

Palladium Supported on Carbon Nanoglobules as a Promising Catalyst for Selective Hydrogenation of Nitroarenes

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Received: 12 August 2019 / Accepted: 20 September 2019 © Springer Science+Business Media, LLC, part of Springer Nature 2019

Abstract

The catalysts 1 wt% palladium supported on carbon nanoglobules (CNGs) were shown to be highly active in the liquid-phase hydrogenation of various nitroarenes and provided nearly 100% selectivity to aromatic amines at complete conversion under mild conditions (323 K, 0.5 MPa, 1 h). The catalytic activity (in terms of turnover frequency and substrate conversion) and selectivity depend on the kind of CNGs support, catalyst preparation method and the reaction conditions (solvent nature). The Pd/CNGs catalyst can be repeatedly used while maintaining the same catalytic performance. The excellent performances of Pd/CNGs catalysts can be due to the globular morphology of the supports as well as the absence of micropores and pronounced surface defects.

Graphic Abstract



Keywords Catalytic hydrogenation · Carbon nanoglobules · Palladium catalysts · Nitroarenes · Aromatic amines

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10562-019-02974-6) contains supplementary material, which is available to authorized users.

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1 Introduction

Catalytic hydrogenation of aromatic nitro compounds over supported metal nanoparticles (NPs) has recently attracted huge attention [1–5]. This is due not only to the importance of the resulting aromatic amines, which are key intermediates in the production of polymers, pharmaceuticals, dyes and pesticides [6, 7], but also because the conventional noncatalytic reduction methods with the use of metallic iron, zinc, tin in acid media, sulfides or inorganic hydrides (e.g., NaBH₄) exhibit serious drawbacks [1–3, 6, 7]. Hydrogenation with H₂ gas in the presence of supported metal catalysts is considered preferable especially from an environmental standpoint.

Meanwhile, the development of highly efficient catalysts for the chemoselective hydrogenation of aromatic nitro compounds to corresponding anilines is still a challenging task. By now, a great number of supported catalysts containing Pt, Pd, Ru, Rh, Ni, Cu, Ag, Au NPs have been examined in the hydrogenation of various substituted nitroarenes [1–12]. Despite the progress made, the procedure for the preparation of some hydrogenation catalysts requires the use of scarce and expensive reagents, and also includes many stages. Additionally, and most importantly, the hydrogenation of nitroarenes in the presence of many of the proposed catalysts often requires the use of harsh conditions to achieve high substrate conversion and high yield of aromatic amines [8–12].

In the synthesis of supported catalysts, the support plays a crucial role in defining the structure and electronic state of supported metal NPs and, ultimately, the activity and selectivity of the resulting catalyst. Recently, carbon materials of different origin and structure (active carbons, carbon nanotubes, carbon nanofibers) are widely used as supports in the catalyst preparation [13-19]. It is well-known that the carbon-supported palladium catalysts are extensively applied for the liquid-phase hydrogenation of various substrates and perhaps are the most common heterogeneous catalysts utilized in organic synthesis [20–24]. It is possible to regulate and improve the catalytic properties of Pd/C, including by varying the nature (structure and physicochemical properties) of the carbon support as well as the conditions of catalyst preparation. These considerations, although they are obvious and important for the production of efficient Pd/C catalysts, are not always taken into account. There are few reviews that discuss in detail the synthesis issues of Pd/C catalysts [24-28]. However, so far it has not always been possible to obtain a catalyst with desired properties, and, as a rule, the development of an optimal procedure for the catalyst synthesis is required. In addition, a reduction in the content of expensive metal in a catalyst while maintaining the catalytic performances at a high level is still a topical task. For instance, commercial Pd/C catalysts used for the hydrogenation of aromatic nitro compounds commonly contain 5–20 wt% of palladium [5, 22]. However, a much smaller Pd loading in the catalyst may be sufficient to achieve excellent catalytic performances.

We recently reported [12] that 1–2% palladium catalysts supported on carbon nanoglobules (CNGs) are highly active in the hydrogenation of ethyl 4-nitrobenzoate (1a) under mild conditions and provide selective formation of ethyl 4-aminobenzoate (2a). CNGs (carbon blacks) we used to prepare the catalysts are produced on a large scale, which makes them quite affordable [29, 30]. However, it is noteworthy that despite several advantages of CNGs for use as a catalyst support [19, 24, 29], numerous works concerning the catalytic application of various carbons pay unreasonably little attention to this carbon material [15, 19]. One should note that the structure, porosity and surface acid–base properties of CNGs can be gently and independently regulated by the variation of the production conditions [12, 24]. This makes it possible to tune the structure and properties of CNGs-supported Pd NPs and thus achieve improved performances of Pd/CNGs catalysts [24].

In the present work, we continued to study 1% Pd/CNGs catalysts in the hydrogenation of **1a**, revealing how the catalytic activity (in terms of turnover frequency (TOF) and substrate conversion) and selectivity depend on the physicochemical characteristics of CNGs, catalyst preparation method and the nature of solvent used as the reaction medium. We also found that these catalysts exhibit excellent performances in the hydrogenation not only of **1a**, but also of other nitroarenes, providing nearly 100% selectivity to aromatic amines under mild reaction conditions.

2 Experimental

2.1 Materials and Reagents

Three samples of CNGs obtained at the Department of Experimental Technologies, (Center of New Chemical Technologies, Boreskov Institute of Catalysis) were used as the supports. These CNGs samples have already been used in our previous study [12], and here, for brevity, we denote them as C-1, C-2 and C-3. Before the experiments, the supports were dried overnight in air at 393 K.

Palladium(II) chloride, PdCl₂ (98%, Aurat, Russia), was used for the catalyst preparation without further purification. Palladium(II) acetate, [Pd(OAc)₂]₃, and *tris*(dibenzylideneacetone)dipalladium(0), [Pd₂(dba)₃], were synthesized by known procedures (see Supplementary Materials for more information). Solvents and most of nitroarenes were purchased from commercial suppliers and used as received (Tables S1 and S2). 1-(2,3-Difluoro-6-nitrophenoxy)acetone was synthesized and supplied by courtesy of Dr. G.L. Rusinov (I.Ya. Postovskiy Institute of Organic Synthesis, Yekaterinburg, Russia). The reduction of catalysts and the catalytic hydrogenation were performed using hydrogen of high-purity grade (99.99%, NCCP, Russia).

2.2 Preparation of Catalysts

Various palladium precursors (see Supplementary Materials) and different techniques were used for the preparation of palladium catalysts. The catalysts denoted as 1% Pd(CCs)/ CNGs were prepared by incipient wetness impregnation of the CNGs supports with aqueous solutions of palladium(II) chloride complexes (CCs) formed by dissolving PdCl₂ in water containing equimolar amount of HCl. After deposition of Pd CCs on the supports, the samples were dried in air at room temperature and then at 393 K. Before catalytic experiments, the catalysts were reduced in flowing hydrogen at 573 K for 2 h.

The second preparation technique used in the present study includes the adsorption of polynuclear hydroxy complexes (PHCs) of Pd(II) onto carbon supports, as described in detail elsewhere [24, 31]. A further reduction of supported Pd PHCs was performed in sodium formate solution at 363 K for 0.5 h. The catalysts obtained by this method are denoted hereinafter as 1% Pd(PHCs)/CNGs.

The catalysts denoted as 1% Pd(Ac)/CNGs and 1% Pd(dba)/CNGs were prepared by incipient wetness impregnation of the CNGs supports with solutions of $[Pd(OAc)_2]_3$ and $[Pd_2(dba)_3]$ in trichloromethane, as described earlier [32, 33]. After deposition of the precursors, the samples were dried in air at room temperature and then at 393 K. Before catalytic experiments, the catalysts were reduced with hydrogen at 573 K for 2 h.

2.3 Characterization of Catalysts

The reducibility of Pd CCs deposited on the carbon supports was examined by H₂-TPR using an AutoChem II 2920 (Micromeritics) chemisorption analyzer equipped with a thermal conductivity detector (TCD). The H₂-TPR experiments were carried out using a mixture of 10 vol% H₂ and argon (the flow rate 30 cm³ min⁻¹) in a temperature range of 303–573 K at a heating rate of 10 K min⁻¹. The catalysts prepared from Pd PHCs and reduced with sodium formate were exposed in a 10 vol% H₂–Ar medium under H₂-TPR conditions in a temperature range of 303–393 K at a heating rate of 10 K min⁻¹ with subsequent cooling in flowing argon.

The dispersion of Pd in the reduced catalysts was estimated by pulse chemisorption of CO (> 99.999 vol% purity) using an AutoChem II 2920 (Micromeritics) instrument, as described in [12]. The palladium dispersion was calculated assuming a stoichiometry Pd:CO = 2 [34, 35]. The mean volume-surface diameter (in nm) of Pd NPs was obtained from the Pd dispersion: d = 1.11/D [36].

Transmission electron microscopy (TEM) images of the reduced catalysts were taken by a JEM-2100 (JEOL) instrument with a lattice resolution of 0.145 nm at an accelerating voltage of 200 kV. The samples were prepared by dispersing the catalysts in ethanol and spraying the suspension onto a copper grid coated with a perforated carbon film. The energy dispersive X-ray (EDX) analysis was carried out with an INCA 250 (Oxford Instruments) spectrometer. The mean volume-surface diameter of Pd NPs was determined by measuring the size of more than 100 NPs. Image processing was performed using the DigitalMicrographTM (Gatan) program package.

Palladium content in the catalysts was measured by atomic absorption spectrometry on an AA-6300 (Shimadzu) spectrometer. Before measurements, the catalyst samples were completely dissolved in a mixture of concentrated HNO₃ and HClO₄. The Pd content measurement error was ± 0.05 wt%.

2.4 Procedure of Catalytic Hydrogenation

Typically, the liquid-phase hydrogenation of nitroarenes in the presence of palladium catalysts was performed in a Miniclave drive (Büchi AG) periodic reactor at 323 K, 0.5 MPa under vigorous stirring at 1000 rpm for 1 h. The ratio of the amount of substrate to that of catalyst was kept constant at 10 g g⁻¹ in all catalytic experiments. The reaction was controlled by measuring the amount of hydrogen consumed. The results of these measurements as well as palladium dispersions derived from CO chemisorption data were used for the calculation of TOF [12]. After completion of the reaction and cooling, the reaction solutions were separated from the catalysts by filtration.

2.5 Analysis of the Reaction Products

Gas chromatography–mass spectrometry (GC–MS) used for the identification of the reaction products was performed on an Agilent 5973 N/6890 N instrument equipped with an HP-5MS column. MS measurements were carried out using electron impact ionization at 70 eV. Identification was performed by comparison of mass spectra with those given in the NIST/EPA/NIH Mass Spectral Library [37] and in the published literature.

The quantitative composition of the reaction solutions was determined by GC on an Hewlett Packard 5890 Series II instrument equipped with an HP-1 capillary column and flame ionization detector. The substrate conversion and selectivity for each product were calculated as follows:

Nitroarene conversion (%) = $\frac{\text{moles of reacted nitroarene}}{\text{moles of initial nitroarene}} \times 100$

Product selectivity (%) = $\frac{\text{moles of product obtained}}{\text{moles of reacted nitroarene}} \times 100$

3 Results and Discussion

3.1 Characterization of Catalysts

The structure, morphology and surface chemistry of the CNGs supports have been discussed in our previous papers [12, 24]. Briefly, the C-1 and C-2 samples obtained by oxidative pyrolysis of aromatic hydrocarbons (furnace black process) are the nanostructured carbons consisting of the 3D aggregated (accreted) globules with an average diameter of 22 and 31 nm, respectively. C-3 was produced by

non-oxidative pyrolysis of methane (thermal black process) and has rather large predominantly single or slightly aggregated globules which are mainly 100–200 nm in diameter. This material exhibits the lowest BET surface area $(10 \text{ m}^2 \text{ g}^{-1})$ compared to the C-1 and C-2 samples (103 and 415 m² g⁻¹, respectively). The total pore volume is of 0.04, 0.91 and 1.00 cm³ g⁻¹ for C-3, C-1 and C-2, respectively. The micropore volume for all the samples does not exceed 0.015 cm³ g⁻¹. According to infrared spectroscopy, the CNGs samples differ to some extent in the intensity of the absorption bands corresponding to C–O stretching vibrations of various surface oxygen functionalities, such as quinones (1550–1650 cm⁻¹), ethers, lactones (1200–1300 cm⁻¹), and hydroxyls (1000–1200 cm⁻¹).

Therefore, mainly the structure and surface area are substantially different for the chosen CNGs supports, and it can be expected that the palladium catalysts will differ in structure of supported Pd NPs as well as their catalytic properties, depending on the nature of interaction between Pd NPs and CNGs. At the same time, this Pd-CNGs interaction and therefore the size and catalytic properties of Pd NPs may also be affected by the composition of the palladium precursor used for the catalyst preparation [24]. Depending on the composition of the palladium precursor and the conditions of its deposition, the localization of Pd NPs on the carbon surface may be very different. In the present study, the following palladium compounds, which are quite affordable and can be easily synthesized, were chosen: Pd CCs, Pd PHCs, [Pd(OAc)₂]₃, and [Pd₂(dba)₃]. These palladium precursors are very different in composition, and various conditions are required for their deposition on CNGs and for the formation of Pd NPs. The Pd CCs and Pd PHCs complexes are highly soluble in water and will be adsorbed predominantly on hydrophilic sites of the carbon surface (e.g., oxygen functional groups). In contrast, the $[Pd(OAc)_2]_3$ and $[Pd_2(dba)_3]$ complexes bearing organic ligands are highly soluble in organic solvents and therefore will be localized on hydrophobic sites of the carbon surface.

The reduction profiles of the catalysts prepared from Pd CCs exhibit a single peak corresponding to the hydrogen consumption due to the reduction of supported palladium precursor (Fig. S2). The Pd chloride precursor supported on C-3 is reduced within a very narrow temperature range with a maximum at 371 K, whereas the peaks for the catalysts based on the C-1 and C-2 supports are wider and shifted towards higher temperatures. Apparently, differences in the structure of aggregates of globules and the surface area value for the supports lead to the fact that the clusters of supported palladium CCs have different size and localization place [31] and therefore are reduced under different temperature conditions.

Since the hydrogen consumption was not observed when studying the Pd(PHCs)/CNGs catalysts by H_2 -TPR (Fig.

S3), this indicates a complete reduction of supported Pd PHCs with sodium formate. The hydrogen release observed at 320–370 K corresponds to the decomposition of palladium β -hydride [38, 39] formed due to the interaction of palladium with hydrogen at low (room) temperature, when H₂-TPR test was started.

According to TEM measurements and CO chemisorption data, the size of Pd NPs in the catalysts may depend on the kind of CNGs as well as the palladium precursor composition (Fig. 1, Table 1). For instance, Pd NPs formed from palladium CCs and supported on C-3 are highly dispersed and their size distribution is very narrow (Fig. 1c), whereas Pd NPs in the 1% Pd(CCs)/C-1 and 1% Pd(CCs)/C-2 catalysts are larger in size with a wider range of distribution (Fig. 1a, b). The size of Pd NPs in the Pd/C-2 catalyst is mostly in the range of 2-3 nm, but in the case of Pd/C-1 sample, the fraction of particles larger than 4 nm is close to 50%. Meanwhile, the kind of CNGs has little effect on the dispersion of Pd NPs obtained from Pd PHCs, and all of the Pd(PHCs) CNGs samples have close average sizes of Pd NPs with a distribution mainly within the range of 2–5 nm (Fig. 1d–f). Apparently, this is due to the fact that Pd PHCs are not sensitive to the size of the nanoglobules and the structure of their aggregates, since, unlike Pd CCs, they do not form surface complexes [25, 31].

As can be seen, for the samples based on C-3, the use of Pd PHCs as the palladium precursor leads to the formation of larger Pd NPs, as compared to the Pd(CCs)/C-3 catalyst (Fig. 1f vs. 1c, Table 1). Besides, unlike the catalysts prepared from Pd CCs, the distribution of PHCs-derived Pd NPs is uneven over the globules (Fig. S4). The C-3-supported catalyst prepared using palladium acetate as the precursor has a wide bimodal size distribution of Pd NPs (Fig. 1i). In some cases, the Pd NPs in this sample are coated with a layer of amorphous carbon. The 1% Pd(dba)/C-3 catalyst contains spherical Pd NPs, many of which are encapsulated with amorphous carbon (Fig. 1k). Possibly, such encapsulation of Pd NPs is due to the interaction between palladium surrounded by organic ligands and carbon support [40, 41]. This may explain the absence of CO chemisorption for the Pd(dba)/C-3 sample (Table 1, entry 11). Certainly, the formation of carbon overlayer on the metal surface causes a discrepancy between the Pd NPs size values determined from TEM and CO chemisorption [24, 41].

3.2 Screening of Pd/CNGs Catalysts in the Hydrogenation of Ethyl 4-nitrobenzoate

The liquid-phase hydrogenation of 1a is currently of great interest as an alternative way to produce 2a which is an important local anesthetic used in medicine [42, 43]. We have previously found [12] that the hydrogenation of 1a in the presence of Pd/CNGs catalysts proceeds through the



Fig. 1 TEM images at different magnifications and the corresponding histograms of the Pd NPs diameter distribution for the catalysts prepared using Pd CCs (\mathbf{a} , \mathbf{b} , \mathbf{c}), Pd PHCs (\mathbf{d} , \mathbf{e} , \mathbf{f}), [Pd(OAc)₂]₃ (\mathbf{g} , \mathbf{h} ,

i) and $[Pd_2(dba)_3]$ (j, k) as palladium precursors, and C-1 (a, d, g, j), C-2 (b, e, h) and C-3 (c, f, i, k) as the supports

formation of intermediate ethyl 4-(hydroxyamino)benzoate (**3a**), diethyl 4,4'-azoxydibenzoate (**4a**) and diethyl 4,4'-azodibenzoate (**5a**) (Scheme 1), i.e. according to the mechanism proposed by Haber [1–3, 44]. Therefore, the selectivity to target amine **2a** can be high if the mentioned intermediates are quickly converted and thus do not accumulate in the reaction mixture.

The 1% Pd/CNGs catalysts were screened in the hydrogenation of **1a** under identical reaction conditions: aqueous ethanol medium, temperature of 323 K, hydrogen pressure of 0.5 MPa, reaction time of 1 h. It was found that the catalysts prepared by deposition of Pd CCs and especially Pd PHCs on the C-3 support demonstrate high activity (in terms of TOF) providing complete conversion of **1a** and nearly 100% selectivity to target amine **2a** (Table 1, entries 8 and 9). The C-3-supported catalysts prepared using [Pd(OAc)₂]₃ and $[Pd_2(dba)_3]$ as the precursors are much less active, and the selectivity to **2a** during the reaction does not reach 100% due to accumulation of intermediate by-products **3a**, **4a** and **5a** (Table 1, entries 10 and 11). The least active catalyst prepared from palladium acetate provides only 75% conversion of **1a** and nearly 67% selectivity to **2a**. Apparently, the encapsulation of Pd NPs with carbon is the reason for the low activity of the 1% Pd(Ac)/C-3 and 1% Pd(dba)/C-3 catalysts, since the carbon layer makes the Pd sites inaccessible to the reactant molecules.

Compared to the catalysts based on C-3, the C-1 and C-2-supported ones are less active in the hydrogenation of **1a**. However, most of them also allow achieving 100% conversion of **1a** for 1 h (Table 1, entries 1–7). Their catalytic performances depend on the composition of Pd precursor and conditions of the catalyst preparation. Thus,

Entry	Catalyst	Mean size of Pd NPs (nm) ^a	TOF (mol H_2 mol Pd_s^{-1} min ⁻¹) ^b	Conversion of 1a (%) ^c	Selectivity (%) ^d			
					2a	3 a	4a	5a
1	1% Pd(CCs)/C-1	3.3	< 30	> 99.9	96.2	1.2	1.6	1.0
2	1% Pd(PHCs)/C-1	4.6	153	> 99.9	> 99.9	0	0	0
3	1% Pd(Ac)/C-1	5.0	< 30	99.3	87.8	8.5	1.5	2.2
4	1% Pd(dba)/C-1	9.3	< 30	> 99.9	98.0	0	0	2.0
5	1% Pd(CCs)/C-2	3.3	< 30	96.1	86.4	5.4	6.6	1.6
6	1% Pd(PHCs)/C-2	5.0	328	> 99.9	> 99.9	0	0	0
7	1% Pd(Ac)/C-2	3.7	< 30	> 99.9	88.9	4.9	3.8	2.4
8	1% Pd(CCs)/C-3	2.8	253	> 99.9	> 99.9	0	0	0
9	1% Pd(PHCs)/C-3	4.3	398	> 99.9	> 99.9	0	0	0
10	1% Pd(Ac)/C-3	4.7	< 30	75.2	66.7	23.4	8.7	1.2
11	1% Pd(dba)/C-3	No chemisorption	< 30	> 99.9	77.8	12.0	8.1	2.1

Table 1 Mean size of Pd NPs in the 1% Pd/CNGs catalysts and their catalytic properties in the hydrogenation of 1a

Reaction conditions: temperature of 323 K, pressure of 0.5 MPa, 1 h, 50 cm³ of aqueous ethanol, 500 mg of 1a, 50 mg of catalyst

^aAccording to CO chemisorption

^bTOF values were calculated using Pd dispersions derived from CO chemisorption data. For the least active catalysts, it was not able to determine the reaction rate and TOF, since a mass flow meter used in the present study does not allow measuring H_2 consumption at too low flow rate (<3 cm³ min⁻¹) due to automatic valve closing

^cSubstrate conversion was determined by GC after 1 h of the reaction

^dSelectivity for the products was determined by GC; the identification was carried out by GC-MS, see Figs. S5-S9

the hydrogenation over the catalysts prepared from Pd PHCs always proceeds with a high rate, resulting in complete conversion of **1a** to the desired amine **2a** with nearly 100% selectivity (Table 1, entries 2 and 6). At the same time, hydrogenation over the catalysts obtained from Pd CCs, $[Pd(OAc)_2]_3$ and $[Pd_2(dba)_3]$ proceeds slowly, and the selectivity to **2a** is < 100% (Table 1, entries 1, 3–5, 7). For example, in the case of the least active C-2-supported catalyst obtained using Pd CCs as the precursor, the conversion of **1a** does not reach 100% after 1 h of the reaction (Table 1, entry 5), and the selectivity to **2a** is decreased (ca. 86%) because intermediate **3a**, **4a** and **5a** accumulate in the reaction mixture.

When comparing the catalytic properties of the CCsderived catalysts, the increased hydrogenation activity of the C-3-based catalysts in comparison with catalysts supported on C-1 and C-2 may be related with the high dispersion of supported Pd NPs (Fig. 1c vs. a and b; Table 1, entries 1, 5, 8), which ensures the accessibility of Pd to molecules of reactants. Besides, the C-3 support has such structure and properties that are apparently favorable to achieve excellent catalytic performances in the hydrogenation of **1a**. This support consists predominantly of single or slightly aggregated CNGs, whereas C-1 and C-2 are constructed of aggregates containing more than a hundred accreted CNGs. In the reaction solution, the catalysts based on these carbon materials form a suspension, the least particle size of which is determined by the size of the corresponding aggregates. Therefore, the particles (i.e., aggregates) of C-1- and

C-2-supported catalysts suspended in the reaction solution have an internal porosity and their surface has a pronounced roughness, while the suspension of C-3-based catalysts consists of spherical particles with a smooth surface. As a result of this difference, the adsorption–desorption processes on the Pd/C-3 catalysts proceed faster than on the Pd/C-1 and Pd/C-2 catalysts. This can contribute to the high hydrogenation activity and selectivity of the catalysts supported on the C-3 support.

According to published data, the hydrogenation of 1a can be performed in the presence of various carbon-supported catalysts containing Ni [10, 45, 46], Pt [47, 48] or Pd [49-53]. The advantage of Pd/C catalysts over nickel and platinum ones is that they allow achieving complete conversion of the substrate and high yield of amine 2a under mild reaction conditions (temperature of 293-333 K, pressure of 0.1–1.3 MPa) for a short time. For instance, Visentin et al. [51] showed that almost 100% yield of 2a can be achieved during the hydrogenation of 1a in the presence of 1% Pd supported on activated carbon in a methanol solution at 323 K, 1.3 MPa for about 2 h. According to other work [53], the use of the Pd catalyst supported on N-modified ordered mesoporous CMK-3 carbon made it possible to achieve almost 100% yield of 2a by the liquid-phase hydrogenation of **1a** at 333 K, 1 MPa for 4 h. The CNGs-supported 1% palladium catalysts studied in the present work exhibit high activity in the liquid-phase hydrogenation of 1a to target amine 2a under mild conditions (323 K, 0.5 MPa, 1 h) and, as can be seen, are not inferior and even superior to the



Scheme 1 Reaction network for hydrogenation of 1a over Pd/CNGs catalysts [12]

Pd/C catalysts previously proposed for this reaction. The catalytic activity (in terms of TOF and substrate conversion) and selectivity depend on the kind of CNGs and the catalyst preparation method. Although most Pd/CNGs catalysts provide complete conversion of **1a** with the selective formation of **2a**, the catalysts based on the C-2 and C-3 supports and prepared using Pd PHCs as the precursor are superior to others apparently due to the optimal combination of the support structure and texture, size and uniformity of Pd NPs, as well as the nature of localization place of Pd sites.

3.3 Effect of the Solvent Nature on the Catalyst Activity and Selectivity in the Hydrogenation of Ethyl 4-nitrobenzoate

To study the influence of solvent nature on the catalytic process, we chose the 1% Pd(PHCs)/C-2 catalyst which is one of the most active and highly selective in hydrogenation of **1a**. According to published data, such solvents as methanol [51], ethanol [11, 54], 2-propanol [50, 52], ethyl acetate [53], tetrahydrofuran (THF) [55] and toluene [49] can be effectively used for the liquid-phase hydrogenation of **1a** over palladium catalysts. These solvents have a good dissolving capacity for substrate **1a**. However, they may differ in their influence on both the rate of hydrogenation and the yield of products due to the difference in ability of formation of adducts with carbon surface or palladium sites.

In the present study, we used the solvents which can be differentiate by polarity into three groups: (1) polar protic solvents, such as methanol, aqueous ethanol (96%) and 2-propanol; (2) polar aprotic solvents, such as ethyl acetate, THF and N,N-dimethylformamide (DMF); (3) nonpolar solvents, such as 1,4-dioxane, benzene and cyclohexane (see also Table S3). To investigate the solvent effect, the hydrogenation of 1a was performed under identical reaction conditions: temperature of 323 K, pressure of 0.5 MPa, reaction time of 1 h. It was found that when using aliphatic alcohols and cyclohexane as the solvents, the substrate 1a is completely hydrogenated with nearly 100% selectivity to **2a** (Table 2, entries 1-3, 9). The highest TOF values are observed during hydrogenation in aqueous ethanol and especially cyclohexane media. Under the same conditions, the hydrogenation of 1a in ethyl acetate, THF (polar aprotic solvents) and such nonpolar solvents as benzene and 1,4-dioxane proceeds very slowly and does not ensure a complete conversion of 1a (Table 2, entries 4, 5, 7, 8); the selectivity to 2a does not always reach 100% (THF and 1,4-dioxane) due to accumulation of intermediate products 3a and 4a. When using DMF as the solvent, no conversion of 1a is observed (Table 2, entry 6).

The dramatic influence of solvents can be clearly seen when plotting the substrate conversion (or another catalytic response) against some parameter that characterizes the polarity of the solvent [56–60]. For this purpose, the empirical solvatochromic parameter E_T^N proposed by Reichardt [61, 62] can be used (see Table S3). Plots of the **1a** conversion after 1 h of the reaction as a function of E_T^N for each group of solvents are shown in Fig. 2. As can be seen, when using nonpolar and polar aprotic solvents, the conversion of **1a** decreases with increasing solvent polarity, whereas in alcohols, which are polar protic solvents, the conversion of **1a** always reaches 100%.

The observed influence of solvent nature on the catalytic performance can be explained by differences in the interactions between molecules of solvent, reactants and the catalyst surface. Thus, the interaction between substrate and nonpolar cyclohexane is obviously weak. Besides, the adsorption of cyclohexane molecules on Pd active sites is also weak. As a result, the hydrogenation of **1a** is not inhibited in cyclohexane, and the substrate is completely converted to **2a** with a high rate. With increasing polarity in the Table 2Hydrogenation of1a over 1% Pd(PHCs)/C-2 invarious solvents

Entry	Solvent	TOF (mol H_2 mol	Conversion of	Selectivity (%)			
		$Pd_s^{-1} min^{-1}$)	la (%)	2a	3 a	4 a	5a
1	MeOH	413	> 99.9	> 99.9	0	0	0
2	EtOH (aq.)	491	> 99.9	> 99.9	0	0	0
3	<i>i</i> -PrOH	216	> 99.9	98.3	1.7	0	0
4	THF	< 30	96.8	95.6	3.5	0.9	0
5	EtOAc	< 30	26.0	> 99.9	0	0	0
6	DMF	< 30	0	-	_	-	-
7	1,4-Dioxane	< 30	54.1	86.8	13.2	0	0
8	Benzene	< 30	60.0	> 99.9	0	0	0
9	Cyclohexane	556	> 99.9	> 99.9	0	0	0

Reaction conditions: temperature of 323 K, pressure of 0.5 MPa, 1 h, 100 cm³ of solvent, 1.000 g of **1a**, 100 mg of catalyst



Fig.2 Conversion of **1a** after 1 h of hydrogenation versus solvent polarity $E_{\rm T}^{\rm N}$. Reaction conditions: temperature of 323 K, pressure of 0.5 MPa, 1 h, 100 cm³ of solvent, 1.000 g of **1a**, 100 mg of 1% Pd(PHCs)/C-2 catalyst

series cyclohexane < benzene < 1,4-dioxane, the mentioned interactions are enhanced and, thus, hamper the substrate conversion.

The molecule of polar aprotic solvent can donate lone pair electrons from the oxygen atoms. The adsorbed solvent molecules block the active sites due to the interaction between suitable atomic orbital of Pd and lone pair electrons of solvent molecule (donor–acceptor interaction). As a result, the hydrogenation activity (TOF) is lowered due to competitive adsorption between reactants and solvent on the metal surface. At the same time, the interaction between polar aprotic solvents and the substrate (solvation) hampers the adsorption of the substrate onto the metal surface [58]. Apparently, in the case of DMF, the solvent–substrate and solvent–catalyst interactions are so strong that the hydrogenation of **1a** in DMF is completely suppressed. This result for DMF is consistent with some earlier observations [59, 63]. For example, Takagi et al. [59] reported a lack of conversion of benzyl alcohol when trying to hydrogenate it in a solution of DMF over ruthenium catalyst.

Like aprotic solvents, the protic ones (i.e., alcohols) are able to strongly interact with the substrate molecules and metal surface [58]. However, the excellent performance observed during the hydrogenation of 1a in alcohols (Table 2, entries 1-3) is apparently not due to the polarity of these solvents, but rather are related to their higher hydrogen-bond donating ability which, unlike nonpolar and polar aprotic solvents, has nonzero values (cf. α-parameters in Table S3). Therefore, since the protic solvents easily form hydrogen bonds with the intermediates and product, a strong interaction between them facilitates the desorption of the intermediates and product from the catalyst surface and, thus, promotes the catalytic hydrogenation [63]. Furthermore, the protic solvents can interact with the nitro groups of adsorbed substrate via the formation of hydrogen bonds, which favors the polarization of N=O bonds and makes them easy to be attacked by chemisorbed hydrogen [60, 63]. For these reasons, the higher TOF value in aqueous ethanol compared to that in other alcohols (Table 2, entries 1–3) may be due to the presence of water which has a higher hydrogenbond donating ability than alcohols [62]. It was previously shown [63] that adding even 5% of water to ethanol leads to a significant acceleration of the hydrogenation of nitro compound.

Note that the high intrinsic rate (TOF) of hydrogenation using cyclohexane and alcohols as solvents could be also explained by hydrogen-transfer processes, since these compounds act as good hydrogen donors and can reduce nitroarenes in the presence of a catalyst without an external source of hydrogen [64–68]. However, in the present study, even traces of by-products that should have been formed during the catalytic transfer hydrogenation (for example, carbonyl compounds and the products of their interaction with the amino group [66–68]) were not detected in the reaction mixtures. The result of a separate experiment (without hydrogen gas) shows that a possibility of reduction by hydrogen transfer from solvent is excluded under the chosen experimental conditions. Obviously, the reaction conditions are too mild to allow catalytic transfer hydrogenation to be sufficiently intensive.

In general, the regularities of the solvent effect found for the Pd/CNGs catalyst turned out to be close to those described in the literature for carbon-supported palladium catalysts. However, the absence of microporosity leads to a greater "manifestation" of the solvent effect due to the absence of blockage of catalytically active sites located in the micropores by solvent molecules.

3.4 Stability of Pd/CNGs Catalyst in the Hydrogenation of Ethyl 4-nitrobenzoate

As shown above, the hydrogenation of **1a** in cyclohexane proceeds with a highest rate. However, the aqueous ethanol was chosen as a solvent for further experiments for the following reasons. Firstly, aqueous ethanol is more affordable than cyclohexane. Secondly, the use of ethanol is preferable from an environmental standpoint, because cyclohexane is recognized as a dangerous substance for the environment (in contrast to ethanol) [69]. Finally, since the hydrogenation of nitroarenes is always accompanied by the formation of water, carrying out the reaction in cyclohexane, especially on a large scale (i.e., at high substrate concentration in the reaction solution), can lead to undesirable formation of emulsion.

We have previously shown [12] that the 1% Pd(PHCs)/C-3 catalyst can be repeatedly used many times without losing activity (100% conversion of **1a**) and maintaining nearly 100% selectivity to amine 2a. In this paper, to study the stability of the 1% Pd(PHCs)/C-2 catalyst in the hydrogenation of 1a, the reusability test was performed at incomplete conversion of the substrate (70-85%) under the same conditions as indicated above (EtOH (aq.), 323 K, 0.5 MPa) but on an enlarged scale (5.000 g of 1a and 500 mg of the catalyst). After each cycle, the catalyst was filtered off, thoroughly washed with acetone, dried and used in the next run with a freshly prepared solution of **1a**. As can be seen from Fig. 3, the catalyst can be repeatedly used five times while maintaining selectivity to 2a at about 80%. The slight deviations in the selectivity to 2a for different cycles are associated with the fact that the reaction proceeds very fast under the chosen conditions (just 5-8 min is enough to achieve the necessary values of substrate conversion and selectivity to 2a), and thus, using the technique for reaction control (measuring the amount of hydrogen consumed in a given time interval), it was not possible to distinctly define the moment when the experiment should be discontinued, so that conversion of **1a** would be incomplete and, at the same



Fig. 3 Stability test for the 1% Pd(PHCs)/C-2 catalyst in the hydrogenation of **1a**. Reaction conditions: temperature of 323 K, pressure of 0.5 MPa, 5–8 min each cycle, 5.000 g of **1a**, 500 mg of catalyst. The selectivity to **2a** was measured at incomplete conversion of **1a** (70–85%)

time, the selectivity to 2a would be the same (about 80%) for each cycle. The intrinsic reaction rate (TOF), although slightly decreases, still remains at a high level for all cycles. This slight decline in activity from cycle to cycle is not due to deactivation but rather to the inevitable catalyst loss during the recycles. Note that the analysis of the spent catalyst (after fifth cycle) showed a slight decrease in palladium content (by 0.2 wt%). However, this is apparently due not to the loss of palladium during the experiment, but to the accumulation of products that are difficult to remove from the catalyst surface.

Therefore, the 1% Pd(PHCs)/C-2 catalyst exhibits stability in hydrogenation of **1a**, which may be related with the absence of microporosity in the support. Thus, catalytically active sites are not blocked by intermediate condensation products (although such a process would have to be very pronounced at incomplete conversion of the substrate), and the hydrogenation proceeds with high selectivity to **2a**.

3.5 Catalytic Hydrogenation of Various Nitroarenes

The 1% Pd(PHCs)/C-2 catalyst, while being not the most active sample, still showed excellent performance in hydrogenation of **1a** under mild conditions (complete conversion of **1a** and nearly 100% selectivity to **2a**) and thus was utilized in hydrogenation of a series of nitroarenes to explore its general applicability. The choice of substrates subjected to hydrogenation was due in particular to the high practical importance of the resulting hydrogenation products [6, 7, 42, 43, 70, 71]. The results summarized in Table 3 show that most of the substrates are completely converted in just 1 h giving corresponding amines with nearly 100% selectivity under mild reaction conditions (323 K, 0.5 MPa). It proves

Entry	Substrate	Product ^a	$\begin{array}{c} \text{TOF} \ (\text{mol} \ \text{H}_2 \ \text{mol} \\ \text{Pd}_s^{-1} \ \text{min}^{-1}) \end{array}$	Conversion (%) ^b	Selectivity (%)
1	NO ₂ 1b	NH ₂ 2b	1204	> 99.9	> 99.9
2	NO ₂ Me	NH ₂ 2c	481	> 99.9	> 99.9
3	F ₃ C, NO ₂ 1d	F ₃ C NH ₂ 2d	498	> 99.9	> 99.9
4	NO ₂ OH	NH ₂ 2e	701	> 99.9	> 99.9
5	HO NO ₂ 1f	HO NH ₂ 2f	<30	95.1	> 99.9
6	MeO 1g	MeO NH ₂ 2g	965	> 99.9	> 99.9
7	NO ₂ NH ₂	NH ₂ 2h	216	> 99.9	> 99.9
8	H ₂ N NO ₂ 1i	H ₂ N 2i	337	> 99.9	> 99.9
9	HOOC NO ₂	HOOC NH ₂ 2j	615	> 99.9	> 99.9
10	HOOC NO ₂ 1k	HOOC NH ₂ 2k	292	> 99.9	> 99.9
11 ^c	F O Me 11	F F	154	> 99.9 ^d	90.0

 Table 3
 Hydrogenation of various nitroarenes over 1% Pd(PHCs)/C-2 catalyst

Reaction conditions unless otherwise noted: temperature of 323 K, pressure of 0.5 MPa, 1 h, 100 cm³ of aqueous ethanol, 1.000 g of substrate, 100 mg of catalyst

^aCompounds **2b–l** were identified by GC–MS, see Figs. S10–S30

^bSubstrate conversion was determined by GC after 1 h of the reaction

^cReaction conditions: temperature of 343 K, pressure of 0.5 MPa, 6 h, 100 cm³ of aqueous ethanol, 1.000 g of substrate, 200 mg of catalyst

^dConversion of **11** after 6 h of the reaction according to GC

that the 1% Pd(PHCs)/C-2 catalyst possesses high activity and selectivity for the hydrogenation of structurally diverse nitroarenes.

As can be also seen from Table 3, the intrinsic reaction rate (in terms of TOF) essentially depends on the structure of the substrate. Thus, the hydrogenation of nitrobenzene (1b) to aniline (2b) proceeds with the highest rate (Table 3, entry 1). Under the same reaction conditions, 4-nitrophenol (1f) is hydrogenated most slowly (TOF could not be determined), and the substrate conversion is incomplete after 1 h of the reaction (Table 3, entry 5), although 100% conversion of 1f could be achieved by extension of the reaction time. The hydrogenation of 1-(2,3-difluoro-6-nitrophenoxy) acetone (**1** I) proceeds slowly even at higher temperature (343 K) and higher content of catalyst than in the hydrogenation of other nitroarenes (Table 3, entry 11). In this case, it takes 6 h to achieve complete conversion of **11**. The reaction is accompanied by intramolecular cyclization to intermediate 7,8-difluoro-3-methyl-2*H*-1,4-benzoxazine (**31**) (Scheme 2). Under the specified reaction conditions, the further hydrogenation of C=N bond in **31** is hampered, and the selectivity to 7,8-difluoro-3-methyl-3,4-dihydro-2*H*-1,4-benzoxazine (**21**) does not exceed 90%. In the



Scheme 2 Reaction pathway of the catalytic hydrogenation of 11

same time, this is a rather high selectivity to **2l**, which is apparently achieved due to the absence of microporosity in the support, as has been previously shown for the palladium catalysts supported on mesoporous SibunitTM [72].

Meanwhile, it is difficult to present a general picture of the influence of a substituent on the hydrogenation rate. It is known that the study of substituent electronic effects is limited (or complicated) for heterogeneous catalytic systems by the involvement of adsorption phenomena, the inhomogeneous distribution and nature of active sites and the contribution of steric effect [73]. Such limitation should be particularly pronounced when using the catalysts supported on microporous supports. However, we found the relationships in some particular cases when studying the Pd/CNGs catalyst. For example, an increase in TOF for the hydrogenation of substrates in a series 4-nitroaniline (1i) < 1-methoxy-4-nitrobenzene (1g) < 1b (Table 3, entries 1, 6 and 8) can be explained taking into account a nucleophilic mechanism for the hydrogenation of nitroarenes [74–76] and the Hammett equation considering substituent electronic effects [73-76]. In a nucleophilic attack, the reaction rate is enhanced by electron-withdrawing substituents. The substituent electron donating/acceptor character can be evaluated by σ factor which increases in a series 1i(-0.66) < 1g(-0.27) < 1b(0) [77]. Therefore, according to the Hammett equation for nucleophilic reactions, the hydrogenation rate increases in proportion to the increase in σ constant of the para-substituent.

When comparing the hydrogenation of nitrophenols **1e** and **1f** (Table 3, entries 4 and 5), the conjugation and inductive effects should be taken into account [78]. Due to the conjugation effect in the molecules of **1e** and **1f**, the negative charge in the nitrophenoxide ion may be delocalized onto the nitro group, making the group more stable. On the other hand, the inductive effect depending on the distance between the substituent group and the NO₂ group also plays a certain role. Obviously, the inductive effect in *ortho*-isomer **1e** is stronger than that in *para*-isomer **1f**. The stronger inductive effect in **1e** makes its nitrogen atom more positively charged, resulting in higher reactivity.

In the case of the hydrogenation of *ortho*-substituted nitroarenes such as 2-nitroaniline (1h), 3-nitrophthalic acid (1 k) and 1 l, the rate of hydrogenation is relatively low (Table 3, entries 7, 10 and 11), which may be due to the steric hindrances that are characteristic of *ortho*-substituted nitrobenzenes.

4 Conclusions

In summary, it was found that 1% palladium catalysts supported on CNGs exhibit high activity and selectivity in the liquid-phase hydrogenation of various nitroarenes under mild conditions (323 K, 0.5 MPa, 1 h). On the example of ethyl 4-nitrobenzoate hydrogenation, it was shown that the catalytic activity (in terms of TOF and substrate conversion) and selectivity depend on the physicochemical characteristics of CNGs, the composition of Pd precursor, catalyst preparation method and the nature of solvent used as the reaction medium.

It is possible to highlight the following advantages of our proposed Pd/CNGs catalysts for their use in the hydrogenation of nitroarenes: (1) low content of expensive palladium in the catalyst (1 wt%); (2) CNGs material used as the catalyst support is produced on a large scale (carbon black), which makes it quite affordable; (3) Pd/CNGs catalysts can be prepared by simple and well-known methods; (4) complete conversion of nitroarene and nearly 100% selectivity to amine can be achieved under mild conditions of hydrogenation; (5) Pd/CNGs catalyst can be repeatedly used while maintaining the same selectivity to target amine, that makes palladium catalysts of this type attractive for the hydrogenation of nitroarenes on a large scale.

The above-mentioned advantages of Pd/CNGs catalysts could arise due to the globular morphology of the chosen supports as well as the absence of micropores and pronounced surface defects. The results of the present study clearly show that variation of the physicochemical properties of CNGs makes it possible to change the formation conditions and size of supported Pd NPs and thus achieve improved performances of Pd/CNGs catalysts.

Acknowledgements We thank O. V. Maevskaya, Dr. R. R. Izmailov, I. V. Muromtsev, Dr. A. B. Arbuzov, E. N. Kudrya, Dr. V. P. Talsi and S. N. Evdokimov for their help with experiments. Besides, the authors are grateful to Dr. A. S. Kostyuchenko (Omsk State Technical University, Omsk, Russia) for the supply of some nitroarenes. The authors also gratefully acknowledge Dr. G. L. Rusinov (I. Ya. Postovskiy Institute of Organic Synthesis, Yekaterinburg, Russia) for the supply of 1-(2,3-difluoro-6-nitrophenoxy)acetone.

Funding This work was supported by the Russian Foundation for Basic Research (Grant Number 16-29-10742).

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