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Ultradispersed Diamond As a New Carbon Support for Hydrodechlorination Catalysts

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Abstract—The properties of palladium and nickel catalysts supported on ultradispersed diamond (UDD) were studied in the vapor-phase hydrodechlorination (HDC) reaction of chlorobenzene and the multiphase HDC of polychlorobenzenes. The catalysts on UDD exhibited a number of advantages: the vapor-phase HDC of chlorobenzene on Ni/UDD occurred at lower temperatures, and the multiphase HDC of chlorobenzene, 1,3,5-trichlorobenzene, and 2,4,8-trichlorodibenzofuran on Pd/UDD occurred more rapidly than that on catalysts supported on activated carbon. The structure of the catalysts and the electronic states of the active components were studied using IR spectroscopy, temperature-programmed reduction, and adsorption techniques. It was found that the properties of the catalysts depend on the electronic state of palladium, which depends on its concentration in the sample; the structural properties, which are responsible for the accessibility of the active surface to adsorption; and the presence of other metal impurities.

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INTRODUCTION

The reductive dechlorination of organochlorine compounds is a convenient and efficient process for the conversion of toxic organochlorine wastes; this process is free of disadvantages characteristic of oxidative utilization processes (the formation of dioxins and the irreversible loss of the hydrocarbon moieties of molecules as a result of their conversion into CO_2 and water) [1, 2]. Reductive dechlorination (unlike dehydrochlorination) is applicable to a wide range of substrates, and the reaction occurs more rapidly than biodegradation. Systems based on palladium are the most active hydrodechlorination catalysts; however, economic considerations prevent the widespread use of these catalysts. Nickel catalysts are also used. The main problems are the insufficient stability of catalytic systems because of the low mechanical strength of the most widespread inert carbon supports [3–5] and the interaction of the active component or oxide support with hydrogen chloride released in the reaction [6]. All of these factors can result in a loss of the active component, especially, in the conversion of heavy polychlorinated compounds in a liquid phase. Moreover, the catalytic systems deactivate as a result of carbonization due to products (more frequently, in the conversion of chlorinated aliphatic hydrocarbons) [7] and particle aggregation under reaction conditions. It was found experimentally [8, 9] that hydrodechlorination is a structure-sensitive reaction; to obtain effective catalysts, active metal nanoparticles of a certain size (3–10 nm) should be immobilized on the support surface and particle aggregation in the course of reaction should be prevented. The interaction of metal nanoparticles with a structured support is considered a way of stabilizing these nanoparticles.

Recently, attention has been focused on the unusual adsorption properties of ultradispersed diamond (UDD), a structurally ordered material obtained upon the utilization of explosives. The particles of UDD can have a size of about 20 nm; the specific surface area of the material is about 300 m^2/g. A number of functional groups, primarily, carboxyl and hydroxyl groups, and metal impurities occur on the surface of UDD. The strength of UDD is much higher than that of standard carbon supports. Bogatyreva et al. [10] found that the oxidation of CO to CO_2 can occur on UDD at temperatures higher than 300°C. The addition of only 0.001 wt % Pd makes it possible to decrease the reaction temperature to 180°C; in this case, the conversion increased from 80 to 100%. Kulakova [11] found that a solvent (tetralin or decalin) underwent a number of transformations with the formation of isomerization, dehydrogenation, disproportionation, and cracking products upon the high-temperature extraction of diamond stock. The polymerization catalyst Cp_2ZrCl_2 ($Cp = \eta^5$-cyclopentadienyl) supported onto UDD exhibited higher activity than an analogous system on aluminum oxide [12]. In addition, unlike the Cp_2ZrCl_2/Al_2O_3 system, which dramatically loses its activity after reaching a maximum rate of polymerization, the catalyst supported on UDD remains sufficiently stable. Youling Yuan et al. [12] explained this phenomenon by the presence of various functional groups on the surface of UDD.

Nickel catalysts supported on purified UDD or UDD blend were found quite good catalysts for methanol decomposition. Their activity and selectivity intricately depend on reaction temperature and pretreatment conditions (for example, heating in an atmosphere of argon affects these characteristics) [13]. Differences in catalytic activity are due to changes in the phase composition, mesoporosity, and the composition and concentration of surface functional groups. These differences clearly manifest themselves in a comparison between catalysts on purified UDD and supports based on a blend. Preparation conditions and purification efficiency seriously affect the adsorption properties of nanodiamonds and hence the catalytic properties of systems based on these nanodiamonds.

A number of studies were devoted to the properties of oxidized nanodiamonds. Catalytic systems including Cr_2O_3 or V_2O_5 supported on oxidized nanodiamond exhibited high activity in the dehydrogenation of light alkanes to alkenes [14]. The activity increased especially strongly if the reaction was performed in the presence of CO_2. Nakagava et al. [14] related special properties of nanodiamonds to the occurrence of functional groups, such as carboxyl and carbonyl groups, which act as organic reagents, on the surface. Moreover, a supported metal or oxide reacts more weakly with nanodiamond than with an oxide support, and this can impart special properties to catalysts based on nanodiamonds.

Published data indicate that Pd particles supported on UDD are especially resistant to agglomeration in an atmosphere of hydrogen: thus, for example, hydrogen reduction at 600°C did not result in an increase in the particle size of palladium on UDD (10–20 nm), although it increased to 100 nm upon an analogous treatment of a catalyst on activated carbon [15]. The high resistance of palladium nanoparticles to agglomeration was also noted in a study of (Pd–Pr)/UDD catalysts [16].

Kachevskii et al. [17] were the first to demonstrate that palladium catalysts supported on UDD exhibit high activity in the multiphase reactions [18] of the hydrodechlorination (HDC) of tri- and hexachlorobenzene, which is higher than the activity of catalytic systems supported on activated carbons with an analogous active metal content (they were compared with both laboratory samples and a commercial 5% Pd/C catalyst from Fluka). Based on a number of physicochemical studies, it was hypothesized that the high activity of catalysts on UDD was due to considerable surface ordering, almost complete absence of micropores, and the presence of promoting trace impurities on the surface. The catalytic properties of the resulting systems depended on the palladium content of these systems. With the use of transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis, it was found that an increase in the metal content from 0.5 to 5 wt % resulted in an increase in metal particle size [19].

In this work, we studied the catalytic properties of nickel- and palladium-containing catalysts supported on UDD in the processes of vapor-phase HDC of chlorobenzene (CB) and multiphase HDC of CB, 1,3,5-trichlorobenzene (TCB), hexachlorobenzene (HCB), and 2,4,8-trichlorodibenzofuran (TCDBF), which is a nontoxic analog of dioxins.

EXPERIMENTAL

UDD from the All-Russia Research Institute of Technical Physics (Snezhinsk) with the specific surface area $S_{BET} = 260$ m^2/g (particle size, <0.01 mm), which was treated with Cr_2O_7 in sulfuric acid to remove amorphous carbon, and activated carbon (AC) with $S_{BET} = 1090$ m^2/g (particle size, <0.01 mm) were used in the experiments. The supports were impregnated with a calculated amount of an aqueous solution of palladium nitrate (Aurat) or nickel nitrate $Ni(NO_3)_2 \cdot 6\ H_2O$ (Reakhim) followed by slow heating (1 h) to 150°C and calcination at this temperature for 2 h. Reduction was performed in a flow of hydrogen ($V_{H_2} =$ 12 ml/min) under slow heating to 280°C and then under isothermal conditions for 2 h. Cooling was also performed in a flow of hydrogen.

For comparison, a 5% Pd/C catalyst (Fluka) was used.

The gas-phase HDC of CB was performed in a flow setup with a fixed bed of a catalyst. The setup included a quartz tube reactor heated with a furnace and a system of two bubblers, one of which contained CB and the other, glass packing moistened with CB. The second bubbler served for damping a nonequilibrium flow of hydrogen at the outlet of the first bubbler. Hydrogen from a GVCh-12 generator was passed through a gas flow controller from Metakhrom, saturated with CB, and supplied to the reactor at the bottom. The reactor temperature was maintained to within ±1°C. The effluent gas was also passed through two bubblers, one of which containing isooctane was intended for trapping hydrocarbon products, and the other with a weak alkali solution was intended for trapping the resulting hydrogen chloride. Analytical samples were taken from the top of the reactor at regular intervals using a syringe.

Analysis was performed by gas–liquid chromatography on a PU4410 instrument with a DBWax capillary column 30 m in length and a flame-ionization detector (injector temperature, 200°C) and on an Agilent 6890N instrument (injector and detector temperatures, 250°C) using temperature programming from 35°C (5 min) to 200°C at a heating rate of 10 K/min followed by a 10-min exposure at 200°C. To refine the composition of products, some samples were analyzed by gas chromatography–mass spectrometry (GC–MS) on a Trace DSQ-2 instrument with a DB-5 column 15 m long.

A weighed portion of a catalyst (50 mg) was placed in the reactor between the layers of a Whatman QM-A quartz filter. Before the onset of an experiment, a flow of hydrogen (12 ml/min) was passed through the reactor, and the catalyst was additionally reduced for 30 min; thereafter, a specified temperature was adjusted. Then, a three-way valve was turned to direct the hydrogen flow to a bubbler and CB was supplied to the reactor. In all of the experiments, the CB supply rate was 1.2 h^{-1}. After reaching a constant degree of conversion, the reactor temperature was increased to the next specified value. The activity of catalysts was measured over the range from 30 to 350°C.

The multiphase HDC of CB, 1,3,5-TCB, and 2,4,8-TCDBF was performed at atmospheric pressure in a reactor described previously [17]. A 6 ml of reaction mixture consisting of a 5% aqueous solution of KOH, 2 ml of isooctane, 100 mg of a catalyst, and a solution of 0.26 mmol of Aliquat 336 in 2 ml of isooctane were placed in the reactor. The mixture was stirred with a magnetic stirrer for 20 min. Then, a solution of 0.01–0.8 mmol of a substrate in 3 ml of isooctane and 0.11 mmol of nonane (internal standard) were introduced into the reactor; thereafter, hydrogen was passed (5 ml/min). The reaction was performed at 50°C. The constant rate of hydrogen supply was maintained using a Metakhrom gas flow controller. Samples for analysis were taken through a rubber septum; the average sample volume was 0.1 ml. The products were analyzed as described above with the use of an internal standard.

To determine the yields of all of the gas-phase HDC products, effluent gases were passed through a solution of KOH and the yield of HCl was determined by titration upon completion of the experiment. The titration of an aqueous phase after multiphase HDC was performed in the same manner. Material balance in the multiphase process and the gas-phase reaction was observed within ±10 and ±20%, respectively.

The diffuse reflectance IR spectra were measured on a Bruker Equinox 55/S Fourier transform IR spectrometer. CO was used as a probe molecule. Carbon monoxide was purified and dried by passing through a trap with liquid nitrogen and long keeping in a cylinder of a vacuum adsorption setup over a layer of precalcined zeolite. The samples of catalysts and supports were placed in quartz ampoules with branches in which calcium fluoride windows were pasted. They were subjected to thermal vacuum treatment at 450°C in air for 20 min and then in a vacuum of no worse than 5×10^{-5} Torr for 3 h. The adsorption of CO was performed in a vacuum adsorption system at room temperature. The equilibrium pressure of CO over the surfaces of the samples was maintained to within ±3 Torr.

The temperature-programmed reduction (TPR) spectra of catalyst precursors were measured after the drying and calcination stages (without reduction) in a laboratory setup containing a gas preparation system, a reactor with a tube furnace, and a thermal-conductivity detector. The gas flow rate of 23 ml/min was chosen based on the results of a preliminary study of the effect of gas flow rate on the reduction of nickel-containing systems. Detector signals were processed using the Ecochrom program package. An unreduced sample was placed in a quartz reactor on a layer of a Whatman QM-A porous filter. The sample weight was 40–50 mg. Reduction was performed with a mixture of 5% H_2 + 95% Ar using linear heating at a rate of 12 K/min. The concentration of hydrogen in a flow was continuously monitored using a thermal-conductivity detector, whose signal arrived at a computer through an analog-to-digital converter.

The energy dispersive spectra were measured for 120 s on a Respect EDXRF spectrometer.

RESULTS AND DISCUSSION

Catalytic Properties of Nickel and Palladium Catalysts Supported on UDD

Liquid-phase HDC. Previous studies of catalysts supported on UDD performed by TEM [17] and XRD analysis demonstrated that UDD particles have a crystal structure; they are aggregated in agglomerates up to 300 nm in size consisting of smaller segments at the edges of which supported metal particles are arranged. The character of point reflections in electron diffraction patterns suggests that palladium supported on UDD is not amorphous. In the course of catalyst preparation, the texture properties of UDD changed only slightly. The palladium catalyst supported on UDD was far superior to 5% Pd/AC and 5% Pd/C (Fluka) catalysts in terms of activity in the HDC reactions of 1,3,5-TCB and HCB [17].

Nickel catalysts did not exhibit activity in a multiphase system. Table 1 summarizes data on the activity of catalysts with various Pd contents in the HDC reactions of CB, 1,3,5-TCB, HCB, and TCDBF under multiphase conditions. The half-conversion time (t_{50}), the time of 90% substrate conversion (t_{90}), and the time of the full conversion of the substrate into a corresponding product containing no chlorine served as the measures of activity. As will be demonstrated below, differences in activity between the catalysts supported on UDD and reference catalysts were very great. In the majority of cases, we failed to reach complete substrate conversion into corresponding nonchlorinated compounds (benzene or dibenzofuran) for reasonable reaction times (to 500 min) on the reference catalysts. Therefore, the comparison of activities in terms of reaction turnover numbers with consideration for the formation of partial HDC byproducts was found ineffective.

According to GC and GC–MS data, only HCl and benzene were formed as products upon the HDC of CB. The HDC of polychlorobenzenes and TCDBF occurred with the consecutive replacement of chlorine atoms by hydrogen; the end products were benzene

Table 1. Half-conversion and 90% conversion times of substrates in a multiphase system in the presence of palladium-containing catalysts

Catalyst	Particle size, nm		CB		1,3,5-TCB		2,4,8-TCDBF		HCB	
	according to HR TEM data	according to XRD data	t_{50}, min	t_{90}, min	t_{50}, min	t_{90}, min	t_{50}, min	t_{90}, min	t_{50}, min	t_{90}, min
5% Pd/C (Fluka)	5–30	–	35	110	275	670	7	24	15	43
5% Pd/AC	4–40	–	109	–	–	–	650	–	83	315
5% Pd/UDD	5–7	5–6	12	47	10	40	5	10	13	38
2% Pd/UDD	4–5	3.0–3.5	7	15	10	60	12	23	23	50
1% Pd/UDD	4–5	2.5–3.0	7	15	10	65	14	30	25	50
0.5% Pd/UDD	2.5–4	1.5–2.0	3	10	75	200	95	–	30	–

Note: Catalyst sample, 0.1 g; substrate content, 0.35 mmol.

and dibenzofuran, respectively. Cyclohexane or other by-products were not formed in the multiphase system. As can be seen in Table 1, the activity of catalysts in the HDC of CB increased as the Pd content was decreased. At a palladium content of 0.5 wt %, the half-conversion time was 3 min, whereas 90% conversion took place after 10 min (for comparison, the corresponding values in the presence of 5% Pd/UDD or 5% Pd/C (Fluka) were 12 and 47 or 35 and 109 min, respectively).

Other behaviors were observed in the HDC of polychlorinated benzenes. The sample of 0.5% Pd/UDD was found the least active in the HDC reaction of 1,3,5-TCB, and the 50% conversion times of this substrate on the catalysts containing 1, 2, and 5% Pd were the same. The almost complete conversion occurred somewhat more rapidly (40 min) in the presence of 5% Pd/UDD. The times t_{90} on catalysts containing 1 and 2% Pd did almost not differ (65 and 60 min, respectively). About 50 min was required for the complete conversion of 1,3,5-TCB into benzene in the presence of 5% Pd/UDD, whereas less than 5% benzene was formed in the specified time on reference catalysts. The total degrees of conversion in the presence of 5% Pd/AC and 5% Pd/C (Fluka) were 12 and 5%, respectively; at this point in time, chlorobenzene was the main product.

The catalysts containing 1 and 2% Pd exhibited very similar activities in reactions with the participation of TCDBF and HCB. Both the half-conversion times and the 90% conversion times of these substrates were almost coincident (Table 1). Note that the sample of 5% Pd/UDD was much more active than 5% Pd/C (Fluka) in the HDC reactions of CB and, especially, 1,3,5-TCB and somewhat more active in the HDC of TCDBF ($t_{90} = 10$ and 24 min, respectively). Complete conversion into dibenzofuran in the presence of 5% Pd/UDD or 5% Pd/C (Fluka) occurred within 50 or 110 min, respectively, whereas a 100% yield of benzene on a catalyst based on activated carbon was not reached even after 500 min.

In the HDC of HCB, the times t_{50} and t_{90} reached with the use of catalysts on various supports differed only slightly. However, a more detailed analysis of kinetic data indicated that the complete conversion of HCB into benzene in the presence of 5% Pd/UDD occurred within 80 min, whereas we failed to reach full conversion into benzene on reference catalysts even after 500 min. From an analysis of kinetic curves (they are not given in this paper), it follows that the complete conversion of TCDBF and HCB in the presence of 0.5% Pd/UDD did not occur at the reaction times used in this work: in the former case, conversion reached a constant value of about 80% after 100-min reaction, whereas it was 55% after 60 min in the latter case, and this conversion continued to increase slowly (by 5% in 10 min). Thus, the catalyst on UDD exhibited a much higher activity in the HDC reactions of chlorobenzenes and TCDBF, as compared with that of the commercial catalyst and the sample on activated carbon; that is, it provides an opportunity to rapidly and efficiently convert chlorobenzenes into benzene and TCDBF into dibenzofuran.

Vapor-phase HDC. Figure 1 compares the samples of 5% Pd/UDD, 5% Ni/UDD, 5% Pd/C (Fluka), 5% Pd/AC, and 5% Ni/AC in the gas-phase process of CB HDC in a catalytic fixed-bed flow reactor. As can be seen, the initiation of reaction in the presence of palladium catalysts occurred at sufficiently low temperatures. Thus, even at 50°C, the conversion of CB in the presence of 5% Pd/AC, 5% Pd/C (Fluka), or 5% Pd/UDD was 52, 69, or 85%, respectively, whereas it was higher than 90% at 100°C; in this case, it was close to 100% on the two last-named samples. Thus, the catalysts on UDD are superior to the reference catalysts in terms of activity at relatively low temperatures.

On the nickel catalysts, the reaction began at temperatures higher than 100°C. At 200°C, the conversion of CB on 5% Ni/UDD or 5% Ni/AC was 61 or 51%, respectively. At all of the test temperatures, the conversion of CB in the presence of catalysts on UDD was noticeably higher than that on AC. On the sample of 5% Ni/UDD, the degree of conversion at 350°C was as high as 80%.

A comparison between the compositions of HDC products formed in the presence of nickel and palla-

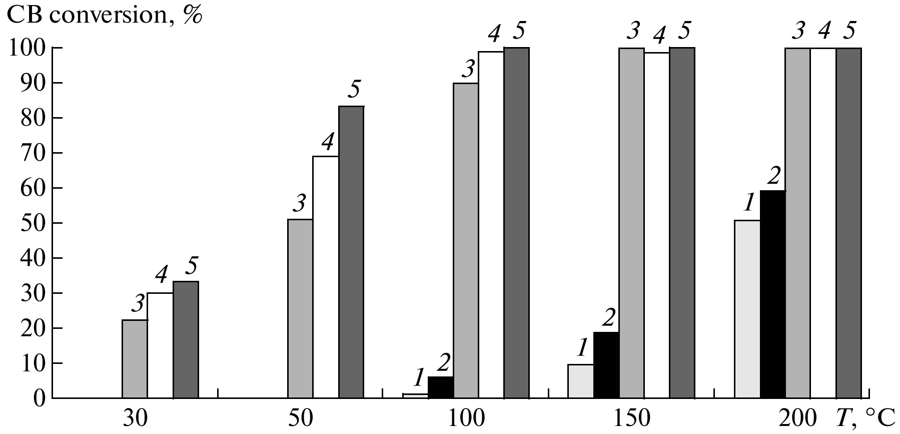

Fig. 1. Gas-phase HDC of CB in the presence of various palladium and nickel catalysts: (*1*) 5% Ni/AC, (*2*) 5% Ni/UDD, (*3*) 5% Pd/AC, (*4*) 5% Pd/C (Fluka), and (*5*) 5% Pd/UDD.

dium catalysts exhibited serious differences. On Ni-containing samples, benzene was the only product over the entire test temperature range. In the presence of Pd catalysts, the concentration of cyclohexane, which resulted from benzene hydrogenation, increased with temperature (it was 0, 3, or 25% on 5% Pd/UDD at 30, 50, or 100°C, respectively). On the less active 5% Pd/AC catalyst, 0, 3, or 14% cyclohexane was formed at the above temperatures, respectively.

Temperature-Programmed Reduction

Figure 2 shows the results of the TPR of NiO/UDD and NiO/AC samples, which were prepared in the same manner as the corresponding catalysts but in the absence of the stage of reduction. For comparison, the TPR spectrum of pure UDD is also given. It is likely that the presence of a double peak in the spectrum of UDD was due to the reduction of carbon with hydrogen with the formation of methane. In the spectrum of NiO/UDD, a peak at 310°C due to the reduction of a NiO species weakly bound to the surface and a broad peak with a maximum at 400–450°C were present. It is likely that the latter peak resulted from a mutual superposition of peaks due to the reduction of a NiO species more strongly bound to the surface and the reduction of UDD with hydrogen. Tsoncheva et al. [13] noted the occurrence of two NiO species on purified UDD; they were reduced at 322 and 365°C, respectively. The interaction of UDD with hydrogen, which leads to methane formation, in Ni-containing catalysts occurred at much lower temperatures (starting at 350°C) than on pure UDD (above 450°C). Above 600°C, the decomposition of methane with the release of hydrogen can also occur in the presence of Ni/UDD [14]; as a result of this, intensity ratios between high-temperature peaks in the TPR spectra of the support and the catalyst changed.

In the spectrum of NiO/AC, the main peak of NiO reduction was broader; it was shifted toward high temperatures by approximately 50°C, as compared with the TPR peak of NiO/UDD. Moreover, a second peak due to Ni reduction occurs in the spectrum of NiO/AC at about 230°C; this suggests the presence of an insignificant amount of NiO particles even more weakly bound to the support or particles with another size as catalyst constituents.

Kachevskii et al. [17] found similar differences between the TPR spectra of PdO/UDD and PdO/AC: the peak due to the reduction of palladium oxide supported on UDD was shifted toward lower temperatures and broadened as compared to the peak of PdO/AC reduction. These differences were explained by the presence of mesopores in UDD, which facilitate the reduction of the supported metal unblocked by the support, and a narrower particle-size distribution of the supported metal in systems on UDD. The conclusions made were supported by the results

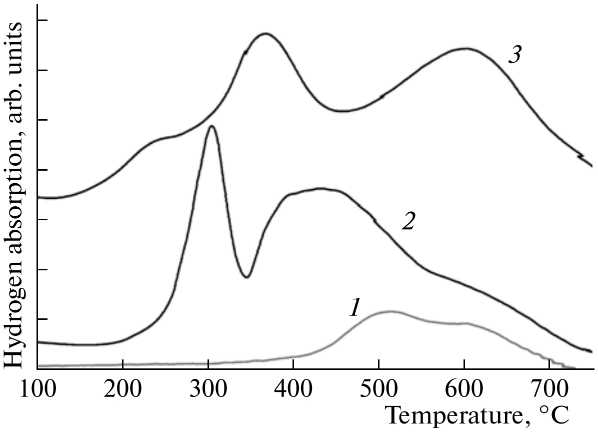

Fig. 2. TPR of (*1*) UDD, (*2*) NiO/UDD, and (*3*) NiO/AC.

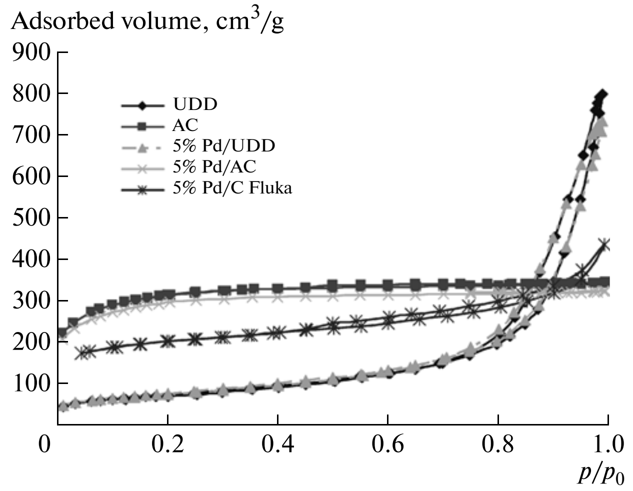

Fig. 3. Isotherms of nitrogen adsorption/desorption on AC, UDD, and 5% Pd/AC, 5% Pd/C (Fluka), and 5% Pd/UDD catalysts.

of studies performed using adsorption techniques and TEM.

Thus, according to TPR data, the major portion of a supported metal (Pd or Ni) supported on UDD more easily underwent reduction. The temperature at which conversion in a gas-phase HDC reaction was higher than 50% was almost the same as the temperature of the onset of nickel or palladium reduction in the supported systems. It is likely that, at lower temperatures, metal oxidation occurred under the action of HCl released in the reaction; this resulted in a decrease in catalyst activity. An increase in the temperature above 50 (in the case of Pd) or 200°C (in the case of Ni) was accompanied by the reduction of an oxidized metal; as a consequence of this, the conversion of CB increased.

With the use of TEM and XRD analysis [17, 19], it was found that the particle size of Pd in catalysts increased as its concentration was increased (Table 1). The particle size distribution in catalysts on UDD was narrow (a range of no greater than 3 nm), whereas particles of sizes from 4 to 40 nm occurred in reference catalysts. It is likely that the narrow particle size distribution was due to the presence of oxygen-containing groups on the surface of UDD and a high degree of crystallinity of the support [5]. The reduction of PdO/UDD occurred at temperatures above 70°C [17], whereas palladium supported on graphite or carbon fibers was reduced even at room temperature [5] and hydride decomposition was observed above 70°C. This was likely due to a higher concentration of Pd (8 wt %) and a greater particle size of Pd in the samples supported on carbon. The micrographs published by Amorim et al. [5] suggest that the size of Pd particles varied from 2 to 20 (Pd/AC) or from 5 to 80 nm (Pd on graphite nanofibers).

Pore Structure of Catalytic Systems

Figure 3 shows the isotherms of nitrogen adsorption/desorption on AC and UDD samples and 5% Pd/AC, 5% Pd/C (Fluka), and 5% Pd/UDD catalysts. The isotherms obtained on individual supports (AC and UDD) almost coincided with the isotherms of supported systems (5% Pd/AC and 5% Pd/UDD). This means that the texture characteristics of the supports remained unchanged in the course of catalyst preparation. The isotherms of AC and 5% Pd/AC correspond to type I according to the IUPAC classification; that is, they describe a microporous material. The isotherms of the samples of UDD, a catalyst on its basis, and 5% Pd/C (Fluka) belong to type IV; that is, they correspond to multilayer adsorption/desorption with capillary condensation, which caused the formation of hysteresis loops as a sign of the presence of mesopores. Tsoncheva et al. [13] observed isotherms of the same type in a study of oxidized nanodiamond; this fact was explained by similar treatments of the systems (with potassium bichromate or chromic anhydride in sulfuric acid). Extremely low nitrogen absorption at low relative pressures, as compared with samples on ACs, suggests a low concentration of micropores (<1%). The most intense nitrogen absorption came into play at the relative pressure $p/p_0 = 0.8$. This circumstance and the occurrence of a hysteresis in adsorption/desorption isotherms over the range of $p/p_0 = 0.8–1$ suggest a narrow distribution of medium-size pores (mesopores). The total pore volumes in the samples of UDD and 5% Pd/UDD were 0.84 and 0.81 cm^3/g, respectively, whereas pores of size about 120 Å were predominant. As compared with other carbon supports, the specific surface areas of UDD and 5% Pd/UDD were low (260–270 m^2/g). As found previously [17], the size of UDD particles varied from 5 to 20 nm, and the average pore size in UDD was ~12 nm. Evidently, these pores were formed upon the agglomeration of UDD particles; that is, they were pores between particles.

The pore size distribution suggests that AC and the 5% Pd/AC catalyst were characterized by the presence of micropores with a size of <20 Å, which were filled with nitrogen even at relative pressures of 0.02–0.1, and the full absence of mesopores. Because of the developed micropore structure, AC had high S_{BET} (1090 m^2/g). The total pore volume in AC was 0.53 cm^3/g, of which more than a half accounted for micropores with an average size of about 15 Å.

The isotherms of N_2 adsorption/desorption on 5% Pd/C (Fluka) are characterized by a monotonic increase in the amount of adsorbed nitrogen; this suggests the presence of pores with various sizes from 10 to 150 Å. The isotherm of adsorption on this catalyst over the relative pressure range of 0.05–0.8 lies lower than the corresponding isotherm on the sample of 5% Pd/AC. Consequently, the total pore volume filled at these pressures in the sample of 5% Pd/C (Fluka) was

Table 2. Assignment of bands in the IR spectra of adsorbed CO

Catalyst	Wavenumber, cm^{-1}				
	Pd^{2+}–CO	Pd^{+}–CO	Pd^{0}–CO	$(Pd^{0})_2$–CO	Pd^{0}–CO_2
0.5% Pd/UDD	2173	2120	2077	1960	–
1% Pd/UDD	2172	2134	2082	1950	–
2% Pd/UDD	2170	2115	2087	1970	2335
5% Pd/UDD	–	–	2085	–	2338

smaller than that in the catalyst on AC. The total pore volumes in the samples of 5% Pd/C (Fluka) and 5% Pd/AC were approximately the same (0.52 cm^3/g); however, the fraction of micropores in the former case was somewhat smaller than that in AC (32%), and the S_{BET} of this catalyst was 700 m^2/g, which is smaller than S_{BET} in the sample of 5% Pd/AC.

Based on the experimental data, we can conclude that pore size rather than specific surface area has a crucial effect on the efficiency of HDC catalysts. An increase in the pore size facilitated an increase in the activity of the catalyst. Difference in the activities of catalysts with different pore sizes can be due to steric hindrances for an organic substrate in contact with the active surface. A possible reason for steric hindrances is the localization of a portion of palladium in pores whose size is smaller than the effective molecular size of the substrate [20].

Diffuse Reflectance IR Spectroscopic Study of Catalysts

The acidic (electron-acceptor) properties of the surface of Pd-containing catalysts were studied using diffuse reflectance IR spectroscopy with carbon monoxide as a probe molecule. The sample surface was rapidly coated in air with a dense layer of adsorbed hydroxide groups and water, which prevent the adsorption of CO and give signals in a wide range corresponding to the adsorption of carbon monoxide on metal particles. Therefore, before treatment with CO, the samples were calcined in air and then in a vacuum at an elevated temperature, which was chosen with consideration for published data on the possible desorption of hydroxyl groups from the surface. Thermogravimetric data suggest the absence of noticeable effects of the oxidation of a carbon support of catalysts in air at temperatures to 450°C. Moreover, weight losses in the samples were not observed after this treatment. Higashi et al. [21] used long-term calcination at 450°C in air to oxidize nickel nitrate in the course of Ni/UDD catalyst preparation using an impregnation method. The catalysts obtained after reduction contained small (10–15 nm) nickel particles. Thus, both our results and published data demonstrate that neither the oxidation of a carbon phase nor the noticeable agglomeration of metal particles occurred upon thermal treatment in air.

In principle, thermal treatment in a vacuum can result in the reduction and agglomeration of metal particles on the surface. However, published data [13, 14] suggest the high stability of palladium particles supported on UDD to aggregation even upon hydrogen reduction at 600°C. The TPR study of the catalytic systems based on UDD prepared in this work (Fig. 2 shows data on Ni catalysts; data on Pd catalysts were reported elsewhere [17]) showed that the reduction of carbon in the presence of Ni began at temperatures higher than 450°C or above 400°C in Pd-containing catalysts. However, it occurred to a very insignificant extent; this was likely due to the fact that amorphous carbon, a small amount of which was present on the surface of nanodiamond, underwent reduction. These results are consistent with TPR data for Ni/UDD reported by Higashi et al. [21]: the methanization of the support occurred at temperatures higher than 600°C; according to DTA data, it was accompanied by a considerable weight loss. In this case, the temperature of methane formation was higher because Higashi et al. [21] used preoxidized nanodiamond as a support, which was almost free of amorphous carbon. Thus, the pretreatment did not exert a considerable effect on metal particle size and did not cause considerable changes in the support. In addition, the results of IR spectroscopic studies given below suggest that oxidized palladium species and small particles were retained in the catalysts thermally treated in a vacuum. Of course, their concentration could be higher in the samples before treatment; because of this, we analyzed the ratios between the amounts of observed active metal species on a qualitative rather than quantitative level.

The IR spectra of adsorbed CO (Fig. 4) include the superpositions of several absorption bands. We related the occurrence of several absorption bands to the presence of Lewis acid sites of various types on the surface; these sites are formed by palladium cations in different oxidation states and several CO species adsorbed at palladium cations. In the spectra of CO adsorbed on the surface of Pd/UDD catalysts containing 0.5, 1, and 2% metal, absorption bands occurred at 2170 and 2115–2134 cm^{-1} (Fig. 4, Table 2), which were attributed to the vibrations of linearly adsorbed CO in the Pd^{2+}–CO and Pd^{1+}–CO systems, respectively [22, 23]. The most intense absorption band at 2077–2087 cm^{-1} and an absorption band at 1950–1970 cm^{-1}

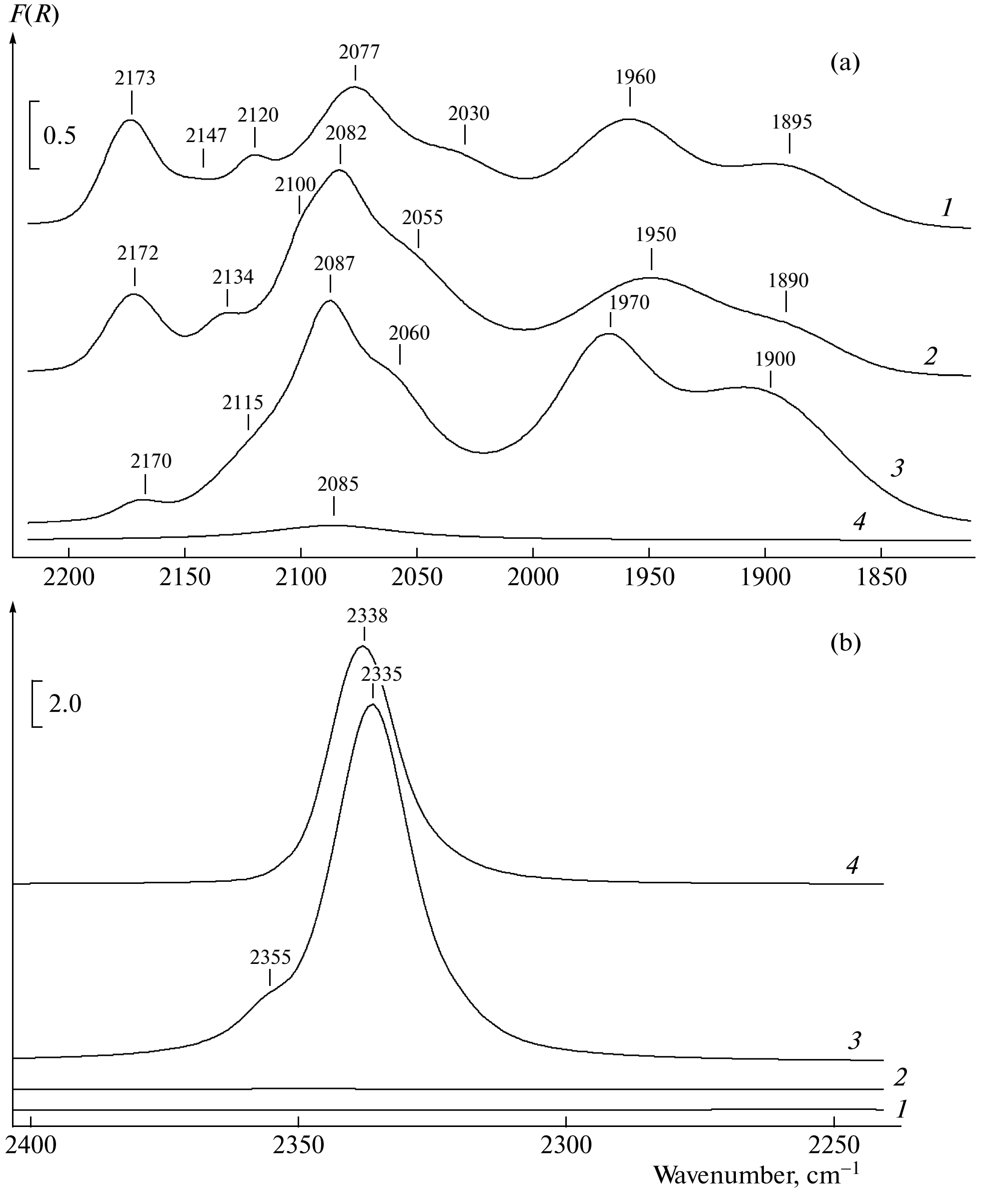

Fig. 4. IR spectra of CO adsorbed at room temperature on (*1*) 0.5% Pd/UDD, (*2*) 1% Pd/UDD, (*3*) 2% Pd/UDD, and (*4*) 5% Pd/UDD over frequency ranges of (a) 1800–2200 and (b) 2200–2400 cm^{-1}. The pressure of CO was 20 Torr.

correspond to the vibrations of CO adsorbed on palladium metal in a linear form (Pd^0–CO) and in a bridging form at two or more palladium atoms ((Pd^0)$_2$–CO). According to Vannice et al. [24], a band at 1950–1970 cm^{-1} is characteristic of the adsorption of CO on Pd metal crystals. The presence of an absorption band at 1890–1900 cm^{-1}, which can also be ascribed to the bridging surface structures of adsorbed carbon monoxide on the surface of Pd crystals [25], argues for an assumption that Pd crystals are formed in the systems.

The IR spectra of the samples of 2% Pd/UDD and 5% Pd/UDD exhibited a band due to weakly disturbed CO$_2$ at 2335 cm^{-1} [23].

Lines corresponding to CO adsorption were almost absent from the IR spectrum of CO adsorbed on the surface of 5% Pd/UDD; the main line corresponded to the adsorption of CO$_2$. This peak was also present in the spectrum of CO on 2% Pd/UDD.

Published data indicate that palladium on UDD can catalyze the oxidation of CO to CO$_2$ [10]. An issue of the source of oxygen required for oxidation is of interest. Because the samples were subjected to long thermal vacuum treatment under weakly reducing conditions, adsorbed water and hydroxyl groups were absent from the surface. However, according to various data, UDD contains from 2 to 10 wt % oxygen. Bogatyreva et al. [10] studied the temperature-pro-

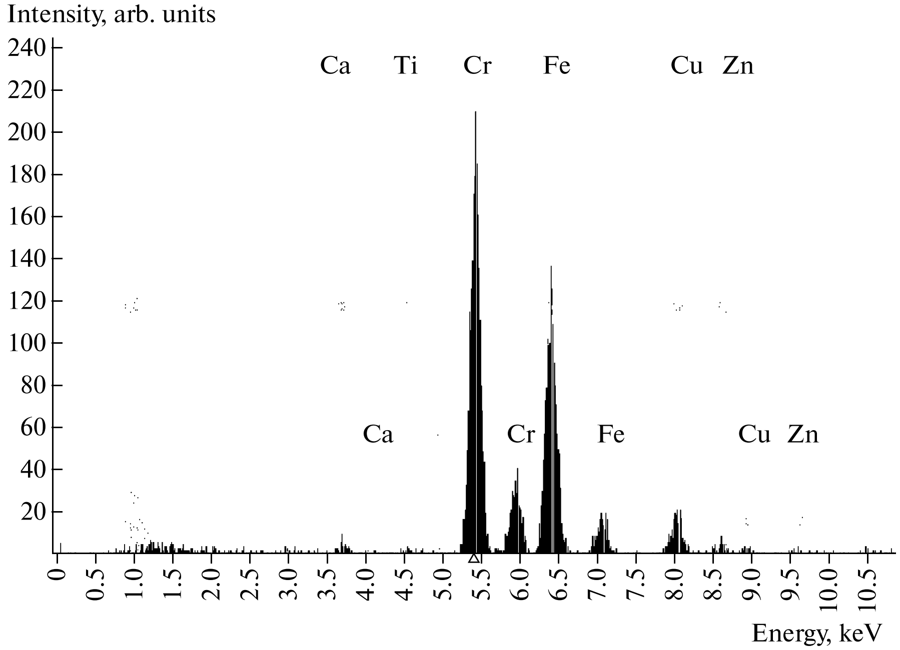

Fig. 5. Energy-dispersive spectrum of UDD

grammed desorption of atomic oxygen from the surface of UDD and found that physically sorbed oxygen (which was released at 150–200°C) and chemisorbed oxygen (which began to liberate at temperatures higher than 450°C; it is likely that it was a constituent of functional groups) were present on this surface. At the same time, if CO is oxidized by oxygen from the support, the peak of CO_2 should be present in the spectra of all of the catalysts because even a small amount of palladium can catalyze the oxidation of CO [10]. However, the peak of CO_2 was not observed in the spectra of catalysts with palladium concentrations of 0.5 and 1%.

CO can also be oxidized by oxygen present in the catalyst. According to IR spectroscopic data (Fig. 4), the concentration of a palladium metal phase increased as its concentration in the catalyst was increased. The formation of PdO can occur upon the oxidation of a palladium phase in air or in the course of the thermal treatment of a catalyst before measuring the spectrum. This PdO can serve as a source of oxygen for the subsequent oxidation of CO to CO_2. However, the estimation of palladium dispersity based on TEM data showed that Pd particles of a size that allowed their oxidation with oxide formation were present as the constituents of low-percentage catalysts. Nevertheless, the presence of CO_2 was not detected in the spectra of these catalysts.

According to calculations, the direct dissociation of carbon monoxide in accordance with the equation $CO = C + O$ is energetically unfavorable; however, if it is coupled to the reaction $O + CO = CO_2$, the overall reaction is the Boudouard reaction ($2CO = C + CO_2$). The Boudouard reaction is highly exothermic, and it can occur in the absence of kinetic hindrances. The signs of dissociation were not detected on the highly ordered surface of palladium using XPS. However, the less ordered the surface, the higher the probability of an inclined orientation of adsorbed CO molecules and the possibility of their dissociation [26]. Moreover, dissociation is facilitated in the presence of impurities, for example, alkali metal impurities. Thus, the dissociation of CO on Pd supported on mica was detected in the presence of potassium [27]. It is well known that UDD is characterized by the presence of impurity metals. According to Gubarevich and Poleva [28], an incombustible residue (0.5–8.0%) of the oxides, carbides, and salts of various elements, such as Fe, Ti, Cr, K, Ca, Si, and Zn, was a constituent of UDD. The presence of Cr, Fe, Co, and Cu impurities and trace amounts of Zn was detected in this work in a study of the sample of UDD by energy-dispersive analysis (see Fig. 5).

It is believed that the particle size and the number of defects increase with Pd content; this results in the disproportionation of CO with the formation of CO_2.

The experimental data suggest the presence of small particles of Pd^0 and Pd^{n+} and larger particles, which behave as a palladium metal phase during CO adsorption, in catalysts. As the concentration of palladium was increased, the fraction of Pd^{n+} decreased and the fraction of a metal phase increased.

According to the opinion of Gomes-Sainero et al. [29], the presence of palladium in two forms, Pd^0 and Pd^{n+}, in the catalyst is required to efficiently perform an HDC reaction. Chlorine-containing substrate RCl is activated on partially oxidized palladium with the formation of a covalent bond [Pd^{n+}–Cl] as a result of the transfer of a 3*p* electron from Cl^- to the $5s^0$ orbital of Pd^{n+}. The resulting electrophilic ion R^+ coordinated to Pd^0 by a donor–acceptor bond with partial electron density transfer from the 4*d* level of Pd to a free orbital of R^+. The role of Pd^0 was reduced to the activation of chemisorbed hydrogen, which reacted with R^+ and [Pd^{n+}–Cl]; HCl and a nonchlorinated product were desorbed from the surface. The catalyst activity in the course of HDC strongly depended on the Pd^0/Pd^{n+} ratio; for example, in the partial HDC of CCl_4 to $CHCl_3$, a maximum activity was observed at a ratio of 1 : 1 [29]. An analogous dependence can also be observed upon the replacement of a chlorine atom by hydrogen, as in the HDC of CB. The ratio changed upon the transition of Pd^{n+} to a metal phase; this could result in a decrease in activity, as it was observed in the HDC of CB in the presence of Pd/UDD with a metal content of 0.5–2%.

In the Pd/UDD catalysts containing from 0.5 to 5% metal, palladium occurs in various forms: as Pd^0 and partially oxidized Pd^{n+}. Using the IR spectroscopy of adsorbed CO, we found that the ratio between these forms depends on catalyst composition. In the sample of 0.5% Pd/UDD, both of the species occurred in approximately equal amounts; as the concentration of Pd was increased, the fraction of oxidized palladium decreased and the fraction of palladium metal increased.

The mechanisms of HDC reactions have been discussed in the literature. It is believed that both substrate and hydrogen can be adsorbed and activated on Pd. At the same time, it was noted that chloroaromatic compounds can be activated on a carbon support. The activation of hydrogen occurs at active metal sites; then, active hydrogen arrives at an activated substrate, where the reaction occurs, by a spillover mechanism. Hydrogen spillover is facilitated if the support possesses certain properties, for example, greater accessibility of delocalized π electrons, which is characteristic of structured supports [30]. The occurrence of oxygen-containing surface groups, for example, acidic groups, is responsible for the occurrence of electron-rich regions, where the formation of donor–acceptor complexes with a substrate is more probable; these complexes make possible the adsorption of the aromatic molecule of chlorinated benzene on the surface of the support [5]. The presence of functional groups (primarily carboxyl groups) on the surface of UDD was supported by published data [31]. Consequently, it is likely that, in the presence of catalysts supported on carbon, the HDC reaction occurs under conditions of separate substrate and hydrogen adsorption, and the surface properties of UDD facilitate the occurrence of the reaction because of an increased adsorption capacity of the substrate and facilitated hydrogen spillover. Amorim et al. [5] also hypothesized that better faceted particles are more active in HDC reactions. As followed from published data [19], Pd occurred on UDD as well-faceted particles; this suggests strong metal–support interaction [32]. All of these special features are not characteristic of catalysts on AC; this fact can explain their low efficiency in HDC processes.

Thus, in this work, we found that nickel and palladium catalysts supported on UDD can perform the HDC of CB in a vapor phase at lower temperatures than with analogous systems on AC. Under multiphase process conditions, Pd/UDD is an efficient catalyst for the conversion of polychlorinated organic molecules, for example, 1,3,5-TCB, HCB, and the dioxin analog TCDBF.

Using the IR spectroscopy of adsorbed CO, we found the occurrence of two Pd species on UDD; the ratio between these species depends on the metal content of the catalyst and correlates with the catalytic activity of the system in the HDC reaction of CB.

The reasons for the enhanced activity of catalysts supported on UDD at comparatively low temperatures can be the absence (due to the mesopore structure of UDD) of steric hindrances for reagent adsorption and a change in the metal–support interaction strength that provides an optimum ratio between palladium species in different oxidation states, which is reflected in TPR spectra.

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