

Reaction Kinetics of Nitrobenzene Hydrogenation on a Palladium Catalyst Supported on Nanodiamonds

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Abstract—The kinetics of nitrobenzene hydrogenation on a palladium triphenylphosphine catalyst supported on nanodiamonds was studied. It was found that the reaction is of first order with respect to the catalyst and hydrogen and of zero order with respect to nitrobenzene. The apparent constant and activation energy of the reaction were calculated. A probable reaction mechanism was proposed. The effects of the triphenylphosphine-to-palladium ratio and the nature of the solvent and an aromatic nitro compound on the activity of the test catalyst were demonstrated.

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INTRODUCTION

The development of versatile catalysts for the selective conversions of individual compounds or groups of compounds is an important problem concerning catalytic processes in organic synthesis [1]. Previously [2], the effect of the structure of various carbon supports (coal and carbon fiber) on the activity, stability, and selectivity of palladium catalysts in the reduction reactions of aromatic compounds was studied. These catalysts allow one to perform highly efficient and environmentally appropriate processes for the reduction of aromatic nitro compounds to corresponding amines with molecular hydrogen. Thus, it was found [3, 4] that a palladium triphenylphosphine catalyst supported on nanodiamonds noticeably increased the rate of hydrogenation of ethyl *para*-nitrobenzoate and provided an opportunity to obtain anesthetin of pharmacopoeial grade in a quantitative yield. The process occurred in a single step under mild conditions without by-products. Moreover, the catalyst allowed one to perform 50 hydrogenation cycles with the subsequent regeneration for further use.

Thus, the use of nanodiamonds as a catalyst support for the hydrogenation reactions of nitro compounds was found to be promising because the catalyst activity was higher than that of analogous catalysts with carbon supports by a factor of ~2 [2, 5].

The kinetics of hydrogenation of nitro compounds on palladium catalysts supported on coal has been studied [5–9]. Klyuev [5] found that the reaction of nitrobenzene hydrogenation was first order with respect to the catalyst and hydrogen and pseudo-zero order with respect to nitrobenzene. We failed to find published data on the kinetics of this reaction with the use of other carbon matrices as supports. It seems pertinent

to study this reaction in more detail because catalysts supported on nanodiamonds exhibit a number of advantages, and they are very promising for use.

This work was devoted to a formal kinetic study of the reaction of nitrobenzene reduction with molecular hydrogen, which was chosen as a model reaction, in the presence of a palladium catalyst supported on nanodiamonds.

Detonation nanodiamond, which was separated from a diamond–carbon mixture and purified to remove various impurities in accordance with a previously developed technology [10, 11], was used as a support for the catalyst. The nanodiamond thus prepared was characterized by a small particle size and homogeneity with a stable particle size of 3–6 nm and a specific surface area of 250–350 m²/g. Moreover, it did not undergo graphitization during long-term storage and use, and it was suited to the requirements of international standards in terms of quality (Tajirinu Trading Co., Japan).

EXPERIMENTAL

The preparation of the catalyst and nitrobenzene hydrogenation were performed in a batch system at a constant pressure. The catalyst and other reactants were placed in a thermostated 50-ml glass reactor with a magnetic stirrer; the reactor was tightly connected to a thermostated burette at atmospheric pressure. With the use of a three-way valve in the burette, the reactor was initially purged with argon and then with hydrogen. The uptake of hydrogen in the course of the reaction was monitored by measuring changes in the volume of the liquid in the burette. Nitrobenzene was introduced into the reactor in a flow of argon; thereafter, the reactor

Table 1. Effect of the P/Pd ratio on the rate of nitrobenzene hydrogenation (w_a)

| P/Pd, mol/mol | 0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.8 | 1.0 |
|--|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| $w_a, 1 \text{ H}_2 (\text{g Pd})^{-1} \text{ min}^{-1}$ | 3.8 ± 0.2 | 4.3 ± 0.3 | 5.4 ± 0.2 | 6.1 ± 0.3 | 7.6 ± 0.3 | 5.2 ± 0.2 | 4.4 ± 0.2 | 4.1 ± 0.2 |

was purged with hydrogen (5 min) and stirring was begun. It was found that the reaction did not proceed without stirring.

To prepare the catalyst, 42.22 mg of palladium acetate $\text{Pd}(\text{OAc})_2$ and 19.93 mg of triphenylphosphine PPh_3 were loaded in the reactor, and 20 ml of acetone was added; the contents were stirred in a flow of hydrogen until the complete dissolution of the reactants. Next, 1 g of nanodiamonds was also added in a flow of argon, and the contents were stirred for 5 min. Then, the reaction system was purged with hydrogen for 5 min without stirring. The subsequent reduction was performed at 40°C with stirring for 2 h. We found by special experiments that this time was sufficient for the reduction of palladium acetate to palladium metal.

The resulting catalyst was filtered, dried, and kept at room temperature in an inert atmosphere.

The synthesis of palladium acetate was performed in accordance with a published procedure [12].

The amounts of components for the preparation of the palladium catalyst supported on nanodiamonds were calculated based on the fact that the palladium content should be ~2 wt %. This palladium content would ensure the most rational consumption of palladium and a hydrogenation rate appropriate for kinetic studies.

In the study of the effect of the partial pressure of hydrogen on the rate of hydrogenation, the fact that the gas atmosphere composition in the batch system continuously changed because of hydrogen uptake was taken into account. In view of this, the measurements were performed at low degrees of conversion so that the volume of consumed hydrogen was no higher than 10% of the total volume of the system.

Blank experiments were performed to adequately evaluate the rate of reaction and to detect side processes. It was found that the reaction of nitrobenzene hydrogenation did not occur in the absence of the catalyst and the support (nanodiamond) did not absorb hydrogen.

All of the experiments were performed under identical conditions (unless otherwise specified): reaction temperature, 40°C; atmospheric pressure; solvent, ethanol (10 ml); catalyst weight, 5 mg; nitrobenzene amount, 0.3 ml; nitrobenzene concentration, 0.29 mol/l; palladium content, ~2%; and P/Pd ratio, 0.4.

The reaction was monitored by measuring changes in the volume of hydrogen in the measuring system at regular time intervals. The termination of hydrogen uptake indicated the completion of the reaction.

All of the measurements were performed at rates of hydrogen uptake lower than 3 ml/min with stirring at 400 rpm in order to prevent diffusion inhibition.

RESULTS AND DISCUSSION

It is well known that, in the preparation of supported palladium catalysts, palladium atoms migrate on the support surface to result in the formation of large palladium clusters [13]. As a consequence, a decrease in the activity of these catalysts was observed. Previously [3], we found that triphenylphosphine can stabilize palladium atoms on support surfaces. In this context, we studied the effect of the triphenylphosphine/palladium acetate ratio (henceforth referred to as P/Pd) on the catalytic activity of palladium catalysts supported on nanodiamonds. Table 1 summarizes the results.

Table 1 indicates that the maximum rate of nitrobenzene hydrogenation was observed in the presence of a catalyst with the ratio $\text{P/Pd} = 0.4$. It is likely that the most stable palladium clusters with phosphorus-containing ligands were formed in this case. Previously [3, 14], it was found that cluster complexes from the $\text{Pd}_5(\text{PPh}_3)_2$ – $\text{Pd}_8(\text{PPh}_3)$ series were formed on the deposition of palladium onto carbon supports in the presence of triphenylphosphine followed by reduction with hydrogen. In these complexes, triphenylphosphine molecules serve to stabilize palladium particles with a certain size, which exhibit the highest catalytic activity. This allows one to increase considerably the rate of hydrogenation and the yield of the desired product and ensures a long lifetime of the catalyst without a noticeable loss of its activity.

It is likely that larger palladium clusters with phosphorus-containing ligands were formed at the ratio $\text{P/Pd} < 0.4$. As a result of this, the number of catalytic centers decreased to cause a decrease in the catalyst activity. A decrease in the catalyst activity was also observed at the ratio $\text{P/Pd} > 0.4$. This was due to the blocking of palladium by phosphorus-containing ligands; as a consequence, the nitrobenzene access to palladium was hindered. It was found experimentally that the activity of the catalytic system was equal to zero at $\text{P/Pd} = 5.0$.

In the absence of triphenylphosphine, the resulting palladium metal can also reduce nitrobenzene. However, it is less active in this reaction than the palladium clusters prepared in the presence of triphenylphosphine; evidently, this is due to the above factors (migration on the support surface).

Thus, $\text{P/Pd} = 0.4$ is the optimum P/Pd ratio for the preparation of palladium catalysts supported on nano-

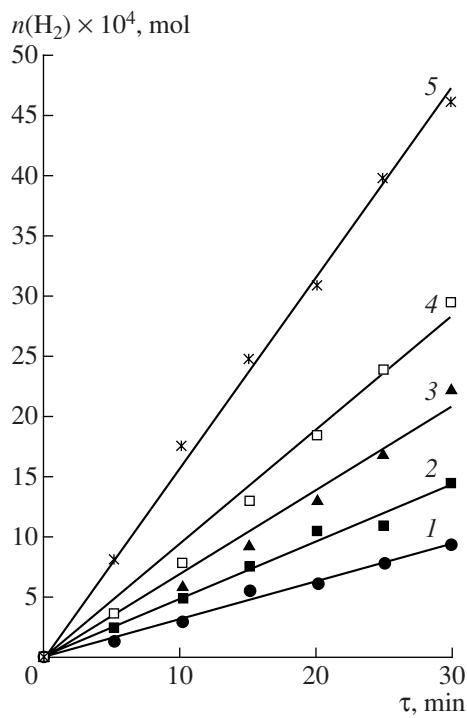


Fig. 1. Dependence of the amount of consumed hydrogen on the duration of nitrobenzene reduction (τ) at the following catalyst amounts: (1) 5, (2) 7, (3) 10, (4) 12, and (5) 20 mg.

diamonds. This ratio was used in the preparation of catalysts for all of the subsequent kinetic studies.

As an example, Fig. 1 shows the dependence of the amount of absorbed hydrogen on the duration of nitrobenzene reduction at various catalyst amounts. The rectilinear shape of the kinetic curves allowed us to characterize the process of reduction by the rate determined at this portion (initial rate) and to study the dependence of the initial rate on various parameters.

Thus, we studied the effects of the catalyst and nitrobenzene amounts, the partial pressure of hydrogen, and temperature. The order of the reaction with respect to all parameters was determined by a differential method.

Figure 2 shows the dependence of $\log w$ on (a) $\log C_{\text{NB}}$, (b) $\log P_{\text{H}_2}$, and (c) $\log m_{\text{Cat}}$, where w is the rate of reaction, C_{NB} is the concentration of nitrobenzene (mol/l), P_{H_2} is the partial pressure of hydrogen (Torr), and m_{Cat} is the weight of the catalyst (mg). Figure 2 indicates that the reaction was of first order with respect to hydrogen and the catalyst and zero order with respect to nitrobenzene under the test conditions.

The average apparent rate constant of the reaction was $0.126 \text{ (g Pd)}^{-1} \text{ min}^{-1}$, as determined graphically from Figs. 2b and 2c.

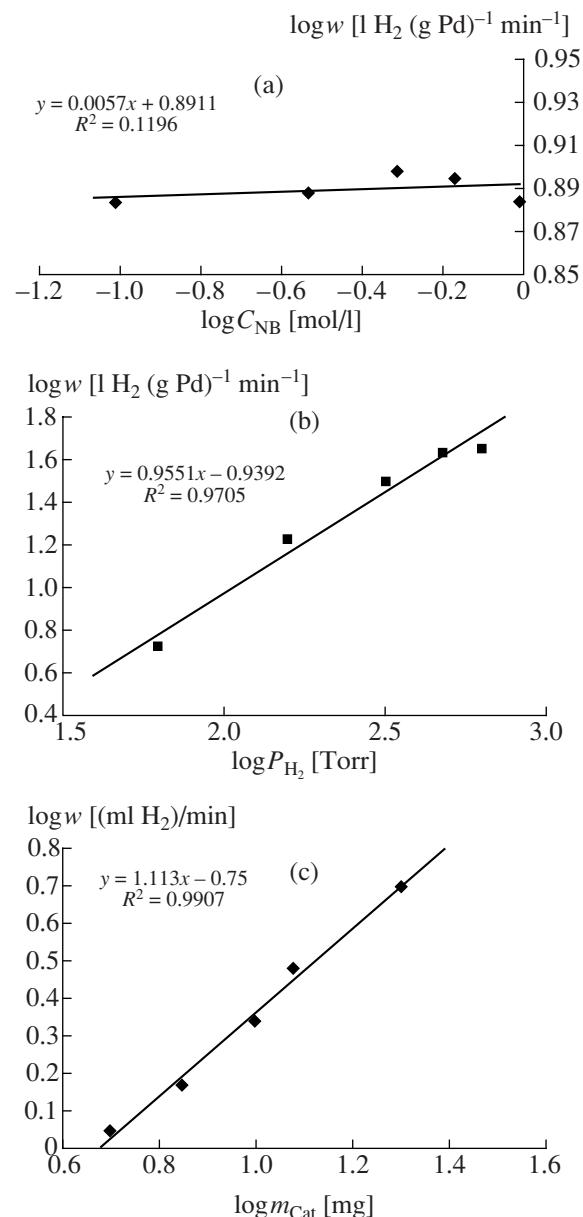


Fig. 2. Dependence of $\log w$ for nitrobenzene hydrogenation on (a) $\log C_{\text{NB}}$, (b) $\log P_{\text{H}_2}$, and (c) $\log m_{\text{Cat}}$.

Figure 3 demonstrates the effect of temperature on the rate of the reaction.

It can be seen in Fig. 3 that, in the given temperature region, a linear Arrhenius plot was observed for the reaction rate of nitrobenzene hydrogenation with molecular hydrogen in the presence of the palladium catalyst supported on nanodiamonds. We found that the rate of reaction increased with temperature. The apparent activation energy derived from experimental data was 12 kJ/mol.

Note that the experimentally found orders of the reaction with respect to all of the reactants are consis-

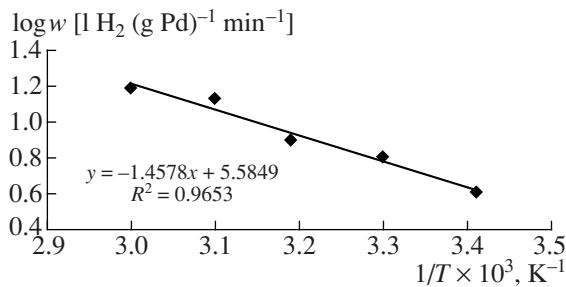
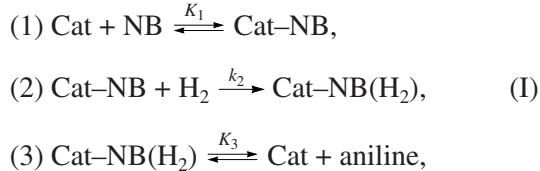


Fig. 3. Arrhenius plot for the temperature dependence of the reaction rate of nitrobenzene hydrogenation.

tent with well-known data for palladium catalysts on other supports [5–9].

Based on the kinetic study and in accordance with a quasi-steady-state approximation (all steps before and after the rate-limiting step are considered equilibrium), the following reaction mechanism can be proposed:



where Cat is the catalyst; NB is nitrobenzene; H_2 is hydrogen; K_1 and K_3 are the equilibrium constants of steps 1 and 3, respectively; and k_2 is the rate constant of rate-limiting step 2.

The expressions for the equilibrium constants K_1 and K_3 are as follows:

$$K_1 = \frac{C_{\text{Cat-NB}}}{C_{\text{Cat}} C_{\text{NB}}}, \quad (1)$$

where $C_{\text{Cat-NB}}$ and C_{Cat} are the concentrations of intermediate catalyst species and C_{NB} is the nitrobenzene concentration;

$$K_3 = \frac{C_{\text{Cat}} C_{\text{aniline}}}{C_{\text{Cat-NB}(\text{H}_2)}}, \quad (2)$$

where $C_{\text{Cat-NB}(\text{H}_2)}$ is the concentration of intermediate catalyst species and C_{aniline} is the aniline concentration.

The total catalyst concentration is the sum of the concentrations of all intermediate species:

$$C_{\text{Cat}}^\circ = C_{\text{Cat}} + C_{\text{Cat-NB}} + C_{\text{Cat-NB}(\text{H}_2)}. \quad (3)$$

Expressing C_{Cat} from Eq. (1) and $C_{\text{Cat-NB}(\text{H}_2)}$ from Eq. (2) and substituting them in Eq. (3), we obtain

$$\frac{C_{\text{Cat-NB}}}{K_1 C_{\text{NB}}} + C_{\text{Cat-NB}} + \frac{C_{\text{Cat-NB}} C_{\text{aniline}}}{K_3 K_1 C_{\text{NB}}} = C_{\text{Cat}}^\circ. \quad (4)$$

From Eq. (4), we express $C_{\text{Cat-NB}}$ as follows:

$$C_{\text{Cat-NB}} = \frac{C_{\text{Cat}}^\circ K_1 C_{\text{NB}}}{1 + K_1 C_{\text{NB}} + \frac{C_{\text{aniline}}}{K_3}}. \quad (5)$$

With consideration for the fact that step 2 (hydrogen activation step) in reaction scheme (I) is a rate-limiting step, we obtain the following rate equation:

$$w = k_2 C_{\text{Cat-NB}} C_{\text{H}_2}. \quad (6)$$

Substituting (5) into Eq. (6), we obtain

$$w = \frac{k_2 K_1 C_{\text{NB}} C_{\text{Cat}} C_{\text{H}_2}}{1 + K_1 C_{\text{NB}} + \frac{C_{\text{aniline}}}{K_3}}. \quad (7)$$

Because nitrobenzene is rapidly adsorbed on the catalyst surface (K_1) and the resulting reaction product (aniline) rapidly passes into solution from the catalyst surface (K_3), we have high values of the equilibrium constants K_1 and K_3 . At the high values of K_1 and K_3 ,

$$K_1 C_{\text{NB}} \geq 1 + \frac{C_{\text{aniline}}}{K_3}, \quad (8)$$

the value of $1 + \frac{C_{\text{aniline}}}{K_3}$ in Eq. (7) can be ignored and rate Eq. (7) changed to the following rate equation, which was observed experimentally:

$$w = k C_{\text{Cat}} C_{\text{H}_2}, \quad (9)$$

where w is the rate of reaction, k is the rate constant, C_{Cat} is the catalyst concentration, and C_{H_2} is the hydrogen concentration.

Based on these data, the following conclusions can be made: Zero order with respect to nitrobenzene suggests the rapid adsorption of nitrobenzene, and equilibrium 1 in scheme (I) is almost completely shifted to the formation of the Cat–NB complex. Equilibrium 1 and first order with respect to hydrogen suggest that step 2 (interaction of the Cat–NB complex with hydrogen) is a rate-limiting step. Then, the direct reduction of nitrobenzene to aniline with activated hydrogen occurs by a complex multistep mechanism [5]. The resulting reaction product is almost not adsorbed on the catalyst surface, and it rapidly goes into solution; therefore, it does not have an inhibiting effect on the process.

The shapes of the kinetic curves shown in Fig. 1 and relationships in Fig. 2 suggest the absence of an effect of aniline in the course of its formation. Moreover, we found that the introduction of an additional amount of aniline into the reaction medium had no effect on the rate of the reaction.

Thus, the reaction scheme proposed adequately describes the processes occurring in the course of nitrobenzene hydrogenation in the presence of a catalyst based on nanodiamonds.

We studied the effect of the nature of the solvent on the rate of nitrobenzene hydrogenation. Table 2 summarizes the results of this study.

In Table 2, it can be seen that the rate of hydrogenation increased with the molecular weight of aliphatic alcohols. The highest rate of hydrogenation was reached with the use of butanol as the solvent. This was due to the fact that the boiling temperature of the solvent increased and the saturation vapor pressure decreased with increasing molecular weight of the solvent and the concentration of hydrogen increased; this favored an increase in the reaction rate. Figure 4 shows the logarithmic plot of the rate of reaction in methanol, ethanol, and butanol on the partial pressure of hydrogen calculated using published data [15] for the vapor pressures of these solvents at 40°C. It can be seen that, within the limits of the experimental errors, a nearly first-order rate law with respect to P_{H_2} was observed; this allowed us to substantiate the above conclusions. It is likely that the low rates of nitrobenzene hydrogenation in benzene, benzyl alcohol, and amyl alcohol solutions are explained by the adsorption of the solvents competing with the adsorption of nitrobenzene. Because of this, the active palladium species of the catalyst becomes inaccessible to nitrobenzene.

In addition to nitrobenzene, other aromatic nitro compounds were hydrogenated (Table 3).

In Table 3, it can be seen that, in general, the rate of hydrogenation of substituted aromatic nitro compounds is lower than the rate of hydrogenation of nitrobenzene. This may be explained by the electronic and steric effects of substituents on different steps of the multistep reduction of the nitro group [5]. The introduction of electron-acceptor substituents into the aromatic ring accelerates electron-transfer steps and decelerates protonation steps. The protonation steps become rate-limiting steps, and a further increase in the electron-accepting power of the substituent will decelerate the overall rate of hydrogenation. On the contrary, electron-donor substituents accelerate the protonation steps and decelerate the electron-transfer steps, which become rate-limiting steps. Therefore, an increase in the electron-accepting power of the substituent will also slow down hydrogenation.

Table 3 also indicates that the selective reduction of the nitro group to the amino group occurred in the presence of palladium catalysts supported on nanodiamonds without the formation of any by-products or intermediate products. In this case, the corresponding aromatic amines were formed in quantitative yields (97–99%, as found by gas–liquid chromatography). This was also evidenced by the stoichiometric absorption of hydrogen in the hydrogenation of aromatic compounds with one and two nitro groups. Thus, the corresponding amount for dinitrophenol was precisely two times larger than that for nitrophenol taken in an equal molar amount.

Table 2. Effect of solvents on the reaction rate of nitrobenzene hydrogenation (w_a) on the palladium catalyst supported on nanodiamonds

| Solvent | $w_a, 1 \text{ H}_2 (\text{g Pd})^{-1} \text{ min}^{-1}$ |
|----------------|--|
| Benzene | 0.3 ± 0.1 |
| Benzyl alcohol | 0.9 ± 0.3 |
| Amyl alcohol | 1.7 ± 0.2 |
| Methanol | 6.9 ± 0.2 |
| Ethanol | 7.7 ± 0.3 |
| Butanol | 11.6 ± 0.2 |

Table 3. Hydrogenation of aromatic nitro compounds

| Compound | $w_a, 1 \text{ H}_2 (\text{g Pd})^{-1} \text{ min}^{-1}$ | Amine yield, % |
|----------------------------------|--|----------------|
| γ -Dinitrophenol | 3.2 ± 0.2 | 98 |
| <i>para</i> -Nitrobenzoic acid | 3.5 ± 0.2 | 99 |
| Ludigol | 3.9 ± 0.3 | 97 |
| α -Dinitrophenol | 4.5 ± 0.1 | 99 |
| <i>ortho</i> -Nitrophenol | 4.6 ± 0.1 | 99 |
| <i>para</i> -Nitrochlorobenzene | 4.7 ± 0.1 | 98 |
| Ethyl <i>para</i> -nitrobenzoate | 4.8 ± 0.2 | 99 |
| <i>ortho</i> -Nitrochlorobenzene | 5.0 ± 0.3 | 98 |
| Nitrobenzene | 7.3 ± 0.3 | 99 |

Thus, we found that nanodiamonds are an effective support for hydrogenation catalysts based on palladium clusters stabilized by triphenylphosphine. The rates of hydrogenation in ethanol were 7.6, 3.73 [5], and $3.74 \text{ l H}_2 (\text{g Pd})^{-1} \text{ min}^{-1}$ [2] on nanodiamonds, carbon, and carbon fiber, respectively. The reaction was of first order with respect to hydrogen and the catalyst, and the reaction rate was independent of the nitrobenzene con-

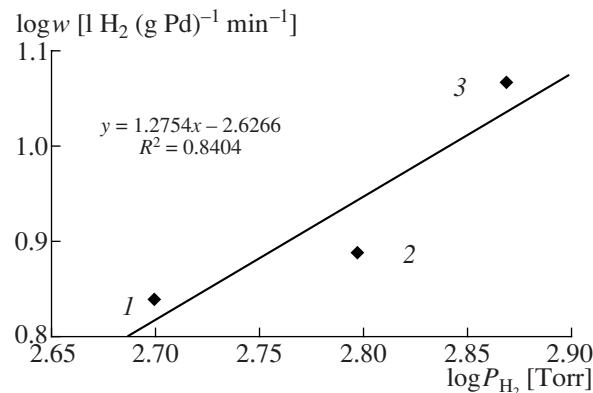


Fig. 4. Dependence of $\log w$ for nitrobenzene hydrogenation on $\log P_{H_2}$ in (1) methanol, (2) ethanol, or (3) butanol.

centration. In principle, the formal kinetics of hydrogenation was identical for traditional catalysts with various carbon matrices. The main distinctive feature of the proposed catalyst is its higher activity and selectivity [3, 4]. The reaction mechanism proposed completely describes the processes occurring in nitrobenzene hydrogenation with molecular hydrogen on a palladium catalyst supported on nanodiamonds.

REFERENCES

1. Chepaikin, E.G. and Khindekel, M.L., *J. Mol. Catal.*, 1978, vol. 4, p. 103.
2. Obraztsova, I.I., Efimov, O.A., Simenyuk, G.Yu., and Min'kov, A.I., *Trudy Mezhdunarodnoi nauchno-prakticheskoi konf. "Khimiya—XXI vek: Novye tekhnologii, novye produkty"* ("Chemistry of the 21st Century: New Technologies and New Products," Proc. Int. Scientific and Practical Conf.), Kemerovo, 2000, p. 62.
3. RF Patent 2203885, 2003.
4. Obraztsova, I.I. and Efimov, O.A., *Zh. Prikl. Khim.*, 2004, vol. 77, no. 3, p. 517.
5. Klyuev, M.V., *Zh. Org. Khim.*, 1987, vol. 23, no. 3, p. 581.
6. Nasibulin, A.A. and Klyuev, M.V., *Neftekhimiya*, 1998, vol. 38, no. 4, p. 277.
7. Budaeva, A.I., Kurunina, G.M., and Zorina, G.I., *Trudy 8 Mezhvuzovskoi nauchno-prakticheskoi konferentsii molodykh uchenykh i studentov* (Proc. 8th Int. Conf. for Young Scientists and Students), Volgograd, 2003, vol. 2, p. 124.
8. Klyuev, M.V., Tershko, N.V., and Solomonova, S.Yu., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1988, vol. 31, no. 9, p. 36.
9. Nakao, Y. and Fujishige, S., *J. Catal.*, 1981, vol. 68, p. 406.
10. RF Patent 2081821, 1997.
11. Obraztsova, I.I. and Eremenko, A.N., *Zh. Prikl. Khim.*, 2003, vol. 76, no. 3, p. 443.
12. Stephenson, F.A., Morhouse, M., Powell, A.R., Heffer, J.P., and Wilkinson, G., *J. Chem. Soc.*, 1965, vol. 6, p. 3632.
13. Semikolenov, V.A., *Usp. Khim.*, 1992, vol. 61, no. 2, p. 320.
14. Eremenko, N.K., Mednikov, E.G., and Kurasov, S.S., *Usp. Khim.*, 1985, vol. 54, no. 4, p. 671.
15. *Spravochnik khimika* (Chemist's Handbook), Leningrad: Goskhimizdat, 1962.