and V. B. Ukraintsev, *Zh. Obshch. Khim.*, 2000, **70**, 886 [*Russ. J. Gen. Chem.*, 2000, **70** (Engl. Transl.)].
23. V. V. Potekhin, V. A. Matsura, and V. B. Ukraintsev, *Zh. Obshch. Khim.*, 2000, **70**, 2058 [*Russ. J. Gen. Chem.*, 2000, **70** (Engl. Transl.)].
24. V. V. Potekhin, V. A. Matsura, and V. B. Ukraintsev, *Zh. Obshch. Khim.*, 2002, **72**, 105 [*Russ. J. Gen. Chem.*, 2002, **72** (Engl. Transl.)].
25. V. V. Potekhin, S. N. Solov´eva, and V. M. Potekhin, *Izv. Akad. Nauk*, *Ser. Khim.*, 2003, 2420 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2668].
26. V. V. Potekhin, N. Yu. Ryadinskaya, and V. M. Potekhin, *Zh. Obshch. Khim.*, 2001, **71**, 1242 [*Russ. J. Gen. Chem.*, 2001, **71** (Engl. Transl.)].
27. N. Yu. Ryadinskaya, V. V. Potekhin, N. K. Skvortsov, and V. M. Potekhin, *Zh. Obshch. Khim.*, 2002, **72**, 1004 [*Russ. J. Gen. Chem.*, 2002, **72** (Engl. Transl.)].
28. L. Elding, *Helv. Chim. Acta.*, 1984, **67**, 1453.
29. S. I. Ginzburg, *Analiticheskaya khimiya platinovykh metallov* [*Analytical Chemistry of Platinum Group Metals*], Nauka, Moscow, 1972, 614 pp. (in Russian).
30. Z. Marczenko, *Kolorymetryczne Oznaczanie Pierwiastkow*, Wydawnictwa Naukowo-Techniczne, Warszawa, 1968, 500 pp. (in Polish).
31. V. V. Potekhin, V. A. Matsura, S. N. Solov´eva, and V. M. Potekhin, *Kinet. Katal.*, 2004, **45**, 707 [*Kinet. Catal.*, 2004, **45**, 707 (Engl. Transl.)].
32. N. B. Shitova, K. I. Matveev, and L. I. Kuznetsova, *Izv. Sib. Otd. Akad. Nauk SSSR*, *Ser. Khim. Nauk*, 1973, **2**, 25 [*Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1973, **2** (Engl. Transl.)].
33. E. G. Zhizhina, N. B. Shitova, and K. I. Matveev, *Kinet. Katal.*, 1986, **27**, 1451 [*Kinet. Catal.*, 1986, **27** (Engl. Transl.)].

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