Liquid-Phase Hydrogenation of Halobenzenes in the Presence of Palladium-Containing Nanodiamonds

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Abstract—The catalytic activity of palladium-containing nanodiamonds (Pd/ND) is studied in the model reaction of liquid-phase hydrodehalogenation of monohalobenzenes (chlorobenzene, bromobenzene, and io-dobenzene) and ortho-, meta-, and para-isomers of dichlorobenzene under mild conditions ($T = 45^{\circ}$ C, $P_{H_2} = 1$ atm). The obtained results are compared with the catalytic behavior of the palladium-containing activated carbon (Pd/C) under identical conditions. It is found that catalyst Pd/ND is more active than Pd/C and is more stable against the poisonous effect of hydrogen halide forming during the reaction. Study of the effect of HCl and NaOH additives on the catalyst activity shows that, in the presence of HCl, poisoning of the catalyst occurs: the rate of reaction decreases; in the presence of NaOH, the catalyst activity grows; the rate of reaction decreases as a result of hydrogen chloride neutralization by an alkali. For both catalysts the rate of reaction decreases in the sequence Cl > Br > I for monohalobenzenes and in the sequence para- > or-tho- > meta-isomer in the case of dichlorobenzenes. The obtained dependences are explained using the quantum-chemical modeling of substrates of model reactions.

Keywords: hydrodehalogenation, palladium, catalysts, nanodiamonds, activated carbon, halobenzenes **DOI:** 10.1134/S0965544118140049

Halogen-containing organic compounds accumulated in the national economy pose a serious threat to the environment. Among them, for example, are pesticides (hexachlorobenzene, DDT) and polychlorobiphenvls, which were banned long ago, and environmentally more dangerous polychlorinated dibenzo-pdioxins and dibenzofurans, chlorofluorocarbons, and other chloroorganic solvents (perchloroethylene, 1,1,1-trichloroethane, carbon tetrachloride, and vinyl chloride) formed upon their burning [1]. In May 2004, Russia ratified the Stockholm Convention on Persistent Organic Pollutants, according to which more than 25000 t of polychlorobiphenyls should be disposed of in our country by 2025 [2]. Among methods currently applied to dispose of haloorganic compounds (burning, burial (including pumping in deep layers), irradiation, photochemical and oxidative degradation), catalytic hydrodehalogenation in the presence of various catalysts, including palladium-containing ones, is the most versatile and ecologically friendly one [1, 3-14].

Catalytic hydrodehalogenation may be carried out both in the gas and liquid phase either using hydrogen or via hydrogen transfer from a hydrogen donor (phosphorous acid, phosphites, formic acid and its salts, alcohols, metal hydrides, hydrazine hydrate, or alkoxides). The hydrodehalogenation of light aliphatic halocarbons, including halogenated solvents, more rarely halobenzenes, is more often conducted in the gas phase [1].

The hydrodehalogenation reaction is frequently studied using chlorobenzene with a strong C–Cl bond which is contained in many organic wastes as a model substrate [1]. Benzene is the main product of chlorobenzene hydrodehalogenation; however, in some studies, the presence of diphenyl [12, 13] and chlorocyclohexane and cyclohexane [14] in the reaction mixture was confirmed by analytical methods.

This study focuses on the liquid-phase hydrodehalogenation of monohalobenzenes (Scheme 1a) and dichlorobenzenes (Scheme 1b) conducted in the presence of palladium-containing nanodiamonds (Pd/ND) as a catalyst. Owing to their structure nanodiamonds possess high strength, chemical resistance, and thermal stability, and the presence of functional groups facilitates the anchoring of metal clusters with a diameter of 5 nm and a thickness of 0.4-1.2 nm [15– 22]. The obtained results are compared with the data on hydrodehalogenation conducted in the presence of conventional catalyst Pd/C (activated carbon of the M200 brand).



EXPERIMENTAL

Preparation of Catalyst Samples

Nanodiamonds containing Pd were synthesized as described in [23]. Detonation nanodiamonds with a specific surface area of $307-314 \text{ m}^2/\text{g}$ (the average size of diamond crystalline nucleus composed of ~4-nm nanodiamond particles united to polycrystals of 100–200 nm) and the total content of noncarbon admixtures not above 0.5 wt % were used. The synthesis was detailed in [15–20]. Previously, this catalyst was explored in the hydrogenation and hydroamination of organic compounds [15–20].

Hydrodehalogenation Procedure

Model hydrodehalogenation reactions were run as follows. Thirty milligrams of the catalyst and 10 mg of NaBH₄ were loaded in a glass reactor equipped with a temperature-controlled jacket and a magnetic stirrer (the rate of stirring was chosen in order to provide occurrence of the process in the kinetic region) under the solvent layer (15 mL), and the content of the reactor was stirred for 10 min. Afterwards, 1 mmol of substrate was added in a hydrogen stream, and hydrodehalogenation was conducted at $T = 45^{\circ}$ C and $P_{H_2} =$ 1 atm.

The observed rate of reaction was measured by the volumetric method according to hydrogen absorption. It is known that the true catalytic activity of heterogeneous catalysts should be reduced to the number of active sites of the catalyst, whose estimation is hardly probable. Under identical reaction conditions, the catalytic activity of the test objects may be compared in terms of the turnover frequency (TOF, min⁻¹), which shows the number of substrate molecules converted per mole of metal per minute [24]. The error in the determination of TOF was no greater than 5%.

Under the studied conditions, the model reactions had the zero order with respect to the substrate and the first order with respect to the catalyst and hydrogen. The occurrence of processes in the kinetic region was confirmed using the Thiele criterion (Φ) [25]:

$$\Phi = R \sqrt{\frac{v}{cD}},$$

where *R* is the average diameter of catalyst particles, cm; v 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 substrate is reached); *c* is the substrate concentration, mol/L; and *D* is the diffusion coefficient, 10^{-5} cm²/s. In the experiments, the Thiele criterion was much smaller than unity ($\Phi = 0.1 - 1.3 \times 10^{-5}$). This fact provides unambiguous evidence that the reaction occurs in the kinetic region.

Investigation Procedures

The content of the catalytically active metal in the Pd/ND sample was determined by micro-X-ray spectral analysis, and the total specific surface area of the sample was measured by the BET method according to nitrogen adsorption using a Quantachrome Nova 3200 instrument. The relative error in the determination of palladium content in the catalyst was not above $\pm 10\%$. X-ray spectral local microanalysis was conducted on a VEGA TS 5130MM digital scanning electron microscope equipped with detectors of secondary and reflected electrons of YAG crystals and an energydispersive X-ray microanalyzer equipped with an INCA Energy2 Si(Li) semiconductor detector. The results of analysis were computed using the INCA Energy 200 program and then were recomputed using the TP3PT software package developed at the Institute of Experimental Mineralogy, Russian Academy of Sciences. Analysis was carried out at an accelerating voltage of 20 kV. The electron current absorbed by the cobalt reference sample was 516–565 pA; by the test sample, 540–620 pA. The size of the electron probe on the sample surface was 157–200 nm. The amount of titanium and chlorine admixtures was no greater than 0.3 and 0.1 wt %, respectively. The ash content of the initial nanodiamonds was not above 2 wt %.

The products of the hydrodehalogenation reaction were analyzed using a 3700 Series gas chromatograph equipped with a flame-ionization detector

Entry	Substrate	C–Hal bond length, Å	Natural charge on halogen atom	Natural charge on carbon atom linked to halogen	Sum of natural charges on carbon and halogen atoms	Dipole moment, D	TOF, min ⁻¹	
							Pd/ND	Pd/C
1	Chlorobenzene	1.760	-0.026	-0.026	-0.052	2.36	14.6	14.3
2	Bromobenzene	1.918	0.043	-0.086	-0.043	2.39	9.8	6.2
3	Iodobenzene	2.125	0.137	-0.159	-0.022	2.16	1.8	1.9
4	o-Dichlorobenzene	1.747	0.009	-0.061	-0.052	3.47	15.9	1.4
5	<i>m</i> -Dichlorobenzene	1.755	-0.008	-0.009	-0.017	2.22	8.2	1.0
6	p-Dichlorobenzene	1.755	-0.013	-0.030	-0.043	0	18.4	1.9

Table 1. Characteristics of halo-organic compounds and activity of catalysts in their hydrodehalogenation reactions

and a 3 mm × 2000 mm chromatographic glass column packed with Lucopren G-1000 (5%) on Chromaton N-AW-DMCS (carrier gas, nitrogen; evaporation temperature, 80–230°C; column temperature, 40–180°C (depending on the analyte); carrier gas flow rate, 1.6 \pm 0.02 L/h; and injected sample volume, 0.5–1 µL).

Quantum-Chemical Calculations

These calculations were performed using the NWChem shoftware package [26]. Geometry optimization and vibrational frequencies were calculated in terms of the functional electron density theory in the B3LYP approximation [27-29] using the correlationconsistent split-valence triple-zeta aug-cc-pVTZ basis set with the diffuse function. In calculations of an iodobenzene molecule, the generated basis set aug-ccpVTZ-pp with relativistic pseudopotential ECP was applied. All calculations were conducted with allowance for nonspecific solvation within the framework of the PCM model in the medium of ethanol (dielectric permittivity of the medium, 24.852). The data on the distribution of electron density on atoms were derived within the framework of the natural bond orbital (NBO) theory incorporated into the NWChem calculation package. The visualization of the molecules and their characteristics was performed using the Chem-Craft program [30].

RESULTS AND DISCUSSION

The synthesized catalyst Pd/ND has a specific surface are of 284 m^2/g , and the size of metal particles is 4–5 nm. Palladium occurs in the zero-valent state providing the hydrogenation process.

The catalytic properties of Pd/ND were studied in the liquid-phase hydrodehalogenation of monohalobenzenes and dichlorobenzene (DCB) isomers (Table 1). In the hydrodehalogenation of monohalobenzenes, the activity of Pd/ND decreased in the sequence chlorobenzene > bromobenzene > iodobenzene. A similar dependence was observed for the Pd/C catalyst (Table 1, samples 1-3). As is seen from Table 1, the activities of both catalysts are close in this reaction. It appears that active sites in Pd/ND and Pd/C are distributed on surfaces in such a manner that they are to be equally accessible to monohalobenzene molecules.

In the hydrodehalogenation of dichlorobenzenes, the activity of both catalysts decreases in the sequence p-DCB > o-DCB > m-DCB (Table 1, entries 4–6). Note that the catalytic activity of Pd/ND is an order of magnitude higher than that of the commercial Pd/C. This experimental fact may be explained as follows. It is known that activated carbon is a porous substance having micropores and mesopores on the surface and metal particles are anchored predominantly via physical adsorption in these pores. This hampers their accessibility to the hydrogenated substrates. Nanodiamonds, in turn, are polycrystals composed of diamond nuclei covered by functional groups which retain metal particles on the surface. Thus, the active sites in Pd/ND are more accessible to substrate molecules, as evidenced by an increased activity of this catalyst compared to Pd/C.

According to the liquid-phase chromatography of reaction products, under the test conditions, the hydrogenation of chlorobenzene, bromobenzene, and dichlorobenzenes over Pd/ND to benzene occurs with a 100% conversion over 4 to 5 h, whereas the hydrodehalogenation of o-, m-, and p-dichlorobenzenes over Pd/C gives rise to chlorobenzene, which is uninvolved in further hydrodehalogenation. This finding may suggest that, after a certain time, the catalyst ceases to operate apparently because of the poisoning of its active sites by HCl evolving during the reaction. The formation of HCl was confirmed by qualitative analysis for chloride ion (via reaction with 1% silver nitrate aqueous solution). The deactivation of palladium catalysts by HCl in hydrodechlorination reactions was reported in [3–6].

An iodide ion is a stronger catalytic poison. As evidenced by liquid-phase chromatography, in the case of both catalysts, the conversion of iodobenzene is no greater than 10%. The poisonous effect of iodine was



Fig. 1. Initial portions of kinetic curves for *p*-DCB hydrodehalogenation over Pd/C: (1) without additives, (2) 1 mmol of HCl, (3) 1.5 mmol of NaOH, (4) 2 mmol of NaOH, (5) 2.25 mmol of NaOH, and (6) 3 mmol of NaOH.

verified experimentally. The model reaction of nitrobenzene hydrogenation fully stops upon addition of 0.1 mol of iodobenzene to the reaction mixture [31].

The poisoning of Pd/C chloride ions by chloride ions was proved by adding hydrochloric acid (1 mmol) to the reaction mixture. As is clear from Fig. 1, actually upon the addition of HCl, the rate of hydrodehalogenation decreased. HCl evolved in the course of reaction was neutralized by adding alkalis, for example, NaOH, to the reaction mixture [3, 4]. Study of the effect of various amounts of NaOH added to bind chloride ions showed that, when NaOH was added to the reaction mixture, the activity of the catalysts increased (Fig. 1). The highest rate of *p*-DCB hydrodehalogenation in the presence of Pd/C was attained upon the addition of 2 mmol of NaOH, which not only neutralized HCl evolving as a result of hydrodechlorination but also enriched the surface of palladium in electrons via the adsorption of OH⁻ ions exhibiting a strong +M effect and a weak –I effect. As the amount of NaOH was increased above 2 mmol, the rate of reaction decreased apparently because of the effect of salting out on the active sites of the catalysts. In addition, the accumulation of water exerting the deactivating effect on palladium and the emergence of competitive adsorption with respect to substrate molecules are feasible. Moreover, at high concentrations of NaOH, destruction of the support may take place [4]. For the hydrodehalogenation of chlorobenzene under the test conditions, the addition of 1.5 mmol of NaOH is optimal.

When the hydrodehalogenation of dichlorobenzene isomers is carried out with the addition of 2 mmol of NaOH, the reaction is completed over 3.5 and 5 h in the case of Pd/ND and Pd/C, respectively. For both catalysts benzene is the single reaction product. Note that the activity of catalyst Pd/ND grows by 2– 4 times; Pd/C, by 10–30 times (Fig. 2).

Figure 3 shows the rate constants of hydrodehalogenation over catalyst Pd/ND as a function of the rate constant over Pd/C (the numbering of closed cubes on plots corresponds to the numbering of halobenzenes in Table 1). Linear dependences are observed in the event of both hydrogenolysis of the carbon—halogen bond in monohaloarenes (Fig. 3a) and hydrodehalogenation of dichlorobenzene isomers in the sequence para- > ortho- > meta-isomer (Fig. 3b). This observation provides evidence that the mechanism of hydrodehalogenation is preserved with a change in the nature of the palladium support. Furthermore, in the case of hydrodehalogenation of dichlorobenzene isomers it may be assumed that the mechanism of reac-



Fig. 2. Activity of palladium catalysts (TOF, min^{-1}) in the hydrodehalogenation of dichlorobenzene isomers: (a) without NaOH additive, and (b) upon the addition of 2 mmol of NaOH.

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Fig. 3. Relation between rate constants of reactions proceeding over Pd/ND and Pd/C for the hydrodehalogenation of (a) monohalobenzenes and (b) dichlorobenzene isomers.

tion evidently remains invariable with a change in the position of the substituent. All correlation points are in the confidence interval >95%. It should be noted that the rate constants for the hydrogenation of o-DCB and p-DCB have comparable values, whereas the rate constant for the hydrogenation of m-DCB is almost two times smaller than these values. Thus, the effect of concerted (ortho- and para-isomers) and disconcerted (meta-isomer) action of substituents (for chlorine both strong +M and –I effects are typical) is observed, which evidently may affect the efficiency of the horizontal adsorption of the substrate (the most preferable for hydrogenation) and the subsequent hydrodehalogenation process.

In order to gain insight into structure-property relationships for the tested substrates, quantumchemical calculations were performed (Table 1). As the sequence number of halogen in monohalobenzenes grows, the length of the C-Hal bond increases. The distribution of charges derived in terms of the natural bond orbitals (NBO) method indicates that a halogen atom in a chlorobenzene molecule carries a negative charge. The charge on the halogen increases in the sequence of substituents Cl < Br < I and its sign changes to positive beginning from bromobenzene. For dichlorobenzenes, the value of charge on chlorine atoms grows in the sequence para- < meta- < orthoisomer.

Figure 4 presents the dependence of charge on the halogen atom on the length of the carbon—halogen bond in the tested halobenzenes. With increasing length of the carbon—halogen bond and decreasing charge on the halogen atom, the rate of the hydrode-halogenation reaction declines. In accordance with [32], during the hydrogenation process, several different forms of hydrogen may reside on the surface of palladium, namely, a partially positively charged form,

a partially negatively charged form, and adsorbed molecular hydrogen. On the basis of the above dependences, it may be assumed that the negative charge on the halogen atom should facilitate hydrodehalogenation. Then, in this reaction, a partially positively charged form of hydrogen is evidently the active form of hydrogen on the surface of palladium. It is known that the longer the bond length, the lower the energy of its breaking. In our case, the rate of the hydrodehalogenation reaction decreases in the sequence Cl > Br >I, while the length of the C–Hal bond grows in the opposite direction: Cl < Br < I. At the same time, on passage from chlorine to iodine, the electronic character of the halogen atom "softens" and, as a consequence, the C-Hal bond strengthens in the perpendicular adsorption of substrate. Taking into consideration this fact, it may be suggested that during hydrodehalogenation substrate molecules coordinate on active sites of the catalyst to form the intermediate complex "substrate-palladium" in which the carbon-halogen bond breaks more easily in the studied monohalobenzenes in the sequence Cl > Br > I.

Figure 5 shows the diagram of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy distribution for the tested halobenzenes. A gap between HOMO and LUMO energies of monohalobenzenes decreases in the sequence Cl > Br > I. Hence, the rate of hydrodehalogenation should increase in this sequence. However, as was mentioned above, the rate constant for the tested compounds decreases in the sequence Cl > Br > II for both catalysts. For dichlorobenzene isomers, a gap in HOMO and LUMO energies also decreases in the direction opposite to an increase in the rate constant of hydrodehalogenation: para- > ortho- > metaisomer. It may be expected that, under the studied conditions in the hydrodehalogenation of monohalo-



Fig. 4. Dependence of charge (q) on halogen atom on the length of (r) carbon—halogen bond.



Fig. 5. Diagram of HOMO and LUMO energy distribution for monohalo-substituted and dichloro-substituted ben-zenes.

benzenes and dichlorobenzenes, the charge control of reaction prevails over the orbital one for both catalysts.

In conclusion it should be mentioned that catalytic hydrodehalogenation is one of the most promising methods for processing of halogen-containing organic compounds. It was shown that palladium-containing nanodiamonds are active catalysts of hydrodehalogenation under mild conditions (solvent, ethanol, $T = 45^{\circ}$ C, and $P_{H_2} = 1$ atm). Evidently, the surface groups of nanodiamonds facilitate formation of the structure of active sites optimal for the hydrodehalogenation reaction. If conditions required for binding of halogenide ions generated during the reaction are chosen, then the conversion of aromatic halogen derivatives on

the order of 90-100% may be attained over a shorter time. Thus, hydrodehalogenation under mild conditions in the presence of Pd/ND calls for further studies.

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