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An X-ray Spectroscopy Study of the Electronic Structure of Products of Carbonization of Polyvinylidene Fluoride on Silicon Dioxide Nanoparticles

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The electronic structure of products of carbonization of polyvinylidene fluoride (PVDF) on SiO_2 nanoparticles was studied using the X-ray emission and photoelectron spectroscopy methods. The shape of the X-ray emission C*K*α band of products of carbonization of PVDF in a SiO_2 matrix resembles that of the band of fullerene C_{60} containing other carbonic structures, but that of products of PVDF carbonization in a matrix consisting of a mixture of SiO_2 and graphite resembles the band of pure graphite. A weak chemical bonding of oxygen atoms of silicon dioxide nanoparticles with products of PVDF carbonization is characteristic in the case of a SiO_2 matrix. The shape and energy positions of fine-structure peculiarities of the X-ray emission O*K*α bands of products of PVDF carbonization in matrices of fine silica and of SiO_2 with a mixture of graphite are similar to those of the analogous band of the initial SiO_2 particles. Surfaces of products of PVDF carbonization consist of C–C, C=C, CO, COO and CHF groups.

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Introduction

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I. Introduction

Porous carbon materials are widely used as high-performance sorption materials, catalyst carriers, membrane systems for filtration of either solutions or gases. Carbon in porous materials often ensures carbonization of polymers and organic precursors. Shapes and compositions of such carbon structures depend strongly upon carbonization conditions: speed of carbonization processes, concentration of precursors, presence and type of catalyst etc. [1-3]. Orientations of polymeric chains also affect significantly the structure of porous carbon materials [2,4].

This work presents results of investigation of the electronic structure of porous carbonic materials, products of carbonization of polyvinylidene fluoride (PVDF), in matrices of fine silica, SiO_2, and of its mixture with graphite.

II. Experimental

As precursors for obtaining composite-matrices in the present work either fine silica (particle size ≤80 nm,

S_{sp}=50 g/m^2) or its mixture with natural graphite (particle size 1–5 μm) were used. The matrices ("precomposites") were prepared employing the method of self-assembly of particles in dispersion of hydrophilic particles of either SiO_2 or a mixture of SiO_2 with graphite using PVDF solutions as a dispersion medium. The "precomposites" were formed at 50 °C using solutions of PVDF in acetone and at room temperature using solutions of PVDF in dimethyl formamide (DMF). It is well known that SiO_2 particles form stable spatial structures (gels) owing to their ability for self-assembling into ordered structures of PVDF solutions in DMF [5]. After drying the "precomposites", PVDF embedded into their pores was carbonized at 750 °C under argon atmosphere. The method of sample synthesis was described in details in Ref. [6].

As can be seen from Fig. 1, scanning electron microscopy (SEM) images derived with an electron microscope JEM100CX-II reveal that products of carbonization of PVDF in a fine SiO_2 matrix possess almost spherical shapes with particles sizes of about 100 nm while those in a matrix of fine silica with mixture of graphite contain (in addition to spherical particles with size of ca. 100 nm) also plate-layer structures (their thickness reaches values of a few nanometers).

Charge states of surface carbon atoms in products of carbonization of PVDF in fine silica matrices were investigated using the X-ray photoelectron spectroscopy (XPS) method. The experiments were made with an electron spectrometer "SERIES 800 XPS" Kratos Analytical employing an X-ray Mg*K*α source ($h\nu$=1253.6 eV).

The X-ray emission C*K*α and O*K*α bands ($K \rightarrow L_{II,III}$ transition), reflecting the energy distribution of the C2*p*- and O2*p*-like states, respectively, in the studied products of carbonization in matrices of fine silica and its mixture with graphite were derived using an RSM-500 spectrometer-monochromator. The energy resolutions of the RSM-500 spectrometer-monochromator in the ranges corresponding to energy positions of the C*K*α and O*K*α bands were found to be better than 0.3 eV and 0.4 eV, respectively. The operation conditions of the X-ray tube were the following: accelerating voltage, U_a = 5 kV; anode current, I_a = 1.5 mA. The detector was a secondary electron multiplier VEU-6 with a CsI photocathode and the dispersing element was a diffraction grating with 600 lines/mm and a radius of curvature of R = 6026 mm. The X-ray emission measurements were made under condition of oil-free evacuation. The residual pressure in the spectrometer chamber was routinely ca. 5×10^{-6} Pa during the present measurements.

III. Results and discussion

Figure 2 displays the XPS C1*s* core-level spectrum recorded for a surface of products of carbonization of PVDF in a fine SiO_2 matrix. As can be seen from the above figure, the C1s spectrum of the mentioned products of carbonization reveals an asymmetry and possesses a comparatively big width. This means that the XPS C1s spectra of the products of carbonization of PVDF in a silica matrix are complex and can be deconvoluted onto individual peaks. Using a conventional procedure of deconvolution of the XPS spectra [7], the XPS C1s core-level spectrum of the products of carbonization of PVDF in a SiO_2 matrix consists of five individual peaks (see Fig. 2).

In accordance with findings of Okpalugo and co-workers [8] for carbon-containing materials, epy peaks *a* and *b* at about 284.0 eV and 285.0 eV correspond to carbon atoms belonging to the C–C and C=C groups, respectively. Additionally, the peak *c* at 286.2 eV is formed by carbon atoms belonging to the CO group, but the peaks *d* and *e* at 288.2 eV and 290.3 eV are created by carbon atoms belonging to the COO and CHF groups, respectively. However, the present X-ray emission spectroscopy data reveal that in the volume of the products of carbonization of PVDF in a silica matrix, as well as in a matrix of SiO_2 with a mixture of graphite, fluorine atoms either are absent or their quantity is minor.

The X-ray emission C*K*α bands recorded for five independent successive measurements of the products of carbonization of PVDF in a SiO_2 matrix are presented in Fig. 3. During the experiments on the above products of carbonization it has been established that the intensity of the O*K*α band does not change, while the intensity of the C*K*α band decreases. Therefore the C*K*α and O*K*α spectra we recorded successively and the C*K*α band presented in Fig. 3 are normalized so that the intensity of the O*K*α band is one and the same for every experiment. From Fig. 3 it is apparent that, the first spectrum of the C*K*α band of products of carbonization of PVDF in a SiO_2 matrix resembles that of fullerene C_{60}. In every successive measurements we observed decreasing the intensity of the C*K*α band and changing its shape. The above effect can be explained by the following: the products of carbonization of PVDF in silica matrix (see Fig. 1) are very fine clusters that either diffuse or evaporate (fullerenes) under the influence of the electron beam.

Figure 4 shows the X-ray emission C*K*α bands recorded for three independent successive measurements of products of carbonization of PVDF in a matrix containing a mixture of SiO_2 and graphite. In this case we did not observe any significant changes of the shape and intensity of the band during successive records. As one can see from Fig. 4, the average spectrum of the products of carbonization of PVDF in a matrix consisting of mixture of SiO_2 and graphite resembles very much that of pure graphite. It is noteworthy to mention that, pyrolitic carbon in the above composite is located mainly on graphite. Therefore, it can be assumed that in such a case carbon composites are thin multi-layer films that are stable and do not neither diffuse nor evaporate under the influence of the electron beam.

The X-ray emission O*K*α bands for the composites with a SiO_2 matrix and a matrix consisting of a mixture of SiO_2 and graphite are presented in Fig. 5. The shapes and energy positions of the main features of the O*K*α bands for the two composites are similar to those of the

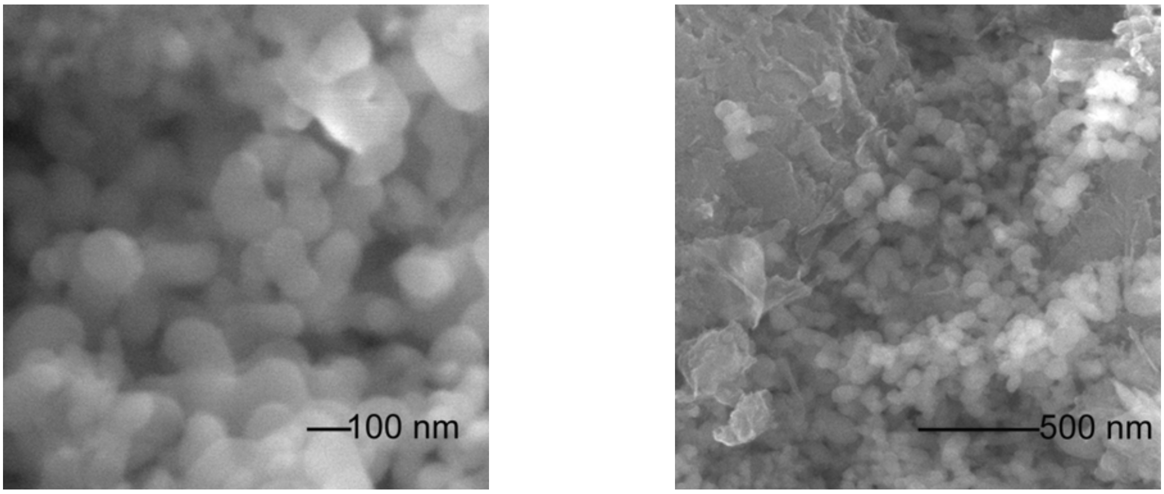

Fig. 1. SEM images of products of carbonization of PVDF in fine SiO$_2$ (**a**) and in fine silica with mixture of graphite (**b**).

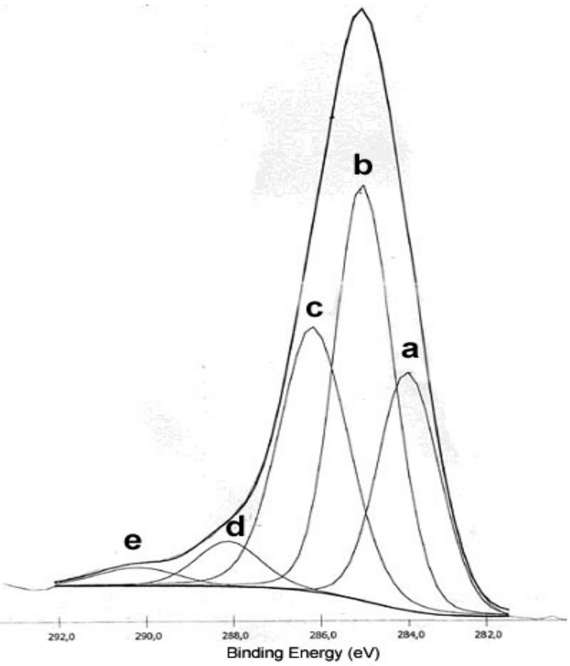

Fig. 2. Deconvolution of the XPS C1*s* core-level spectrum recorded for a surface of products of carbonization of PVDF in a fine SiO$_2$ matrix onto individual C1*s* lines.

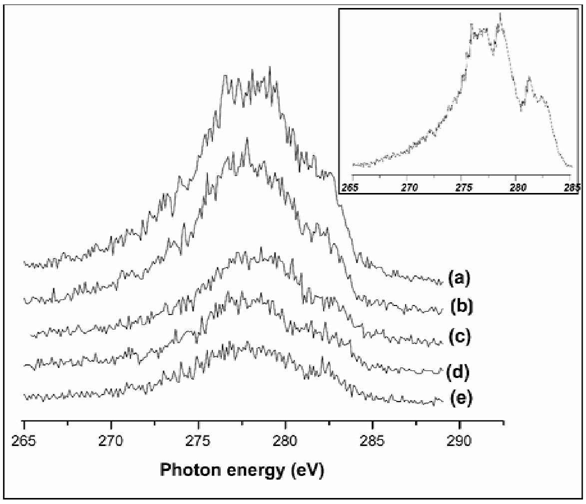

Fig. 3. X-ray emission C$K\alpha$ bands recorded for five independent successive measurements of products of carbonization of PVDF in a SiO$_2$ matrix: a – 1st record, b – 2nd record, c – 3rd record, d – 4th record, e – 5th record (for comparison, the C$K\alpha$ band of fullerene C$_{60}$ is presented in the insert).

band of pure quartz (α-SiO$_2$) [9,10]. Due to self-consistent pseudopotential calculations of Garvie et al. [10] for partial densities of states in α-quartz, it is characteristic that the main contributors into the central part of the valence band of the compound are the Si3*p*-like states, while contributions of the valence Si*s*- and Si*d*-like states dominate the bottom and the upper part of the valence band, respectively. Taking into account results of Ref. [10], the peculiarity *a* of the X-ray O$K\alpha$ band is due to σ-bonding of the Si3*s*–O 2*p*-like states, the feature *b* is formed by σ-bonding of the Si3*p*–O2*p*-like states, the peculiarity *c* is due to contributions of the O2*p*-like states bonded weakly with the Si*s*,*d*-like states and, finally, the peak *d* of the band is formed by contributions of the non-bonding O2*p*-like states. From Fig. 5 it is obvious that the half-width of the O$K\alpha$ band for the composites with a SiO$_2$ matrix is significantly bigger (by 0.6±0.1 eV) as compared with that for the composites with a matrix consisting of a mixture of SiO$_2$ and graphite. The broadening occurs in the energy region corresponding to the position of the main maximum *d* of the band. Since, as it has been already mentioned above, in the energy region corresponding to the position of the main maximum *d* of the X-ray emission O$K\alpha$ band the non-bonding O2*p*-like states are located, the mentioned broadening can be a result of involving non-bonding in pure quartz the O2*p*-like states in the chemical bonding with products of carbonization of PVDF in a silica matrix. The bonding between the SiO$_2$ matrix and

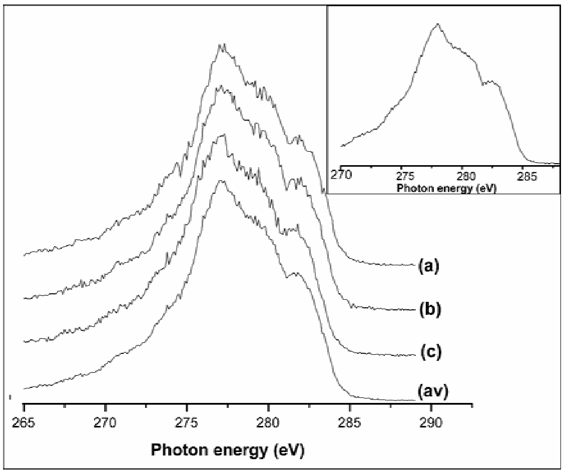

Fig. 4. X-ray emission C*K*α bands recorded for three independent successive measurements of products of carbonization of PVDF in a matrix containing a mixture of SiO_2 and graphite: a – 1st record, b – 2nd record, c – 3rd record, av – average spectrum (for comparison, the C*K*α band of graphite is presented in the insert).

products of carbonization of PVDF is very weak, and the mentioned products of carbonization are removed from the region of bombardment of the electron beam. This fact is confirmed by decreasing the half-width of the X-ray emission O*K*α band during its successive records (see the inset in Fig. 5) as well as by monotonous decreasing the intensity of the C*K*α band with its every successive record (see Fig. 3).

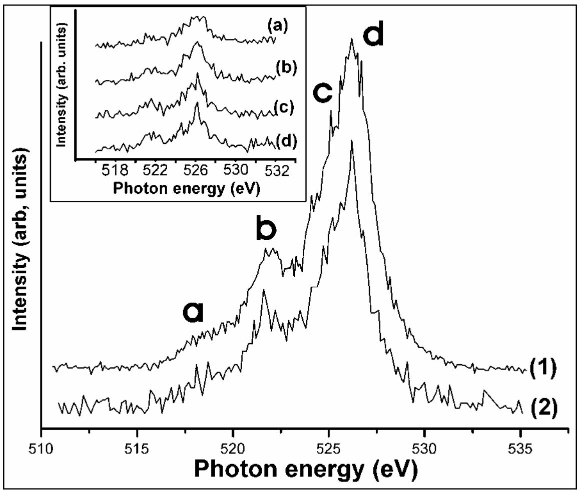

Fig. 5. X-ray emission O*K*α bands for the composites with a SiO_2 matrix (curve 1) and a matrix consisting of a mixture of SiO_2 and graphite (curve 2) [X-ray emission O*K*α bands, recorded in the second order of reflection, for four independent successive measurements of products of carbonization of PVDF in a SiO_2 matrix are presented in the inset: a – 1st record, b – 2nd record, c – 3rd record, d – 4th record].

Conclusions

The X-ray emission C*K*α band of products of carbonization of PVDF in a SiO_2 matrix resembles that of the band of fullerene C_{60} containing other carbonic structures. During an acquisition of the X-ray emission C*K*α bands of products of PVDF carbonization in a SiO_2 matrix we have detected an almost monotonous decreasing intensity of the C*K*α band and changes of its shape. This fact indicates a weak chemical bonding of oxygen atoms of silicon dioxide nanoparticles with products of PVDF carbonization. An intensity and the shape of the X-ray emission C*K*α band of products of PVDF carbonization in a matrix consisting of a mixture of SiO_2 and graphite do not alter during the data acquisition. The shape of the C*K*α band of the above products of carbonization resemble that of pure graphite. It should be mentioned that the shape and energy positions of fine-structure peculiarities of the X-ray emission O*K*α bands of products of PVDF carbonization in matrices of fine silica and of SiO_2 with mixture of graphite are similar to those of the analogous band of the initial SiO_2 particles. Results of the present work reveal that surfaces of products of PVDF carbonization consist of C–C, C=C, CO, COO and CHF groups.

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Рентгеноспектральне дослідження електронної структури продуктів карбонізації полівініліденфториду на наночастинках диоксиду кремнію

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Електронна структура продуктів карбонізації полівініліденфториду (ПВДФ) на матриці SiO_2 вивчалася за допомогою методів рентґенівської емісійної та фотоелектронної спектроскопії. Форма отриманих рентґенівських емісійних С*Kα*-смуг продуктів карбонізації ПВДФ на матриці диоксиду кремнію (SiO_2) нагадує форму смуги фулерену C_{60} з домішками інших вуглецевих структур. Форма С*Kα*-смуги продуктів карбонізації ПВДФ на матриці SiO_2 з домішками графіту нагадує таку ж смугу чистого графіту. Однією з характеристик матриці є слабкий хімічний зв’язок атомів кисню в диоксиді кремнію з продуктами карбонізації ПВДФ. Форма та енергетичне положення особливостей тонкої структури рентґенівських емісійних О*Kα*-смуг продуктів карбонізації ПВДФ на матриці диоксиду кремнію та SiO_2 з домішками графіту нагадують такі аналогічних смуг вихідних частинок SiO_2. Поверхня продуктів карбонізації ПВДФ містить С–С, С=С, СО, СОО та СНF групи.