ISSN 0023-1584, Kinetics and Catalysis, 2008, Vol. 49, No. 5, pp. 748–755. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © E.S. Lokteva, T.N. Rostovshchikova, S.A. Kachevskii, E.V. Golubina, V.V. Smirnov, A.Yu. Stakheev, N.S. Telegina, S.A. Gurevich, V.M. Kozhevin, D.A. Yavsin, 2008, published in Kinetika i Kataliz, 2008, Vol. 49, No. 5, pp. 784–792.

III INTERNATIONAL CONFERENCE "CATALYSIS: FUNDAMENTALS AND APPLICATIONS"

High Catalytic Activity and Stability of Palladium Nanoparticles Prepared by the Laser Electrodispersion Method in Chlorobenzene Hydrodechlorination

E. S. Lokteva[a], **T. N. Rostovshchikova**[a], **S. A. Kachevskii**[a], **E. V. Golubina**[a], **V. V. Smirnov**[a], **A. Yu. Stakheev**[b], **N. S. Telegina**[b], **S. A. Gurevich**[c], **V. M. Kozhevin**[c], **and D. A. Yavsin**[c]
[a] *Faculty of Chemistry, Moscow State University, Moscow, 119992 Russia*
[b] *Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*
[c] *Ioffe Physicotechnical Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia*
e-mail: rtn@kinet.chem.msu.ru

Received August 23, 2007

Abstract—Palladium nanoparticles deposited on thermally oxidized silicon and on the carbon support Sibunit by the laser electrodispersion method are extremely active in the gas-phase hydrodechlorination of chlorobenzene at 100–200°C. High conversion of chlorobenzene (above 90%) has been achieved with catalysts with an unusually low metal content (from 10^{-4} to 10^{-3} wt %). The cyclohexane-to-benzene ratio in the reaction products depends on the process duration, palladium content, and support nature. According to X-ray photoelectron spectroscopy (XPS) data, palladium in the catalysts retains its metallic state over a long time under the reaction conditions. Possible causes of the high catalytic activity (10^5 mol (mol Pd)$^{-1}$ h^{-1}) of the palladium nanoparticles and their stability to chlorination are discussed.

DOI: 10.1134/S0023158408050212

INTRODUCTION

It has recently been found that the activity of metal-containing catalysts depends on the particle size and on the average interparticle distance [1–6]. The properties of the catalytic system can change dramatically at the critical (threshold) value of the surface coverage or at an average interparticle distance allowing intercluster charge transfer. The discovery of this effect opened up a new possibility for controlling the catalytic properties of supported metal particles by the formation of coatings with the optimal surface density of these particles. This would allow one to enhance the efficiency of the catalysts based on nanosized particles, which can be especially useful for the development of catalytic systems containing precious and rare metals. In this case, the metal content can be decreased by several orders of magnitude without changing the main characteristics of the catalyst.

In the present work, knowledge of the second-order size effects [4–6] that are due to the appearance of charged states of nanoparticles near the threshold interparticle distance was used to develop new, highly efficient and stable catalysts for hydrodechlorination. Catalytic hydrodechlorination is the only environmentally friendly method for treatment of toxic polychloroorganic technogenic waste [7–10]. This process has not found wide use so far only because of the large consumption of precious metals and the low stability of the catalysts. The development of new, highly efficient catalysts prepared by laser electrodispersion makes it possible to solve these problems.

The laser electrodispersion method [11] is based on the ablation of a metallic target under the action of a powerful pulsed periodical laser under conditions of the formation and detachment of molten metal drops from the target surface. This is possible under severe target irradiation conditions, specifically, a high temperature of the laser torch plasma [6]. As a result of the subsequent cascade separation of micronic and submicronic drops formed in the laser torch plasma, a huge number of charged nanosized particles with a narrow size scatter are formed. A nonuniform steady-state electric field is created in the gap between the target and support for further separation of the resulting particles. The electric field configuration and strength are chosen in such a way that the nanosized drops are "focused" on the support without disturbing the motion of the larger particles. The nanoparticle size at given electrophysical parameters of the system is a function of the metal nature alone [1–6]. The surface density of the particles and the number of granular layers are controlled by the selecting the film deposition time. At short deposition times, the metal particles are arranged on the support as a single layer. On contact with the atmosphere, the metal nanoparticles oxidize only to a negligible extent and even the copper particles do not undergo complete oxidation [12]. These specific features of the nanostructured metal coatings prepared by laser electrodisper-

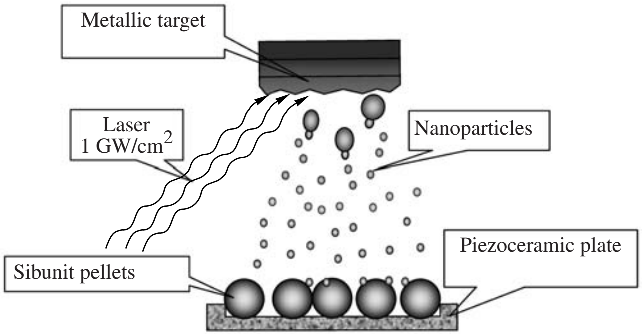

Fig. 1. Scheme of Pd nanoparticle sputtering on the surface of the Sibunit pellets stirred on a vibrating piezoceramic plate.

sion make them highly efficient and stable under catalytic conditions.

EXPERIMENTAL

Thermally oxidized silicon (SiO_2/Si) was used as a support for the deposition of the palladium nanoparticles by laser electrodispersion as described previously [4]. The other support was the granular carbon material Sibunit (C) with a pellet size of 0.6 to 3.0 mm and a specific surface area of 406–410 m^2/g. The scheme of nanoparticle deposition on the granular support is shown in Fig. 1. This procedure differs from the earlier described procedure of nanoparticle deposition on planar supports [4] in that the Sibunit pellets are placed on the surface of a piezoceramic holder. To achieve a uniform coating of the pellets by the metal nanoparticles, the support was continuously stirred by vibrations of the piezoceramic plate with a frequency of 16 kHz.

The average size and size scatter of the Pd nanoparticles were determined by transmission electron microscopy (TEM) and scanning tunneling microscopy (STM). It was shown previously that these characteristics are independent of the support material [6]. Images were obtained using Philips EM-42 (resolution of ~0.34 nm) and JEM 2100F (ultrahigh resolution of ~0.1 nm) transmission electron microscopes. Samples for TEM examinations were prepared by deposition of Pd nanoparticles onto standard grids using the laser electrodeposition method. The electron beam current was minimized to avoid the transformation (annealing) of the structure during imaging. The STM images of the Pd nanoparticle coatings were obtained using an NT-MDT Solver P47 instrument, which makes it possible to scan images on a surface area up to 50×50 μm^2 with an object height determination accuracy of at least 0.1 nm. The coatings were deposited on the surface of polished silicon supports or on the atomically smooth surface of pyrolytic graphite plates. The sizes of the Pd nanoparticles measured by the TEM and STM methods coincided. The analysis of the TEM and STM images shows that the average density of the Pd nanoparticles on the support surface is constant and is determined only by the deposition time. This is another typical feature of the laser electrodispersion method.

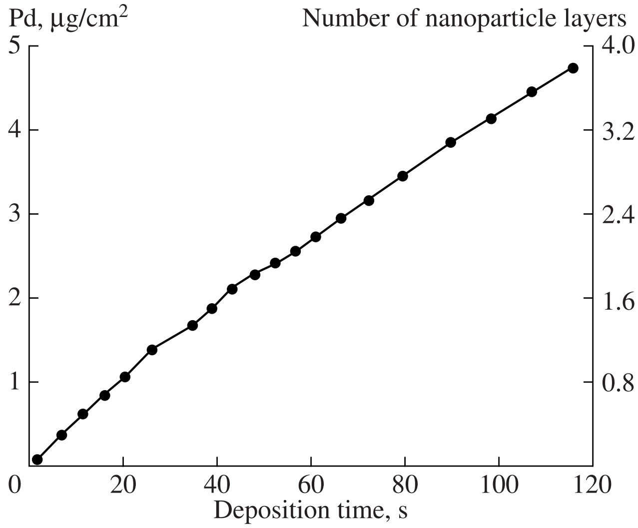

Fig. 2. Weight of supported palladium versus the time of its deposition on thermally oxidized silicon.

The particle density on the support surface or the quantity of the supported metal was varied by changing the film deposition time. A piezoceramic sensor with an intrinsic frequency of 3.3 MHz designed for magnetronic material sputtering was used to study the dependence of the amount of deposited palladium on the deposition time. The sensor was preliminarily calibrated under standard conditions of metal film sputtering using a special-purpose setup (Alkotel, Russia). The dependence of the amount of palladium deposited on the unit area of the support surface on the deposition time is shown in Fig. 2 along with the data on the number of metal particle layers on the support. The number of layers was calculated from an average particle size of ~2 nm found by microscopic analysis.

As can be seen from Fig. 2, the weight of Pd in the deposited film under the specified experimental conditions depends almost linearly on the time of structure deposition and the deposition rate corresponds to a deposition of approximately 2 layers per minute. This result agrees well with the estimate obtained by measuring the conductivity of the Pd films and by the TEM method [1]. According to these data, the deposition time of a nanoparticle monolayer on a silicon plate is also 30 s. Based on these results, the time of palladium deposition on the silicon support with a surface area of 1 cm^2 and a weight of about 0.08 g was varied between 5 and 30 s. The palladium content ranged from 2×10^{-4} to 2×10^{-3} wt %. When the nanoparticles were deposited on Sibunit, 1.5 g of the support was used, and the deposition time was between 80 and 200 s. The catalyst composition data are given in Table 1.

Table 1. Composition of the Pd/C catalysts

Catalyst	Pellet size, mm	Pd content, wt %
1	2.5–3.0	0.0004
2	1.6–2.0	0.0004
3	0.63–1.25	0.0010

The supported catalyst with a Pd content of 0.5 wt % prepared by the conventional impregnation of ultrafine diamond with palladium nitrate followed by reduction was used for comparison.

X-ray photoelectron spectra were recorded on an XSAM-800 spectrometer using Al$K_{\alpha 1,2}$ radiation. The C 1s line (BE = 285.0 eV) of Sibunit was chosen as the binding energy (BE) standard. The catalyst pellets were glued on a special-purpose band mounted on the holder. A portion of the initial pellets was thoroughly ground and was also glued on the band. The samples were prereduced with hydrogen at 50°C for 15 min in a specially designed reactor attached to the spectrometer. The reduced samples were transferred into the spectrometer chamber without contact with air.

A palladium foil was used as the reference sample. Before recording a spectrum, the foil was purified by Ar^+ ion sputtering (2 kV, 0.25 μA, ~30 min). The measured Pd 3$d_{5/2}$ binding energy was 335.3 eV, which agrees well with published data [13, 14].

Chlorobenzene (Acros Organics, 99.5%) was hydrodechlorinated in a vertical tubular quartz reactor with an internal diameter of 10 mm equipped with a tubular oven and a thermocouple. Chlorobenzene was poured into one part of a double glass bubbler, whose second part contained glass rings wetted with chlorobenzene to maintain equilibrium in the flow. A hydrogen flow from the generator was passed at a rate of 35 ml/min through the bubbler connected with the reactor. The chlorobenzene feed rate was determined as the difference between the bubbler weights before and after the reaction divided by the duration of the experiment. The chlorobenzene feed rate was 0.15 g/h or 3 h^{-1} in all experiments.

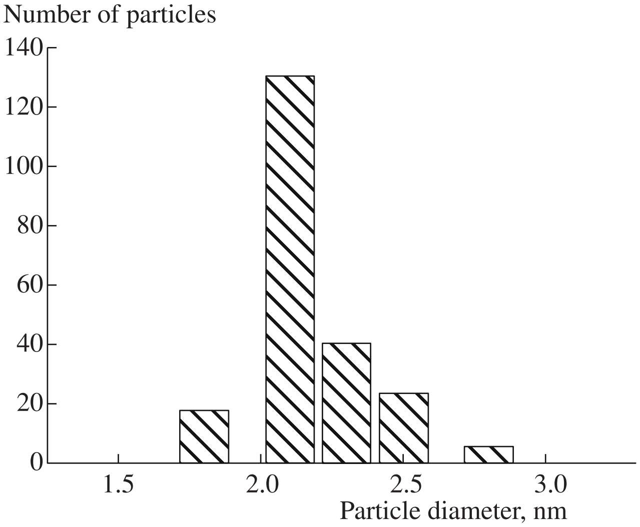

Fig. 3. Size distribution of the palladium nanoparticles in the Pd/SiO_2/Si sample (according to TEM data).

The nonground catalyst (50 mg) was placed in the middle of the reactor between the quartz paper layers. A mixture of chlorobenzene and hydrogen was introduced into the reactor at its bottom, and, in the current of this mixture, the reactor was heated to the preset temperature. The catalyst was not prereduced. After the working temperature (150°C) was achieved, the reaction mixture was sampled at intervals for chromatographic analysis. The analysis was carried out on a PU4410 chromatograph equipped with a DB Wax capillary column 30 m in length (column temperature of 100°C, flame-ionization detector, injection port temperature of 200°C, He as the carrier gas, pressure of 1 atm at the column inlet). The quantitative composition of the reaction mixture was determined using an internal standard precalibrated against each component of the reaction mixture.

The amount of palladium in the reactor did not exceed 10^{-8} mol. The catalytic activity was derived from the yield of the product in 1 h as the molar ratio of its amount to the total amount of the metal or to the amount of the metal in the surface layer. The product yield did not exceed 1% in blank experiments, in which the supports containing no Pd were loaded into the reactor. The accuracy of determination of the catalytic activity was 15%.

RESULTS AND DISCUSSION

Catalyst Structure

When palladium is deposited on a silicon support, the nanoparticles uniformly cover the surface and the average particle density on the surface is constant. This uniform character of surface coverage is typical of nanostructured films obtained by laser electrodispersion. This character is due to the Coulomb interaction between metallic particles, which gain a charge in the laser torch plasma and retain this charge at the moment of deposition on the support [6].

The results of a statistical analysis of the TEM images of the palladium films are presented in Fig. 3. The average size of the palladium particles is about 2 nm. The laser electrodispersion method provides a very narrow particle size distribution, and the relative scatter for palladium does not exceed 10%. The same narrow distribution is typical of nanoparticles of other metals prepared by this method [1–6].

Another important feature of the nanoparticles deposited by laser electrodispersion is their unusual stability to oxidation [12], which can be a consequence of their amorphism. The amorphous state of the nano-

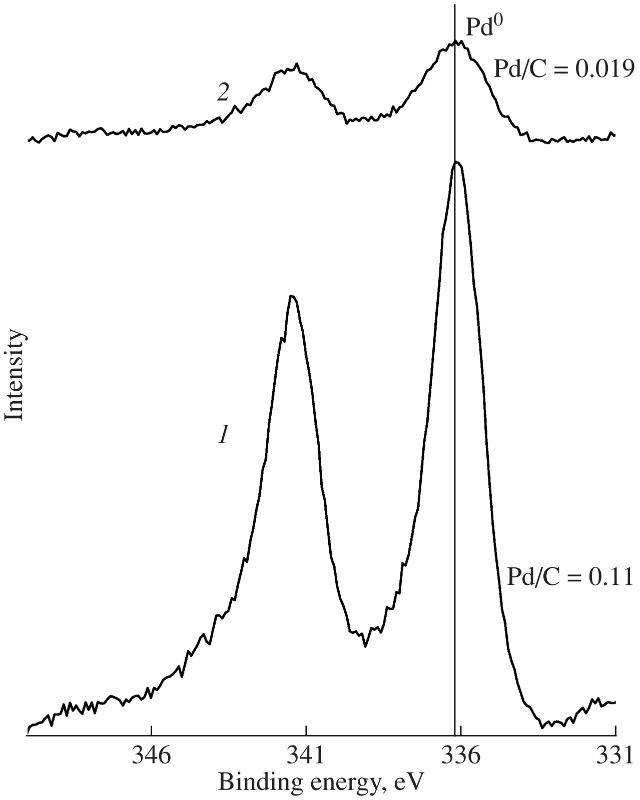

Fig. 4. Pd 3*d* XPS spectra of the granular Pd/C catalyst (*1*) before and (*2*) after hydrodechlorination.

particles is indicated by the absence of well-defined diffraction fringes in the electron diffraction patterns of the palladium films obtained using a transmission electron microscope.

According to the XPS data, all palladium on the catalyst surface is in the metallic state after its activation in a hydrogen atmosphere. This is indicated by the binding energy of the Pd $3d_{5/2}$ line (336.1 eV) and by the shape of the Pd 3*d* line (Fig. 4).

It should be mentioned that the above binding energy is 0.8 eV higher than that for the palladium foil (335.3 eV), which is likely due to the small size of the Pd particles in the supported catalyst. According to published data, the increase in the Pd $3d_{5/2}$ binding energy for small palladium particles is caused by the effects of the initial and final states, and it can reach 1.5 eV [15, 16]. The actual shift is somewhat smaller and can be assigned to 2-nm particles. It can be assumed that the decrease in the shift of the Pd $3d_{5/2}$ line is due to the interaction between Pd particles, which can result in an increase in the energy of extraatomic relaxation and, hence, a decrease in the binding energy of a photoelectron emitted from the core level.

A comparison between the X-ray photoelectron spectrum of the external surface of the catalyst pellets and the spectrum of the ground catalyst indicates a high degree of surface enrichment of the catalyst pellets with palladium. The Pd/C ratio in the spectra of the external pellet surface is ~30 times larger than that in the spectra of the ground catalyst (0.11 versus 0.0036) (Fig. 5). From this we infer that the use of the laser electrodispersion method results in the pronounced “crustlike” palladium distribution over the catalyst pellet. The entire active metal is on the external particle surface, which is most accessible to the reactants, and the degree of its penetration into the internal porous structure is insignificant.

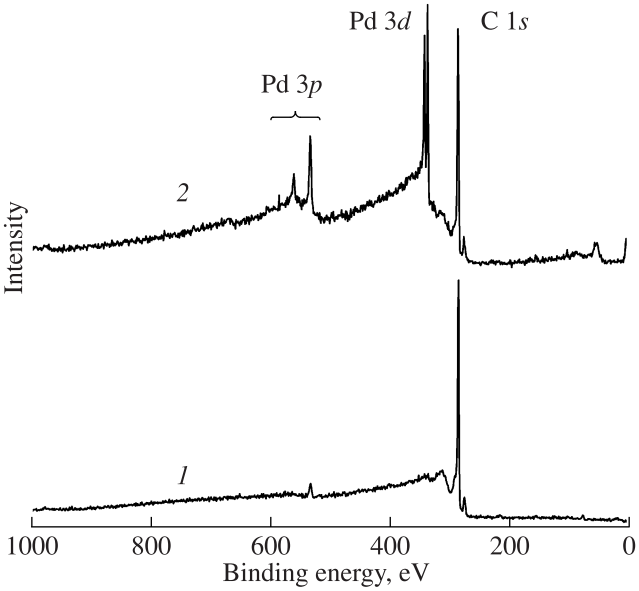

Fig. 5. Survey XPS spectra of (*1*) ground and (*2*) granular Pd/C catalysts before the beginning of the reaction.

Catalytic Hydrodechlorination of Chlorobenzene

Palladium nanoparticles deposited by laser electrodispersion on the silicon plates and Sibunit are active in the gas-phase hydrodechlorination of chlorobenzene. An important distinctive feature of the catalysts prepared by laser electrodispersion is that they need no prereduction. Moreover, preheating of these catalysts in a hydrogen flow decreases their activity. For this reason, all subsequent experiments were carried out simply by passing a mixture of the chlorine-containing hydrocarbon and hydrogen through the catalyst.

Catalysis by the Pd nanoparticles deposited on thermally oxidized silicon. Benzene and cyclohexane are the products of chlorobenzene hydrogenation at 150–200°C in the presence of the palladium nanoparticles deposited on thermally oxidized silicon ($Pd/SiO_2/Si$). The efficiency and selectivity of the process depend on the metal content of the support surface. Selected results are presented in Tables 2 and 3.

As can be seen, the catalysts with an extremely low palladium content manifest considerable activity in the

Table 2. Evolution of the reaction mixture during chlorobenzene hydrodechlorination at 200°C on the Pd/SiO_2/Si catalyst with a palladium content of 2×10^{-4} wt %

Time, min	Content, %		
	cyclohexane	benzene	chlorobenzene
0	–	–	100
48	0	18	82
144	11	17	72
168	10	18	72
228	6	23	71

Table 3. Evolution of the reaction mixture during chlorobenzene hydrodechlorination on the Pd/SiO_2/Si catalyst with a palladium content of 4×10^{-4} wt %

T, °C	Time, min	Content, %		
		cyclohexane	benzene	chlorobenzene
150	0	0	0	100
	12	100	0	0
	24	97	0	3
	84	96	0	4
	96	97	0	3
	108	80	16	4
	120	73	23	4
	132	81	15	4
	144	73	20	7
	156	63	30	7
	168	66	27	7
200	228	56	37	7
	288	41	51	8
	372	51	41	8

hydrodechlorination reaction. For a palladium content of 4×10^{-4} wt %, at the early stages of the process chlorobenzene is hydrogenated completely to form only cyclohexane. Subsequently, at a reaction temperature of 150°C, the catalyst efficiency somewhat decreases. This is indicated by the slight decrease in the chlorobenzene conversion and by the appearance of benzene in the product. If the temperature is increased to 200°C without interrupting the reactant supply, the conversion remains above 90% and a product ratio close to 1 : 1 is observed. As can be seen from the data in Table 3, the temperature increase does not enhance the conversion of chlorobenzene and only slightly affects the selectivity of the process. On the catalysts with a palladium content above 8×10^{-4} wt %, complete conversion of chlorobenzene was also achieved even at 150°C, but benzene was the only hydrogenation product. No decrease in the activity of these catalysts was observed within 7 h.

Catalysis by the Pd nanoparticles deposited on Sibunit. Chlorobenzene is also hydrodechlorinated at 150–200°C on the catalysts prepared by the deposition of palladium nanoparticles on Sibunit using laser electrodispersion. In this case, however, the only product is benzene. The further hydrogenation of benzene to cyclohexane does not occur even at 200°C. The dependences of the chlorobenzene conversion to benzene on the Pd nanoparticles on Sibunit with different pellet sizes (catalysts **1**–**3**) on the duration of the process at 150 and 200°C are shown in Fig. 6. At 100°C chlorobenzene conversion on the most active catalyst **3** does not exceed 13%. It should be mentioned that the palladium catalysts prepared by the standard supporting method exhibit no activity at this temperature.

It can be seen from the data in Fig. 6 that the high initial conversion of chlorobenzene on catalysts **1** and **3**, as distinct from the Pd/SiO_2/Si catalysts, at 150°C decreases to a steady-state level of 33–35% during the process. However, as the temperature is raised to 200°C, the activity of all three Pd/C catalysts increases and the chlorobenzene conversion in the steady-state region approaches 90%. Thus, the steady-state activity of these catalysts is almost independent of the Sibunit pellet size.

The size of the support pellets has an effect only on the catalyst development time. Catalyst **3**, prepared using large Sibunit pellets (up to 3 mm in size), reaches a high activity level immediately after the temperature rise. All three catalysts are very stable. As can be seen from the data in Fig. 4, a high conversion of about 90% persists as the catalysts are repeatedly tested without being regenerated.

Specific Features of the Catalytic Behavior of the Pd Nanoparticles Prepared by Laser Electrodispersion

The specific catalytic activities (A) of the catalysts based on Pd/SiO_2 and Pd/C and containing palladium nanoparticles were calculated from the chlorobenzene conversion achieved at the stage of steady catalyst operation. The results are presented in Table 5. For comparison, Table 5 also includes the data obtained for the supported catalyst prepared by the conventional impregnation of ultrafine diamond. Note that the catalysts on ultrafine diamond are more active than many carbon-supported catalysts. Their efficiency is due to the high specific surface area and the small size of the palladium particles. The particle size in such a catalyst ranges from 2 to 10 nm [17]. The catalytic activities of the different Pd catalysts presented in Table 5 refer either to the total metal content of the catalyst or to the amount of the metal in the surface layer of the particle. In our calculations, we used the data reported in [18], according to which the metal fraction in the surface layer of

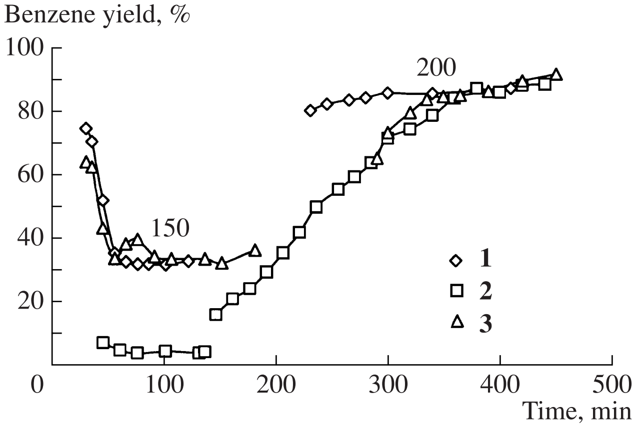

Fig. 6. Benzene yields in chlorobenzene hydrodechlorination versus the reaction time at 150 and 200°C on for Pd/C catalysts **1**, **2**, and **3**.

particles 2 and 2–10 nm in size is 0.63 and 0.45, respectively. It can be seen from the data in Table 5 that the catalysts prepared by the deposition of palladium nanoparticles using laser electrodispersion exceed the supported catalysts in activity by three orders of magnitude. The same high activity of the catalysts of this type was observed earlier in some other reactions of chlorine-containing hydrocarbons and in olefin hydrogenation [1–6].

The palladium nanoparticles deposited on the silicon support are more active at 150°C than the catalysts on Sibunit with a similar metal content. At 200°C, the activities of the catalysts on different supports are comparable. Samples **1** and **2** prepared using large and medium-sized Sibunit pellets manifested the same activity in the steady-state region, and the activity of catalyst **3**, prepared using a finer Sibunit fraction, was lower. This may be due to the fact that the palladium particle coverage of the surface, along with the size of the support pellets, exerts a substantial effect on the catalytic activity.

The influence of the metal content on the specific catalytic activity of catalysts of two types is shown in Fig. 7. For the catalysts prepared on thermally oxidized silicon, the largest *A* value is observed at a metal content of 4×10^{-4} wt %. Probably, the optimal surface coverage is achieved at this metal content, making possible charge transfer between closely spaced particles. A similar extreme dependence of the catalytic activity on the surface density of the particles is typical of several other processes occurring on analogous catalysts supported on dielectrics [1–6]. A plausible explanation of this fact is that a change in the charge state of the nanoparticles takes place, which is indicated by both experimental data and theoretical calculations [1–6, 19]. The similar occurrence of various catalytic processes on nanoparticles of different metals suggests that the substantial enhancement of the catalytic ability observed upon the formation of ensembles of nanoparticles is a rather general phenomenon. As shown by structural and electrophysical studies of palladium films [19], an increase in the metal content of the support surface is accompanied by the formation of small conducting agglomerates, i.e., ensembles of palladium nanoparticles.

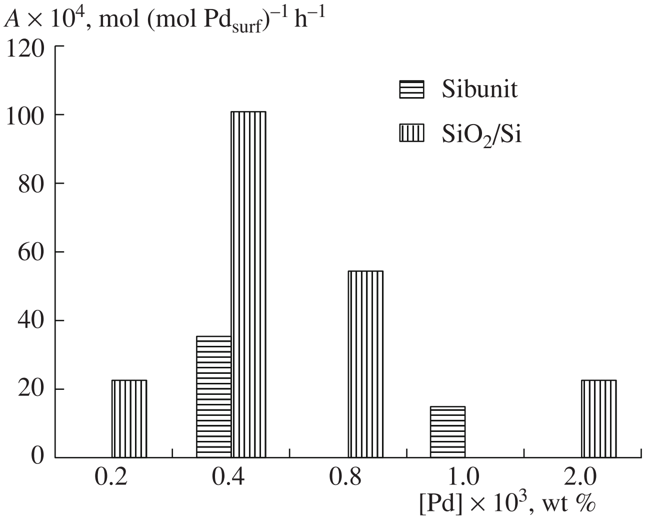

Fig. 7. Activity of the Pd/C and Pd/SiO_2/Si catalysts in chlorobenzene hydrodechlorination at 150°C versus the palladium content.

Concerning the catalysts on Sibunit, the available data suggest only that the decrease in the catalytic activity is caused by a change in the size of the support pellets and by an increase in the metal content of their

Table 4. Evolution of the reaction mixture during chlorobenzene hydrodechlorination on the Pd/C catalysts during their repeated testing (200°C)

Catalyst	Time, min	Content, %	
		chlorobenzene	benzene
2	40	15	85
	55	16	84
	70	16	84
	100	15	85
	230	11	89
	265	8	92
	305	7	93
3	25	7	93
	60	11	89
	85	11	89
	125	11	89
	160	12	88
	180	12	88

Table 5. Activity of the catalysts prepared by laser electrodispersion compared with the activity of the impregnated catalyst in the gas-phase hydrodechlorination of chlorobenzene

Support	Pd content		T, °C	Conversion, %	Activity	
	total, wt %	in the surface layer, mol $\times 10^8$			mol (mol Pd_{tot})$^{-1}$ h^{-1}	mol (mol Pd_{surf})$^{-1}$ h^{-1}
SiO_2/Si	2×10^{-3}	0.9	150	100	143000	227000
	8×10^{-4}	0.4	150	100	340000	540000
	4×10^{-4}	0.2	150	96	640000	1016000
			200	92	620000	984000
	2×10^{-4}	0.1	150	10	140000	222000
			200	29	390000	619000
Sibunit (1.6–3.0 mm pellets)	4×10^{-4}	0.2	150	33	221000	351000
			200	88	590000	937000
Sibunit (0.63–1.25 mm pellets)	1×10^{-3}	0.5	150	35	94000	149000
			200	91	244000	387000
Ultrafine diamond	0.5		200	100	570	1270

surface. Similar dependences were observed for nickel nanoparticles deposited on another conducting support, specifically, crystalline silicon [4]. They can be fuel for electron exchange between the supported nanoparticles and the conducting support. This process becomes more significant when isolated particles appear at low surface coverages [19].

An important feature of the Pd nanoparticles prepared by laser electrodispersion is their high stability in hydrodechlorination accompanied by hydrogen chloride formation. An analysis of the X-ray photoelectron spectra of the catalyst before and after the reaction (Fig. 4) suggests that only some agglomeration of palladium occurs during the reaction and the average size of the metal particles increases. This is indicated by the decrease in the Pd/C ratio from 0.11 (in the fresh catalyst before the beginning of the reaction) to 0.019 (in the catalyst that has participated in the reaction cycle). It can be assumed that the induction period or the phenomenon of catalyst “development” on Sibunit during hydrodechlorination is due to palladium agglomeration and to the increase in the average size of the palladium particles. It is known [20, 21] that palladium particles of optimum size often exhibit a higher catalytic activity in hydrodechlorination than fine particles.

It should be specially emphasized that, according to XPS data, the valence state of palladium remains unchanged during catalytic hydrodechlorination. This means that neither the oxidation nor the chlorination of palladium occurs during the reaction. The high stability is also typical of nanoparticles of other metals obtained by laser electrodispersion. In particular, the unusually high stability to oxidation was observed for copper nanoparticles deposited by laser electrodispersion onto silicon supports [12]. The enhanced stability of the nanoparticles prepared by laser electrodispersion can also be due to their small size and to the amorphous state of the metal persisting for a long time.

According to the XPS data, the chlorine content of the catalyst surface after hydrodechlorination is rather low (Cl : C = 0.01). It can be assumed that the stability of the catalyst surface to chlorination is due to the high palladium concentration on its external surface. Because of this, only a few, if any, C–Cl bonds form during the reaction and, at a high palladium content of surface, all the chlorine is removed rapidly from the surface, most likely as HCl. This result is very important because the problem of catalyst stability is central in the development of methods for processing toxic organochlorine compounds by catalytic hydrodechlorination. The use of the laser electrodispersion method in the preparation of highly efficient catalysts with enhanced stability can contribute to the solution of this problem. The results obtained indicate that the high catalytic activity of the materials examined is also due to the pronounced “crustlike” palladium distribution and the high palladium concentration on the catalyst surface, which makes the active sites readily accessible to the components of the reaction medium.

Thus, unusually high activity and stability of the palladium nanoparticles in catalytic chlorobenzene hydrodechlorination were observed in this work. This is partially due to the use of the laser electrodispersion method, which favors uniform coverage of the support surface with monodisperse amorphous spherical metal nanoparticles. The charge transfer processes favoring the formation of catalytically very active charged states can proceed via different routes. It is not necessary to use only monodisperse systems. Conversely, a wide particle size and shape distribution can facilitate charge transfer. It is quite natural that similar effects were observed in metal–polymer composites with an optimum metal content [22]. An important condition for achieving the maximum catalytic activity is incomplete coverage of the support surface with nanoparticles. A high efficiency of the process is achieved on the catalysts with a very low metal content, which makes it possible to reduce consumption of the precious metal by several orders of magnitude. This fact, along with the high stability of the catalysts, provides new interesting prospects for the development of the technology of toxic organochlorine waste processing.

ACKNOWLEDGMENTS

This work was supported by the International Science and Technology Foundation (grant no. 2955), the Russian Foundation for Basic Research (project no. 07-03-01017), and the Federal Purpose-Oriented Program "Research and Development in Priority Areas of the Science and Technology of Russia in 2007–2012" (state contract no. 02.513.11.3204).

REFERENCES

1. Kozhevin, V.M., Rostovshchikova, T.N., Yavsin, D.A., Zabelin, M.A., Smirnov, V.V., Gurevich, S.A., and Yassievich, I.N., *Dokl. Akad. Nauk*, 2002, vol. 387, no. 6, p. 785 [*Dokl. Phys. Chem.* (Engl. Transl.), vol. 387, nos. 4–6, p. 324].
2. Rostovshchikova, T.N., Yavsin, D.A., Smirnov, V.V., Kozhevin, V.M., and Gurevich, S.A., *Kinet. Katal.*, 2003, vol. 44, no. 4, p. 607 [*Kinet. Catal.* (Engl. Transl.), vol. 44, no. 4, p. 555].
3. Rostovshchikova, T.N., Smirnov, V.V., Gurevich, S.A., Kozhevin, V.M., Yavsin, D.A., Nevskaya, S.M., Nikolaev, S.A., and Lokteva, E.S., *Catal. Today*, 2005, vol. 105, p. 344.
4. Nevskaya, S.M., Nikolaev, S.A., Noskov, Yu.T., Rostovshchikova, T.N., Smirnov, V.V., Gurevich, S.A., Zabelin, M.A., Kozhevin, V.M., Tret'yakov, P.A., Yavsin, D.A., and Vasil'kov, A.Yu., *Kinet. Katal.*, 2006, vol. 47, no. 4, p. 657 [*Kinet. Catal.* (Engl. Transl.), vol. 47, no. 4, p. 638].
5. Rostovshchikova, T.N., Smirnov, V.V., Kozhevin, V.M., Yavsin, D.A., Zabelin, M.A., Yassievich, I.N., and Gurevich, S.A., *Appl. Catal., A*, 2005, vol. 296, p. 70.
6. Rostovshchikova, T.N., Smirnova, V.V., Kozhevin, V.M., Yavsin, D.A., and Gurevich, S.A., *Ross. Nanotekhnol.*, 2007, vol. 2, nos. 1–2, p. 47.
7. Alonso, F., Beletskaya, I.P., and Yus, M., *Chem. Rev.*, 2002, vol. 102, p. 4009.
8. Urbano, F.J. and Marinas, J.M., *J. Mol. Catal. A: Chem.*, 2001, vol. 173, p. 329.
9. Zanaveskin, L.N. and Aver'yanov, V.A., *Usp. Khim.*, 1998, vol. 67, no. 8, p. 788.
10. Lunin, V.V. and Lokteva, E.S., *Izv. Akad. Nauk, Ser. Khim.*, 1996, no. 7, p. 1609.
11. Kozhevin, V.M., Yavsin, D.A., Kouznetsov, V.M., Busov, V.M., Mikushkin, V.M., Nikonov, S.Yu., Gurevich, S.A., and Kolobov, A., *J. Vac. Sci. Technol., B*, 2000, vol. 18, no. 3, p. 1402.
12. Kozhevin, V.M., Yavsin, D.A., Smirnova, I.P., Kulagina, M.M., and Gurevich, S.A., *Fiz. Tverd. Tela*, 2003, vol. 40, no. 10, p. 1895.
13. Teschner, D., Vas, E., Havecker, M., Zafeiratos, S., Schnorch, P., Sauer, H., Knop-Gericke, A., Schlogl, R., Chamam, M., Wootsch, A., Canning, A.S., Gamman, J.J., Jackson, S.D., McGregor, J., and Gladden, L.F., *J. Catal.*, 2006, vol. 242, no. 1, p. 26.
14. Chary, K.V.R., Naresh, D., Vishwanathan, V., Sadakane, M., and Ueda, W., *Catal. Commun.*, 2007, vol. 8, no. 3, p. 471.
15. Kohiki, Sh., *Appl. Surf. Sci.*, 1986, vol. 25, nos. 1–2, p. 81.
16. Stakheev, A.Yu. and Sachtler, W.M.H., *J. Chem. Soc., Faraday Trans.*, 1991, vol. 87, no. 22, p. 3703.
17. Kachevskii, S.A., Golubina, E.V., Lokteva, E.S., and Lunin, V.V., *Zh. Fiz. Khim.*, 2007, vol. 81, no. 6, p. 998 [*Russ. J. Phys. Chem. A* (Engl. Transl.), vol. 81, no. 6, p. 866].
18. Bukhtiyarov, V.I. and Slin'ko, M.G., *Usp. Khim.*, 2001, vol. 70, p. 167.
19. Gurevich, S.A., Kozhevin, V.M., Yassievich, I.N., Yavsin, D.A., Rostovshchikova, T.N., and Smirnov, V., in *Thin Films and Nanostructures: Physico-Chemical Phenomena in Thin Films and at Solid Surfaces*, Trakhtenberg, L.I., Lin, S.H., and Ilegbusi, O.J., Eds., Amsterdam: Elsevier, 2007, vol. 34, p. 726.
20. Coq, B. and Figueras, F., *Coord. Chem. Rev.*, 1998, vol. 178–180, p. 1753.
21. Aramendia, M.A., Borau, V., Garcia, I.M., et al., *J. Mol. Catal. A: Chem.*, 2002, vol. 184, p. 237.
22. Trakhtenberg, L.I., Gerasimov, G.N., Potapov, V.K., Rostovshchikova, T.N., Smirnov, V.V., and Zufman, V.Yu., *Vestn. Mosk. Univ., Ser. 2: Kim.*, 2001, vol. 42, no. 5, p. 325.