Palladium-Containing Nanodiamonds in Hydrogenation and Hydroamination

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Abstract—Palladium catalysts in the form of Pd nanoparticles supported on nanodiamonds have been studied in the hydrogenation of nitrobenzene, allyl alcohol, and cyclohexene and in the hydrogenating amination of propanal with 4-aminobenzoic acid. The ratio of two valence states of palladium, i.e., Pd^{2+} and Pd^0, in the catalysts has been determined by XPS. The dependence of hydrogenation reaction rate on electron density at the reaction site of nitrobenzene, allyl alcohol, cyclohexene, and 4-(propylideneamino)benzoic acid molecules has been studied using quantum chemical calculations (HF/6-31G, PCM).

Palladium catalysts are extensively used in various chemical and petrochemical processes. Commercially available products are activated carbons that contain a certain amount of palladium. Carbon nanomaterials (CNMs) have been recently used as supports: fullerenes and fullerene black [1, 2], carbon nanotubes and nanofibers [1, 3, 4], nanodiamonds (NDs) [3, 5–9], etc.; they significantly improve the catalyst characteristics, such as activity, selectivity, and stability; in addition, the nature and sizes of metal centers, as well as their accessibility to the molecules of converted compounds, are largely determined by the nature of the support [1, 3, 4].

Catalysts based on NDs are of particular interest. It was shown in [10, 11] that the use of NDs as a support for platinum group metals gives the possibility to obtain clusters of platinum and palladium with a diameter of 5 nm and a thickness of 0.4–1.2 nm. This is attributed to the fact that the surface carbon atoms in NDs have uncompensated bonds [12–15], which provide the homogeneity of metal centers and thus the maximum catalytically active surface area required for the adsorption of chemical agents, the occurrence of the reaction, and the desorption of the product. The more homogeneous the metal centers in the catalyst, the more selective they are.

We previously showed [3] that Pt- and Pd-NDs are more active and effective in catalytic liquid-phase hydrogenation than other metal-containing CNMs. In this study, we have analyzed the catalytic properties of Pd/NDs in the hydrogenation of nitrobenzene, allyl alcohol, and cyclohexene and in the hydrogenating amination of propanal with 4-aminobenzoic acid.

EXPERIMENTAL

The synthesis of Pd-containing NDs was carried out according to the procedure described in [15]. Detonation NDs with a specific surface area of 307–314 $m^2 g^{-1}$ (the average size of the crystalline diamond nucleus of ND particles is about 4 nm) and a total noncarbon impurity concentration of no more than 0.5 wt %. The synthesized Pd/ND samples were mixed with activated carbon in a ratio of 180 to 820 mg (a total weight of 1 g).

The composition of the Pd/ND samples was determined by X-ray microanalysis, and the specific surface area was found by the BET method. The local X-ray microanalysis was carried out using a VEGA TS 5130MM fully PC-controlled scanning electron microscope ((CamScan MV2300)TP1PT) equipped with secondary electron (SE) and backscatter electron (BSE) detectors of YAG-crystals and an energy dispersive X-ray (EDX) microanalyzer with an INCA Energy2 semiconducting Si(Li) detector. The computation of the X-ray microanalysis data was performed using the INCA Energy 200 software with the subsequent recalculation of the results using the TP3PT software package developed at the Institute of Experimental Mineralogy, Russian Academy of Sciences. The studies were carried out at an accelerating voltage of 20 kV. The absorbed electron current was 516–565 pA on the reference cobalt sample and 540–620 pA on the sample under study. The size of the electron probe on the sample surface was 157–200 nm. Titanium and chlorine impurities made no more than 0.3 and 0.1 wt %, respectively. The ash content of the original ND was more than 2 wt %.

The analysis of the catalyst by X-ray photoelectron spectroscopy (XPS) was performed using a

Riber LAS-3000 instrument equipped with an OPX-150 hemispherical retarding-field electron-energy analyzer. To excite photoelectrons, we used an AlKα 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. Vacuum in the working chamber was 5×10^{-9} torr. Photoelectron peaks were calibrated against the C 1s carbon line with a binding energy (E_b) of 285 eV. The measurement error for E_b was ±0.1 eV.

The hydrogenation of nitrobenzene, allyl alcohol, and cyclohexene (Scheme 1) was performed as follows: 30 mg of the catalyst and 10 mg of NaBH$_4$ were placed into the reactor under a solvent layer (10 mL ethanol) and subjected to activation for 10–120 min; after that, 1 mmol of the substrate was introduced in a stream of hydrogen, and hydrogenation was conducted at $T = 318$ K and $P_{H_2} = 0.1$ MPa.
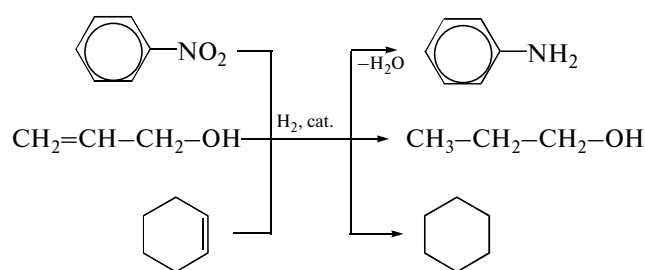
Scheme 1.

The hydrogenating amination of propanal with 4-aminobenzoic acid (Scheme 2) was performed as follows: 30 mg of the catalyst and 10 mg of NaBH$_4$ were placed into the reactor under a solvent layer (5 mL) and subjected to activation for 1 h; after that, 2 mmol of 4-aminobenzoic acid (0.274 g) and 2 mmol of propanal (0.15 mL) dissolved in 20 mL of ethanol were introduced and purged with hydrogen, and the process was carried out at $T = 318$ K and $P_{H_2} = 0.1$ MPa.
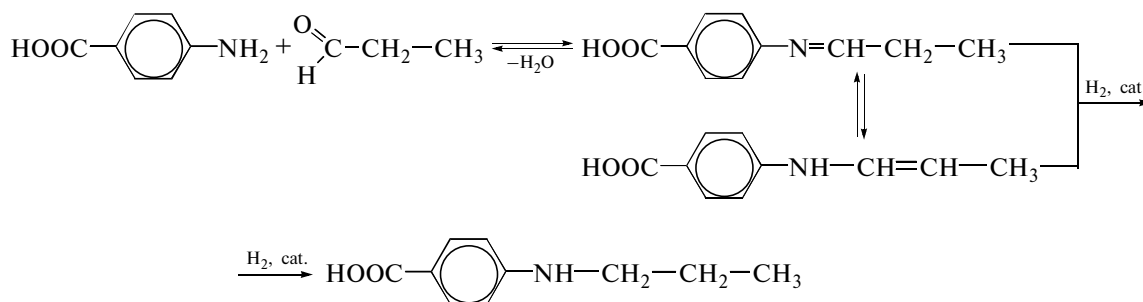
Scheme 2.

The apparent reaction rate was measured by the volumetric method from hydrogen absorption measurements. To compare the catalytic activity of the samples under study, we used the turnover number of the catalyst (TON, min^{-1}), which shows the number of substrate moles converted per mole of palladium per minute.

Under these conditions, the two reactions are zero order with respect to the substrate and first order with respect to the catalyst and hydrogen. In studying the stability of the catalysts, upon the completion of the conversion of one portion of substrates, another portion was introduced without separation of the catalyst and isolation of target products from the reaction mixture.

The hydrogenation and hydroamination products were analyzed using a 3700 Series gas chromatograph with a flame ionization detector and a chromatographic glass column (2 m × 3 mm ID) packed with Lucopren G-1000 (5%) on Chromaton N-AW-DMCS (carrier gas, argon; evaporation temperature, 200°C; column temperature, 230°C; carrier gas flow rate, 1.60 ± 0.02 L/h; injected sample volume, 0.1–0.5 µL).

RESULTS AND DISCUSSION

The synthesized Pd/ND samples contained 3, 6, 9, 10, 12, and 15 wt % palladium. The diameter of the supported palladium clusters was 5 nm. The specific surface area (S_{sp}) of the resulting samples was 263–305 m^2/g, and the highest value was observed for 3% Pd/ND. An increase in the supported palladium concentration leads to a decrease in the specific surface area of Pd/ND, and S_{sp} is 263 m^2/g for 15% Pd/ND. The activity of the resulting catalysts was studied in the above hydrogenation reactions. According to the GLC analysis of the reaction products, the substrates completely reacted. No by-products were found.

In the case of the hydrogenating amination of propanal with 4-aminobenzoic acid, the catalyst activity decreases with increasing palladium concentration (Table 1); at the same time, there is no direct dependence: similar values were obtained for the 3 and 6% Pd/ND catalysts and for the 10 and 15% Pd/ND samples. The 3% Pd/ND catalyst was found to be the most active (TON = 14.0 min^{-1}); the catalysts containing 6 and 10% palladium showed similar TON values. It should be noted that Pd/Nd exhibits significantly

Table 1. Hydrogenating amination of propanal with 4-aminobenzoic acid in the presence of Pd/ND and 1% Pd/C

Catalyst	$S_{sp.}$, m^{2}g^{-1}	$W_{H_2} \times 10^6$, mol/(L s)	k, L/(mol s)	TON, min^{-1}	TON/S, min^{-1}m^{-2}
3% Pd/ND	305	10.7	62.8	14.0	8.5
6% Pd/ND	284	11.0	31.5	7.0	4.5
10% Pd/ND	267	17.7	30.9	6.8	4.7
15% Pd/ND	263	17.0	20.1	4.4	3.1
1% Pd/C (200 mg)	14	2.0	1.2	0.3	0.1

Table 2. Nitrobenzene hydrogenation in the presence of Pd/ND and 1% Pd/C

Parameters	Catalyst					
	3% Pd/ND	6% Pd/ND	9% Pd/ND	12% Pd/ND	15% Pd/ND	1% Pd/C (200 mg)
$S_{sp.}$, m^{2}g^{-1}	305	299	293	291	263	14
k, L/(mol s)	733.7	524.2	481.9	429.0	379.5	10.1
TON, min^{-1}	164.1	116.2	106.9	95.2	84.2	2.2
TON/S, min^{-1}m^{-2}	99.7	71.9	67.7	60.6	59.0	0.8

higher catalytic properties in hydroamination than a commercial 1% Pd/C catalyst.

In the case of nitrobenzene hydrogenation, it was shown (Fig. 1) that, with each increase in the metal concentration in the catalyst by 3%, the reaction rate (W_{H_2}) increases by a factor of 1.4–1.1. It is evident from the experimental data in Table 2 that the catalyst activity, on the contrary, decreases. This suggests an inefficient use of palladium. Taking the surface area (TON/S) of the catalysts (Table 2) into account does not change the tendency. In the hydrogenation of nitrobenzene, as in hydroamination, the catalytic activity of the Pd/ND samples is an order of magnitude higher than that of the 1% Pd/C catalyst (Table 2).

Using the example of 9% Pd/ND and 15% Pd/ND, we studied the effect of catalyst activation time on nitrobenzene hydrogenation rate and catalyst activity (Table 3). It was found that the reaction rate and turnover number increase with increasing activation time; apparently, this can be explained by the formation of a higher amount of Pd^0.

This assumption was confirmed in the XPS study of the 10% Pd/ND catalyst with a specific surface area of 267 m^2/g and a metal particle size of 4–5 nm. Three samples were analyzed: (1) original, (2) after activation with hydrogen for 1 h, and (3) after the hydrogenation of a model substrate, i.e., nitrobenzene. The C 1s spectrum of all three original samples exhibits a peak at a binding energy of 285.18 eV, which consists of two components: a diamond phase with the sp^3 hybridization and a graphite phase with the sp^2 hybridization of the valence electron states of the carbon atom, which is characteristic of activated carbon (284.7 eV); similar data were given in [16, 17]. In the

O 1s spectrum (E_b = 531.14 eV), oxygen was found in carboxyl and carbonyl forms as well as in an oxide form, which corresponds in energy to the PdO bond (529.3 eV). Chlorine was not detected in any of the three samples.

Figure 2a depicts the Pd3d spectrum of sample, which shows the presence of palladium in two valence states: Pd^{2+} and Pd^0 in a ratio of 1.06 to 1. After the hydrogen reduction of the catalysts for 1 h (sample 2), the two forms remain present (Fig. 2b); however, the Pd^{2+} to Pd^0 ratio is shifted to zero-valent palladium (1 to 1.23). After hydrogenation (sample 3), only Pd^0 was detected (Fig. 2c). In this case, the catalyst is effi-
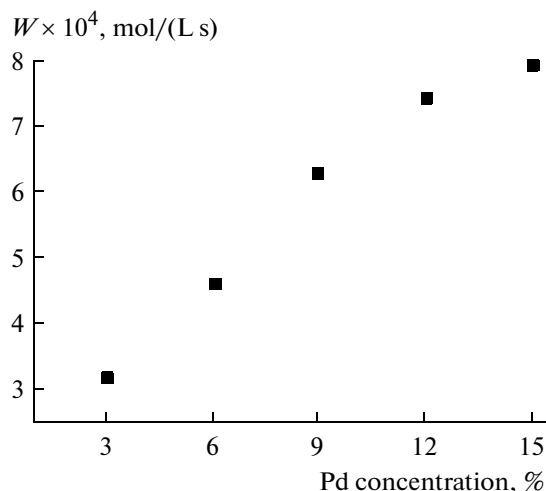

Fig. 1. Dependence of nitrobenzene hydrogenation rate on palladium concentration in Pd/ND.

Table 3. Characteristics of nitrobenzene hydrogenation over Pd/ND with varying catalyst activation time

Catalyst	Activation time	Characteristics			
		$W_{H_2} \times 10^4$, mol/(L s)	k, L/(mol s)	TON, min^{-1}	TON/S, min^{-1} m^{-2}
9%Pd/ND	10 min	6.3	481.9	106.9	67.7
	30 min	6.8	569.3	119.4	75.4
	60 min	7.0	547.7	121.5	76.7
	90 min	7.5	576.9	128.1	81.0
15%Pd/ND	10 min	8.0	379.5	84.2	59.0
	30 min	7.2	359.0	75.4	53.1
	60 min	8.4	417.4	87.3	61.5
	90 min	8.7	429.3	89.7	63.1

Table 4. Activity of 10% Pd/ND in the hydrogenation of organic compounds with functional groups

Parameters	Substrates			
	nitrobenzene	allyl alcohol	cyclohexene	4-(propylideneamino)benzoic acid
Sq, arb. units (according to Levdin)*	−0.703	−0.393	−0.298	−0.194
$W \times 10^4$, mol/(L s)	5.8	3.8	3.4	0.2
k, L/(mol s)	405.9	269.6	227.2	30.9
TON**, min^{-1}	89.6	59.9	50.4	6.8
TON/S, min^{-1} m^{-2}	62.2	41.5	35.0	4.7

Notes: * The HF/6-31G method; continuum approach of the PCM method; ethanol as a solvent; PCGAMESS 7.1 [23].
** Measurement error for reaction rate and TON does not exceed 4%.

cient. It can be used repeatedly with no apparent loss of activity (Fig. 3).

Figure 3 shows the hydrogenation rates for nitrobenzene, allyl alcohol, and cyclohexene in the presence of 10% Pd/ND. In the hydrogenation of the second portion of each substrate, the reaction rate is slightly higher than for the first portion; after that, upon the introduction of the next portion of the substrate, the reaction rate remains approximately the same; this indicates the stability of the catalytic properties of the Pd/ND samples under study.

The "catalyst conditioning" effect is more pronounced in the case of the sample activated for 10 min (Fig. 4). In the hydrogenation of a greater number of portions of cyclohexene, the reaction rate was constantly increasing. In the case of nitrobenzene hydrogenation, the reaction rate was almost constant starting with the third portion of the substrate. This experimental finding can be indicative of a different coordination of cyclohexene and nitrobenzene molecules at the active sites of the catalyst.

The active sites of the Pd/ND catalyst are most probably clusters of zero-valent palladium directly involved in all stages of the hydrogenation reaction: the formation of activated hydrogen, the adsorption of substrates, the reduction of an unsaturated bond or a functional group, and the desorption of the product. It was shown in [18] that, during the activation of hydrogen by palladium, bond dissociation occurs in the hydrogen molecule, resulting in the formation of chemisorbed hydrogen atoms carrying a partial positive charge. It was also shown that during the hydrogenation of some nitro compounds [19] and some azomethines [20−21] over palladium-containing catalysts of different types, the reaction rate increases with
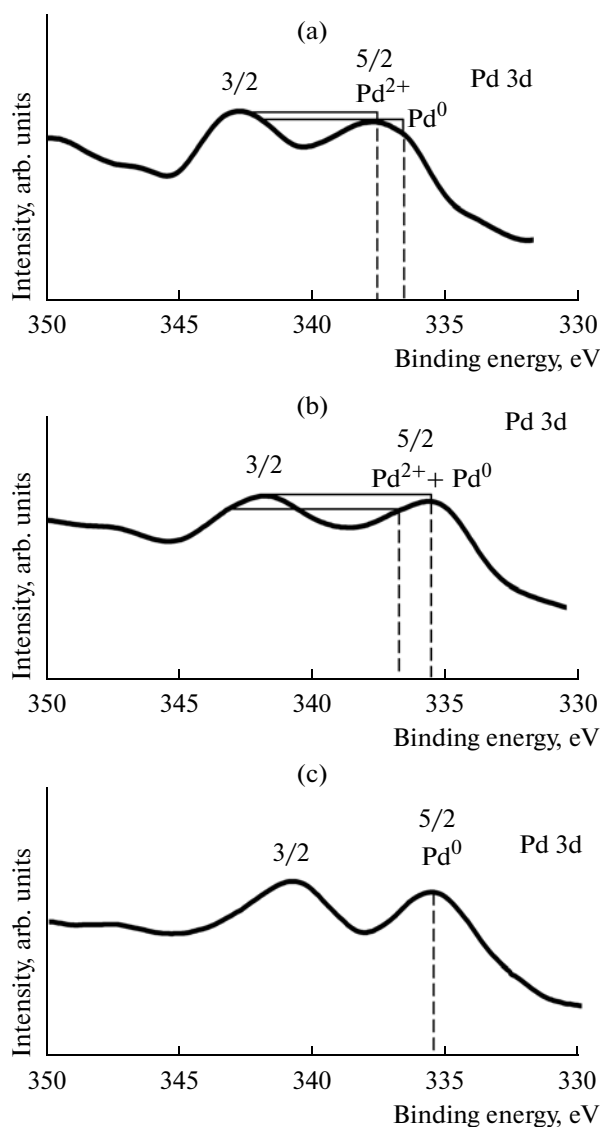
Fig. 2. Pd 3*d* photoelectron spectra of the 10% Pd/ND catalyst: (a) after the exposure of ND to K_2PdCl_4, (b) after catalyst activation with hydrogen for 1 h, and (c) after nitrobenzene hydrogenation.

Fig. 3. Stability of Pd/ND in the hydrogenation of nitrobenzene, allyl alcohol, and cyclohexene upon catalyst activation for 60 min.

increasing negative charge on the nitro group and the >C=N− bond of the substrates, respectively.

Table 4 lists the values of total effective charges at the reaction sites of the substrates, which were derived through quantum-chemical calculations of hydrogenated molecules by the HF/6-31G method. Since the hydrogenation reactions occurred in ethanol, the calculations were performed taking into account the solvent effect using the continuum approach of the polarizable continuum model (PCM) method. It was found that the hydrogenation rates for the substrates do increase with increasing electron density at the reaction site (the oxygen atoms in the NO_2 group, the atoms of the >C=C< and >C=N− bonds) of the
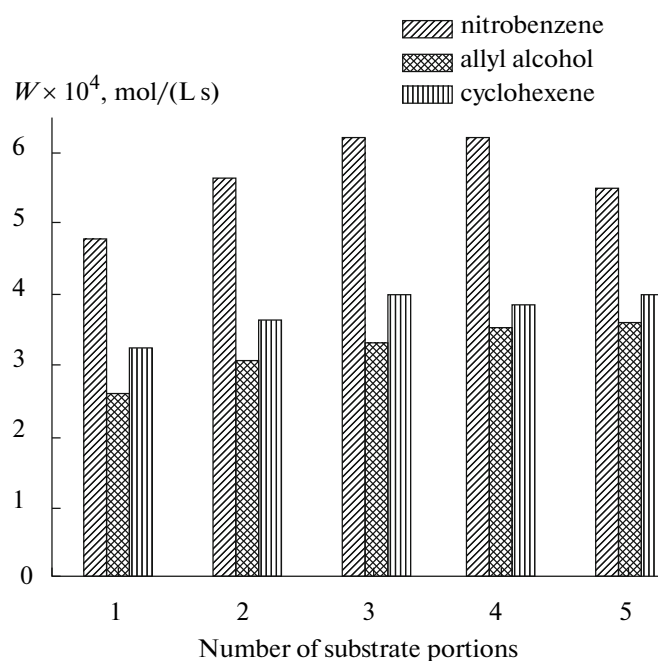
reduced substrate. The hydrogenation of nitrobenzene occurs most easily: the reaction rate is 1.4 and 1.8 times higher than for allyl alcohol and cyclohexene, respectively, and 26 times higher than for 4-(propylideneamino)benzoic acid (Table 4). This can be explained by the fact that the NO_2 group is sterically more accessible and more electronegative. The >C=C< terminal double bond in allyl alcohol is also more accessible than the >C=C< cyclic bond in cyclohexenyl and even more so than the >C=N− bond shielded on both sides in 4-(propylideneamino)benzoic acid.

Thus, the active sites in Pd/ND catalysts are Pd^0 nanoparticles. The hydrogenation reaction rate depends on electron density at the reaction site of the reduced substrate, which is apparently explained by the formation of chemisorbed hydrogen with a partial positive charge on the surface of palladium.
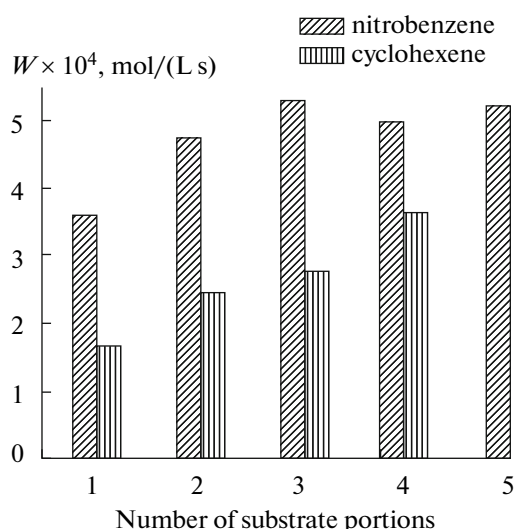
$W \times 10^4$, mol/(L s)

Fig. 4. Stability of Pd/ND in the hydrogenation of nitrobenzene and cyclohexene upon catalyst activation for 10 min.

Base and Precious Metals, Moscow) for conducting the XPS analysis of the catalyst samples.

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