An X-ray Spectroscopy Study of the Electronic Structure of Tolylene-diisocyanate Carbonization Products in an Al₂O₃ Matrix

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Abstract. Results of studies of the electronic structure of carbon-containing porous materials derived by tolylene-diisocyanate (TDI) carbonization in a matrix of Al₂O₃ are presented in this paper. It has been established that products of TDI carbonization are fine spherical clusters (with their sizes of about 10 nm) that reveal a strong bonding with the matrix. The shapes of X-ray emission C⁷Kα and O⁷Kα bands are different for volume and surface parts of the materials. Our study reveals different electronic structures of the materials in volume and surface parts. It has been established that the shape of the X-ray emission C⁷Kα band of the volume part of products of carbonization of TDI in the Al₂O₃ matrix corresponds to that of mixture of the bands of fullerene C₆₀ and graphite, but the shape of the band of the surface part resembles that of the C⁷Kα band of graphite. The shape of the X-ray emission O⁷Kα band of the volume part of the products of TDI carbonization resembles that of the band of γ-Al₂O₃, while that of the surface part corresponds to the shape of the OKα band of Al(OH)₃.

1. Introduction

Porous carbon materials are prospective for their use as high-performance sorption materials, catalyst carriers, membrane systems for filtration of solutions and gases. Porous carbon materials are usually synthesized as a result of carbonization of polymers and organic precursors. During thermal decomposition of a precursor in a solid phase carbon nanoparticles, activating carbon, molecular sieves, fibers etc are formed. Shapes and compositions of such carbon structures depend strongly upon carbonization conditions: velocity, concentration of precursors, presence and type of catalyst etc. [1–3]. Orientations of polymeric chains also influence significantly the structure of porous carbon materials [2, 4, 5].

In this research, results of investigation of the electronic structure of porous carbon materials, products of carbonization of tolylene-diisocyanate in an Al₂O₃ matrix, are presented.
2. Experimental
Fine Al₂O₃ particles (S_p=200 m²/g) were used as a structure-forming agent. A carbonization precursor for obtaining carbon was a mixture of 2,4- and 2,6-tolylene-diisocyanate in ratio 80:20 (TDI). On the first stage alumina was added to dispersion medium, which consisted of TDI dissolved in ethyl acetate. Al₂O₃ particles form with the dispersion medium stable spatial structures, mainly gels [6, 7]. After drying these gels at room temperature, porous xerogels were obtained. On the next stage, xerogels were carbonized at 750 °C under argon atmosphere.

Scanning electron microscopy (SEM) measurements were carried out by Philips FEG SEM XL30; surface of the composite was coated with platinum by a sputter coater 208HR (Cressington) and the thickness of the layer was controlled by a thickness controller MTM20 (Cressington). Transmission electron microscopy (TEM) was carried out by JEM 100CX-II (JEOL).

An electron spectrometer “SERIES 800 XPS” Kratos Analytical equipped with an X-ray Mg Kα source (hv=1253.6 eV) was used for measurements of X-ray photoelectron C 1s core-level spectra. A powder of the samples under consideration was supported on an adhesive tape. The effect of the adhesive tape on the C 1s spectra of the samples studied should be minor because the powder samples were prepared in forms of thick pressed films covering the tape completely in every experiment.

The X-ray emission C Kα and O Kα bands (K → L II, III transition), reflecting the energy distribution of the C2p- and O2p-like states [8, 9], 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 operation conditions of the X-ray tube were the following: accelerating voltage, U_a = 5 kV; anode current, I_a = 2.5 mA. The X-ray emission measurements were made under condition of oil-free evacuation of the spectrometer chamber. 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 residual pressure in the spectrometer chamber during the present measurements was routinely 5×10⁻⁶ Pa.

3. Results and discussion
TDI reacts with OH-groups and molecules of water on the surface of Al₂O₃ that results in formation of arynes, ureas and urethanes some of which are bonded to the alumina particles [10]. After carbonization of these compounds in an Al₂O₃ matrix, a carbon composite is formed.

Carbonized composite was black with a characteristic metallic luster of the sample surface. The interior part of the samples was not lustrous. This fact can be explained by different electronic structure of volume and surface parts of the material, a product of TDI carbonization in an Al₂O₃ matrix. Therefore, we have carried out investigations of the electronic structure of products of TDI carbonization in an Al₂O₃ matrix separately for surface and volume parts.

Figure 1. SEM micrograph of a carbon-loaded composite (a) and TEM image (b) of carbon nanostructures obtained by TDI carbonization in an Al₂O₃ matrix.
As can be seen from Fig. 1, products of TDI carbonization in an Al₂O₃ matrix are almost of spherical shape with particle size of about 10 nm.

The average X-ray emission CKα band records for surface and volume parts of products of TDI carbonization in an Al₂O₃ matrix are presented in Fig. 2. For comparison, CKα bands of fullerenes C₆₀ and C₇₀, graphite, carbon nanotubes with different diameters have been also recorded at the same experimental conditions with the aim of identification of carbon materials in the samples obtained as a result of TDI carbonization in the matrix under consideration. From Fig. 2 it is apparent that, the shapes of CKα bands of surface (1) and volume (2) parts of products of TDI carbonization in an Al₂O₃ matrix are different. The shape of the band recorded for the surface part of the sample studied resembles that of graphite, however the shape of the band measured for the volume part of products of TDI carbonization resembles that of fullerene C₆₀ with an admixture of graphite (the CKα bands of graphite (a) and fullerene C₆₀ (b) are presented in the inset in Fig. 2).

![Figure 2. Average X-ray emission CKα bands of surface (1) and volume (2) parts of products of TDI carbonization in an Al₂O₃ matrix. In the inset the CKα bands of graphite (a) and fullerene C₆₀ (b) are presented.](image)

The X-ray emission OKα bands recorded for the volume (a) and surface (b) parts of the composite, a product of TDI carbonisation in an Al₂O₃ matrix, are presented in Fig. 3. The shape and energy positions of main features of the OKα band for the volume part of the composite are similar to those of the band of γ-Al₂O₃. The shape of the OKα band obtained for the surface part of the composite resembles that of the band of Al(OH)₃ [11]. The X-ray emission OKα bands of γ-Al₂O₃ and Al(OH)₃ are presented in Figs. 3A and 3B, respectively. As can be seen from Fig. 3, there are two peculiarities on the long-wave slope of the OKα bands. Taking into account results of Ref. [10], the peculiarity a of the X-ray emission OKα band is due to σ-bonding the Al₃s-O₂p and Al₃p-O₂p-like states, the feature b is formed by the bonding Al₃d-O₂p-like states, the peak c of the band is formed by contributions of the non-bonding O₂p-like states.
From Figs. 2 and 3 one can see that the shapes of the X-ray emission spectra for the surface and volume parts of products of TDI carbonization in an Al₂O₃ matrix are quite different. The cause of this difference is different conditions of TDI carbonization of the volume and surface parts under consideration. The carbonization was processed in argon atmosphere with some admixture of oxygen. As a result, during TDI carbonization in such conditions, the surface was partly oxidized and the shapes of the C Kα and O Kα bands recorded for the surface and volume parts of the samples studied are somewhat different.

During the spectra acquisitions, we did not observe any changes of the shape and intensity of the X-ray emission C Kα and O Kα bands. This fact indicates the strong chemical bonding of the matrix with products of TDI carbonization.

Figure 3. (A) Average X-ray emission O Kα bands of γ-Al₂O₃ (1) and the volume part of products of TDI carbonization in an Al₂O₃ matrix (2). (B) Average X-ray emission O Kα bands of Al(OH)₃ (1) and the surface part of products of TDI carbonization in an Al₂O₃ matrix (2).

Figure 4 displays the XPS C 1s core-level spectrum recorded for the volume part of products of TDI carbonization in an Al₂O₃ matrix. As can be seen from the above figure, the C 1s spectrum of the mentioned products of carbonization reveals an asymmetry and is characterized with a comparatively big width. This means that the XPS C 1s spectrum studied is complex and can be deconvoluted onto individual peaks. Using a conventional procedure of XPS spectra deconvolution [12], the XPS C 1s core-level spectrum of products of TDI carbonization in an Al₂O₃ matrix consists of five individual peaks (see Fig. 4). In accordance with findings of Okpalugo and co-workers [13] for carbon-containing materials, peaks a and b at about 284.3 eV and 285.0 eV correspond to carbon atoms belonging to the C=C and C–C groups, respectively. Additionally, peak c at 286.2 eV is formed by carbon atoms belonging to the C–O group, while peaks d and e at 287.8 eV and 289.2 eV are created by carbon atoms belonging to the C–NH₇ and COO groups, respectively.

4. Conclusions
A monolithic sample of products of TDI carbonization in an Al₂O₃ matrix was obtained. This sample was found to be a porous carbonic material. The products of TDI carbonization are spherical particles with their sizes of about 10 nm. The electronic structure of products of TDI carbonization in an Al₂O₃ matrix for the surface and volume parts was investigated using the X-ray emission spectroscopy method. The shape of the CKα band of the volume part of products of TDI carbonization in an Al₂O₃
matrix resembles that of the band of fullerene C_{60} with graphite admixture. Additionally, the shape of the C\text{Kα} band of the surface part of products of TDI carbonization in an Al_{2}O_{3} matrix corresponds to that of the band of pure graphite. The shape of the O\text{Kα} band of the volume part of products of TDI carbonization in an Al_{2}O_{3} matrix resembles that of the band of \gamma-Al_{2}O_{3} but the band of the surface part corresponds to that of Al(OH)_{3}. The chemical bonding between products of TDI carbonization and the matrix is rather strong. Results of the present work reveal that the volume part of products of TDI carbonization in an Al_{2}O_{3} matrix contain C\text{C}, C=C, C═O, COO and C\text{NH}_{x} groups.

Figure 4. Deconvolution of the XPS C\text{1s} core-level spectrum, recorded for products of TDI carbonization in an Al_{2}O_{3} matrix, onto individual C\text{1s} lines.

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