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Pt- and Pd-Containing Nanodiamonds in Hydrogenation and Hydroamination Reactions[1]

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Abstract—The catalytic activity of platinum- and palladium-containing nanodiamonds has been investigated in liquid-phase nitrobenzene, allyl alcohol, and cyclohexene hydrogenation and propanal hydroamination with 4-aminobenzoic acid as model reactions. The catalysts suggested are significantly more active than commercial Pd/C. The catalysts with a low metal weight content are the most effective in liquid phase catalytic hydrogenation.

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In recent years, special attention has been given to obtaining catalysts based on various carbon nanomaterials: fullerenes [1, 2], fullerene black [1, 2], carbon nanotubes and nanofibers [1, 3, 4], nanodiamonds (NDs) [5–9], etc., which, owing to their structure, show high activity, selectivity, and stability [1]. Earlier [3, 4], we demonstrated that the nature and size of the metal sites and their accessibility to the substrate molecules are determined by the nature of the support.

Nanodiamonds are a carbon nanostructure with a diamond-type crystal lattice. Usually, the size of nanocrystals is 1 to 10 nm. The surface of ND crystals is always defective, and its structure depends on the ND production and purification procedure [10–13]. The surface carbon atoms in ND have dangling bonds, which are favorable for generation of uniform metal sites and ensure the maximum increase in the catalytically active surface area, which is necessary for adsorption of reactants, for the reaction itself, and for product desorption. The "righter" the configuration of the metal sites and the higher their uniformity, the higher the selectivity of the catalyst. We have shown [14, 15] for the first time that use of detonation NDs as supports for platinum group metals makes it possible to obtain platinum and palladium clusters with a characteristic diameter of 5 nm and a characteristic thickness of 0.4 to 1.2 nm.

In the present work, we consider the possibility of employing the ND-based catalysts in model liquid-phase reactions, namely, nitrobenzene, allyl alcohol, and cyclohexene hydrogenation and propanal hydroamination with 4-aminobenzoic acid, which are of practical interest to the pharmaceutical industry.

EXPERIMENTAL

Nanodiamonds containing Pd or Pt were synthesized according to a patented method [12]. The detonation NDs had a specific surface area of 307–314 $m^2 g^{-1}$ (the average size of the crystalline diamond core of the ND particles was ~4 nm). The total percentage of non-carbon admixtures in the NDs was no higher than 0.5 wt %. Samples of the Pd- and Pt-containing NDs were combined with active carbon (180 mg of catalyst + 820 mg of carbon), so the total weight was of the sample was 1 g.

The proportion of the catalytically active metal in the Pt/ND and Pd/ND samples was determined by electron probe X-ray microanalysis; the total specific surface area, by the BET method. The relative error in the determination of the platinum and palladium contents of the catalyst was no larger than ±10%. Electron probe X-ray microanalysis was carried out on a VEGA TS 5130MM fully PC-controlled scanning electron microscope (CamScanMV2300)TP1PT) equipped with secondary electron and backscatter electron detectors and an energy dispersive X-ray microanalyzer with an INCA Energy2 semiconducting Si(Li) detector. The results of electron probe X-ray microanalysis were calculated using the INCA Energy 200 program, which was followed by recalculation of the resulting data using the TP3PT program package, developed at the Institute of Experimental Mineralogy, Russian Academy of Sciences. The analysis was carried out at an accelerating voltage of 20 kV. The absorbed electron current on the standard cobalt sample was 516–565 pA, and that on the samples examined was 540–620 pA. The size of the electron probe on the sample surface was 157–200 nm. The amount of titanium and chlorine impurities was mo larger than

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[1] This article was translated by the authors.

0.3 and 0.1 wt %, respectively. The ash content of the initial BDs did not exceed 2 wt %.

The specific surface area of palladium and platinum (S_M) was calculated as

$$S_M = [S_\Sigma - S_{ND}m_{ND}(1 - k_1k_2)]/m_M,$$

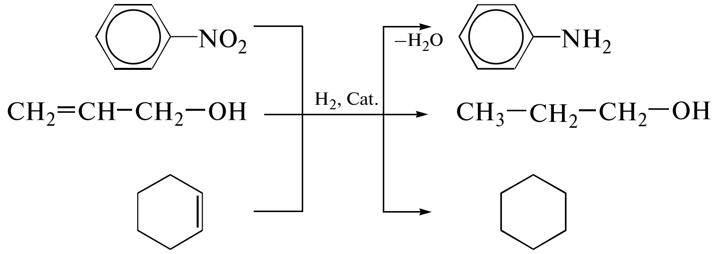
where m_{ND} is the ND content of the catalyst (in grams per gram of catalyst), m_M is the Pd or Pt content of the catalyst (in grams per gram of catalyst), S_{ND} is the specific surface area of ND determined by extrapolation to zero Pd or Pt content, S_Σ is the total specific surface area of the catalyst (ND + metal), k_1 is the constant accounting for the decrease in the ND surface area at the metal cluster–ND contact places, and k_2 is the constant that accounts for the fact that part of the Pd or Pt particles is not located on the ND surface, forming separate clusters. In previous studies [14, 15] it was found that 20–30% of the catalytic metal particles of the total metal weight form separate clusters. The value of k_2 is 0.7–0.8. The value of k_1 for an average metal cluster thickness of 0.8–1.1 nm can be defined using the formula

$$k_1 = \frac{m_M}{m_{ND}}\frac{\rho_{ND}}{\rho_M},$$

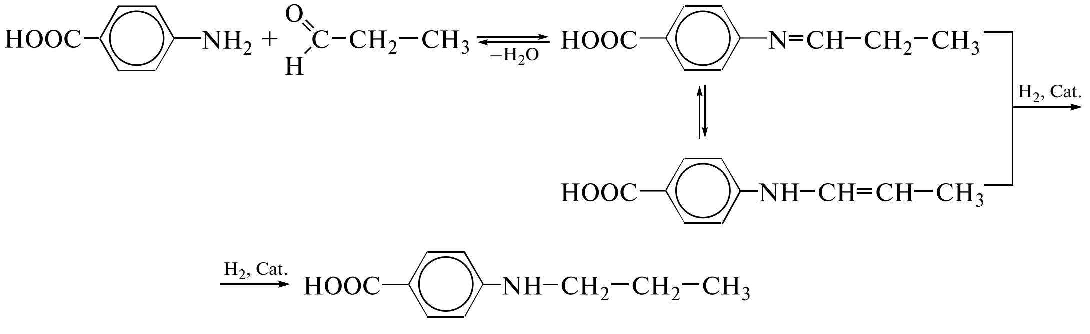
where ρ_{ND} is the density of diamond and ρ_M is the density of the metal. The following values were used in the calculations: ρ_{ND} = 3.5 g/cm^3, ρ_{Pd} = 12.02 g/cm^3, ρ_{Pt} = 21.45 g/cm^3, S_{ND} = 312 m^2/g (for ND with palladium), and S_{ND} = 313 m^2/g (for ND with platinum). The S_M values are presented in Table 1.

The hydrogenation reaction was performed as follow (Scheme 1): 30 mg of a catalyst and 10 mg of $NaBH_4$ were placed under a solvent layer (10 mL of ethanol) in a reactor, and the catalyst was activated for 10 min. Next, 1 mmol of a substrate (nitrobenzene, allyl alcohol, or cyclohexene) was introduced under flowing hydrogen. The reaction temperature was 318 K, and the hydrogen pressure was 0.1 MPa.

The hydroamination of propanal with 4-aminobenzoic acid (Scheme 2) was performed as follow: 30 mg of a catalyst and 10 mg of $NaBH_4$ were placed under a solvent layer (5 mL of ethanol) in a reactor, and the catalyst was activated for 10 min. Next, a solution of 4-aminobenzoic acid (0.274 g, 2 mmol) and propanal (0.15 mL, 2 mmol) in 20 mL of ethanol were introduced. The reaction mixture was purged with hydrogen, and the process was carried out under the above conditions.



Scheme 1.



Scheme 2.

The reaction rate was measured as hydrogen uptake using the volumetric method. The catalytic activity of the samples was evaluated in terms of the turnover number of the catalyst (TON, min^{-1}), i.e., the number of moles of the substrate converted per mole of metal per minute. The efficiency of the ND-based catalysts was compared with the efficiency of the commercial Pd/C catalyst (1 wt % Pd, S_Σ = 14 m^2/g).

Under the conditions examined, both reactions were zeroth-order with respect to the substrate and first-order with respect to the catalyst and hydrogen.

The hydrogenation and hydroamination products were analyzed on a Model 3700 commercial chromatograph with a flame-ionization detector using a glass column (diameter of 3 mm, length of 2000 mm) packed with Lucopren G–1000 (5%) on Chromaton

Table 1. Characteristics of the Pd/ND and Pt/ND catalysts and the rates of nitrobenzene hydrogenation over them

Metal content, wt %	Parameter			
	S_Σ, m^2/g	S_M, m^2/g	$W \times 10^4$, mol L^{-1} s^{-1}	TON, min^{-1}
Pd				
3	305	140 ± 70	3.2	127 ± 13
6	299	160 ± 40	4.6	90 ± 9
9	293	165 ± 40	6.3	83 ± 9
12	281	120 ± 40	7.5	74 ± 8
15	263	50 ± 20	8.0	65 ± 6
Pt				
5	311	324 ± 60	0.7	29 ± 3
10	307	304 ± 40	0.6	12 ± 1
15	295	244 ± 40	3.1	42 ± 5
20	288	240 ± 40	3.0	32 ± 3
25	277	220 ± 40	3.0	26 ± 3

Table 2. Activity of the 10 wt % Pd/ND catalyst in the hydrogenation of some organic compounds

Substrate	Parameter	
	$W \times 10^4$, mol L^{-1} s^{-1}	TON, min^{-1}
Nitrobenzene	5.2	60 ± 6
Allyl alcohol	3.8	45 ± 5
Cyclohexene	2.9	35 ± 4
4-(Propylidenamino)benzoic acid	0.2	5 ± 1

N-AW-DMCS. The carrier gas was argon; injection port temperature, 200°C; oven temperature, 230°C; carrier gas flow rate, 1.60 ± 0.02 L h^{-1}; sample volume, 0.1–0.5 μL.

RESULTS AND DISCUSSION

The platinum- and palladium–containing NDs with different weigh percentages of supported metal had a total specific surface area of 263 to 311 m^2/g and S_M = 50–324 m^2/g (Table 1). Experimental data on nitrobenzene hydrogenation in the presence of Pd/ND and Pt/ND (Table 1) show that, every time the metal content of the Pd/ND catalyst is increased by 3 wt %, the reaction rate (W) increases by a factor of 1.4–1.1. For the Pt/ND samples with a platinum content of 5 and 10 wt % and 15–25 wt %, the reaction rate has similar values. For the 15 wt % Pt/ND catalyst, W is 5 times higher than for the samples containing 5 and 10 wt % Pt (Table 1).

A comparison of the TON values for nitrobenzene hydrogenation shows that the activity of the catalyst decreases as the metal (Pt or Pd) content is increased (Table 1). This finding points to the inefficiency of the metal-rich samples. The TON value for commercial Pd/C under the same conditions is 2.2 min^{-1}.

A number of substrates, namely, nitrobenzene, allyl alcohol, cyclohexene, and 4-(propylydenamino)benzoic acid (product of propanal and 4-aminobenzoic acid condensation, Scheme 2), were studied in hydrogenation hydrogenated over 10 wt % Pd/ND. According to GLC data, the substrates underwent total conversion without yielding any by-products.

The choice of substrates was dictated by their practical significance and by interest in the mechanisms of reduction of their functional groups (–NO$_2$, >C=C<, >C=N–), which differ in their nature and occupy different positions.

Nitrobenzene hydrogenation proceeds most readily: the reaction rate is 1.4 and 1.8 times higher than in the case of allyl alcohol and cyclohexene, respectively, and 26 times higher than the hydrogenation rate of 4-(propylydenamino)benzoic acid (Table 2). This may be due to the higher steric accessibility and higher electronegativity of the NO$_2$ group, which is favorable provided that activated hydrogen bears a positive charge [16]. The terminal double bond >C=C< in allyl alcohol is also more accessible than the inner double bond in cyclohexene. The low rate of hydrogenation of 4-(propylydenamino)benzoic acid is due to the >C=N– bond being difficult to access because of steric effects.

The results obtained can also be explained in terms of the significant difference between the mechanisms of –NO$_2$, >C=C<, and >C=N– hydrogenation.

In the hydroamination reaction (Scheme 2) over the commercial catalyst Pd/C under similar conditions, TON = 0.3 min^{-1}, almost 17 times smaller than the TON value for Pd/ND.

Thus, the Pt- and Pd-containing NDs can be used in the hydrogenation of unsaturated and functionalized organic compounds. The most effective catalysts for liquid-phase hydrogenation are Pd/ND and Pt/ND with a relatively low weight percentage of metal.

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