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Preparation of highly dispersed $Ni_{1-x}Pd_x$ alloys for the decomposition of chlorinated hydrocarbons

Yuliya V. Rudneva [a,*], Yury V. Shubin [a,b], Pavel P. Plyusnin [a,b], Yury I. Bauman [c], Ilya V. Mishakov [b,c], Sergey V. Korenev [a,b] and Aleksey A. Vedyagin [c]

[a] Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia;
[b] Novosibirsk State University, Novosibirsk, Russia
[c] Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia;
* Corresponding author. Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia. E-mail address: rudneva@niic.nsc.ru (Yu.V. Rudneva)

Abstract: A convenient procedure to synthesize highly dispersed $Ni_{1-x}Pd_x$ alloys has been developed. The procedure is based on thermal decomposition in the reducing atmosphere of specially synthesized multicomponent precursor. The formation of single-phase solid solutions in the entire range of palladium concentrations was confirmed by powder XRD. The alloys have a porous structure composed of grains whose size depends on the synthesis temperature. The study of the catalytic properties of $Ni_{1-x}Pd_x$ alloys (5 wt.% Pd) showed their high activity in the 1,2-dichloroethane decomposition process. After 5 h of catalytic experiment the yield of carbon material was 160 g_C/g_{cat} for $Ni_{1-x}Pd_x$. This is more than 3 times higher than the yield of reference samples (porous Ni, Ni–Co, Ni–Cu). The carbon material formed has a segmented fibrous structure. It is characterized by high morphological uniformity. The specific surface area of the obtained carbon material is 580 m^2/g.

Keywords: Ni-Pd alloys; dispersed alloy; combined precipitation; 1,2-dichloroethane; alloy catalysts; carbon fibers

1. Introduction

Over the past decades, the problem of reducing environmental pollution by highly toxic Cl-containing organic wastes is of great interest. These wastes are accumulated as a result of the growing production of polymer materials. Recycling of these wastes is a tough problem due to their high chemical resistance. The catalytic decomposition on nickel and its alloys is one of the most promising methods for recycling Cl-containing organic wastes [1–4]. This method enables the conversion of multicomponent waste to easily utilized HCl and carbon material [5]. The forming carbon material represents fibers of different morphology, which have hydrophilic properties and are characterized by a high specific surface area. These properties make them promising for various applications [6], in particular, the development of heat-resistant materials [7], composite materials with increased strength properties [8], the preparation of sorbents and catalytic supports [9, 10].

Recent studies have shown that the decomposition process of Cl-containing organic wastes can proceed on both highly disperse supported catalysts [5] and bulk materials (wire, mesh, macrocrystalline powder) made of nickel or its alloys with transition metals [11]. The formation of a carbon fiber during the reaction proceeds according to the carbide cycle mechanism [5, 12, 13]. This mechanism consists of the following steps: 1) catalytic decomposition of chlorinated hydrocarbons on the metal particle surface; 2) diffusion transfer of carbon atoms through the of a metal particle bulk; 3) formation of graphite-like phase nuclei and the growth of carbon fibers.

Spontaneous dispersion of bulk metal catalysts as a result of carbon erosion is a special feature of the catalytic decomposition method [14]. In this case, catalytic particles (~ 200-250 nm) form and detach from the initial catalyst. Then the particles are transferred into the formed carbon fibers. This process provides high accessibility of the particle surface for the reagents and promotes their long-term activity. As a result, a high yield of the carbon material is achieved [15, 16]. The basic features of the carbon erosion process were investigated during the catalytic decomposition of 1,2-dichloroethane in the presence of hydrogen on massive nickel and various nickel alloys (nichrome, chromel, etc.) [17]. It is shown that the concentration and type of components in the alloy significantly influence the activity and resistance to oxidation and deactivation of the formed catalytic particles.

We have previously demonstrated the possibility of preparing highly dispersed powders of $Ni_{1-x}M_x$ alloys (M = Cu, Co, Cr, Fe) in a wide range of compositions without alloying metals [15, 16, 18]. In the synthesis of alloys, the thermolysis of multicomponent precursors (namely, compounds or microheterogeneous mixtures) under reducing conditions was used. In the precursors, the atoms of the alloy components are mixed. During the reduction of these precursors in a H_2 flow homogeneous alloy particles are formed. It has previously been shown that in the 1,2-dichloroethane decomposition process the most active catalysts are nickel alloys with metals capable to form non-stoichiometric carbides: MeC_x. These carbides are solid solutions in which carbon atoms are at interstitial positions in the metal host structure [13]. The role of these carbides is related to the carbide cycle mechanism responsible for the catalytic activity of metal particles in the process under study. Pd is a metal with a wide range of Pd–C solid solutions [19]. In addition, dispersed palladium particles are known to catalyze the growth of carbon nanofibers (CNFs) and nanotubes (CNTs) in the gas-phase decomposition of hydrocarbons [20-23]. It should also be noted that heterogeneous catalysts based on metallic palladium are characterized by high stability in a reaction medium containing chlorine compounds (for example, HCl). Palladium is less subjected to deactivation under the influence of HCl in comparison with traditional catalysts based on nickel, cobalt, and iron for the synthesis of carbon material. Therefore, palladium catalysts are widely used in the reactions of liquid and gas phase hydrodechlorination of polychlorinated hydrocarbons [24-27].

There are reasons to suppose that the introduction of a small amount of palladium (up to wt. 5%) into the composition of a nickel-based alloy can promote an increase in the catalytic activity of nickel in the synthesis of carbon material (CM) and increase the catalyst stability in an aggressive reaction medium containing hydrogen chloride. In this work, bimetallic porous nickel-based $Ni_{1-x}Pd_x$ alloys with a Pd concentration in the range 1-10 wt.% were obtained. The catalytic activity of alloys in the decomposition of 1,2-dichloroethane with the formation of a carbon fibrous material was investigated. The characteristics of CM obtained were studied.

2. Materials and Methods

2.1. Reagents

For the synthesis of Ni1-xPdx alloys the following compounds were used: $Ni(NO_3)_2{\cdot}6H_2O$ (puriss.), $K_2[PdCl_4]$ (puriss.), $NaHCO_3$ (puriss.).

To carry out the catalytic experiments 1,2-dichloroethane (puriss.), argon (puriss. spec.) and hydrogen (puriss. spec.) were taken. For catching hydrogen chloride gas a NaOH solution was used.

2.2. Preparation of $Ni_{1-x}Pd_x$ solid solution

Weighed amounts of precursor salts $K_2[PdCl_4]$ and $Ni(NO_3)_2{\cdot}6H_2O$ calculated to obtain 1 g of the alloy and taken in the required Ni:Pd ratio were dissolved in 100 mL of deionized water. The obtained solution of metal salts was added dropwise to an aqueous 0.1 M solution of $NaHCO_3$ with vigorous magnetic stirring and elevated temperature (70 °C). During the synthesis pH was maintained within 7.0–9.0 via a controlled addition of the precipitator: 1 M aqueous solution of $NaHCO_3$. The resulted grey green precipitate was centrifuged, washed abundantly with distilled water, and dried at 105 °C for 12 h. Dried samples were then reduced in a hydrogen flow of 130 cm^3/min at 800 °C for 30 min. Reduced $Ni_{1-x}Pd_x$ alloy samples were cooled down to room temperature in a hydrogen flow. The cooled reactor was purged with helium. A pure Ni sample was prepared as the reference in accordance with the procedure described above.

2.3. Characterization and measurements

The powder X-ray diffraction (XRD) analysis of the samples was performed at room temperature on a Shimadzu XRD-7000 diffractometer (CuK_α radiation, Ni filter on the reflected beam). XRD patterns were recorded in the step mode in the angular range 2θ = 7–107°, step 0.05° (for the phase identification) and 2θ = 140–147°, step 0.02° (for the precise determination of lattice parameter). Polycrystalline silicon (a = 5.4309 Å) was used as the external standard. Data from the JCPDS data base were used as Ref. [28]. The lattice parameters were determined by an angular position of the (331) reflection using the PowderCell 2.4 software. The composition of $Ni_{1-x}Pd_x$ bimetal alloys was determined using a calibration curve constructed based on lattice parameters of the known alloys. The volume-averaged crystallite sizes were estimated from the integral broadening of the (111), (200), (220) peaks using the Scherrer formula [29] and the WINFIT 1.2.1 program [30].

The morphology of synthesized $Ni_{1-x}Pd_x$ alloy and carbon nanomaterials (CNMs) was studied by scanning electron microscopy (SEM) on a JSM-6460 (Jeol, Japan) electron microscope with a resolution of 4 nm and magnifications from 5 × to 300,000. Transmission electron microscopy (TEM) examinations were performed on a JEM-1400 (Jeol, Japan) instrument (accelerating voltage 80 kV).

The SEM/EDX study of the $Ni_{1-x}Pd_x$ alloy precursor was carried out on a JSM-5100LV microscope with an EX-23000BU energy-dispersive X-ray spectroscopy attachment at operating voltage of 15 kV. The samples were compressed into tablets at 500 MPa prior to the test.

The chemical composition of synthesized $Ni_{1-x}Pd_x$ alloys was determined by atomic absorption spectroscopy (AAS) on a Solaar IC-3000 spectrophotometer. Prior to the measurement procedure, the samples were dissolved in nitric acid.

The textural parameters (S_{BET}, m^2/g; V_{pore}, cm^3/g) of the obtained catalysts and CNM samples were determined by low-temperature N_2 adsorption (BET method). Nitrogen adsorption isotherms were measured at 77 K on ASAP-2400 (Micromeritics, USA).

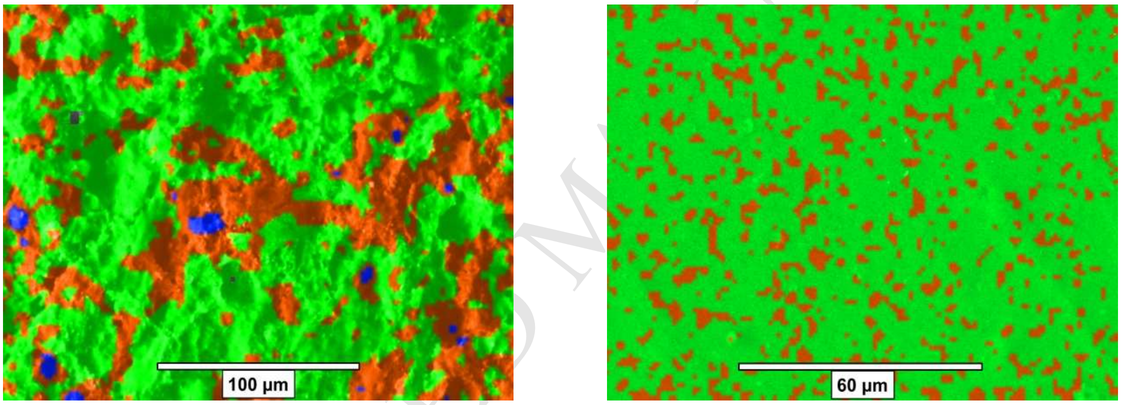
2.4. Study of the $Ni_{1-x}Pd_x$ catalytic activity

The kinetic measurement of the carbon product accumulation was conducted in a flow quartz reactor equipped with McBain balances at 600 °C [31]. Prior to the catalytic experiment the $Ni_{1-x}Pd_x$ alloy specimens were subjected to in situ reduction in a hydrogen stream at 500 °C for 30 min. The amount of each sample was 2.00±0.02 mg. After reduction the sample was brought to contact with the reactant mixture containing a constant concentration of DCE vapor (7.5 vol.%), H2 (37.5 vol.%) and argon (55 vol.%) as a balance. The total flow rate was 15 L/h. HCl released to the gas phase was trapped at the reactor outlet with a NaOH solution.

3. Results and Discussion

3.1. Synthesis of $Ni_{1-x}Pd_x$

Mixed nickel-palladium hydroxycarbonates were used as multicomponent precursors for the preparation of alloys. These precursors were obtained by the combined precipitation of $Ni(NO_3)_2$ and $K_2[PdCl_4]$ from an aqueous solution. The precipitation was carried out with a $NaHCO_3$ solution at its constant excess. At the same time, due to supersaturation, hydroxycarbonates of both metals precipitate simultaneously. As a result, a high degree of mixing of Ni and Pd in the obtained product is achieved. The structure determination and the phase composition of the obtained precursor were impossible since it was amorphous. Combined SEM/EDX method reveals that this method of alloy synthesis has a significant advantage over mechanical grinding of the precursors (Fig. 1). We studied two samples: 1) precursor obtained by grinding of $Ni(NO_3)_2 \cdot 6H_2O$ and $K_2[PdCl_4]$ in a mortar; 2) precursor synthesized by our method (sediment). To obtain the map of regions enriched and depleted in palladium (Fig. 1) for both precursors, the SEM/EDX method was used. The size of these regions varies from 10 to 200 μm in the grinded sample, and from 2 to 10 μm in the sediment. In addition, in sediment these regions are located much more evenly than in the grinded sample. Thus, it is clearly shown that in grinded samples the necessary extent of homogenization of the substances is not achieved.



(**a**) (**b**)

Fig. 1. SEM/EDX data of $Ni_{1-x}Pd_x$ alloy precursors (10 wt.% Pd) before reducing: a) grinding of alloy precursors in a mortar; b) sediment obtained by our technique.

When the dried precursor was reduced in an H_2 atmosphere at 400, 500, 600, and 800 °C, powders of differently dispersed $Ni_{1-x}Pd_x$ alloys formed. According to the elemental analysis (AAS) data, the composition of prepared alloys strictly corresponds to the preset alloy composition in the synthesis (Fig. 2). The crystallite size in the obtained alloys depends on the synthesis temperature. In the SEM images of the obtained samples, porous structures with different morphologies are observed (Fig. 3). Thus, at a temperature of 400 °C, a porous structure constructed of coupled bridges with a diameter of ~ 200 nm was obtained (Fig. 3a, b). With an increase in the temperature to 500, 600, and 800 °C, the diffusion rate of Ni and Pd atoms increases significantly, consequently, the crystallites enlarge. At T = 500 °C, the bridges are sintered into small blocks consisting of grains with a diameter of 200-300 nm (Fig. 3c, d). At 600 °C the blocks are sintered even more with an increase in the grain diameter to 500-600 nm (Fig. 3e, f). The alloys obtained by calcination of the precursor samples at 800 °C consist of 1-2 μm grains (Fig. 3g, h). Despite that with increasing calcination temperature the alloys are close in structure to bulk materials, they are still dispersed powders. The crystallite size of the obtained samples, determined from the XRD data, varies from 30 nm at T = 400 °C to 100 nm at 800 °C (Table 1).

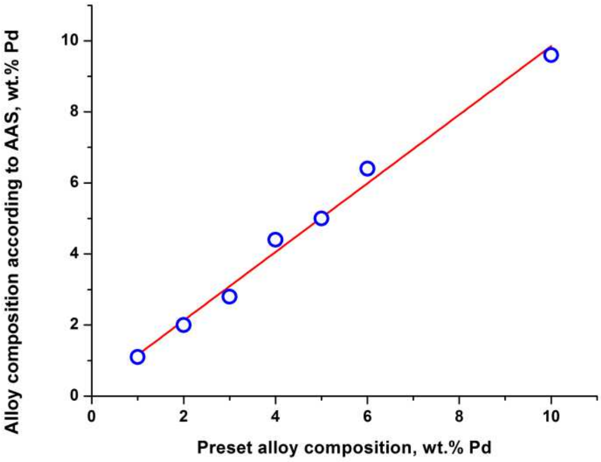
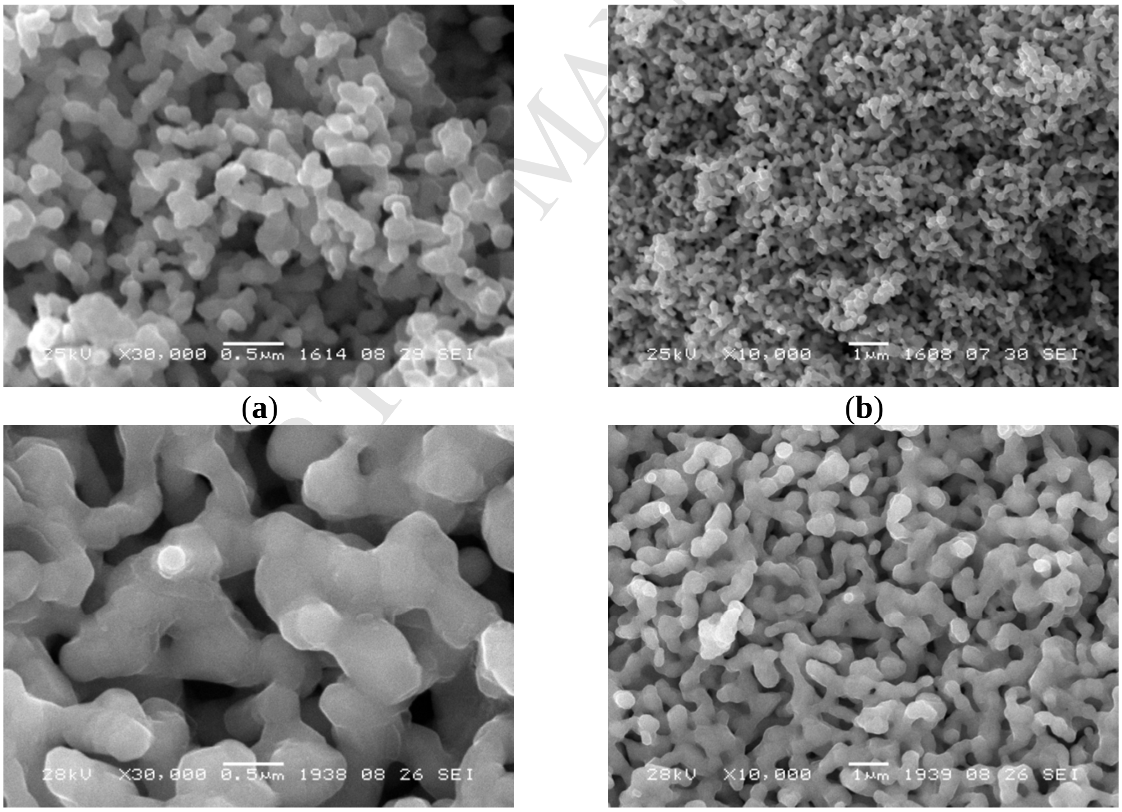
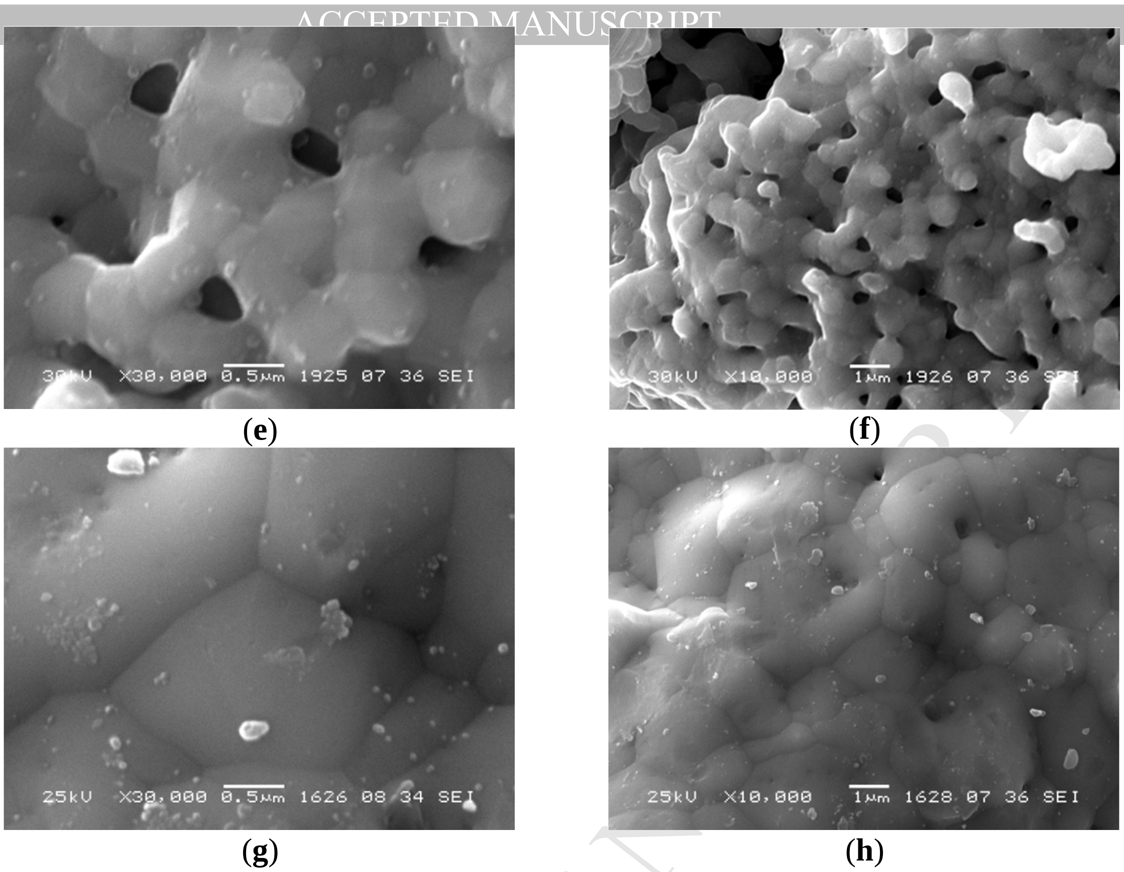


Fig. 2. Correspondence between the composition of synthesized alloys (according to AAS data) and the preset alloy composition in the synthesis.



(**a**) (**b**)

(**c**) (**d**)



(**e**) (**f**)

(**g**) (**h**)

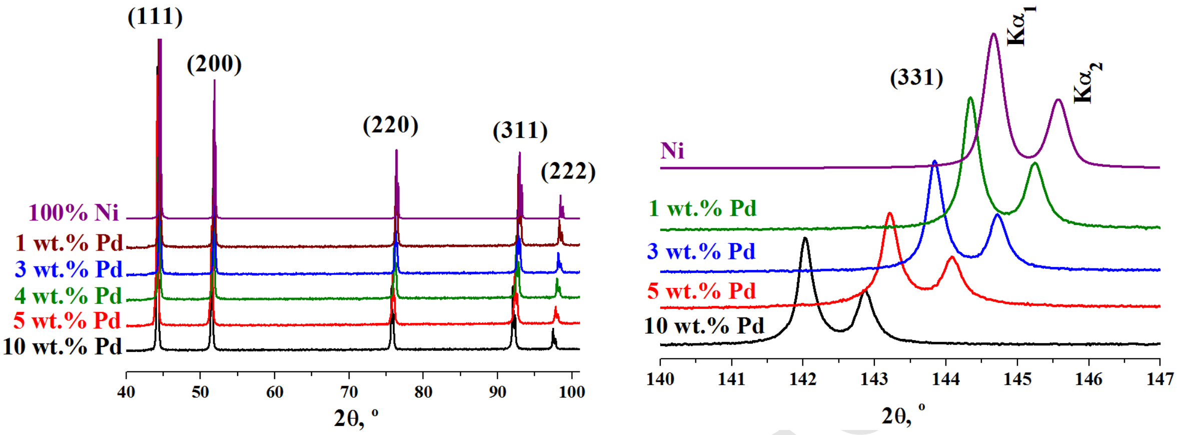
Fig. 3. SEM micrographs of $Ni_{1-x}Pd_x$ alloys (5 wt.% Pd) synthesized at 400 °C (a, b), 500 °C (c, d), 600 °C (e, f), and 800 °C (g, h).

Table 1. Characteristics of the obtained $Ni_{1-x}Pd_x$ samples.

№	Synthesis temperature, °C	Preset composition, wt. % Pd	Composition by AAS, wt.% Pd	**XRD data**			
				***a*, Å**	**Composition, at.% Pd**	**Composition, wt.% Pd**	**Crystallite size, nm**
1	400	5	4.2	3.539(1)	2.5	4.4	27
2	500	5	5.3	3.536(1)	2.7	4.8	36
3	600	5	5.2	3.537(1)	2.8	5.0	62
4	800	1	1.1	3.527(1)	0.7	1.3	76
5	800	2	2.0	3.529(1)	1.2	2.2	100
6	800	3	2.8	3.532(1)	1.7	3.0	81
7	800	4	4.4	3.536(1)	2.7	4.8	60
8	800	5	5.0	3.538(1)	3.6	6.3	73
9	800	6	6.4	3.543(1)	3.9	6.9	50
10	800	10	9.6	3.551(1)	5.5	9.5	82

3.2. Powder XRD analysis

In the diffraction patterns of all samples within 2θ= 40-100°, a set of reflections typical of a face-centered cubic (fcc) lattice is observed (Fig. 4a). Impurity peaks are absent. The position of the reflections is shifted to the low-angle range with respect to pure nickel. The shift of the reflections is most pronounced in the far-angle range (Fig. 4b).



(a) (b)

Fig. 4. XRD profiles for $Ni_{1-x}Pd_x$ alloys: (a) survey patterns; (b) (331) reflections in the far angle range.

The XRD qualitative data of the obtained alloys are summarized in Table 1. As can be seen, an increase in the Pd content in the alloy leads to a consistent increase in the lattice parameter of the solid solution. The lattice parameters of synthesized solid solutions fit well with the graph of the dependence of lattice parameters on the chemical composition of the $Ni_{1-x}Pd_x$ alloy (Fig. 5), which is constructed from the literature data [32-34]. This calibration reveals an insignificant deviation from Vegard's law [35] and in the low concentration range is close to linear. The composition of solid solutions based on the Ni crystal lattice, which is determined from the XRD data, is in good agreement with the nominal content of metals in the samples (AAS data). These data, as well as the absence of impurity peaks in the diffraction patterns, indicate that the obtained alloys are homogeneous.

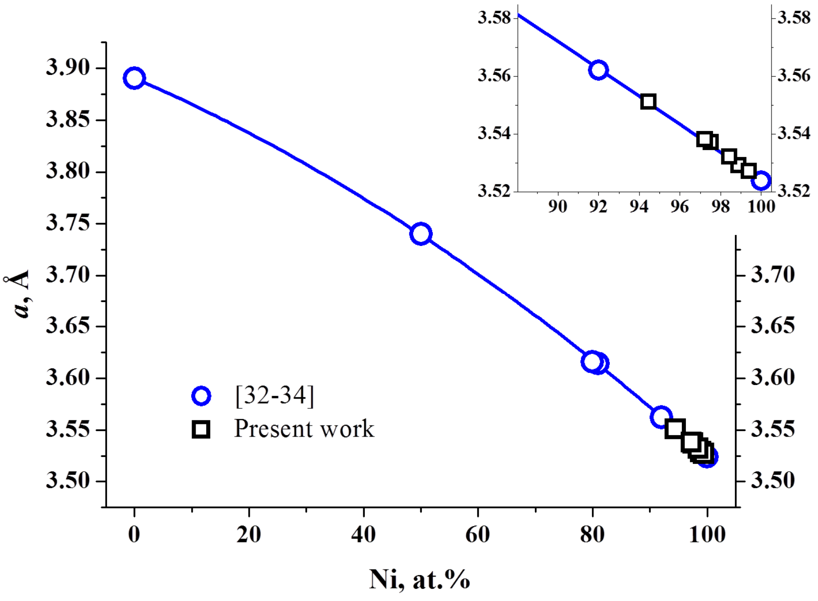


Fig. 5. Dependence of the lattice parameter of $Ni_{1-x}Pd_x$ alloy upon the nickel atomic fraction (X_{Ni}): experimental (□) and literature (○) data.

3.3. Catalytic properties of $Ni_{1-x}Pd_x$ alloys in the decomposition reaction of 1,2-dichloroethane

A sample of $Ni_{1-x}Pd_x$ containing 5 wt.% of Pd was investigated in a decomposition of 1,2-dichloroethane with producing of carbon material. As a result of contact of the sample with $C_2H_4Cl_2$ vapors in excess H_2, a rapid disintegration of a massive alloy occurs with the appearance of submicron metal particles. These particles catalyze the growth of carbon filaments. The phase of disintegration of the alloy is characterized by an induction period (10–20 min). After the induction period, a rapid growth of the carbon product takes place. The activity of the catalyst forming in this way can be represented as the yield of the carbon product (in grams) over a certain time, referred to 1 g of alloy.

The results of comparative catalytic tests are shown in Fig. 6. The same figure presents for comparison the previously published catalytic data [15] obtained for 100% Ni (reference sample), $Ni_{1-x}Co_x$, and $Ni_{1-x}Cu_x$ samples. These samples were prepared by a similar method. It can be seen that after two hours of the experiment the $Ni_{1-x}Pd_x$ catalyst activity is slightly higher than that of other samples. However, the advantage of using palladium as a promoting additive to nickel becomes evident in 3 hours from the start of the process (Fig. 6). A further increase in the experiment time to 5 hours showed that the $Ni_{1-x}Pd_x$ system retained a high catalytic activity in the synthesis of CM. By this time, samples based on Ni, $Ni_{1-x}Co_x$ and $Ni_{1-x}Cu_x$ are completely deactivated when CM is accumulated in an amount of 40-50 g/g_{cat} [18]. After the 5-hour reaction the yield of the carbon product was almost 160 g/g_{cat} for the $Ni_{1-x}Pd_x$ catalyst, which is more than 3 times better than the efficiency of the reference samples.

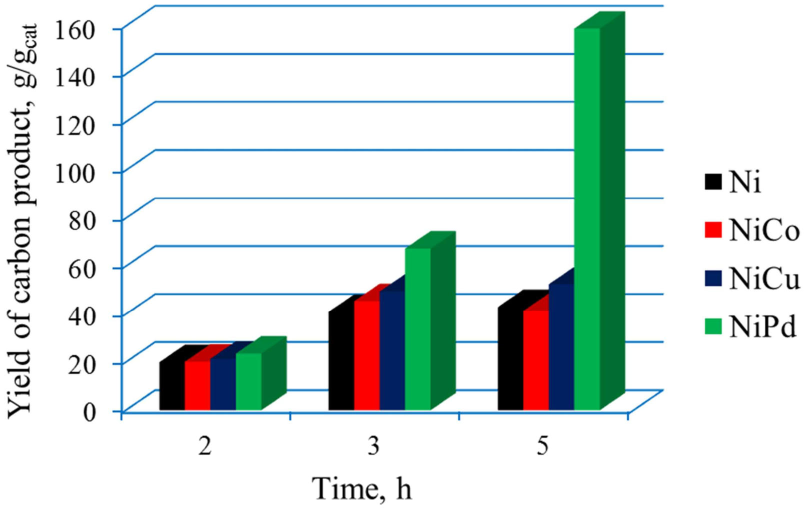
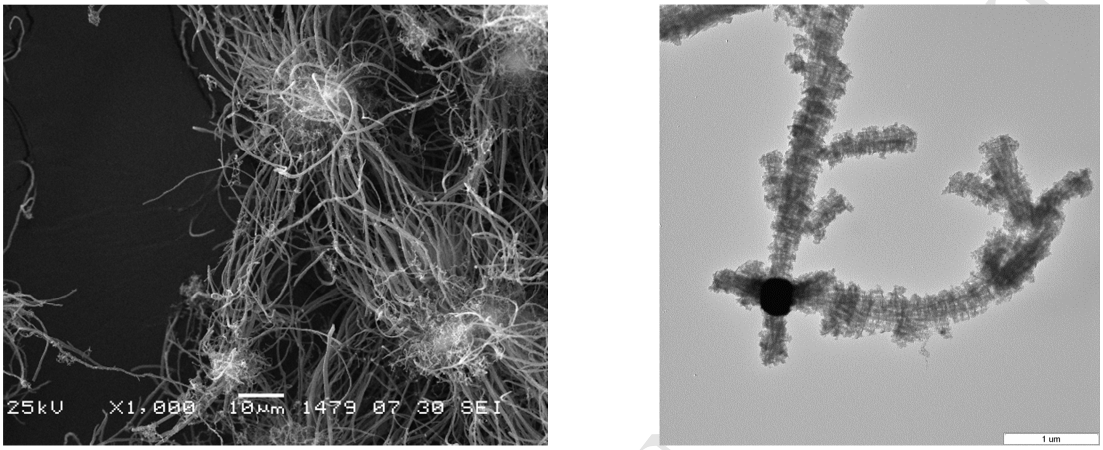


Fig. 6. Yield of CM obtained by decomposing the DCE/H_2/Ar reaction mixture on Ni, $Ni_{1-x}Cu_x$, $Ni_{1-x}Co_x$, and $Ni_{1-x}Pd_x$ catalysts for 2, 3, and 5 hours. The process temperature is 600 ° C.

Thus, the introduction of a small amount of palladium into the nickel alloy, resistant to the poisoning effect of hydrogen chloride, contributes to a sharp increase in the catalyst stability. This property is expressed in the absence of deactivation of the $Ni_{1-x}Pd_x$ catalyst in resource tests. Due to this, a high yield of CM exceeding 100 g/g_{cat} may be achieved.

The structure and morphology of the carbon product obtained as a result of the 1,2-dichloroethane decomposition on a $Ni_{1-x}Pd_x$ catalyst was investigated by SEM and TEM. The characteristic images are shown in Fig. 7. It can be seen that on the catalyst CM is formed only in the form of long carbon filaments of a submicron diameter which grow by conventionally parallel beams. The average diameter of carbon fibers is in the range 0.2–0.9 μm. The formation of carbon filaments is preceded by the process of complete destruction of the initial massive alloy. As a result of this destruction, dispersed active particles are formed (Fig. 7b). It should be noted that the special character of the growth of the carbon phase on $Ni_{1-x}Pd_x$ catalysts leads to the formation of a product with an extremely low bulk density of less than 0.03 g/cm^3. At the same time, for CMs synthesized on the other analogous $Ni_{1-x}M_x$ (M = Co, Cu, Fe) catalysts this parameter varies in the range 0.08–0.15 g /cm^3.



(**a**) (**b**)

Fig. 7. Filamentary morphology of the carbon product: (a) SEM data and the structure of carbon filaments, (b) TEM data. The sample was obtained by decomposing a $C_2H_4Cl_2/H_2/Ar$ mixture on a $Ni_{1-x}Pd_x$ catalyst (5 wt.% Pd) at 600 °C.

Metal particles playing the role of active centers of CM growth are located in the mass of the carbon product formed. Most often, the formation of a graphite-like phase on the surface of an active particle occurs immediately in several directions. Fig. 7b shows an active particle catalyzing the simultaneous growth of four carbon filaments. Usually, carbon fibers have a pronounced segmented structure [16] (Fig. 7b). This fact indicates a discrete character of carbon deposition. Due to a high degree of structure defectiveness, obtained CM has a high specific surface area (up to 580 m^2/g) and a developed pore system with a volume of 0.5–0.6 cm^3/g.

4. Conclusions

By reductive thermolysis of multicomponent precursors highly dispersed binary $Ni_{1-x}Pd_x$ alloys are synthesized. The proposed method makes it possible to obtain solid solutions with a preset composition in the concentration range 1-10 wt.% Pd. It is established that the introduction of a small amount of palladium into the nickel alloy contributes to a noticeable increase in the catalyst stability, which is expressed in the absence of its deactivation in resource tests. After the 5-hour reaction the yield of the carbon product was 160 g/g$_{cat}$ for the $Ni_{1-x}Pd_x$ (5 wt.% Pd) catalyst. Thus, the obtained alloys can be successfully used as catalysts for the catalytic decomposition of DCE to produce a carbon product.

Acknowledgements

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Highlights

- A new procedure for synthesis of highly dispersed $Ni_{1-x}Pd_x$ alloys is proposed.
- The particle size of the alloys depends on the synthesis temperature.
- $Ni_{1-x}Pd_x$ shows high stability in the carbon fiber formation reaction.
- Carbon fiber is characterized by high morphological uniformity.