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X-ray Photoelectron Study of Carbon-Nickel-Containing **Nanostructures Obtained in Nanoreactors** in Polyvinyl Alcohol Gels and in Gels Prepared from a Mixture of Polyvinyl Alcohol and Polyethylene Polyamine

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Abstract-The interaction of nickel ions with walls of nanoreactors in mixed gels based on polyvinyl alcohol and polyethylenepolyamine was investigated. The formation of positively charged nitrogen and unsaturated carbon-carbon bonds coordinated to nickel has been revealed. It is found that thermal effect leads to reduction of metal and carbonization. The carbon films obtained roll up into nanotubes and form shells of nickel nanocrystals.

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INTRODUCTION

The need for ecologically pure productions open wide prospects of application of synthesis of chemical materials in nanoreactors of different matrices. However, it is difficult to implement directed syntheses in nanoreactors without preliminary computational experiment, which predicts the behavior of chemical particles, and development of diagnostic methods, which would allow to control the intermediate and final products of occurring processes. Application of nanostructures in nanoreactors of polymer matrices for synthesis seems to be expedient due to the decrease in the energy consumed in the process and, in the ideal case, reduced output of minor products into the environment. In this context, development of X-ray photoelectron spectroscopy (XPS) for monitoring synthesis and testing obtained nanostructures is of particular importance. An essential feature of this method is its nondestructive character, since the X rays used to excite photoelectrons do not damage most materials. This does not hold true for the methods of surface analysis based on ion or electron bombardment. In this study, along with the XPS data, we used the results obtained by transmission electron microscopy (TEM), electron diffraction (ED), and IR spectroscopy.

The purpose of this study is to develop a model of formation of carbon-metal-containing nanostructures in active media and a technology of their fabrication.

EXPERIMENTAL

The XPS investigation was performed on an X-ray electron magnetic spectrometer with the following characteristics: automated control system, double focusing, resolution 0.1 eV, excitation by the Al K_{α} line (1486.6 eV), and vacuum 10^{-6} - 10^{-7} Pa. This spectrometer has a number of advantages over electrostatic spectrometers, specifically: constant aperture ratio, independence of resolution on the electron energy, and high spectral contrast.

The XPS method is used to monitor the fabrication of nanostructures from the relative content of C-C and C-H bonds, type of hybridization of valence s and pelectrons of carbon atoms and the satellite structure of the C 1s spectrum, and the type of interaction between metal atoms with carbon. This method makes it possible to identify C 1s spectra and determine the chemical bonds of elements, nearest environment of atoms, and the type of sp hybridization of valence electrons in nanostructures with the use of the satellite structure of the Cls spectra [1]. The XPS data make it possible to monitor the formation and growth of nanostructures. It



Fig. 1. (a) Results of the calculation of the multiplet structure of electron spectra of the 3p of nickel in complexes [3] and (b) the Ni3p X-ray photoelectron spectra of the samples obtained from the (1) 2PVA + 1NiCl₂, (2) 1PVA + 1PEPA + 1NiCl₂, (3) 2PVA + 2PEPA + 1NiCl₂, and (4) 1AA + 2PVA + 2PEPA + 1NiCl₂ mixtures.

has been established that, in the C1s spectrum, the satellite spaced at a distance of 22 eV from the main peak, is characteristic of the C–C bond with sp^2 hybridization of valence electrons; its relative intensity is 10% of the main spectrum intensity. The satellite can be caused by plasmon losses. If the C1s spectrum exhibits a satellite at a distance of 27 eV, the C–C bonds are characteristic of the sp^3 hybridization of valence electrons of carbon atoms (diamond, fullerene). One might suggest that the satellite ratio should change, depending on the diameter and shape of the nanostructures obtained. For rolls and multilayer tubulenes of large diameter, one might expect a much higher intensity of the satellite corresponding to the sp^2 hybridization in comparison with the satellite characteristic of the sp^3 hybridization.

The C1s spectrum of the single-wall nanotubes contains two satellites near 306 and 313 eV. Therefore, the spectrum of carbon single-wall nanotubes contain a component characteristic of the C-C bonds with sp^2 and sp^3 hybridization of valence electrons at carbon atoms. The intensity of the component characteristic of the sp^3 -hybridized C-C bond of valence electrons is lower by a factor of 2 in comparison with that of the component characteristic of the sp^2 -hybridized C-C bond. Hence, single-wall nanotubes are formed as a result of roll-up of a graphite plane. A similar situation is observed in the C1s spectrum of multilayer nanotubes of small diameter; however, in this case, the intensity of the component characteristic of the sp^3 hybridized C-C bonds of valence electrons is higher; apparently, due to the screening effect.

In this paper, we report the results of the XPS study of the nanoproducts obtained in nanoreactors of polymer matrices in the form of gels of polyvinyl alcohol (PVA); PVA and polyethylenepolyamine (PEPA); and PVA, PEPA, and acetylacetone (AA) in the presence of nickel chloride NiCl₂.

The PVA, PVA-PEPA, and PVA-PEPA-AA polymer matrices were obtained by mixing solutions of the corresponding components, according to the technique described in [2]. Then, the gels formed during predrying were treated with a nickel chloride solution. According to the IR spectra, interaction of nickel ions with oxygen of hydroxyl and ketone groups and nitrogen of amine groups occurs in the color films formed. In this case, the coordination number of Ni²⁺ is 4 in PVA gels and 6 in PVA-PEPA and PVA-PEPA-AA gels. Upon subsequent thermal treatment (step heating to 400°C), the film color changed to black and a porous semiproduct was formed, which was rinsed and dispersed with subsequent isolation and drying of the nanoproduct. The formation of nanostructures is a redox process, which implies metal reduction and carbonization of the organic components that form nanoreactor walls.

RESULTS AND DISCUSSION

In the XPS study, we analyzed the C1s and Ni3p spectra of the nanoproducts obtained from nickel chloride and PVA, PVA-PEPA, and PVA-PEPA-AA gels. Figure 1a shows the results of the calculations of the multiplet structure related to the 3p-3d interaction of unoccupied shells in nickel complexes. The Ni3p spectrum consists of three strong peaks: the main one and two peaks located at distances of 2.5 and 5.0 eV from the main peak; in addition, a series of weak peaks is observed at a distance of 10 eV [3].

The XPS data on the samples are presented in the table and Figs. 1 and 2.

The C1s XPS spectrum of the nanoproduct obtained from the 2PVA-NiCl₂ mixture showed the presence of the sp^2 -hybridized C-C bond; i.e., similar to graphite, as is evidenced by the satellite structure at 306 eV, as well as the presence of hydrocarbons and carbon-oxy-

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No.	Composition	Ratio of carbon bonds in the C 1s spectrum	Ratio of nickel bonds in the Ni 3 <i>p</i> spectrum
1	2PVA + INiCl ₂	$C-C(sp^2): C-H: C-O = (50: 40: 10)\%$	Ni-O(H): Ni-Cl = (55:45)%
2	1PVA + 1PEPA + 1NiCl ₂	Ni(C) : C–C(sp^2) : C–C(sp^3) : C–H = (21 : 42 : 11 : 26)%	$Ni-C$: $Ni-O(H)$: $Ni(N^+) =$ (12 : 35 : 53)%
3	$2PVA + 2PEPA + 1NiCl_2$	Ni–C : C–C(sp^2) : C–C(sp^3) : C–H = (15 : 28 : 14 : 43)%	Ni : Ni(N ⁺) = (23 : 77)%
4	$1AA + 2PVA + 2PEPA + 1NiCl_2$	Ni–C : C–C(sp^2) : C–C(sp^3) : C–H = (10 : 39 : 11 : 40)%	Ni : Ni–O(H) : Ni(N ⁺) = $(22 : 34 : 44)\%$

Relative Ni and C contents in the samples under study

gen (C–O) bond. The sp^3 -hybridized C–C bond is weakly pronounced for this mixture. The O1s spectrum indicates the presence of adsorbed and bound oxygen. The percent ratio of all these components is 50 : 40 : 10 (Table, row 1; Fig. 2a).

Analysis of the chemical shifts in the Ni3p spectrum (Fig. 1b, curve 1) indicates the presence of nickel bonds: Ni–O or Ni–O(H), as well as Ni–Cl or (H)O–Ni–Cl with approximately the same percent ratio. Reduced Ni atoms are absent in the analyzed layer. However, according to the X-ray diffraction (XRD), ED, and TEM data, metal (nickel) is present in multi-



Fig. 2. C1s X-ray photoelectron spectra of the samples obtained from the (1) 2PVA + $1NiCl_2$, (2) $1PVA + 1PEPA + 1NiCl_2$, (3) $2PVA + 2PEPA + 1NiCl_2$, and (4) $1AA + 2PVA + 2PEPA + 1NiCl_2$ mixtures.

layer tubular nanostructures, which form dense bundles ("aggregates") [4]. This fact can explain the sp^2 hybridization of carbon. The TEM images show that the formed carbon films roll up into nickel-containing "rolls". In this case, the lateral surfaces of such nanostructures can be fairly active to form aggregates. The instant of roll-up of a nanofilm, as well as the product of the process (aggregates of nickel-containing tubulenes), are shown in Fig. 3.

The C1s spectrum of the nanoproduct (Table, row 2; Fig. 2b) obtained from the mixture of PVA, PEPA, and NiCl₂ in the ratio 1 : 1 : 1 contains components that are due to the Ni–C interaction, C–C bond with sp^2 hybridization of the valence electrons of carbon, C–C bond with sp^3 hybridization of the valence electrons of carbon, and C–H bond. These components are in the following percent ratio: Ni–C : C–C (sp^2) : C–C (sp^3) : C–H = 21 : 42 : 11 : 26.

Analysis of the Ni3*p* spectrum (Fig. 1b, curve 2) showed the presence of nickel (12%), N–O or Ni–O(H) (35%), and Ni(N⁺) (53%) in the nanoproduct. Comparison of the IR and XPS N1*s* spectra indicates the presence of =N⁺= groups in the nanoproduct, which have an electronegativity of 3.3 [5]. This fact explains the corresponding chemical shift in the Ni3*p* spectrum. The formation of =N⁺= groups was noted in the analysis of the IR spectrum of the obtained color films (xerogels). These groups are evidenced by the existence of bands in the ranges 2280–2130 and 1710–1570 cm⁻¹ [6]. The spectra revealed bands associated with the C=N and



Fig. 3. TEM image demonstrating the instant of roll-up of a nanofilm and aggregates formed.

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Fig. 4. TEM images demonstrating the formation of small nanotubes and nickel nanocrystals on nanofilms and nanoribbons.



Fig. 5. TEM image demonstrating the instant of roll-up of a nanofilm with small graphite pieces and nickel nanocrystals.

N=N bonds. Analyzing the spectra, one can conclude that conjugation chains are formed; this process indicates possibility of forming of a thermostable coordination polymer with participation of Ni atoms. In this case, the coordination number of nickel, as in inorganic analogs, can be 6.

The presence of C--C bonds with sp^2 and sp^3 hybridization of valence electrons of carbon in the ratio 2 : 1 indicates the presence of nanotubes; however, since the number of sp^2 -hybridized C--C bond is larger, we can suggest that graphite inclusions are present, which arise due to the crystallization of the polymer precursor. This fact is confirmed by the TEM data. One might suggest that the presence of PEPA in the mixture leads to reduction of nickel, partially oriented to carbon, and increases the probability of breaking nanofilms at phase boundaries with formation of single-layer nanostructures of smaller diameter. This mechanism can be illustrated by the TEM data (Fig. 4). The micrograph demonstrates nanotubes with a diameter of about 10 nm and a length of about 200 nm against the background of amorphous thin "rumpled" nanofilms and small graphite particles with metal-containing nanocrystals.

With an increase in the content of the polymer phase and a decrease in the content of NiCl₂ (Table, row 3; Fig. 2c) in the C1s spectrum of the nanoproduct obtained from the 2PVA-2PEPA-NiCl₂ mixture, the component ratio changed as follows: Ni-C : C-C (sp^2) : C-C (sp^3) : C-H = 15 : 28 : 14 : 43.

Analysis of the Ni3p spectrum (Fig. 1b, curve 3) showed the presence of nickel in the sample and the $Ni(N^+)$ interactions in the ratio Ni(C) : $Ni(N^+) = 23 : 77$, which is indicative of coordination of nickel with positively charged nitrogen. In this case, the amount of interacting nitrogen greatly exceeds the amount of oxygen that can be present in the nanoproduct. The decrease in the content of Ni ions in the initial composition changed the character of the coordination interaction, which enhanced nickel reduction and increased the content of the heat-resistant polymer phase. The intensity ratio of the satellites reflecting the sp^2 and sp^3 hybridizations decreased. Therefore, one can state that the content of small single-wall nanotubes increased, all the more that, according to the TEM and ED data, graphite inclusions and a large number of small tubular nanostructures were observed. This fact can be explained by the formation of more stable crystalline polymer phases with an increase in the PEPA content.

During formation of nanostructures in nanoreactors of the PVA–PEPA–AA gel (table, row 4; Fig. 2d), the satellite ratio increased, apparently, due to the change in the mechanism of nickel coordination to the nitrogen and oxygen present in the walls of nanoreactors. Therefore, the fraction of the hydrocarbon part of the heatresistant polymer phase increased and the content of reduced carbon-saturated nickel somewhat decreased, because, during thermal action and catalytic process, stresses in the nanofilms increase, leading to their break and roll-up of pieces of amorphous film fragments under the action of Ni ions or atoms. The roll-up of a nanofilm is shown in the TEM image in Fig. 5.

The ratio of components in the C1s spectrum is as follows: Ni(C) : C-C(sp^2) : C-C(sp^3) : C-H = 10 : 39 : 11 : 40. From the ratio of the C-C(sp^2) and C-C(sp^3) components, one can judge about the shape and sizes of the nanostructures obtained. The TEM and ED data confirm the presence of graphite films in the sample and increase in the nanostructure diameter; i.e., they correlate with the XPS data (the contribution of the sp^3 hybridized component decreased). In addition, individual aggregates of nanostructures are observed; their presence explains the increase in the intensity of the satellite assigned to the sp^2 hybridization. Analysis of the Ni3p spectrum (Fig. 1b, curve 4) showed the pres-

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ence of reduced nickel, Ni–O(H) bonds, and Ni(N⁺) interactions in the ratio 22:34:44.

CONCLUSIONS

Based on the results of the XPS study and the TEM, ED, and IR spectroscopy data, we can propose the following model of formation of carbon nickel-containing nanostructures.

Carbon nanotubes or tubulenes containing nickel nanoclusters (in some cases, nickel nanocrystals) are formed during the redox process, in which nickel compounds play the role of an oxidant and hydrocarbon or amine groups serve as reducers.

During this process, chlorine and oxygen are removed from the sphere of interactions, and carbonization occurs with the formation of corresponding nanostructures. In this case, amorphous nanofilms are formed first; under the action of Ni ions or atoms, they roll up into cylindrical nanostructures of certain diameter. In the case of nanoreactors in the PVA gel, multilayer tubulenes are formed, which are prone to formation of aggregates due to the presence of sp^2 -hybridized C-C bonds.

Formation of gels of complex composition, including polyethylenepolyamine or polyethylenepolyamine and acetylacetone, facilitates metal reduction and graphitization. The formation of crystalline phases in carbon nanofilms is accompanied by an increase in the internal stress and break of the nanofilm with isolation of its amorphous part. Pieces of amorphous parts of the film roll up into single-wall nanotubes or form shells for nickel nanocrystals.

On the basis of the results obtained, we can draw the following conclusions.

(i) In contrast to the PVA gel, complex PEPA-containing gels exhibit an increase in the amount of reduced nickel, coordinated to the C=C bond, during the process under study.

(ii) With a decrease in the nickel content in a nanoreactor, the amount of thermostable coordination polymer increases, and small nanotubes are formed.

(iii) Addition of AA to PVA and PEPA increases the content of graphite inclusions without decreasing the content of the coordination polymer.

Thus, XPS can be successfully used to establish the character of nanostructures, their sizes, and characteristics of the processes of formation of metal nanoclusters.

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