

Catalytic Hydrodechlorination on Palladium-Containing Catalysts

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Abstract—The catalytic liquid-phase hydrodechlorination of chlorobenzene on supported palladium-containing catalysts has been investigated. The following processes capable of deactivating the catalyst occur during the liquid-phase hydrodechlorination: the coarsening of supported metal particles, the washoff of the active component with the reaction medium, and potassium chloride deposition on the catalyst surface. The effects of the active component composition and of the preparation method on the hydrodechlorination activity and deactivation stability of the catalysts have been studied. The catalysts have been characterized by several physical methods.

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INTRODUCTION

Catalytic hydrodehalogenation (or hydrogenolysis) is presently acknowledged as the most universal and promising method for treatment and neutralization of halogen-containing organic waste, since this process makes it possible to convert hazardous compounds to useful products without isolating the toxic substances [1].

Catalytic hydrogenolysis can be carried out both in the liquid phase and in the gas phase. Gas-phase processes are most frequently used in the treatment of light aliphatic compounds. At the same time, there have also been reports on the catalytic hydrodehalogenation of aromatic halides [2, 3]. One of the main factors preventing the use of the catalytic hydrodechlorination of chloroaromatic compounds is catalyst deactivation. This can be caused by the inhibiting effect of hydrogen chloride, which is a by-product of the reaction; the formation of carbon deposits; the sintering of the active phase; and the washoff of the active component during the reaction [4].

Different factors can affect catalyst deactivation, depending on the phase where hydrogenolysis occurs.

One of the earliest works concerned with catalyst deactivation [5] revealed the poisoning effect of forming hydrogen chloride in the gas-phase dehalogenation of ethyl chloride on sprayed palladium, platinum, and nickel films. Presently, it is known for certain that hydrogen halides resulting from the hydrodehalogenation of organohalogen compounds on supported palladium metal catalysts can inhibit the reaction in both the gas and liquid phases. The adverse effect of HCl can be

neutralized using proton acceptors, such as NaOH and NH₃.

The effect of bases on the liquid-phase hydrodechlorination of chlorobenzene was studied by Aramendia et al. [6]. The bases were introduced into the system using three different methods: (1) adding an amount of NaOH stoichiometric with respect to chlorobenzene, (2) using a Na-modified catalyst prepared by introducing sodium into the support before impregnating the latter with a metal precursor, and (3) modifying the catalyst with NaOH and NaNO₃ prior to hydrodechlorination. The substantial decrease in the activity of oxide-supported palladium catalysts upon the addition of a stoichiometric amount of alkali was explained by the change in terms of pore modification and Pd⁰ washoff in the alkaline medium.

The washoff of the active component with the reaction medium is among the causes of catalyst deactivation in the liquid phase. Catalyst destruction cannot be excluded either. For instance, a 25% decrease in the specific surface of the Pd/C catalyst and a 20% loss of active metal due to leaching were detected after the 20-h-long hydrodechlorination of polychlorobiphenyls [7]. Similar results were obtained for the liquid-phase hydrodechlorination of chlorobenzene on Pd/MgO [8]. It was shown that palladium can dissolve under the action of HCl resulting from the liquid-phase hydrogenolysis of chlorophenol on Pd/C [9]. The dissolution of palladium can be diminished by using an appropriate solvent.

Among the causes of catalyst deactivation, the formation of carbon deposits is particularly important for gas-phase hydrodechlorination. Coke deposits on

Pd/Al₂O₃ [10, 11] and Pd/C [12–15] catalysts were observed at the initial stages of CCl₂F₂ hydrogenolysis.

Another mechanism of deactivation is the sintering of the active metal [16–18], which can occur in both the liquid and gas phases. Sintering was recognized to be among the main factors causing the deactivation of the palladium catalyst in the gas-phase hydrodechlorination of CClF₂CF₃ [18]. The fluorination of the support by HF resulting from the reaction facilitates the migration and sintering of Pd particles. Palladium is more stable on the fluorinated support AlF₃ than on the initial oxide support. The interaction of the support with evolving hydrogen halide initiates the sintering of palladium particles. The coarsening of palladium particles on active carbon during dichlorodifluoromethane (CCl₂F₂) hydrodehalogenation at 263°C was observed by Wiersma et al. [14].

Thus, hydrodehalogenation catalysts can be deactivated in both gas- and liquid-phase reactions; however, the causes of deactivation depend strongly on process conditions. The advantages of the liquid-phase hydrodechlorination of chlorobenzene over the gas-phase reaction are a lower process temperature and easier hydrogen chloride neutralization.

The purpose of this work is to synthesize supported palladium catalysts, to study their activity and stability in liquid-phase hydrodechlorination, and to elucidate the factors causing catalyst deactivation during the reaction.

EXPERIMENTAL

Preparation of Catalysts

Supported palladium–platinum bimetallic catalysts were prepared by impregnating the support with palladium(II) chloride and chloroplatinic acid solutions followed by drying at 130–150°C for 5 h. The support was the carbon material Sibunit with a particle size of 0.04 to 0.50 mm, a BET specific surface area of $S_{sp} = 370 \text{ m}^2/\text{g}$, a total pore volume of $V_{pore} = 0.4 \text{ cm}^3/\text{g}$, and a micropore volume of $V_{micro} = 0.15 \text{ cm}^3/\text{g}$ at an average pore size of 40 Å.

Series A samples were reduced with an aqueous solution of sodium tetrahydroborate and washed with water. Sodium borohydride was taken in threefold molar excess over the amount of supported metal.

Series B samples were reduced with the same solution and washed with water. Thereafter, they were placed in a heated steel flow reactor, were dried in flowing nitrogen for 20 min, and were heated in flowing hydrogen at 250°C for 1 h.

Series C catalysts, reduced by the same method and washed with water, were placed in a porcelain crucible and were heated in a muffle furnace in air at 250°C for 1 h.

Catalyst Characterization

Catalysts were characterized by X-ray fluorescence spectroscopy on a VRA-30 analyzer with an X-ray tube equipped with a Cr anode. The element content was determined with an accuracy of 0.02%.

Electron micrographs of catalysts were obtained on a JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV and a resolution of 0.14 nm.

Diffraction patterns were obtained on a URD-6 diffractometer (CuK α radiation, $\lambda = 1.5418 \text{ \AA}$) in the scan mode in a 2θ range of 10°–90° with 0.05° increments and a counting time of 10 s per point. The PCPDF and ICSD databases were used to identify crystalline phases. Unit cell parameters were determined with an accuracy of $\pm 0.005 \text{ \AA}$.

Catalyst Activity

The weight of a catalyst sample was such that metal : chlorobenzene = 1 : 1000. A reduced catalyst of the series A, B, or C was placed in the reactor, and (CH₃)₄N⁺Cl⁻ and 4 ml of a 50% KOH solution (for binding the forming HCl) were added. Tetramethylammonium chloride served as a phase-transfer agent: it favored the removal of chloride ions from the catalyst surface and accelerated their transfer to the aqueous phase, where they were neutralized with the alkali. Such effects have already been described [19].

Next, the catalyst was activated at 55°C under flowing hydrogen at atmospheric pressure with continuous stirring for 1 h. A solution of chlorobenzene and undecane in an organic phase (11 ml) consisting of toluene (7 ml) and isopropanol (4 ml) was added to the system. Undecane was used as the internal standard.

The hydrodechlorination of chlorobenzene was carried out under the atmospheric pressure of hydrogen at a constant temperature of 55°C in a glass temperature-controlled reactor fitted with a magnetic stirrer. The stirring speed was varied between 100 and 1200 rpm.

Catalyst Stability

The weight of a catalyst sample was such that metal : chlorobenzene = 1 : 100. The reduced catalyst was placed in the reactor, and the phase-transfer agent (CH₃)₄N⁺Cl⁻ and a 50% solution of KOH (6 ml) for binding the resulting HCl were added. Next, the catalyst was activated as described above, and a solution of chlorobenzene and undecane in the organic phase (17 ml) consisting of toluene (11 ml) and isopropanol (6 ml) was added.

The reaction was carried out in the same way as in the study of the catalyst activity. The stirring speed was 1200 rpm. After the chlorobenzene added was completely converted, a new portion of the reactant was introduced into the reactor. If an insoluble precipitate of potassium chloride was formed in the reactor, a 50%

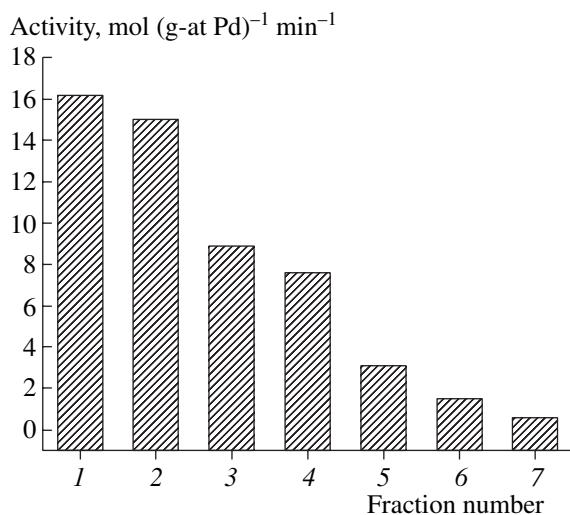


Fig. 1. Initial activity of the series A 1% Pd/C catalyst versus the particle diameter of the support: (1) <0.04, (2) 0.04–0.08, (3) 0.08–0.10, (4) 0.10–0.125, (5) 0.125–0.25, (6) 0.25–0.50, and (7) 0.20–0.50 mm (initial Sibunit).

KOH solution was additionally introduced into the system. Type A, B, and C 1% Pd/C catalysts were tested for stability.

Reaction products were analyzed on a Tsvet 500M gas chromatograph with a flame-ionization detector (Ar as the carrier gas, hydrogen flame, temperature range 50–250°C, column length 3 m, column diameter 2.5 mm, 5% SE-30 on Chromaton N-AW as the column packing).

Catalytic Activity

The total activity of the metals (M) in chlorobenzene hydrodechlorination was estimated as

$$A = \frac{C_{CB}^0 X_B}{v_M \Delta t},$$

where C_{CB}^0 is the initial concentration of chlorobenzene (mol/l). X_B is the fraction of benzene formed (conversion), v_M is the metal concentration in the system (g-atom/l), and Δt is the reaction time (min).

RESULTS AND DISCUSSION

Effect of Diffusion on the Reaction Rate

Numerous works have been devoted to liquid-phase hydrodechlorination. However, it is difficult to compare data obtained by different researchers on different catalysts under different conditions. In most of these works, the process controlling the reaction is not determined and the dependence of the reaction rate on mass-transfer processes is not estimated.

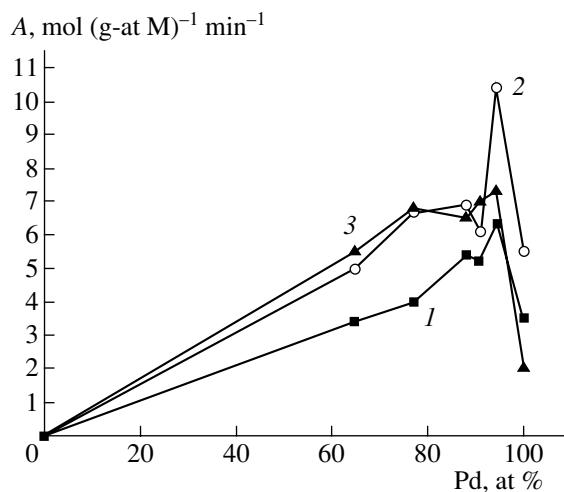


Fig. 2. Activity of hydrodechlorination catalysts pretreated in different ways versus the active component composition: (1) series A catalysts (reduction with a NaBH_4 solution), (2) series B catalysts (reduction with a NaBH_4 solution followed by thermal treatment in a hydrogen atmosphere), and (3) series C catalysts (reduction with a NaBH_4 solution followed by thermal treatment in air).

In the present work, we carried out chlorobenzene hydrogenolysis on the series A 1% Pd/C catalyst at different stirring speeds and different support particle sizes in order to study the effect of external and internal diffusions on the hydrodechlorination rate.

At rotational speeds of the stirrer greater than 800 rpm, the reaction rate is independent of the stirring speed and, hence, the effect of external diffusion can be neglected.

In order to estimate the effect of internal diffusion, chlorobenzene hydrodechlorination was carried out on palladium catalysts with different support particle sizes. Figure 1 shows that the initial activity of the 1% Pd/C catalyst increases as the particle size is reduced. For the particle size 0.1 mm, which was standard in our study, the reaction is controlled by internal diffusion.

In further studies, the support particle size was 0.1 mm and the stirrer speed was 1200 rpm.

Catalytic Activity

The monometallic and bimetallic catalysts of the series A, B, and C were tested in the liquid-phase hydrodechlorination of chlorobenzene. Activity data for these catalysts are presented in Table 1.

The 1% Pt/C catalyst is almost inactive under these conditions. This finding is in agreement with earlier data [20–22] and can be due to the fact that, as compared to palladium, platinum is less capable to accelerate hydride transfer and adsorb hydrogen.

Based on the data presented in Table 1, we plotted the dependences of the activity of the catalysts on their composition for different preparation methods (Fig. 2). Clearly, the bimetallic catalysts heat-treated in a reduc-

tive or oxidative atmosphere are more active in chlorobenzene hydrodechlorination than the catalysts that were simply reduced with borohydride. This is not true for the monometallic catalysts. For a reaction time of 60 min, the 1% Pt/C catalyst treated in a reductive atmosphere is the most active ($5.5 \text{ mol (g-at M)}^{-1} \text{ min}^{-1}$) and the catalyst treated in an oxidative atmosphere is the least active ($2.0 \text{ mol (g-at M)}^{-1} \text{ min}^{-1}$). The catalyst that was not subjected to any additional treatment shows an intermediate activity ($3.5 \text{ mol (g-at M)}^{-1} \text{ min}^{-1}$). However, the time of complete chlorobenzene conversion is 90 min for the series A and C catalysts and 150 min for the series B catalyst. Thus, the activity of the series B catalyst decreases considerably during the reaction.

Catalyst Stability

The supported palladium catalysts treated using the above three procedures were tested for stability in the liquid-phase hydrodechlorination of chlorobenzene. Eight 100% substrate conversion cycles were carried out on the 1% Pd/C catalyst reduced with NaBH_4 (series A). The total test time was 930 min. Four cycles (total test time 900 min) were carried out on the 1% Pd/C catalyst reduced with NaBH_4 and treated in a reductive atmosphere (series B). The substrate conversion in the fourth cycle was 80%. The 1% Pd/C catalyst reduced with NaBH_4 and treated in an oxidative atmosphere (series C) was tested for 1240 min to carry out nine 100% chlorobenzene conversion cycles. The conversion of one portion of chlorobenzene was considered to be one cycle. Figure 3 illustrates the dependence of the catalyst stability on the catalyst pretreatment method. The complete conversion of the substrate in the first cycle was achieved in 90 min for the series A and C catalysts and in 150 min for the series B catalyst.

The above data suggest that thermal treatment in an oxidative atmosphere enhances the stability of the palladium catalysts.

Characterization of the Catalysts by Physical Methods

In order to establish the factors affecting the activity and stability of catalysts pretreated in one way or another and to elucidate the processes causing catalyst deactivation, we examined the catalysts using physical methods.

The elemental composition of the catalysts was determined by X-ray fluorescence spectroscopy before and after stability tests in order to detect the washoff of active metal during the reaction. The data presented in Table 2 show that the highest loss of active metal during the reaction is observed for the 1% Pd/C catalyst reduced with NaBH_4 and heat-treated in a hydrogen atmosphere (series B). Apparently, the rate of hydrogenolysis on this catalyst decreases because of the decrease in the active phase content. For the catalyst simply reduced with borohydride (series A) and the cat-

Table 1. Activity of supported bimetallic catalysts in chlorobenzene hydrodechlorination as a function of the catalyst composition (reaction duration, 60 min)

Entry	Catalyst	$A, \text{ mol (g-at M)}^{-1} \text{ min}^{-1}$
1	1% Pd/C (A)	3.5
2	1% $\text{Pd}_{90}\text{Pt}_{10}/\text{C}$ (A)	6.3
3	1% $\text{Pd}_{85}\text{Pt}_{15}/\text{C}$ (A)	5.2
4	1% $\text{Pd}_{80}\text{Pt}_{20}/\text{C}$ (A)	5.4
5	1% $\text{Pd}_{65}\text{Pt}_{35}/\text{C}$ (A)	4.0
6	1% $\text{Pd}_{50}\text{Pt}_{50}/\text{C}$ (A)	3.4
7	1% Pt/C	0
8	1% Pd/C (B)	5.5
9	1% $\text{Pd}_{90}\text{Pt}_{10}/\text{C}$ (B)	10.4
10	1% $\text{Pd}_{85}\text{Pt}_{15}/\text{C}$ (B)	6.1
11	1% $\text{Pd}_{80}\text{Pt}_{20}/\text{C}$ (B)	6.9
12	1% $\text{Pd}_{65}\text{Pt}_{35}/\text{C}$ (B)	6.7
13	1% $\text{Pd}_{50}\text{Pt}_{50}/\text{C}$ (B)	5.0
14	1% Pd/C (C)	2.0
15	1% $\text{Pd}_{90}\text{Pt}_{10}/\text{C}$ (C)	7.3
16	1% $\text{Pd}_{85}\text{Pt}_{15}/\text{C}$ (C)	7.0
17	1% $\text{Pd}_{80}\text{Pt}_{20}/\text{C}$ (C)	6.5
18	1% $\text{Pd}_{65}\text{Pt}_{35}/\text{C}$ (C)	6.8
19	1% $\text{Pd}_{50}\text{Pt}_{50}/\text{C}$ (C)	5.5

Note: The series A catalysts were reduced with a NaBH_4 solution and were not subjected to any thermal treatment, the series B catalysts were additionally heat-treated in a hydrogen atmosphere, and the series C catalysts were heat-treated in air.

Table 2. Palladium content of the series A, B, and C 1% Pd/C catalysts before and after chlorobenzene hydrodechlorination

Catalyst	Pd content, rel. units	
	before reaction	after reaction
Initial 1% Pd/C	0.98	—
Series A sample	1.02	0.89
Series B sample	1.04	0.68
Series C sample	1.00	0.88

Note: The reaction duration for samples A, B, and C is 930, 900, and 1240 min, respectively.

Table 3. Average size of the supported metallic particles in the 1% Pd/C catalysts before and after chlorobenzene hydrodechlorination

Catalyst	Particle size, nm	
	before reaction	after reaction
Series A sample	2.2	3.4
Series B sample	2.7	3.6
Series C sample	2.2	3.8

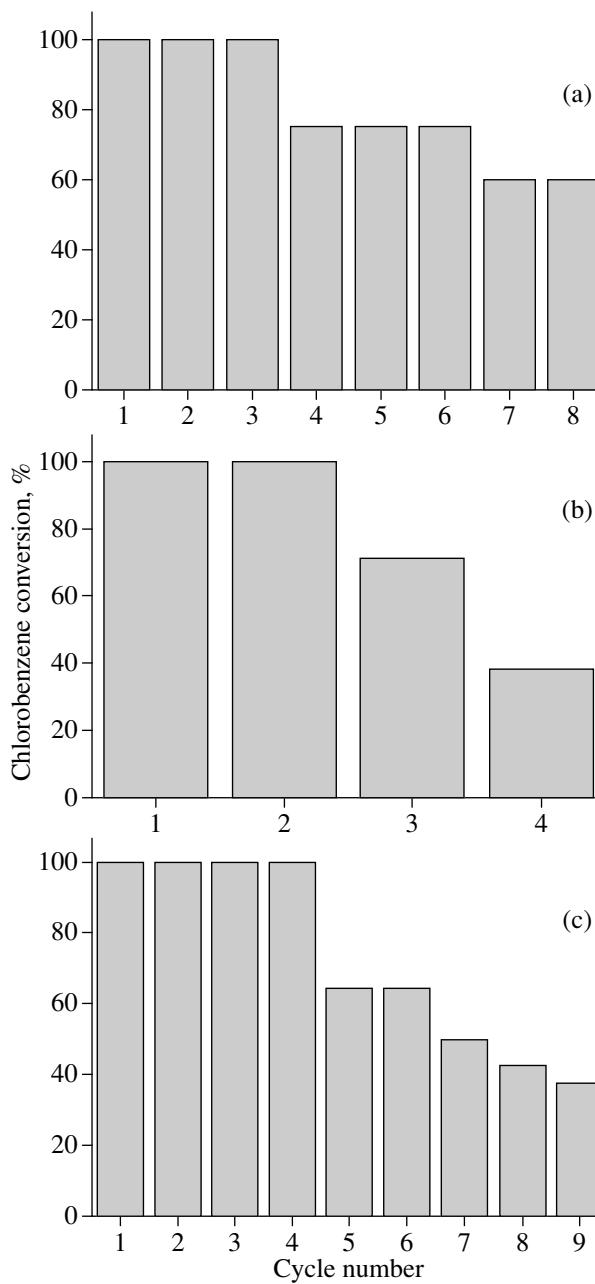


Fig. 3. Conversion of chlorobenzene on the series (a) A, (b) B, and (c) C 1% Pd/C catalysts in successive liquid-phase hydrodechlorination cycles. The duration of each cycle on the series A, B, and C catalysts is 90, 150, and 90 min, respectively.

alyst subjected to additional heat treatment in air (series C), the decrease in the metal content is approximately the same and is ~22%. Since the service life of the series C catalyst is 1240 min and that of the series A catalyst is only 930 min, thermal treatment in the oxidative atmosphere reduces the washoff of the active component during the reaction to the greatest extent.

The changes in the particle size of the supported active component of the catalysts during the reaction

were studied by transmission electron microscopy (TEM). Before the reaction, the active component in all catalysts was monodisperse. The TEM data (Table 3) demonstrate that the average particle size and the extent of particle coarsening during the reaction depend only slightly on the pretreatment procedure. Thus, the main factor determining the average size of supported active component particles and their stability under the reaction conditions is the reduction of the precursors with sodium borohydride. The electron micrographs of the series A 1% Pd/C catalyst before and after liquid-phase hydrodechlorination are shown in Fig. 4.

According to X-ray powder diffraction data, the 1% Pd/C monometallic catalysts of the series A and B contain supported particles of metallic palladium before and after the reaction. The diffraction pattern from the series C 1% Pd/C catalyst before the reaction has a peak at $2\theta = 33^\circ$ presumably due to the palladium(II) oxide phase. The state of the active component after hydrodechlorination is substantially different, as is indicated by a reflection from metallic palladium appearing at $2\theta = 40^\circ$. Thus, it can be assumed that the increasing activity and the high stability of the catalyst pretreated in the oxidative atmosphere are due to the palladium oxide phase. Palladium oxide is much less reactive toward hydrochloric acid than metallic palladium, and its gradual reduction to active palladium metal during the reaction favors an increase in catalytic activity.

Potassium chloride peaks at $2\theta = 28.3^\circ$, 40.5° , 50.2° , 58.6° , and 66.4° were observed in the diffraction patterns from series A, B, and C 1% Pd/C samples after a series of hydrodechlorination cycles. During long-term service-life tests, potassium chloride forms in the aqueous phase via the neutralization of hydrogen chloride with potassium hydroxide. Potassium chloride can build up on the catalyst surface and cover the active sites of the metal and/or the carbon support to decrease the catalytic activity. Similar effects were described earlier [23].

X-ray powder diffraction data for the bimetallic catalysts suggest that the phase composition of the active component depends only slightly on the heat-treatment medium. The diffraction patterns from the series B and C catalysts before and after the reaction exhibit diffraction peaks at $2\theta = 41^\circ$, which are apparently due to palladium–platinum solid solutions. The similarity between the states of the active component in these two series of catalysts is confirmed by the similarity between the activity data for these series (Fig. 2). The unit cell parameter of the palladium–platinum solid solutions in the series B catalysts (Table 4) does not obey Vegard's rule. Probably, this can be explained by the incorporation of hydrogen into the lattice of the solid solution. Unfortunately, the diffraction peaks from most of the series C catalysts are weak and diffuse and, therefore, the unit cell parameter and the size of the coherent scattering region (CSR) of the phase cannot be determined. The only exception is 1% Pd₉₀Pt₁₀/C, whose

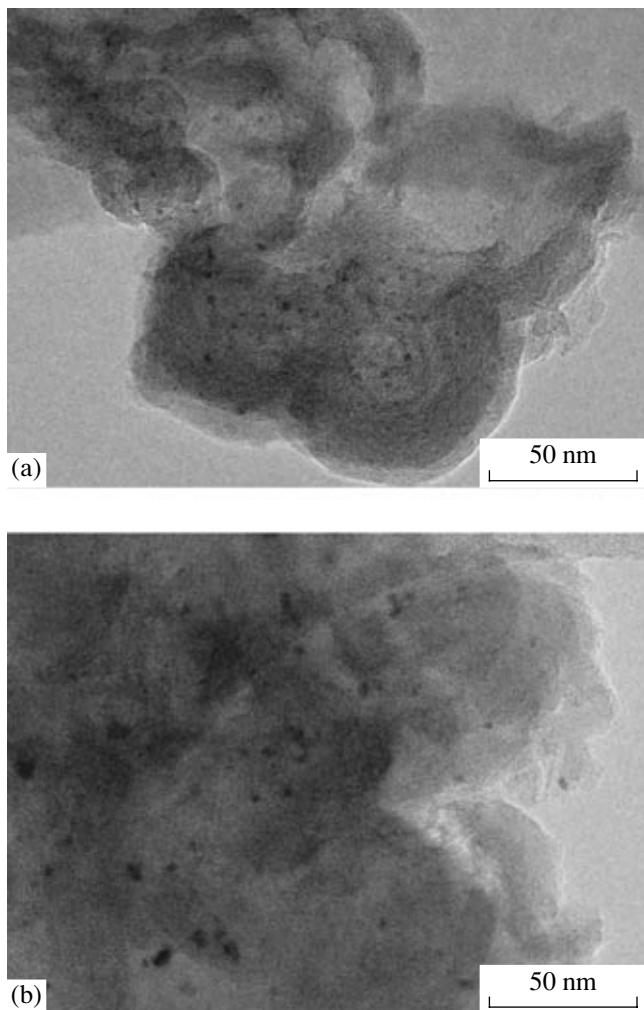


Fig. 4. Electron micrographs of the series A 1% Pd/C catalyst (a) before and (b) after the liquid-phase hydrodechlorination of chlorobenzene.

Table 4. Selected X-ray diffraction data for the supported Pd–Pt bimetallic catalysts after hydrodechlorination (HDC)

Catalyst	Unit cell parameter, Å	CSR size, Å	Phase
1% Pd ₉₀ Pt ₁₀ (A)	3.951	55	Pd–Pt*
1% Pd ₅₀ Pt ₅₀ (A)	3.938	40	Pd–Pt*
1% Pd ₉₀ Pt ₁₀ (B)	3.912	70	Pd–Pt
1% Pd ₉₀ Pt ₁₀ (B) after liquid-phase HDC	3.909	60	Pd–Pt
1% Pd ₈₀ Pt ₂₀ (B)	3.907	50	Pd–Pt
1% Pd ₆₅ Pt ₃₅ (B)	3.907	90	Pd–Pt
1% Pd ₅₀ Pt ₅₀ (B)	3.913	120	Pd–Pt
1% Pd (B)	3.885	–	Pd
1% Pd ₉₀ Pt ₁₀ (C)	3.897	60	Pd–Pt

* This phase is apparently a poorly crystallized solid solution containing impurities altering the unit cell parameter.

characteristics are given in Table 4. Series A catalysts, which were not subjected to any thermal treatment, contain poorly crystallized phases that are apparently solid solutions containing impurities altering the unit cell parameter.

Thus, the study of the liquid-phase hydrodechlorination of chlorobenzene has demonstrated that the reaction on the palladium-containing catalysts is controlled by internal diffusion. The thermal treatment of the reduced, supported, Pt–Pd bimetallic catalysts in a reductive or oxidative atmosphere enhances their activity. The phase composition of the active component remains virtually unchanged.

The pretreatment of the supported monometallic palladium catalyst in an oxidative atmosphere results in an increase in catalytic activity during the reaction, prevents the washoff of the active component, and improves the catalyst stability. The latter effect is apparently due to the formation of the palladium oxide phase, which is more resistant toward HCl. During the reaction in the reductive atmosphere, the palladium oxide phase gradually passes into the active metallic state, resulting in an increase in the catalyst activity. The thermal pretreatment of the monometallic palladium catalyst in a reductive atmosphere leads to an increase in the initial catalytic activity; however, the catalytic activity decreases substantially during the reaction. This is due to the rapid washoff of palladium by the reaction medium.

We believe that the washoff of the active component is among the processes causing the deactivation of the catalyst in the liquid-phase hydrodechlorination of chlorobenzene. Another cause of the loss in catalytic activity is the deposition of potassium chloride (hydrogen chloride neutralization product) on the catalyst surface, which blocks catalytically active sites.

In the catalysts that were subjected to service life (stability) tests, we observed the coarsening of supported metallic particles. Neither the particle size of the active component in the fresh catalysts nor the way the particle size changes during the reaction depends on the pretreatment procedure.

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