# Tetrachloromethane Hydrodechlorination over Palladium-Containing Nanodiamonds

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**Abstract**—Using nanodiamonds of the UDD-STP brand 1 wt % palladium-containing nanodiamonds are obtained and tested as catalysts of tetrachloromethane hydrodechlorination under mild conditions (solvents, ethanol and methanol; T = 298-318 K;  $P_{H_2} = 0.1$  MPa). The catalytic properties of the obtained material and a palladium-containing analog based on activated carbon are compared. It is shown that the hydrodechlorination reaction occurs in a stepwise manner via two pathways: to form products with a smaller content of chlorine, for example, chloroform, and to yield oxygen-containing products, for example, diethyl carbonate. The qualitative and quantitative compositions of reaction products are determined by gas chromatography/mass spectrometry.

Keywords: hydrodechlorinatione, palladium-containing nanodiamonds, tetrachloromethane, chloroform, diethyl carbonate

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Catalytic systems based on carbon nanomaterials (nanotubes, nanofibers, nanodiamonds, graphenelike nanomaterials) containing transition metals are of potential interest for the chemical and pharmaceutical industries because of their high catalytic activity in the hydrogenation reactions of unsaturated organic compounds and compounds containing various functional groups [1]. The study of these systems may help in solving one of the key environmental issues related to the utilization of chloro-organic compounds employed in various areas of human activity.

One of the methods of utilizing chloro-organic compounds is an environmentally friendly catalytic hydrodechlorination. However, high cost and low stability of the existing catalysts limit the development of this method. A solution to this problem may be the use of catalysts based on nanodiamonds exhibiting unique properties and nanosized palladium particles, which are efficiently used in the hydrogenation of organic compounds [2, 3].

The catalytic hydrodechlorination of tetrachloromethane ( $CCl_4$ ), a representative of the family of chloro-organic compounds, in the presence of palladium-containing activated carbon and Sibunite, alumina, and titania is carried out both the gas phase and in the presence of solvents at high hydrogen pressures (up to 10 atm) and high temperatures (up to  $350^{\circ}$ C). The conversion of  $CCl_4$  is 30–90%, and a mixture of products is always formed, which indicates that this is a multistage process. In the case of palladium-containing carbon supports (activated carbon, Sibunite) the quantitative CCl<sub>4</sub> conversion under gas-phase conditions occurs to form methane and hydrocarbons  $C_2-C_5$ . When the liquid-phase tetrachloromethane hydrodechlorination is run over Pd/C chloroform is the main reaction product and the side products are hexachloroethane, tetrachloroethylene, dichloromethane, monochloromethane, and methane [4-11]. The main products of CCl<sub>4</sub> hydrodechlorination carried out in sodium hydroxide aqueous solutions over Pd/Sibunite ( $T = 80-120^{\circ}$ C,  $P_{H_2} = 0.3-1.5$  MPa) are sodium formate, hexachloroethane, and perchloroethylene [8]. According to chromatographic analysis, acetaldehyde, 1,1-dioxyethane, ethyl vinyl ether, and diethyl carbonate are present in reaction products. along with chloro-organic compounds, when CCl<sub>4</sub> hydrodechlorination is run in ethanol over Pd/C (T =353–413 K,  $P_{\rm H_2}$  = 3 MPa) [11].

As was shown in [2, 3], the process of liquid-phase hydrodechlorination of monohalobenzenes may proceed under mild conditions (solvents, ethanol and 2-propanol; T=318 K;  $P_{\rm H_2}=0.1$  MPa) in the presence of various catalysts based on platinum-containing and palladium-containing carbon nanomaterials [2, 3].

This work is aimed at studying the catalytic characteristics of palladium-containing nanodiamonds (1 wt % Pd/nanodiamonds) in the reaction of CCl<sub>4</sub> hydrodechlorination carried out under mild conditions (solvents: ethanol, absolute ethanol, and methanol; T = 298-318 K;  $P_{H_2} = 0.1$  MPa) and comparing the kinetic parameters of the catalyst 1 wt % Pd/nanodiamonds (reaction rate, reaction rate constant, turnover frequency) and a M200 activated carbonbased catalyst prepared in a similar manner (1 wt % Pd/C).

# **EXPERIMENTAL**

The technique of preparing 1 wt % Pd/nanodiamonds and 1 wt % Pd/C catalysts, their characterization, and some catalytic parameters were described in [2].

The hydrodechlorination reaction (Scheme 1) was carried out as follows. Thirty milligrams of the catalyst and 10 mg of NaBH<sub>4</sub> were loaded in a glass reactor equipped with a temperature-controlled jacket and a magnetic stirrer (the rate of stirring was chosen so that the process occurred in the kinetic region) under the solvent layer (10 mL), and the content of the reactor was stirred for 10 min. Afterwards, 1 mmol of substrate was added in a hydrogen stream and hydrogenation was carried out at T = 298-318 K and  $P_{H_2} = 0.1$  MPa.

The observed rate of reaction was measured by the volumetric method according to hydrogen absorption. The true catalytic activity of heterogeneous catalysts is commonly determined from the number of active sites of the catalyst; their evaluation is hardly probable. The catalytic activities of the test objects under identical reaction conditions may be compared in terms of the turnover frequency (TOF, min<sup>-1</sup>), which shows the number of substrate molecules converted per mole of metal per minute.

Under the used conditions, the hydrodechlorination reaction has the zero order with respect to the substrate and the first order with respect to the catalyst and hydrogen [2, 3]. The occurrence of processes in the kinetic region was confirmed using the Thiele criterion ( $\Phi$ ):

$$\Phi = R \sqrt{\frac{W}{C \times 10^{-5}}},$$

where R is the average diameter of catalyst particles, cm; W is the rate of reaction, mol/(L s), in the linear portion of the kinetic curve (usually until a 10% conversion from the theoretically calculated value for each

PETROLEUM CHEMISTRY Vol. 60 No. 10 2020

substrate is reached); *C* is the substrate concentration, mol/L; and *D* is the diffusion coefficient,  $10^{-5}$  cm<sup>2</sup>/s. In our experiments, the Thiele criterion was much smaller than unity  $(0.7-2.0 \times 10^{-5})$ . This fact provides unambiguous evidence that the reaction occurs in the kinetic region.

The products of the liquid-phase hydrodehalogenation reaction were analyzed by liquid-phase chromatography using the internal standard method. The reaction mixture was placed in chromatography vials and analyzed on an Agilent 7890B gas chromatograph equipped with a flame-ionization detector (250°C) and an Agilent DB-624 column (sorbent composition: 6% cvanopropylphenyl and 94% methylpolysiloxane (G43 USP) using helium as a carrier gas. Analysis conditions: sample volume, 1 µL; sample inlet temperature, 50°C; split, 1 : 10; and gas flow, 4 mL/min. The programmable thermostat regime was as follows: heating to 50°C, holding for 5 min, heating to 150°C at a rate of 20°C/min, holding for 7 min, cooling to 50°C at a rate of 50°C/min, and holding for 5 min. The flow rate of air, hydrogen, and helium (heaving) was 300, 30, and 35 mL/min, respectively. Resolution between the detected components was above 1.5. The relative standard deviation with respect to the peak area and intensity was less than 3%. The degree of purity of calibration solutions was taken into account in calculations.

The qualitative analysis of reaction mixtures was carried out by gas chromatography/mass spectrometry with electron ionization on a Kristall 5000.2 gas chromatograph equipped with a flame ionization detector. Analysis conditions: ionization energy, 70 eV; the mass analyzer scan range, 10-550 a.e.m.; the detector temperature, 220°C; and the evaporator temperature, 200°C. The temperature-programmed regime of a thermostat with a TR-FFAP (50 m  $\times$  0.32 mm  $\times$ 0.5 µm) column was as follows: heating from 75 to 110°C at a rate of 15°C/min, cooling to 80°C at a rate of 10°C/min, and heating to 210°C at a rate of 15°C/min. Special-purity grade nitrogen was used as a carrier gas. The injected sample volume was 1.0 µL. The sample was injected in the 30 : 1 split mode. Measurements were performed under conditions of the stead-state gas flow velocity. The instrument was calibrated against the retention times of the components using the model mixture manufactured by the All-Russia Research Institute of Food Biotechnology.

## **RESULTS AND DISCUSSION**

The liquid-phase hydrodechlorination of tetrachloromethane was carried out under mild conditions  $(T = 298-318 \text{ K}, P_{\text{H}_2} = 0.1 \text{ MPa})$  in ethanol in the presence of catalysts 1 wt % Pd/nanodiamonds and 1 wt % Pd/C, which were prepared according to the same technique. The activity of the catalysts based on nanodiamonds was 1.4 times higher compared with

Catalyst	Temperature, K	Turnover frequency, min <sup>-1</sup>	Reaction rate $\times 10^5$ , mol/(L s)	Rate constant, L/(mol s)	Activation energy, kJ/mol	Activation entropy, J/(mol K)
1 wt % Pd/nanodiamonds	298	1.7	0.8	7.9	$27.3\pm0.6$	$-143.8\pm1.9$
	308	2.4	1.7	11.2		
	318	3.5	8.2	15.8		
1 wt % Pd/C	298	1.8	0.8	8.3	$11.2 \pm 1.3$	$-197.4 \pm 4.2$
	308	2.2	1.0	9.9		
	318	2.5	1.2	11.1		

**Table 1.** Activity of catalysts 1 wt % Pd/nanodiamonds and 1 wt % Pd/C in tetrachloromethane hydrodechlorination and the kinetic and activation parameters of the reaction

**Table 2.** The degree of conversion and yield of tetrachloromethane hydrodechlorination reaction products in the presence of catalysts 1 wt % Pd/nanodiamonds and 1 wt % Pd/C

Catalyst	Reaction time, min	CHCl <sub>3</sub> *, %	CH <sub>2</sub> Cl <sub>2</sub> *, %	1,1-Dimethoxyethane**, %	Methyl acetate**, %	1-Methoxy- 1-ethoxymethane**, %	Diethyl carbonate *, %	Degree of CCl <sub>4</sub> conversion*, %
1 wt % Pd/nanodiamonds	10	0.6	_	2.9	3.0	38.0	10.8	29.6
	60	1.2	—	6.5	13.0	44.0	30.0	45.2
	300	6.8	1.0	_	3.3	40.0	21.0	81.2
1 wt % Pd/C	10	1.8	—	_	0.2	17.9	4.3	27.6
	60	2.4	—	—	3.7	43.7	17.6	38.2
	300	8.2	1.2	—	3.0	41.1	22.3	72.2

\* A mixture of 1 mmol of CCl<sub>4</sub> in 10 mL of ethanol was taken as the 0% conversion.

\*\* The quantitative analysis was carried out by the simple normalization method.

the palladium-containing activated carbon (Table 1). As expected, the rate of reaction increased with increasing temperature; however, in the case of 1 wt % Pd/nanodiamonds the growth was more substantial in comparison with 1 wt % Pd/C. The activation energy of the  $CCl_4$  hydrodechlorination reaction catalyzed by 1 wt % Pd/nanodiamonds was almost 2.5 times higher than that in the case of 1 wt % Pd/C. In turn, the activation parameters of chlorobenzene hydrodechlorina-

tion ( $E^{\neq} = 23 \pm 4 \text{ kJ/mol}$ ,  $\Delta S_{298}^{\neq} = 143 \pm 15 \text{ J/(mol K)}$ ) carried out in the presence of 1 wt % Pd/C [12] were close to the parameters of CCl<sub>4</sub> hydrodechlorination catalyzed by 1 wt % Pd/nanodiamonds.

In both cases, the hydrodechlorination reaction occurs with a fairly high degree of  $CCl_4$  conversion (Table 2). Over the first 10 min, the degree of conversion of  $CCl_4$  is about 30% for both catalysts (Table 2). After reaction for 1 and 5 h, the qualitative composition of the reaction mixture remains unchanged; however, for the catalyst 1 wt % Pd/nanodiamonds the degree of conversion of  $CCl_4$  becomes almost 10 times higher than that for the catalyst 1 wt % Pd/C.

Note that in the case of both catalysts marked amounts of 1-methoxy-1-ethoxymethane and diethyl carbonate are formed.

It may be assumed that after abstraction of the first chlorine atom and formation of CCl<sub>3</sub> the hydrodechlorination reaction occurs via the two main pathways. The first pathway (Scheme 1) is associated with the abstraction of chlorine atoms from tetrachloromethane to form dechlorination products (trichloromethane, dichloromethane) and the dimerization of the initially formed radical CCl<sub>3</sub> (pentachloroethane). In turn, the formation of dichloromethane and its interaction with water in the presence of the catalyst yields carbonic acid dichloride, which starts reactions affording oxygen-containing products (1,1-dimethoxyethane, 1-methoxy-1-ethoxyethane, methyl formate, methyl acetate, acetone, and oxalic acid): their presence is attested by gas chromatography/mass spectrometry. It is noteworthy that the qualitative and quantitative compositions of CCl<sub>4</sub> hydrodechlorination oxygen-containing products depend on the nature of the solvent used.

$$CCl_{4} \xrightarrow{H_{2},cat} CHCl_{3} \xrightarrow{H_{2},cat} CH_{2}Cl_{2} \xrightarrow{H_{2},cat} CH_{3}Cl \xrightarrow{H_{2},cat} CH_{4}$$
  
Scheme 1.

Tetrachloromethane dehalogenation was run in ethanol, absolute ethanol, and methanol. It may be assumed that during the reaction not only substrate but also solvent molecules are adsorbed on catalytic active sites. For example, when experiments were carried out in ethanol containing 4% water 1,1-dimethoxyethane, 1-methoxy-1-ethoxyethane, methyl formate, methyl acetate, acetone, and oxalic acid were observed in reaction products. This finding may be apparently explained by the interaction of a trichloromethane radical with water to form carbonic acid dichloride (Scheme 2, Eqs. (2), (3)), from which methanol, methyl formate, acetone, and methyl acetate may be formed through formic acid and methanal (Scheme 2, Eq. (4)). The reduction of trichloromethane radicals may give rise to pentachloroethane fixed in the presence of Pd/C (Scheme 2, Eq. (5)). The interaction of carbonic acid dichloride or its radical with water affords oxalic acid (Scheme 2, Eqs. (6) or (7), respectively). On the surface of palladium ethanol undergoes dehydration to form acetaldehyde, which subsequently interacts with methanol and ethanol molecules to give rise to 1,1-dimethoxyethane and 1-methoxy-1-ethoxyethane, respectively (Scheme 2, Eqs. (8), (9)).



1,1-Diethoxyethane and diethyl carbonate are the only oxygen-containing products formed in absolute alcohol containing no water. Their formation may be explained as follows. Acetaldehyde, which is formed from ethanol, is involved in the reaction with ethanol to form 1,1-dioxyethane (Scheme 2, Eq. (10)). The formation of acetaldehyde from ethanol is also confirmed by the occurrence of the nitrobenzene hydro-

PETROLEUM CHEMISTRY Vol. 60 No. 10 2020

#### KALMYKOV et al.

Fable 3.	Effect of solvents or	n tetrachloromethane	hydrodechlorination	n in the presence	e of 1 wt % Pd	/nanodiamonds
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Solvent	Turnover frequency, min <sup>-1</sup>	Reaction rate $\times 10^5$ , mol/(L s)	Rate constant, L/(mol s)		
Methanol	2.2	1.0	11.3		
Absolute ethanol	3.6	1.7	19.0		

Table 4.	Products of the	tetrachloromethane	hydrodechlo	rination reaction
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Catalysts	Solvent	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	1,1-Dimethoxyethane	Methyl acetae	1-Methoxy- 1-ethoxyethane	1,1-Diethoxyethane	Diethyl carbonate	Pentachloroethane	Oxalic acid	Acetaldehyde	Acetone
1 wt % Pd/C	Ethanol	+	+	+	+	+	+	+	+	_	+	+
1 wt % Pd/nanodiamonds		+	+	+	+	+	+	+	_	+	+	_
1 wt % Pd/C	Absolute ethanol	+	_	—	_	_	+	+	_	_	+	_
1 wt % Pd/nanodiamonds		+	_	_	—	_	+	+	—	_	+	_
1 wt % Pd/nanodiamonds	Methanol	+	_	_	—	—	—	—	_	—	—	_

genation reaction under analogous conditions; therefore, *N*-ethylaniline is detected along with the main product, aniline.

Carbonic acid dichloride interacts with ethanol to afford diethyl carbonate (Scheme 2, Eq. (11)).

In methanol the hydrodechlorination reaction occurs much more slowly (Table 3), the tetrachloromethane conversion is low, and no oxygen-containing products of  $CCl_4$  dehalogenation are observed (Table 4).

When hydrodechlorination is run in the presence of both Pd/C and Pd/nanodiamonds in ethanol containing 4% water, the composition of the products mostly coincides (Table 4). The exception is pentachloroethane and acetone, which are formed only over the Pd/C-based system, and oxalic acid, which is observed only when hydrodechlorination is run over the catalyst Pd/nanodiamonds. In absolute ethanol the compositions of the product mixture are substantially the same for both catalysts.

Thus, the catalyst 1 wt % Pd/nanodiamonds are more active than Pd/C. The CCl<sub>4</sub> conversion over Pd/nanodiamonds is higher than that over palladiumcontaining activated carbon during the same reaction time. In the presence of the both studied catalysts in common ethanol the CCl<sub>4</sub> hydrodechlorination reaction proceeds via two pathways and yields mixed chloro- and oxygen-containing products. In absolute ethanol the amount of oxygen-containing products is much smaller. In methanol the hydrodechlorination reaction occurs much more slowly and does not afford oxygen-containing products.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interest to be disclosed in this paper.

#### ADDITIONAL INFORMATION

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PETROLEUM CHEMISTRY Vol. 60 No. 10 2020

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