Catalytic Properties of Palladium Nanoparticles Deposited on Undoped and Nitrogen Doped Carbon Nanofibres in Selective Hydrogenation of Acetylene

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Abstract

Palladium in the concentration of 0.04–0.5 mass % was deposited on carbon nanofibres with the stack structure. The state of finely dispersed palladium nanoparticles deposited on the carbon nanofibres was studied by physical methods. Decrease of the concentration of supported palladium on the carbon nanofibres below 0.2 mass % led to the stabilization of the metal in atomic state. It was found that palladium nanoparticles in the atomic state were responsible for the high selectivity of the catalyst in acetylene hydrogenation to ethylene. Doping of carbon nanofibres by nitrogen atoms substantially alters the properties of supported palladium nanoparticles. The activity of the catalysts decreases whereas their selectivity substantially increases

Key words: palladium nanoparticles, carbon nanofibres, nitrogen doping, hydrogenation

INTRODUCTION

Olefins are the most important feedstock for industrial organic synthesis. Industrial synthesis of unsaturated hydrocarbons commonly includes cracking of various oil alkanes, from light gaseous fractions C_2–C_3 to heavy liquid fractions such as naphtha and gas oil [1, 2]. The process is inevitably accompanied by the formation of acetylene compounds; these impurities are extremely undesirable because they can irreversibly deactivate catalysts that are employed for further processing of the obtained olefins. For example, in stereoregular polymerization of ethylene these impurities rapidly poison Ziegler–Natta catalysts and drastically lower the quality of resulting polymers. In this connection, the content of acetylene impurities should be decreased to 10 ppm [3–5].

It should be noted also that the reactions of selective hydrogenation of alkynes or dienes are structure-sensitive. According to studies with model catalysts, the (110) face of Pd showed a higher selectivity in the formation of butenes as compared to the (111) face [6, 7]. It was also found [8, 9] that catalyst deactivation under the action of reaction medium depends on the accessible faces of crystals.

It was supposed [10] that alumina was a source of the strongest acid sites that catalyze oligomerization processes on the catalyst surface. In distinction to conventional supports (for example, Al_2O_3), carbon supports do not contain acid sites that are responsible for oligomerization of acetylene with the formation of "green oil" interacting with palladium and deteriorating its catalytic activity [11].

Carbon materials are of particular interest as supports of heterogeneous catalysis due to their inertness and the possibility to control porosity and modify the surface chemically by introducing various functional groups, which can facilitate a controllable synthesis of highly dispersed metal nanoparticles. Among such

materials, carbon nanostructures, nanotubes and nanofibers were shown to possess remarkable physical and chemical properties. Owing to these properties, carbon nanostructures can be employed as supports in heterogeneous catalysis, in particular for hydrogenation reactions [12−16].

Some works demonstrated that the electronic effects originating from specific metal-support interaction can change the behaviour of metal-carbon catalysts in hydrogenation reactions [17−22].

In the last decade a new area of research devoted to synthesis [23−26] and application [27−33] of carbon nanofibers doped with nitrogen atoms is actively developed.

The goal of our research was to study the effect of the carbon nanofibers structure and doping of the carbon nanofibers by nitrogen on the catalytic properties of the deposited palladium nanoparticles in selective hydrogenation of acetylene.

EXPERIMENTAL

Carbon supports

Supports used in the study were represented by carbon nanofibres (CNFs). The CNFs with stacked structure were obtained by decomposition of methane on the Ni−Cu−Fe/Al_2O_3 catalyst at 650 °C. CNFs with the stacked structure are short thick nanofibres. The diameter of CNFs varies from 30 to 120 nm.

Nitrogen doped carbon nanofibres (N−CNFs) were synthesized by decomposition of 40 % C_2H_4−60 % NH_3 mixture over 65 % Ni−25 % Cu−10 % Al_2O_3 catalyst at 550 °C. According to the elemental analysis and XPS data, the total nitrogen concentration in N-CNFs was 3 mass %.

Synthesis of Pd/CNFs and Pd/N-CNFs catalysts

To remove a catalyst from the obtained nanocarbon, the synthesized CNFs and N−CNFs were etched with aqua regia (HNO_3/HCl = 1 : 3) upon heating and stirring on a magnetic stirrer for 30 min. The etched samples was filtered and washed out with distilled water to remove acids by bringing pH of wash water to ca. 7. After that, the nanocarbon was dried and calcined in a muffle furnace at 150 °C for 30 min.

Palladium was deposited on CNFs and N-CNFs from an aqueous solution of $PdCl_2$ acidified with hydrochloric acid. The concentration of $PdCl_2$ in the solution was 0.3 mass %. Metal content in Pd/CNF catalysts was varied from 0.04 to 0.5 mass %. Metal content in Pd/N-CNF catalysts was varied from 0.05 to 0.15 mass %. The calculated volume of the $PdCl_2$ solution was poured into a beaker, supplemented with 5−10 mL of distilled water, and 1.00 g of carbon was then added under stirring on a magnetic stirrer. Water was evaporated to dryness; the solid residue was transferred to a porcelain dish and calcined in a muffle furnace at 150 °C for 30 min.

Pd/C catalysts having different concentrations of palladium were studied by various physical methods.

The X-ray diffraction study was carried out on a Siemens D-500 diffractometer using monochromatic CuK_α radiation (a reflected beam graphite monochromator).

CNFs and Pd/CNFs catalysts were examined by high resolution transmission electron microscopy (HRTEM) combined with electron diffraction on a JEM-2010 instrument with an accelerating voltage of 200 kV and a line resolution of 0.14 nm.

The nitrogen amount in N−CNFs was determined by the elemental analysis. Charging states of nitrogen in N−CNF samples were analyzed by X-ray photoelectron spectroscopy (XPS). After the reaction, samples were quenched in an argon medium to prevent the catalyst changes. Spectra were collected on a KRATOS ES300 photoelectron spectrometer with a non-monochromatized AlK_α radiation (photon energy of 1486.6 eV). The core-level Au $4f_{7/2}$ gold line with the binding energy 84.0 eV was used for spectrometer calibration. The survey spectra were acquired at the analyzer transmission energy 50 eV and step 1 eV. The narrow spectral regions were collected at the analyzer transmission energy 25 eV and step 0.1 eV.

TABLE 1

Specific surface area of CNFs and N−CNFs

Carbon supports	S_{BET}, m^2/g
CNFs	100
N−CNFs	250

TABLE 2

Properties of carbon nanomaterials according to X-ray diffraction analysis

Carbon nanomaterials	Synthesis temperature, °C	Lattice parameter of graphite, nm
CNFs	650	0.340
N−CNFs	550	0.342

The specific surface area of CNFs and N−CNFs was measured by thermal desorption of argon. The measurement data are listed in Table 1.

As shown by the XRD study, all carbon samples are represented by graphite with different degrees of ordering (Table 2). An intense line of graphite is observed on all X-ray patterns in the 2θ region of ~26°. Depending on the type of carbon nanomaterial, interplanar distance changes in a range of $d_{002} = 3.40-3.42$ Å.

Catalytic testing

The hydrogenation reaction was carried out in a quartz flow reactor. A model mixture containing 99.5 % ethylene and 0.5 % acetylene served as the ethylene-acetylene fraction. Flow rates of the hydrocarbon mixture and hydrogen were determined by rotameters.

A mixture at the reactor outlet was analyzed on a Crystal-2000 gas chromatograph using a column with Porapak T, length 1.5 m and internal diameter 2 mm. Temperature of a detector was 150 °C; evaporator, 50 °C; and column, 35 °C. Sampling was made using a 100 mL syringe.

RESULTS AND DISCUSSION

Investigation of the catalytic activity of palladium nanoparticles deposited on CNFs and N-CNFs

Preliminary experiments showed that CNFs and N−CNFs are not active in hydrogenation of the ethylene-acetylene mixture.

The catalytic activity of the 0.1 % Pd/CNF samples was measured at different temperatures. The measurement data are presented in Fig. 1. The mass of the catalyst sample was 0.10 g, flow rate mixture $C_2H_4-C_2H_2 - 3$ L/h, $C_2H_2/H_2 = 1 : 10$.

As seen from Fig. 1, the catalytic activity of all catalytic systems increases and selectivity de-
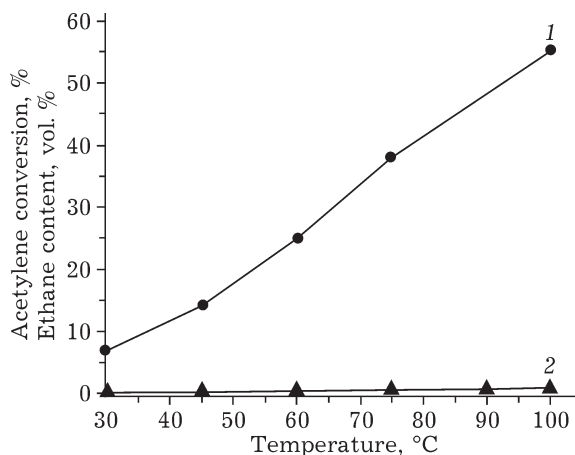

Fig. 1. Temperature dependence of acetylene conversion (*1*) and of ethane content in a mixture at the reactor outlet (*2*) for the 0.1 mass % Pd/CNFs catalysts.

creases with raising the temperature. The ethane content in a mixture at the reactor outlet increases from 0.05 (30 °C) to 0.7 % (100 °C).

Table 3 shows catalytic properties of the Pd/CNF system with various contents of palladium at temperature of 90 °C.

Pd/CNFs catalysts with the Pd content below 0.04 % do not show any catalytic activity; this may be related to intercalation of the metal in the interlayer space of graphite.

According to Table 3, an increase in palladium content of the sample is accompanied by a growth of catalytic activity, the acetylene conversion reaches 90 %; however, ethane content in a mixture at the reactor outlet also increases.

Electron microscopy study of Pd/CNFs

Results of the electron microscopy examination of Pd/CNFs are summarized in Figs. 2 and 3.

TABLE 3

Acetylene conversion and ethane content in a mixture at the reactor outlet for the Pd/CNFs with different palladium content at 90 °C

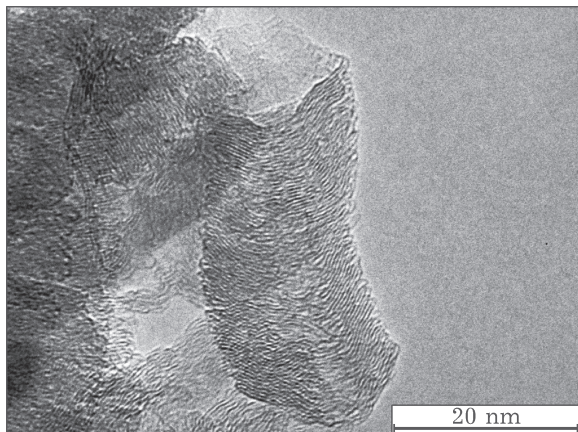| Palladium content, mass %	Acetylene conversion, %	Ethane content, vol. %
0.00	0	0.0
0.04	0	0.0
0.06	15	0.2
0.08	25	0.4
0.10	54	0.6
0.20	78	4.3
0.30	90	9.2

Fig. 2. Electron microscopy image of the catalyst 0.1 mass % Pd/CNFs (stacked).

Figure 2 depicts an electron microscopy image of the 0.1 mass % Pd/CNFs with the stacked structure. The electron microscopy study did not detect palladium particles on the surface of the catalyst. Highly disperse dots in Fig. 2 can be attributed to defects in the CNF structure. This indicates a high dispersion of palladium particles on the surface of carbon nanofibres with the stacked structure.

When palladium concentration in the catalyst was increased to 0.3 mass %, only very rare palladium particles with the size of ca. 0.8–1 nm were found (see Fig. 3). Effect of the concentration of supported palladium on palladium dispersion in Pd/C catalysts represent in Table 4.
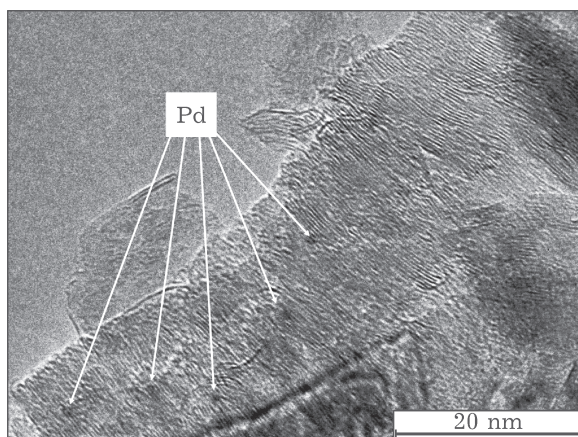
TABLE 4

Effect of the concentration of supported palladium on palladium dispersion in Pd/CNFs

Carbons	Palladium content, mass %	Diameter of palladium particles, nm
CNFs	0.1	Not visible
CNFs	0.3	0.8–1

EXAFS study of Pd/CNFs catalysts

The EXAFS spectra of 0.05–0.5 % Pd/CNFs are shown in Fig. 4.

Two peaks are observed in the EXAFS spectrum of the tested samples Table 5. The first peak corresponds to the R value of ~2.25 Å. Such interatomic distance corresponds to the Pd–C distance. This peak is typical of all the samples that contain carbon. The second peak corresponds to the R value of 2.75 Å, which belongs to the Pd–Pd distance. The highest amplitude is observed for the peak corresponding to the 0.5 % Pd/CNFs sample. For the sample with palladium content of 0.2 %, the peak corresponding to the Pd–Pd distance substantially decreases. This peak is not observed for the sample with 0.05 % of palladium (the amplitude at a noise level). This gives grounds to conclude that in the samples with palladium content below 0.2 % the metal is mostly (ca. 95 %) in the atomically dispersed state.
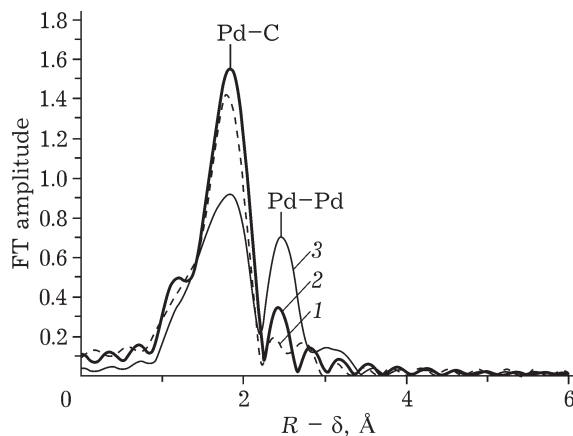

Fig. 3. Electron microscopy image of the catalyst 0.3 mass % Pd/CNFs (stacked).

Fig. 4. Amplitudes of Fourier transform of EXAFS spectra for the tested samples: *1* – 0.05 % Pd/CNFs; *2* – 0.2 % Pd/CNFs; *3* – 0.5 % Pd/CNFs.

TABLE 5

Distances between atoms (R), coordination numbers (N), Debye$-$Waller factors (σ^2) and discrepancy factors (R) for the local environment of palladium in the Pd/CNFs samples

Samples	Pd$-$C			Pd$-$Pd			R-factor, %
	R, Å	N	σ^2, Å$^{-2} \cdot 10^4$	R, Å	N	σ^2, Å$^{-2} \cdot 10^4$	
0.05 % Pd/CNFs	2.26	4.8	20.4				22.5
0.2 % Pd/CNFs	2.25	4.3	18.8				17.7
0.5 % Pd/CNFs	2.19	3.5	58.1	2.75	1.4	48.9	24.0

Properties and catalytic activity of Pd/N$-$CNFs

The properties of Pd/N$-$CNF catalysts were studied in selective hydrogenation of acetylene. The palladium concentration in the Pd/N-CNF catalysts was varied in the range of 0.05$-$0.15 mass %.

Figure 5 reports the data on the dependence of acetylene conversion on reaction temperature for the 0.05$-$0.15 % Pd/N$-$CNFs. For all Pd/N$-$CNF catalysts 100 % selectivity in acetylene hydrogenation to ethylene was observed, no ethane was registered in reaction mixture.

The 0.05 % Pd/N$-$CNFs has low activity (see Fig. 5, curve 1). No catalytic activity is observed in the temperature range of 25$-$100 °C. Selective acetylene hydrogenation to ethylene is observed at higher temperatures. However the acetylene conversion reaches only 12 % at 150 °C.

The data reported in Fig. 5, curve 2, demonstrate that the 0.1 % Pd/N$-$CNFs has higher activity than the 0.05 % Pd/N$-$CNF catalyst.
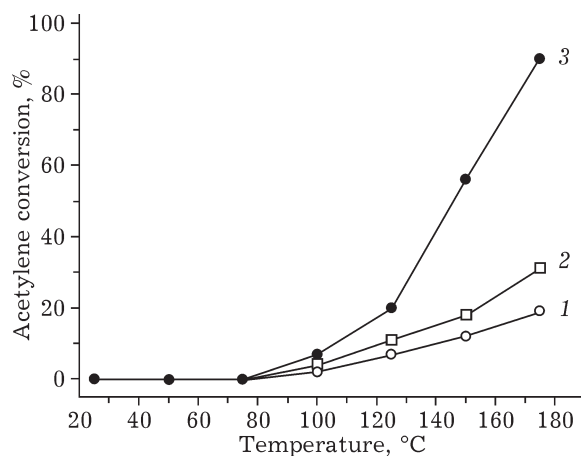
Acetylene hydrogenation over the 0.1 % Pd/N$-$CNF starts at 100 °C. The temperature growth leads to the increase of the catalytic activity in acetylene hydrogenation to ethylene. At 150 °C acetylene conversion reaches 18 %.

The increase of Pd concentration in the Pd/N$-$CNF catalyst up to 0.15 % (see Fig. 5, curve 3) leads to further growth of the catalytic activity. Acetylene hydrogenation over the 0.15 % Pd/N$-$CNF also begins at 100 °C. The activity of the 0.15 % Pd/N$-$CNF in selective acetylene hydrogenation to ethylene is higher than that of the 0.1 % Pd/N$-$CNF. The conversion of acetylene at the level of 90 % is observed at 175 °C in the absence of ethane.

Thus, the CNF doping by nitrogen substantially modifies the catalytic properties of supported palladium nanoparticles: the activity of the catalysts decreases whereas their selectivity substantially increases. This is primarily related to stabilization of palladium atoms on the surface nitrogen sites.
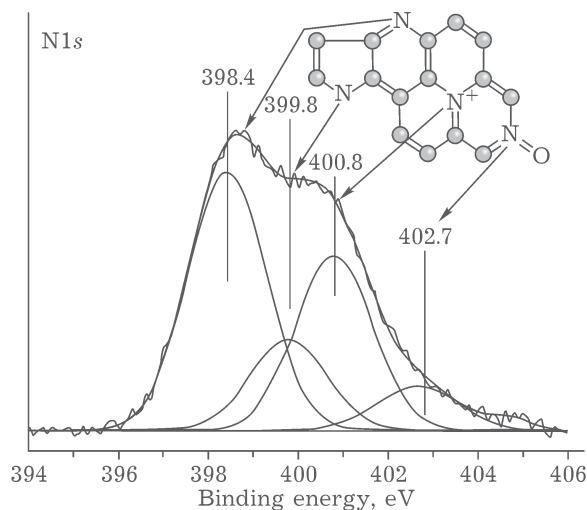

Fig. 5. Temperature dependencies of acetylene conversion for the Pd/N$-$CNFs with different content of palladium (mass %): 1 $-$ 0.05, 2 $-$ 0.1, 3 $-$ 0.15.

Fig. 6. Different nitrogen states in N$-$CNFs: XPS data of 3 % N$-$CNFs.

It was shown using XPS that nitrogen in N-CNFs exited in several electronic states: pyridine-like ($E_b = 398.5$ eV), pyrrole ($E_b = 400$ eV), graphite-like ($E_b = 401$ eeV) and oxidized ($E_b = 402-403$ eV) (Fig. 6).

In [34] it was demonstrated that single isolated Pd^{2+} cations were present on the N-doped carbon. Pd^{2+} cation is coordinated by a couple of pyridine-type nitrogen atoms located on the open edge of the graphene sheet. In our case we also consider that palladium ions are stabilized on the surface of CNF edge facets.

CONCLUSION

CNFs and N−CNFs synthesized were used to prepare palladium supported catalysts; their catalytic properties in selective hydrogenation of acetylene to ethylene were studied.

Regularity was found for CNF support: the higher the content of palladium in a catalyst, the higher the activity in hydrogenation reaction. However, selectivity of the catalysts showed a substantial decrease. The obtained regularity is determined by the features of "palladium−carbon support" interaction. At a low Pd content (below 0.04 mass %) in a catalyst, the metal is intercalated in the interlayer space of graphite and the catalytic activity is equal to zero. The EXAFS study revealed that the main part of palladium in the 0.05−0.1 % Pd/CNFs catalysts is present as a metal in the atomically dispersed state. Carbon atoms reside in the coordination environment of palladium atoms. The Pd/CNFs catalysts where palladium is mostly in the atomically dispersed state have the highest selectivity in hydrogenation of acetylene. An increase in palladium content of the Pd/CNFs catalyst to 0.3 mass % is accompanied by the formation of highly dispersed 0.8−1 nm Pd particles.

The CNF modification with nitrogen atoms substantially modifies the properties of Pd/N−CNFs catalysts. The activity of the catalysts decreases, whereas their selectivity substantially increases. Carbon nanofibres with stacked structures modified by nitrogen atoms are the most promising supports for the development of new Pd/N−CNF catalysts for the purification of ethylene from acetylene.

Acknowledgement

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Каталитические свойства палладиевых наночастиц, нанесенных на недопированные и допированные азотом углеродные нановолокна, в селективном гидрировании ацетилена

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Аннотация

Палладий в концентрациях 0.04−0.5 мас. % нанесли на углеродные нановолокна со стопчатой структурой. Состояние высокодисперсных палладиевых частиц, нанесенных на углеродные нановолокна было изучено с помощью физических методов исследования. Уменьшение концентрации нанесенного палладия на углеродном нановолокне со стопчатой структурой меньше 0.2 мас. % приводило к стабилизации металла в атомарном состоянии. Палладий в атомарном состоянии в Pd/C катализаторах обладает наивысшей селективностью в реакции селективного гидрирования ацетилена в этилен. Допирование углеродных нановолокон атомами азота значительно изменяет каталитические свойства нанесенных наночастиц палладия. Активность катализаторов уменьшается, тогда как их селективность существенно увеличивается.

Ключевые слова: палладиевые наночастицы, углеродные нановолокна, допирование азотом, гидрирование