

Effect of the reduction conditions of the supported palladium precursor on the activity of Pd/C catalysts in hydrogenation of sodium 2,4,6-trinitrobenzoate*

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The study addresses the effect of the reduction conditions of palladium polynuclear hydroxo complexes (PHC) supported on the Sibunit carbon material on the dispersion of the metal particles and the activity of 0.5%Pd/Sibunit catalysts in the selective hydrogenation of sodium 2,4,6-trinitrobenzoate to 1,3,5-triaminobenzene in an aqueous solution (temperature of 323 or 343 K, pressure of 0.5 MPa). The palladium PHC were reduced using the most common methods pertaining to catalyst preparation: liquid-phase reduction with sodium formate and reduction in a hydrogen flow at elevated temperature. It was found that high-temperature reduction in the gas phase gives rise to Pd particles with a markedly lower dispersion compared with the sample obtained under mild liquid-phase reduction conditions. The catalytic activity of the sample containing large Pd particles proved to be higher than the activity of the catalyst obtained by reduction with sodium formate.

Key words: 2,4,6-trinitrobenzoic acid, catalytic hydrogenation, palladium catalyst, reduction.

The supported palladium catalysts have found wide use in organic synthesis processes.^{1–3} Fairly popular among them are catalysts of the "palladium on carbon" type, which are used, in particular, in the catalytic hydrogenation of various organic compounds for the synthesis of dyes, fragrances, pharmaceuticals, and biologically active compounds.^{1–6} Considerable researchers' interest is aroused in both the structures of these catalysts and the physico-chemical aspects of their synthesis.^{6–11} The properties of supported catalysts can be optimized, in particular, by varying the size and morphology of metal particles.^{12,13} This control over the catalyst properties can be accomplished during the catalyst preparation, which consists in the deposition of a precursor of the active component on the support, heat treatment (drying, calcination), and/or reduction.

Previously, we studied in detail^{14–17} the liquid-phase hydrogenation of the sodium salt of 2,4,6-trinitrobenzoic acid (Na-TNBA) in the presence of Pd/C catalysts. This reaction is of interest, first of all, in relation to safe utilization of explosives to obtain valuable chemicals for civil purposes. We were able to optimize the reaction conditions and catalyst composition, which allowed the synthesis of 1,3,5-triaminobenzene (TAB) in a nearly 100% yield.^{15,16} In a study of a series of Pd/C catalysts differing in the dispersion of supported palladium, we found that hydrogenation of Na-TNBA is a structure-sensitive reaction: the turnover frequency (TOF) increased with increasing average size of supported palladium particles.¹⁷ These catalysts were synthesized by deposition of palladium polynuclear hydroxo complexes (PHC) with the composition $\{M_n[Pd(OH)_2]_m\}^{n+}$ (M = Li, Na, K) on the Sibunit carbon material and subsequent reduction with sodium formate. The dispersion of Pd particles was con-

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trolled by varying the nature of M in the reactant forming the PHC and the pH of hydrolysis, *i.e.*, conditions of the initial stages of synthesis of the Pd/C catalyst. Meanwhile, it is of interest whether it is possible to control the particle size of the supported metal and catalytic properties of the resulting Pd/C composite at the final stage of catalyst preparation by selecting conditions of reduction of the (Pd PHC)/C system.

The reduction (activation) step is significant for the use of catalyst in the catalytic hydrogenation and oxidation reactions, because the degree of reduction of supported palladium can vary.¹⁸ The reducing agents used for supported palladium precursors include sodium formate, sodium borohydride, formaldehyde, hydrazine, and gaseous hydrogen.^{5,6,10,13,18,19} The effect of the reduction conditions on the dispersion and catalytic action of supported palladium in various reactions has been addressed in numerous studies.^{8,13,18–21} In particular, it has been shown²¹ that the dispersion of palladium particles in the Pd/C catalysts subjected to reduction with hydrogen (in water under pressure) is 2–5 times higher than that in the samples reduced in sodium formate solutions. The method used to reduce the palladium precursor was found to affect the activity of Pd/C catalysts towards the selective hydrogenation of isophorone. According to another study dealing with the Pd/C catalysts,¹⁹ the reduction of the supported precursor in a sodium formate solution gives rise to highly dispersed palladium particles. The average particle size is more than twice smaller than that in the samples obtained by reduction with hydrogen gas at elevated temperature. In the latter case, increase in the reduction temperature leads to enlargement of the supported palladium particles. The conditions of reduction of palladium precursor and the size of the palladium particles being formed were found to affect the activity and selectivity of the Pd/C catalysts towards liquid-phase hydrogenation of 2,4-dinitrotoluene.

Each reduction method has its own specific features that are to be taken into account in the synthesis of catalysts with specified physicochemical properties. Thus after the reduction of palladium precursor with sodium formate, thorough washing is needed, because the finished catalyst may be contaminated with sodium cations, while in the case of reduction with hydrogen gas, too high temperature of reduction may lead to sintering of palladium particles and their interaction with the carbon support.^{10,19,22,23}

The purpose of this study is to elucidate the effect of the conditions of reduction of the Sibunit-supported palladium PHC on the Pd particle size and the Pd/Sibunit catalyst activity towards hydrogenation of Na-TNBA. The reduction techniques used most widely in the catalyst preparation practice were chosen, namely, liquid-phase reduction with sodium formate and reduction in a hydrogen flow at elevated temperature.

Experimental

Catalysts containing 0.5 wt.% Pd were prepared by hydrolytic precipitation of palladium PHC on the surface of the Sibunit carbon material.^{24–26} This material with a BET specific surface area of 422 m² g⁻¹ and grain size of 50–140 μm was synthesized at the Department of Experimental Technologies of the Institute of Hydrocarbons Processing, Siberian Branch of the Russian Academy of Sciences. The deposition of palladium was carried out as follows. Palladium chloride was dissolved in hydrochloric acid in the Pd to HCl molar ratio of 1 : 2 and the solution was diluted with water to the required concentration. A solution of KHCO₃ was added dropwise to the obtained aqueous solution of H₂PdCl₄ until pH 5 was reached. The resulting brown solution of PHC was mixed with an aqueous suspension of Sibunit. This was accompanied by complete adsorption of the complexes by the support and discoloration of the solution. Then the Sibunit with the supported complexes was separated from the solution by filtration and washed. The reduction of Sibunit-supported palladium PHC was carried out in an HCOONa solution at 363 K for 0.5 h or in a flow of hydrogen gas at 573 K for 1 h.²⁷ The sample obtained after the sodium formate reduction was thoroughly washed with water and stored wet (relative water content of ~50%). This catalyst is designated below as Pd/C-F. The sample obtained upon the reduction with hydrogen is designated as Pd/C-H (Fig. 1).

Methods for catalyst investigation. The palladium content in the catalysts was determined by atomic absorption spectrometry (AAS) on an AA-6300 instrument (Shimadzu) after sample dissolution in a mixture of nitric and perchloric acids. The measured palladium content was the same in both samples (0.5 wt.%).

The palladium dispersion in reduced Pd/C-F and Pd/C-H samples (see Fig. 1) was determined by pulse chemisorption of CO molecules at room temperature using an AutoChem II 2920 chemisorption analyzer (Micromeritics) equipped with a thermal conductivity detector. A mixture containing 10 vol.% CO in helium was injected in pulses at regular intervals into a flow of helium carrier gas. The injection was continued until the detector signal became constant. The metal dispersion was calculated from the CO chemisorption data with the assumption that CO : Pd = 1, relying on published data^{19,22,28} for the Pd/C catalysts synthesized and pretreated under similar conditions. The pretreatment of the Pd/C-F catalyst before the measurements included drying at 393 K in air and subsequent reduction in a flow of 10 vol.% H₂ in argon in the temperature-programmed mode in the temperature range of 303–343 K (heating rate of 10 °C min⁻¹), with the hydrogen consumption profile being recorded. The conditions of formation of metal particles from the Sibunit-supported palladium PHC during the synthesis of the Pd/C-H catalyst were studied using the temperature-programmed reduction (TPR) technique in a flow of 10 vol.% H₂ in argon in the temperature range of 303–573 K (heating rate of 10 °C min⁻¹). The TPR and pulse chemisorption experiments were conducted using special purity gases (not less than 99.999 vol.% purity) and gas mixtures manufactured by the Pure Gases, LLC.

The obtained palladium dispersion (*D*) values in the catalysts were used to calculate the average volume-surface diameter of Pd particles (the particles were assumed to be spherical):^{29,30}

$$\langle d \rangle_{\text{vs}}^{\text{CO}} = 6V_{\text{Pd}}/(a_{\text{Pd}}D), \quad (1)$$

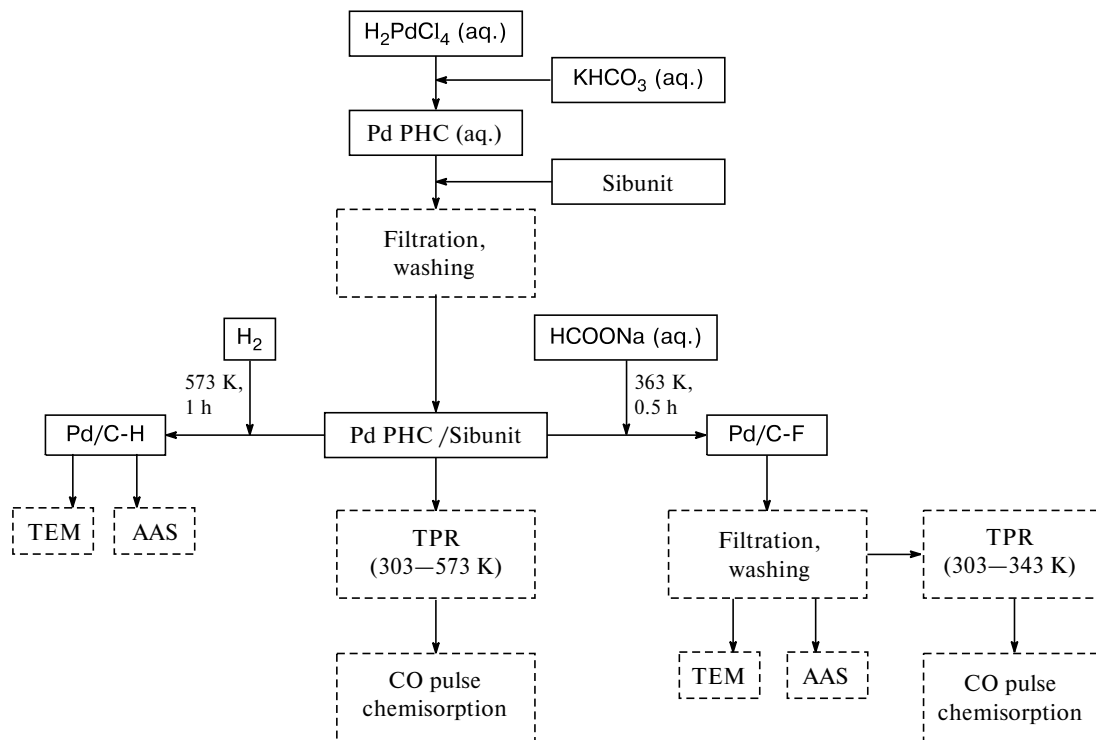


Fig. 1. Block diagram of the preparation and subsequent examination of Pd/C-F and Pd/C-H catalysts: TEM is the transmission electron microscopy, AAS is the atomic absorption spectrometry, TPR is the temperature-programmed reduction.

where V_{Pd} is the atomic volume of the metal phase, which is equal to 0.0147 nm^3 for Pd; and a_{Pd} is the average effective area occupied by one metal atom on the surface, which is 0.0793 nm^2 for Pd.

Transmission electron microscopy (TEM) images were obtained on a JEM-2100 (JEOL) electron microscope with a lattice resolution of 0.14 nm at an accelerating voltage of 200 kV . The samples were prepared as suspensions in ethanol and deposited on copper grids coated by perforated amorphous carbon film, which were then mounted in the electron microscope. The TEM images were analyzed using the DigitalMicrograph program package (Gatan).

The average volume-surface diameter of Pd particles was calculated from the formula^{29,30}

$$\langle d \rangle_{\text{vs}} = \left(\frac{\sum N_i d_i^3}{\sum N_i d_i^2} \right), \quad (2)$$

where N_i is the number of particles with an average diameter of d_i .

Catalytic hydrogenation of Na-TNBA and analysis of the reaction products.^{14–17} An aqueous solution of Na-TNBA was prepared by adding powdered NaHCO_3 (0.59 g) to a gently stirred aqueous suspension of TNBA (2.00 g) up to complete dissolution and the cessation of CO_2 evolution. Hydrogenation of Na-TNBA in the aqueous solution ($2 \text{ wt.}\%$, 100 mL) was carried out with hydrogen gas in the presence of a catalyst (500 mg) in a steel autoclave at a temperature of 323 K or 343 K and a pressure of 0.5 MPa . The reaction mixture was magnetically stirred at 1400 rpm . The completion of the reaction was determined from the volume of hydrogen consumed per unit time.

As the reaction was over (hydrogen was no longer consumed), the autoclave was cooled down and the reaction mixture was sampled with a syringe.

The TOF was calculated from the equation

$$\text{TOF} = r(\text{H}_2)/(nD), \quad (3)$$

where $r(\text{H}_2)$ is the reaction rate (moles of H_2) s^{-1} measured 10 min after the reaction has started, *i.e.*, in the linear segment of the hydrogen consumption curve; n is the amount of supported palladium, moles; D is the dispersion of palladium determined by CO pulse chemisorption or by TEM.

The hydrogenation products were analyzed by ^1H NMR spectroscopy. The spectra were measured on an Avance-400 NMR spectrometer (Bruker). The signal of the residual methyl protons of methanol- d_4 (δ_{H} 3.30 , quintet) was used as the internal standard. The water signal was suppressed by zgpr presaturation pulses (Bruker).

Results and Discussion

Effect of the reduction conditions of supported PHC on the dispersion of the formed palladium particles. The procedure of synthesis of Pd/C catalysts by alkaline hydrolysis of palladium chloride complexes followed by adsorption of the resulting palladium PHC on the carbon support surface has been described in detail previously.^{10,31–33} The formation and the fraction of supported palladium particles exposed are largely determined by the initial conditions of synthesis such as the nature of the alkali metal

Table 1. Average particle size of palladium in the 0.5%Pd/Sibunit catalyst samples and catalytic activity of the samples in hydrogenation of Na-TNBA

Catalyst	$\langle d \rangle_{vs}^{CO}$ ^a	$\langle d \rangle_{vs}$ ^b	$r(H_2)/(\mu\text{mol } H_2) \text{ s}^{-1}$ ^c		TOF/ $(\text{mol } H_2) (\text{mol Pd}_s)^{-1} \text{ s}^{-1}$ ^d	
	nm		323 K	343 K	323 K	343 K
Pd/C-F	7.9	5.9	31.2	38.3	9.4 (6.0)	11.6 (7.3)
Pd/C-H	27.8	7.7	41.0	51.2	43.5 (9.1)	54.2 (11.3)

^a Average volume-surface diameter of Pd particles calculated from the CO pulse chemisorption data by Eq. (1).

^b Average volume-surface diameter of Pd particles calculated from TEM data by Eq.(2).

^c Reaction rate measured 10 min after the start of reaction, *i.e.*, in the linear segment of the hydrogen consumption curve.

^d TOF values were calculated by Eq. (3) and using dispersion values derived from CO chemisorption data. The TOF values calculated using the dispersion values derived from TEM data are given in parentheses.

in the compound involved in PHC formation and pH of hydrolysis.¹⁷ Therefore, in order to identify the effect of the reduction method, the PHC synthesis and adsorption on Sibunit were carried out under identical conditions using KHCO_3 as the alkaline reagent at pH 5. The Sibunit-supported palladium PHC were reduced either in a sodium formate solution at 363 K or in a hydrogen flow at 573 K (see Fig. 1).

As follows from the CO pulse chemisorption data, the dispersion of supported palladium depends on the reduction method. The dispersion of Pd particles is 14% for the Pd/C-F sample (sodium formate reduction) and 4% for the Pd/C-H sample (hydrogen reduction). The obtained dispersion values are in line with the calculated average diameters of the palladium particles ($\langle d \rangle_{vs}^{CO}$): 7.9 nm for Pd/C-F and 27.8 nm for Pd/C-H (Table 1).

The observed difference in the dispersion values may be due not only to the difference between the Pd particle size in the Pd/C-F and Pd/C-H samples, but also to different adsorption behaviors. The chemisorption of CO molecules on Pd particles is known to be structure-sensitive; therefore, in addition to the metal particle size, the mode of CO adsorption (linear *vs.* bridging) also changes, and so does the CO : Pd ratio, which is necessary to calculate the dispersion.^{22,29,30}

In addition, according to TPR data (Fig. 2), the catalyst samples differ in the amount of hydrogen consumed during the synthesis. Despite the fact that the Pd/C-F sample was reduced with sodium formate before the measurements and contained palladium metal particles (according to TEM data), it additionally consumed hydrogen during pretreatment in an autoclave at the reaction temperature, that is, at 323 or 343 K. Indeed, according to TPR data, hydrogen consumption takes place in the 303–343 K range (see Fig. 2, *a*). However, the amount of hydrogen additionally consumed by this sample is relatively low under these conditions ($H_2 : Pd = 0.5$) and is likely to be associated with the reduction of oxidized palladium species formed on the particle surface upon contact of the sample with air. The reduction of supported

palladium PHC with hydrogen involves palladium β -hydride formation³⁴ and subsequent decomposition in the 303–353 K range (see Fig. 2, *b*). However, at higher temperature, intense hydrogen consumption by reduced palladium particles is observed. The consumption of hydrogen in the 353–573 K temperature range in an amount much exceeding the stoichiometric amount, that is, the

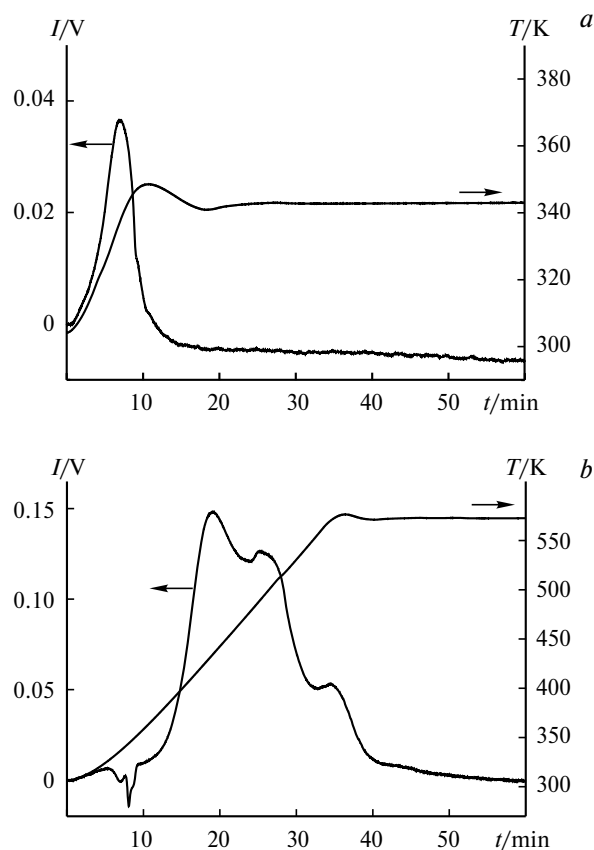


Fig. 2. Hydrogen consumption—evolution profiles recorded during TPR of the Pd/C-F catalyst (*a*) and Sibunit-supported palladium PHC (*b*); I is the thermal conductivity detector signal, T is temperature.

amount needed to reduce the supported complexes, can also affect the adsorption properties of palladium. This excessive consumption of hydrogen may be caused by the formation of large palladium particles during high-temperature reduction, as it is known²⁸ that the amount of hydrogen consumed by palladium particles increases with increasing particle size.

Due to uncertainty in the measurement of dispersion inherent in the chemisorption method, the determined D should be taken as apparent.²² Nevertheless, even though the absolute values of the dispersion determined at a specified CO : Pd ratio are not quite adequate, they correctly reflect the relative particle size, which can be used to compare the catalysts.

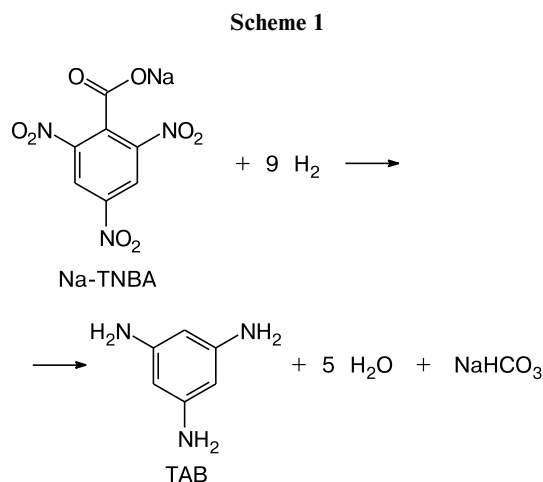
The average Pd particle size was additionally determined using TEM, that is, a direct technique (Fig. 3). This method also has limitations associated with the measurement of sizes of highly dispersed particles, especially when the strong interaction with the support deteriorates the image contrast. Several assumptions have to be made to measure the size of aggregates with a complex shape. The $\langle d \rangle_{\text{vs}}$ values determined by TEM were 5.9 and 7.7 nm for the Pd/C-F and Pd/C-H catalysts, respectively (see Table 1). The considerable difference between the $\langle d \rangle_{\text{vs}}$ and $\langle d \rangle_{\text{vs}}^{\text{CO}}$ values for the sample obtained by high-temperature reduction with hydrogen is consistent with published results¹⁹ and can be attributed to predominance of the bridge-site adsorption of CO on large Pd particles. In this case, the use of the CO : Pd = 1 ratio for the calculation of $\langle d \rangle_{\text{vs}}^{\text{CO}}$ may be improper.

Despite the differences between the absolute values obtained by chemisorption measurements and TEM, the general trend of the influence of the reduction method on the particle size of supported palladium is retained. The catalyst obtained by the high-temperature reduction with hydrogen is characterized by a lower dispersion of supported palladium than the sample obtained under mild conditions by sodium formate reduction. As can be seen from the Pd particle size distribution histograms, the Pd/C-F sample has a relatively narrow size distribution with a maximum in the 3–6 nm range (see Fig. 3, e), whereas the Pd/C-H sample has a higher percentage of large particles (see Fig. 3, f), which are often aggregates of smaller spherical particles. Thus, the reduction in a hydrogen flow at elevated temperature results in sintering of Pd particles, which is consistent with the earlier results for Pd/C systems.^{19,22}

Effect of reduction conditions of the supported PHC on the activity of 0.5%Pd/Sibunit catalysts towards hydrogenation of Na-TNBA. The Pd/C-F and Pd/C-H catalysts differing in the conditions of reduction and dispersion of supported palladium were studied in the hydrogenation of Na-TNBA in an aqueous solution at temperatures of 323 and 343 K and a pressure of 0.5 MPa. The reaction products were identified by ¹H NMR spectroscopy. All

¹H NMR spectra of reaction mixtures (one spectrum is shown in Fig. 4) exhibit an intense singlet with δ_{H} 5.74, which corresponds to TAB aromatic protons.^{14–17} The other signals correspond to intermediate hydrogenation products whose concentrations are very low in all reaction mixtures.

The exhaustive reduction of three nitro groups (*i.e.*, conversion of Na-TNBA to TAB) requires 9 moles of H₂ per mole of Na-TNBA. As can be seen from the hydrogen consumption curves (Fig. 5), the amount of hydrogen consumed during hydrogenation is close to the stoichiometric value. Thus, irrespective of the palladium precursor reduction conditions, Na-TNBA is completely converted during hydrogenation catalyzed by 0.5%Pd/Sibunit with selective formation of TAB at both 323 K and 343 K (Scheme 1).



The TOF values were determined from the reaction rates calculated from the amount of consumed hydrogen in the initial linear segments of the consumption curves (10 min after the start of the reaction) and the amount of the surface Pd atoms for each sample. It follows from the results (see Table 1) that the TOF of the Pd/C-H catalyst is considerably higher than that of Pd/C-F in which the dispersion of the supported palladium is higher. This result is consistent with our recent results¹⁷ and published data on the hydrogenation of 2,4-dinitrotoluene,¹⁹ nitrobenzene,^{35,36} and 4-chloronitrobenzene³⁷ in the presence of supported palladium catalysts. The increase in the TOF with increasing average particle size of supported palladium in the catalyst provides the conclusion that the catalytic reaction in question is structure-sensitive.³⁸ It is evident that the rate of catalytic reactions depends on the state of both substrate and hydrogen molecules on the catalyst surface. It is known that as the supported metal particle size decreases, the interaction of palladium with the substrate nitro groups becomes stronger than the interaction with hydrogen molecules.³⁷ As a result of strong adsorption of the substrate (and intermediate hy-

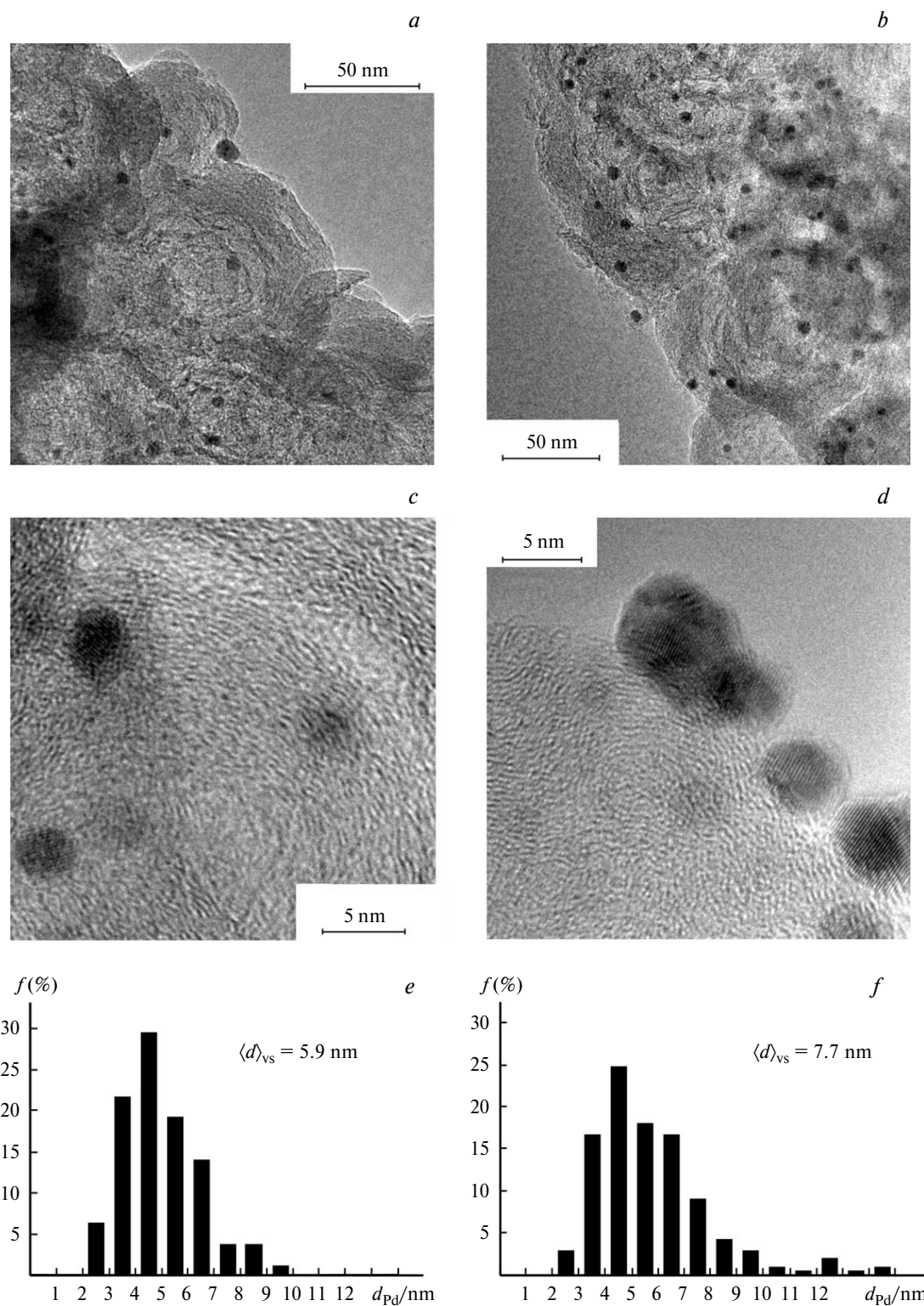


Fig. 3. TEM images of Pd/C-F (*a, c*) and Pd/C-H (*b, d*) catalysts at different magnifications and the corresponding histograms for Pd particle size distribution (*e* and *f*).

drogenation products containing nitro group) on highly dispersed palladium particles, the reaction rate and TOF would be lower than in the case of large Pd particles.

Thus, we studied the influence of conditions of the reduction of Sibunit-supported palladium PHC on the dispersion of the resulting metal particles and activity of

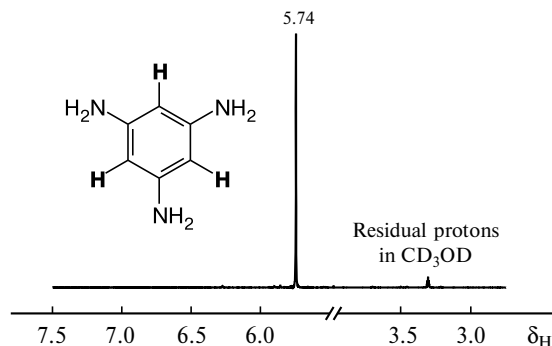


Fig. 4. ^1H NMR spectrum of the reaction mixture during hydrogenation of Na-TNBA in an aqueous solution at a temperature of 343 K and a pressure of 0.5 MPa catalyzed by Pd/C-H. The spectra of mixtures obtained after hydrogenation at 323 K in the presence of Pd/C-F and Pd/C-H catalysts are similar to that presented in the Figure.

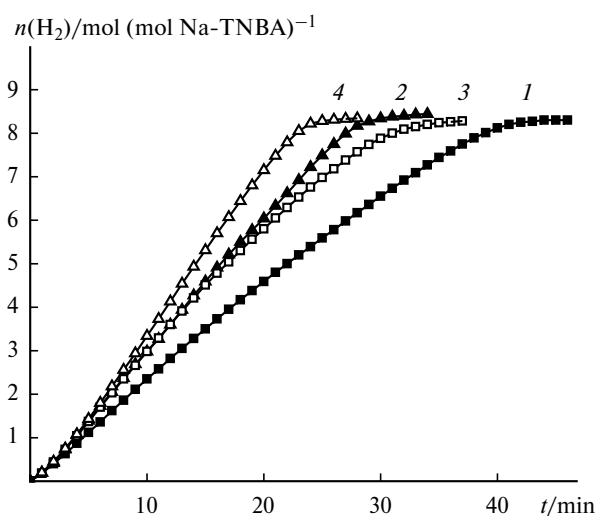


Fig. 5. Hydrogen consumption curves during hydrogenation of Na-TNBA in an aqueous solution in the presence of Pd/C-F (1, 2) and Pd/C-H (3, 4) catalysts at temperatures of 323 (1, 3) and 343 K (2, 4); $n(\text{H}_2)$ is the amount of consumed H_2 .

the Pd/C catalysts thus formed towards selective hydrogenation of Na-TNBA to TAB. The reduction was carried out by the most common methods used in the catalyst preparation practice: liquid-phase reduction with sodium formate and reduction in a hydrogen flow at elevated temperature. It was found that the reduction technique affects the dispersion of the supported metal and its catalytic activity in the considered reaction. The high-temperature gas-phase reduction gives rise to Pd particles with a much lower dispersion than the mild liquid-phase reduction conditions. The TOF value proved to be higher for the sample containing large Pd particles than for the catalyst obtained by sodium formate reduction. These results could be useful for optimization of the conditions of synthesis of high-performance Pd/C type

catalysts for selective hydrogenation of polyfunctional organic compounds.

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