Comparison of Palladium Catalysts Based on Nanodiamonds and Activated Carbon in Hydrogenation Reactions

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Abstract—Comparison of palladium catalysts (1 wt % Pd) based on nanodiamonds and activated carbon in the liquid-phase hydrogenation of organic compounds of different nature (some aromatic nitro compounds, unsaturated hydrocarbons, alcohols, and acids) under mild conditions (T = 318 K; $P_{H_2} = 0.1$ MPa; solvent,

ethanol) has been conducted. It has been found that the palladium catalyst based on nanodiamonds is more active in the hydrogenation reaction and more sensitive to a change in the nature of the substrate than its counterpart based on activated carbon.

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Hydrogenation is one of the basic processes of the petrochemical industry. At present, various types of supports, such as activated carbon, alumina, pumice, and Sibunit, are used for industrial hydrogenation catalysts. Each support has advantages and disadvantages. A good support must have a developed specific surface area, exhibit the ability to retain transition metals, and be chemically and physically stable. Supports made of nanodiamonds (NDs) meet these requirements. These supports exhibit unique properties: a fairly high specific surface area, a functional cover (which optionally can be subjected to chemical modification) capable of effectively binding transition-metal atoms, and certainly the physicomechanical properties of a diamond (primarily, high strength and fairly high thermal stability). The presence of uncompensated bonds on the ND surface leads to the formation of metal clusters with a diameter of 5 nm and a thickness of 0.4-1.2 nm [1-4] and thus provides the uniformity of active sites and the maximal catalytically active surface area required for the implementation of all steps of the catalytic process. Catalysts based on NDs have been tested in the CO conversion to CO_2 [1, 4] and the hydrodehalogenation of aromatic compounds [5-8]; they are promising for use in catalytic decomposition of alcohols (ethanol, methanol) [4].

It should be emphasized that detonation NDs of various particle sizes are commercially available products in Russia (http://www.diamond-nanodia-mond.com/; http://www.skn-nd.ru/products.html; http://frpc-altai.rosbizinfo.ru/products/4.html). Pre-viously, we have studied NDs with palladium loadings of 3, 6, 9, 10, 12, and 15 wt % as catalysts for the liq-

uid-phase hydrogenation of nitrobenzene, allyl alcohol, and cyclohexene and for the hydrogenating amination of propanal with 4-aminobenzoic acid [9, 10]. It has been shown that the use of NDs containing 3 wt % palladium is the most effective. Therefore, it is of interest to study the catalytic properties of NDs with a lower palladium loading and compare these catalysts with a counterpart based on activated carbon.

EXPERIMENTAL

Sample Preparation

The detonation NDs used in the study had a specific surface area of $307-314 \text{ m}^2 \text{ g}^{-1}$ (average size of the crystalline diamond core of ND particles was about 4 nm) and a total content of noncarbon impurities of no more than 0.2 wt %. Prior to the deposition of palladium, a slurry of 0.38–0.42 g of NDs in 100 mL of water was subjected to sonication at 40-50°C for 15 min (0.5 maximum power of a Bandelin electronic HD 3200 ultrasonic homogenizer). After that, a mixture of 100 mL of a PdCl₂ salt solution in 1 N hydrochloric acid, which was prepared so as to contain palladium in an amount of 1% of the weight of NDs (0.004 g, 0.038 mmol), and a 5% aqueous solution of lithium formate taken in a molar ratio of 1:10 and heated to 55°C was poured to the ND slurry. Synthesis was conducted at 55°C. After 20-30 min, a black precipitate was formed. The reaction mixture was heated to 70°C, allowed to stand for 24 h, and subjected to decantation with distilled water three or four times at 24-h intervals. After the final decantation, the catalyst was dried in the air at 20–30°C. Next, the 1 wt % Pd/ND sample was

mixed with M200 activated carbon at a mass ratio of 180 : 820 mg (total mass of 1 g) to form a homogeneous mixture. This procedure was conducted to reduce the weighing error.

The 1 wt % Pd/C catalyst was prepared by a similar technique using M200 activated carbon.

Hydrogenation Procedure

In this study, the catalytic properties of NDs containing 1 wt % palladium are compared to the properties of a 1 wt % Pd/C catalyst prepared by a similar technique in the model hydrogenation of cyclohexene, hexene-1, allyl alcohol, acrylic, methacrylic, crotonic, and cinnamic acids, nitrobenzene, and *p*-substituted analogs of nitrobenzene: *p*-nitroaniline, *p*-nitrophenol, and *p*-nitrobenzoic acid.

Hydrogenation of aromatic nitro compounds and unsaturated organic compounds was conducted as follows: 30 mg of the catalyst and 10 mg of NaBH₄ were placed into a glass reactor, which was equipped with a jacket for temperature control and a magnetic stirrer, under a solvent layer (10 mL of ethanol) and subjected to activation for 10 min; after that, 1 mmol of the substrate (cyclohexene, hexene-1, allyl alcohol, acrylic, methacrylic, crotonic, and cinnamic acids, nitrobenzene, *p*-nitroaniline, *p*-nitrophenol, and *p*-nitrobenzoic acid) was introduced in a hydrogen stream. Hydrogenation was conducted under mild conditions: solvent, ethanol; $T = 45^{\circ}$ C; $P_{H_2} = 1$ atm). The apparent reaction rate was measured by the volumetric method from hydrogen absorption measurements.

It is known that the true catalytic activity of heterogeneous catalysts must be related to the number of active sites of the catalyst, which is difficult to estimate. Under similar reaction conditions, the catalytic activity of the studied objects can be compared using the turnover number (TON, min⁻¹), which shows the number of substrate moles converted per mole of palladium per min.

Under the test conditions, the studied reactions are zero order with respect to the substrate and first order with respect to the catalyst and hydrogen [11]. To confirm the occurrence of the processes in the kinetic region, the Thiele criterion (Φ) was used [12]:

$$\Phi = R \sqrt{\frac{W}{CD}},$$

where *R* is the average diameter of the catalyst particles, cm; *W* is the reaction rate, mol/(L s), in the linear portion of the kinetic curve to a 10% conversion from theoretically calculated value for each substrate; *C* is the substrate concentration, mol/L; and *D* is the diffusion coefficient, 10^{-5} cm²/s. In the experiments, the Thiele modulus was significantly lower than unity ($\Phi = 0.1 \times 10^{-5}$ to 1.3×10^{-5}), thereby undoubtedly indicating the occurrence of the reaction in the kinetic region.

The hydrogenation reaction products were analyzed using a 3700 Series gas chromatograph equipped with a flame ionization detector and a 3 mm × 2000 mm chromatographic glass column packed with Lucopren G-1000 (5%) on Chromaton N-AW-DMCS (carrier gas, nitrogen; evaporator temperature, $80-230^{\circ}$ C; column temperature, $50-180^{\circ}$ C (depending on the analyte); carrier gas flow rate, 1.60 ± 0.02 L/h; and injected sample volume, 0.5-1.0 µL.

Research methods. X-ray photoelectron spectroscopy (XPS) studies of the catalysts were conducted on a Kratos Axis Ultra DLD instrument at a pass energy of 160 eV (survey scans) and 40 eV (individual lines). Photoelectrons were excited using the AlKa X-ray emission of an aluminum anode (E = 1486.6 eV) at a tube voltage of 12 kV and an emission current of 20 mA. The vacuum in the working chamber was $5 \times$ 10^{-9} torr. The photoelectron peaks were calibrated against the nitrogen N1s line at a binding energy $(E_{\rm b})$ of 400.0 eV. The measurement error for $E_{\rm b}$ was ± 0.1 eV. Scanning electron microscopy studies of the samples were conducted using a Versa 3D HiVac microscope (FEI, United States) equipped with a twobeam electron-ion microscopy system with a Schottky field emission cathode and a gallium liquid-metal ion source, an energy dispersive (EDS) analyzer (EDAX, EDX), a secondary electron detector (STEM), a unique DBS detector, and an electron beam retarding unit. The vacuum in the working chamber was 6×10^{-9} torr; accelerating voltage, 10 kV; current density, 0.17 nA to 0.26 pA; working distance, 9.8-10.2 mm; and magnification, 25000× to 35000×.

RESULTS AND DISCUSSION

The catalyst samples containing 1 wt % Pd supported on NDs and M200 activated carbon were prepared. The Pd content in the samples corresponded to the theoretically calculated value as determined by XPS and EDX analyses. Results of the XPS and EDX studies of the catalysts are described in detail in [13].

Comparison of the analysis results for the catalysts suggests that palladium supported on NDs was not washed off from the support during reaction, whereas the metal losses in the case of Pd/C were almost 50%of the initial content. This fact can be apparently attributed to the involvement of the nitrogen-containing groups of the NDs in the supporting of Pd. In fact, the XPS spectra recorded before and after the reaction over Pd/NDs exhibited the presence of nitrogen, and no nitrogen was found in the case of Pd/C. In the last-mentioned catalyst, a portion of the metal (7-9%) is located in places that are inaccessible to the reducing agent and, therefore, remains inactive. After reaction, in the two catalysts, the base peaks—both Pd3d_{5/2} and Pd3d_{3/2}—are shifted to higher binding energies apparently owing to the partial oxidation of metal sites through the formation of

Substrate	1 wt % Pd/NDs		1 wt % Pd/C		
	TON, min ^{-1}	<i>k</i> , L/(mol s)	TON, min ^{-1}	<i>k</i> , L/(mol s)	
Nitrobenzene	133.0	788.0	43.4	255.9	
<i>p</i> -Nitroaniline	87.7	528.9	40.2	237.6	
<i>p</i> -Nitrophenol	56.7	333.9	41.5	246.9	
<i>p</i> -Nitrobenzoic acid	46.1	280.1	22.8	136.2	

Table 1. Activity of Pd/NDs and Pd/C and the rate constant of hydrogenation of aromatic nitro compounds

Reaction conditions: $T = 45^{\circ}$ C, $P_{H_2} = 0.1$ MPa, 30 mg of the catalyst, 10 mg of NaBH₄, 10 mL of ethanol, 1 mmol of the substrate (nitrobenzene, *p*-nitroaniline, *p*-nitrophenol, *p*-nitrobenzoic acid). The error in determining the rate constants and the TON does not exceed 5%.

palladium-to-substrate charge transfer surface complexes. In addition, the nature of the support has an effect on the electron binding energy of Pd. On the Pd3d_{5/2} level, this value is 335.0 and 335.3 eV in the case of NDs and activated carbon, respectively. Properties of the catalysts were studied in the hydrogenation of nitrobenzene, its *p*-substituted analogs (*p*-nitroaniline, *p*-nitrophenol, and *p*-nitrobenzoic acid), cyclohexene, hexene-1, allyl alcohol, acrylic, methacrylic, crotonic, and cinnamic acids:



The proposed substrates differed in the nature and location of the reducible groups; this made it possible, under comparable conditions, to determine the effect of the nature of the catalyst on the kinetic parameters of hydrogenation and study the effect of the substituent in the nitroarenes on the reduction rate of the NO₂ group.

The choice of the substrates was stipulated not only by their practical significance, but also by interest in studying the mechanisms of reduction of the functional groups ($-NO_2$, >C=C<) differing in nature and location in the molecule and the effect of the substituent in the *para* position in nitroarene molecules using the example of *p*-nitroaniline, *p*-nitrophenol, and *p*-nitrobenzoic acid.

According to the analysis of the reaction products by gas—liquid chromatography, the conversion of all the hydrogenated substrates was 100%. Byproducts were not found. The data on the hydrogenation are shown in Tables 1 and 2.

It was found that the 1 wt % Pd/ND catalyst is more active in the hydrogenation of nitrobenzene and its

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p-substituted analogs (*p*-nitroaniline, *p*-nitrophenol, and *p*-nitrobenzoic acid) than 1 wt % Pd/C (Table 1). Apparently, the $-NO_2$ group is sterically more accessible to the contact sites of the 1 wt % Pd/ND catalyst and less accessible to the 1 wt % Pd/C sample, which can be attributed to the strictly ordered nanostructure of NDs compared to activated carbon. The last-mentioned support has pores with different diameters [6] in which a portion of palladium is fixed and thus becomes inaccessible to the XPS data, the fraction of unreduced palladium does not exceed 7–9%.

The hydrogenation of nitrobenzene occurs most readily for each of the catalysts. In the presence of 1 wt % Pd/NDs, the reaction rate constant for nitrobenzene is higher than that for *p*-nitroaniline, *p*-nitrophenol, and *p*-nitrobenzoic acid by a factor of 1.5, 2.4, and 2.8, respectively (Table 1). In the case of 1 wt % Pd/C, the reaction rate constant of the reduction of the nitro group decreases almost twofold in the series: nitrobenzene, *p*-nitrophenol, *p*-nitroa-

Entry	Substrate	1 wt % Pd/NDs		1 wt % Pd/C	
Littiy		TON, min^{-1}	k, L/(mol s)	TON, min ⁻¹	<i>k</i> , L/(mol s)
1	Cyclohexene	49.9	294.2	39.1	236.9
2	Hexene-1	93.7	551.8	60.2	357.5
3	Allyl alcohol	91.4	538.4	50.3	300.3
4	Acrylic acid	104.3	625.9	61.3	355.3
5	Methacrylic acid	49.9	282.3	33.6	201.0
6	Crotonic acid	48.7	284.3	26.3	155.6
7	Cinnamic acid	33.7	196.6	23.9	140.9

Table 2. Activity of Pd/NDs and Pd/C and the rate constant of hydrogenation of unsaturated organic compounds

Reaction conditions: $T = 45^{\circ}$ C, $P_{H_2} = 0.1$ MPa, 30 mg of the catalyst, 10 mg of NaBH₄, 10 mL of ethanol, 1 mmol of the substrate (cyclohexene, hexene-1, allyl alcohol, acrylic, methacrylic, crotonic, cinnamic acids). The error in determining the rate constants and TON does not exceed 5%.

niline, p-nitrobenzoic acid. This fact can be attributed to the presence of fixed metal clusters of different nature and geometry on the surface of the activated carbon. The donor substituent in the para position has an insignificant effect on the rate constant of hydrogenation of the nitro group; however, the introduction of an acceptor substituent (carboxyl group) decreases this parameter almost twofold. Figure 1 shows the dependence of the hydrogenation reaction rate constants on the nature of the 1 wt % Pd/C and 1 wt % Pd/ND catalysts plotted in accordance with an increase in the process constant. The rate constants of hydrogenation of nitrobenzene and its para-substituted compounds over the 1 wt % Pd/ND catalyst are 1.5-3 times higher than over 1 wt % Pd/C (Fig. 1a). In addition, note that the sensitivity of the 1 wt % Pd/ND catalyst significantly depends on the nature of the substituent in the para position. The reduction of nitrobenzene occurs at the highest rate; the reduction rate of *p*-nitrophenol and *p*-nitroaniline is 1.5 and 2.5 times lower, respectively. The compound with the carboxyl group has the lowest rate constant. In the case of the catalyst supported on activated carbon, the reaction rate constant was affected only by the nature of the substituent. Thus, the rate constant of *p*-nitrobenzoic acid is 1.5 times lower than that of nitrobenzene or its para-substituted compounds with donor substituents. This fact suggests that the ratelimiting steps of the reduction of the nitro group can be different depending on the nature of the substrate for given catalysts. The nature of the substituent can have an effect on the reduction mechanism; the size of the substituent imposes steric constraints while the molecule approaches the catalytic site.



Dependence of the hydrogenation reaction rate constant over 1 wt % Pd/C on the reaction rate constant over 1 wt % Pd/NDs (a) for (1) p-nitrobenzoic acid, (2) p-nitroaniline, (3) p-nitrophenol, and (4) nitrobenzene and (b) for (5) cinnamic acid, (6) methacrylic acid, (7) crotonic acid, (8) cyclohexene, (9) allyl alcohol, (10) hexene-1, and (11) acrylic acid.

In general, it can be stated that the catalyst based on activated carbon is 1.5-2.8 times less sensitive to changes in the nature of the substrate than 1 wt % Pd/NDs (Table 1).

A linear dependence in the case of reduction of the multiple bond of compounds with different functional substituents (Fig. 1b) is indicative of the preservation of the hydrogenation mechanism upon a change in the nature of the support for Pd. All the correlation points are in a 95% confidence interval. The standard Pearson correlation coefficient (R) is 0.95.

In the hydrogenation of unsaturated organic compounds (cyclohexene, hexene-1, allyl alcohol, acrylic, methacrylic, crotonic, and cinnamic acid), it was found that the activity of 1 wt % Pd/NDs is 1.3-1.8 times higher than that of 1 wt % Pd/C (Table 2). Apparently, the key factor that determines the reduction rate of the multiple bond is the spatial arrangement of the bond. Compounds with a more sterically accessible multiple bond—acrylic acid, allyl alcohol, and hexene-1 (Table 2, entries 2-4)-undergo hydrogenation significantly faster than the sterically screened multiple bond in methacrylic, crotonic, and cinnamic acids (Table 2, entries 5-7): by a factor of 2-3 and 1.8–2.6 for the 1 wt % Pd/ND and 1 wt % Pd/C catalysts, respectively. In addition, the last-mentioned compounds contain a carboxyl group, which decreases the electron density on the multiple bond. The unsaturated cyclic compound holds an intermediate position in this series of substrates and is reduced to cyclohexane 1.3-1.5 times worse than compounds 2-4 and 1.2-1.6 times better than compounds 5-7 in the presence of the 1 wt % Pd/C catalyst (Table 2). In the case of 1 wt % Pd/NDs, the TON values for cyclohexene and methacrylic and crotonic acids are similar (Table 2, entries 1, 5, 6). It can be assumed that the multiple bond of cycloalkene in the half-chair conformation [14] is as hardly accessible to catalytic sites as the multiple bond of methacrylic acid screened by the methyl and carboxyl groups.

Thus, 1 wt % Pd/NDs can be used as a catalyst in hydrogenation of various organic compounds (nitro compounds, unsaturated hydrocarbons, alcohols, and acids). It has been shown that the reduction mechanism of unsaturated compounds is preserved upon switching from the catalyst based on activated carbon to the ND-supported sample, while in the hydrogenation of nitro compounds the reaction mechanism is apparently determined by the nature of the catalyst. In the hydrogenation of the >C=C< bond, the nature of this bond plays an important role: the more accessible and open the bond, the higher the process rate for the two catalysts. The activity of the metal in the catalyst systems based on NDs is higher than that on activated carbon: by 1.4–1.7 times in the hydrogenation of

unsaturated substrates and 2–3 times in the reduction of the nitro group in nitrobenzene and its *para*-substituted analogs. This can be apparently attributed to the fact that, in the case of NDs, the palladium is reduced more completely: the binding energy on the $Pd3d_{5/2}$ level is 335.0 eV, whereas for activated carbon it is 335.3 eV.

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