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## Coal-Tar Pitch Asphaltene Powders as a Precursor for the Production of Carbon Graphite Nanostructured Materials

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### Abstract

Asphaltenes as self-organizing supramolecular structures are of great scientific and practical interest. An urgent problem is to reveal the regularities of the directed formation of planar associates of asphaltenes and condensed graphite-like structures. For the purpose of investigating the self-organization of the molecular aggregates of coal-tar pitch asphaltenes, the morphology and structure of the particles of asphaltene powder obtained from coal-tar pitch asphaltenes by means of selectively soluble groups was studied using a set of physicochemical methods. It was shown that the crystal structure of asphaltene powder particles is represented mainly by turbostratic carbon structures. According to XRD data, the coke residue after thermolysis of asphaltenes is characterized by the presence of crystallites consisting of naphthenoaromatic layers.

**Keywords:** coal-tar pitch, asphaltene, composition, structure, films

### INTRODUCTION

The variety of allotropic modifications of carbon and a great number of new functional materials on this basis promote the search for new methods to obtain and use graphitized carbon nanostructured materials [1–3]. Precursors for these materials may be either various natural fossils (coal, natural graphite, oil) or the components of the products of their processing (pitch, resins, asphaltenes). The most difficult problem is to obtain the crystal modification of carbon with extended ordered structure.

In search for a promising precursor for obtaining structured materials based on carbon, special attention should be paid to asphaltenes: unlike for other components of oil, coal or pitch, asphaltene molecules undergo spontaneous arrangement and form multilayered macromolecular structures composed of two-dimensional practi-

cally planar polycyclic layers [4] forming the basis of asphaltene macromolecules.

There are some examples of the successful implementation of the transformation of asphaltene macromolecules in carbon nanolayers (graphene) [5], fullerenes [6] or carbon fibres [7, 8].

The authors of [9] succeeded in revealing the geometry, conformation and charge state of separate asphaltene macromolecules by means of atomic force microscopy (AFM). The data obtained by those authors confirmed the previous ideas concerning the structure of separate asphaltene molecules [10] as naphthene aromatic condensed structures with not quite planar structure. With this structure of the molecules, it is still unclear what is the mechanism of the formation of asphaltene crystallites (graphite-like structures) accounting for not more than 6 % in oil [11]. The major part of asphaltene macromolecules forms X-ray amorphous associates of

spherical shape which are micellar macroparticles in which asphaltene molecules form the nuclei of micelles and are surrounded by the sorbed molecules of heteroatomic and hydrocarbon components of complex systems [12].

The term 'oil disperse systems' (ODS) is used to describe macromolecular micelles distributed in the disperse medium in liquid products of petroleum chemistry from the viewpoint of colloid chemistry, while the term 'mesophase' is accepted for similar forms of the arrangement of asphaltene molecules in pitch. In the usual state, pitch is solid, so the behaviour of the particles of mesophase was previously studied at elevated temperature providing the mobility of particles in the matrix of the disperse medium of pitch.

Comparison of the experimental data obtained in the studies of asphaltene detected in various products of coal and petroleum chemistry demonstrated the general similarity of their chemical nature in the formation of supramolecular particles of the dispersed phase in the disperse medium and at the same time the difference in physicochemical properties connected with the quantitative characterization of asphaltene macromolecules. A comparison of the structures of asphaltenes isolated from different kinds of raw material revealed [13–15] that asphaltenes of coal tar pitch (CTP) contain the smallest amount of paraffin fragments. So, one may expect the more efficient formation of graphite-like structures from CTP asphaltenes with the subsequent transfer into carbon forms with an ordered structure under the action of temperature.

In the present work, for the purpose of investigating the self-assembling of the molecular aggregates of CTP asphaltenes, we studied the morphology and structure of asphaltene powders formed during the precipitation by *n*-hexane from the toluene extract of CTP.

## EXPERIMENTAL

Asphaltenes were isolated from the toluene extract of medium-temperature (softening temperature 87 °C) CTP under varied conditions of the dilution of the extract with *n*-hexane. CTP extract was prepared at a ratio of 1 g of pitch/40 mL of toluene. The toluene extract contains toluene-soluble  $\beta$ - (asphaltenes) and  $\gamma$ -fractions (petrolenes) of pitch, and dilution of the extract with *n*-hexane allows us to precipitate  $\beta$ -fraction which is insoluble in *n*-hexane.

Asphaltene precipitation was carried out under the action of ultrasound and without it at room temperature and a pressure of 1 atm. The time of ultrasonic treatment was 10 min. After flocculation, asphaltene precipitate was kept in solution for 1 day, then the precipitate was separated by filtering, washed from petroleum with hexane and dried at a temperature of 80 °C.

The morphology of the particles of asphaltene powders, their elemental composition were studied with the help of scanning electron microscope JEOL JSM6390 SEM (Japan) with a JED 2300 attachment for elemental analysis.

Phase composition and structure of the powders were determined according to the procedure described in [16–18] using a Bruker D8 ADVANCE A25 diffractometer (Germany) in monochromatic  $\text{CuK}_\alpha$  radiation ( $\lambda = 0.15406$  nm), with a Ni filter at the secondary beam. The investigation was carried out within angle range 5–100° over  $2\theta$  with a scanning step of 0.02°. Diffraction patterns were analyzed using the software package for data collecting and processing Diffrac. Suite.Eva (V3.1). Diffraction patterns were interpreted on the basis of ICDD PDF-2 database.

## RESULTS AND DISCUSSION

Solid and fragile brown-coloured asphaltene powders were obtained from medium-temperature CTP. The yield of asphaltenes from pitch was ~6 %.

Under our experimental conditions aggregation and precipitation of asphaltenes from the toluene extract under the action of *n*-hexane proceeded in the presence of petrolenes playing the role of stabilizing agents in the dispersion through the formation of the shells of colloid particles with asphaltene nuclei [12]. The concentrations of extract components are constant and prescribed by pitch composition, so, to study the formation of solid-phase particles, we varied the order in which the precipitating agent – *n*-hexane was mixed with the toluene extract of  $\beta$ - and  $\gamma$ -fractions of CTP. In the first case, 200 ml of hexane was poured into 50 ml of toluene extract (A1 sample), and in the second case, the toluene extract of CTP was poured into *n*-hexane (A2 sample). The conditions of the formation of asphaltene particles may be characterized in the first case as soft – closer to equilibrium, when flocculation and sedimentation of the precipitate after the addition of the whole amount of hexane

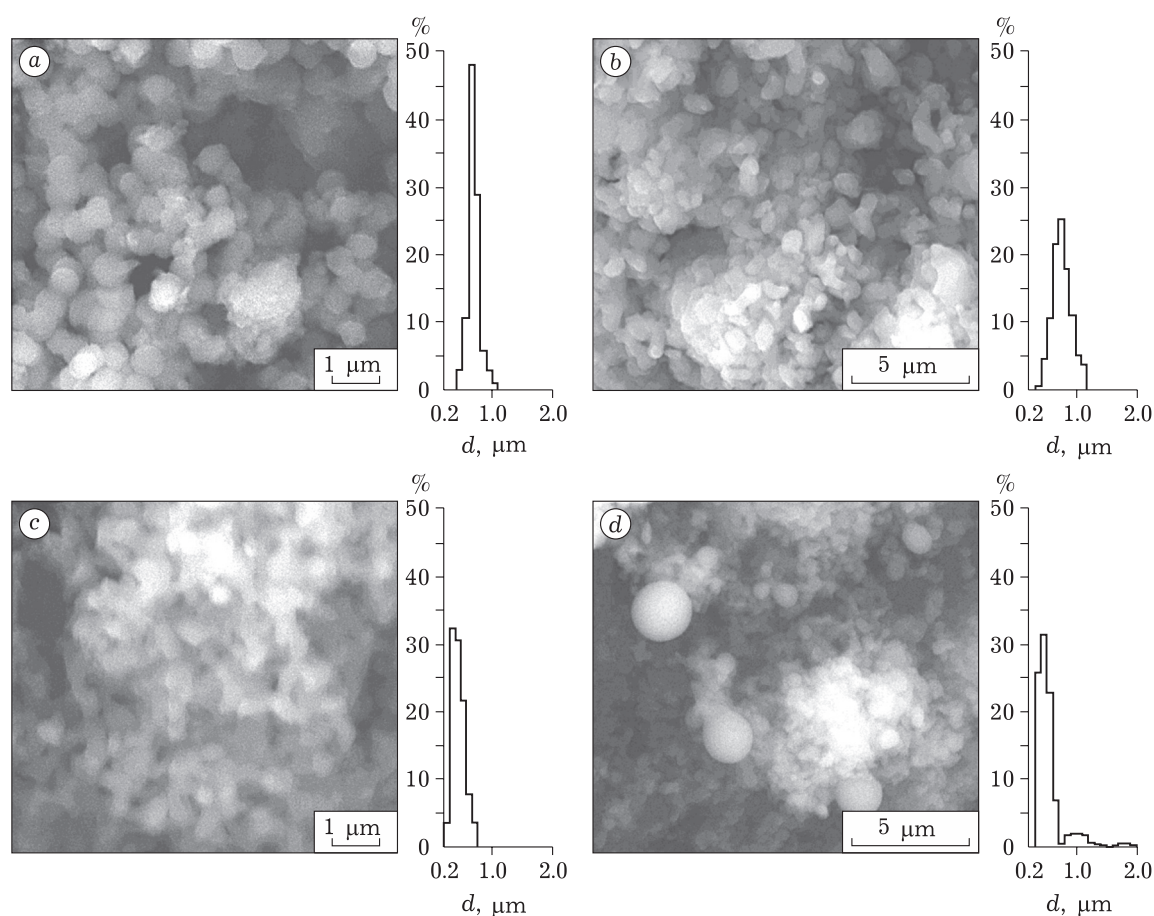


Fig. 1. Electron microphotographs and histograms of the distribution of asphaltene powder particles precipitated without (a, b) and with ultrasonic treatment (c, d).

proceeds over the whole volume of the system, while in the second case the conditions are rigid – nonequilibrium, with rapid flocculation of the particles as a consequence of petrolene desorption from the surface of micelles in hexane. The effect of ultrasound was also investigated, as a factor altering the intensity of mixing in the system and affecting the desorption petrolene substances, which stabilize the colloid stability of asphaltene nuclei (samples A1-UZ, A2-UZ).

Electron microphotographs and the histograms of the distribution of asphaltene powder particles precipitated under different conditions are shown in Fig. 1. One can see that the asphaltene powders are composed of spherical and polyhedral particles.

Precipitation under the soft conditions promotes the formation of the particles (see Fig. 1, a, c) with narrow size distribution. The rigid conditions result in the formation of polyhedral particles with a broader size distribution. Asphaltene particles precipitated under soft conditions without the action of ultrasound form a monodisperse system of particles with a size of about 0.6 mm,

mainly spherical (see Fig. 1, a). The particles precipitated under the same conditions under the action of ultrasound (see Fig. 1, c) form a monodisperse system (with the size variation coefficient  $C_v = 9\%$ ) [19] of polyhedral particles with an average size of  $\sim 0.3$  mm. Ultrasonic action on asphaltene precipitation under rigid conditions leads to the formation of particles which may be separated in two size fractions. One of them is fine fraction composed of polyhedral particles with the average size  $\sim 0.3$  mm (see Fig. 1, d). The largest ( $\sim 1$  mm) particles of this fraction are represented by the aggregates having complicated shapes. The second fraction is composed of spherical particles with a size of  $\sim 1.9$  mm. Ultrasonic action causes not only a decrease in the average size of the formed asphaltene particles but also promotes an increase in flocculation rate due to the acceleration of petrolene desorption from the surface of asphaltene nuclei. For this reason, under rigid conditions at the high rate of particle flocculation, ultrasound promotes the enhancement of aggregation. The formation of coarse

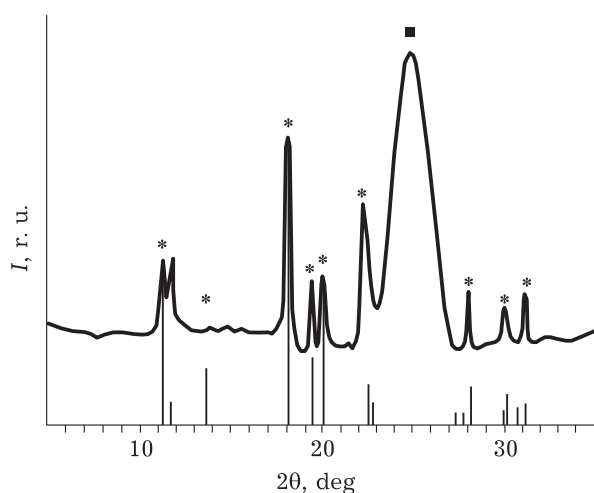


Fig. 2. X-ray diffraction patterns of asphaltene powder (A1-UZ sample) (Vertical lines show the positions and intensities of fullerene reflections according to the Database [21]).

spherical particles may be explained by the fact that after the initial formation of a large number of small particles in a unit volume, their spontaneous flocculation into aggregates of arbitrary shapes occurs, and then their maturing starts, which is accompanied by the redistribution of particle mass.

Typical X-ray diffraction patterns of the resulting asphaltene powder are presented in Fig. 2. One can see that the structure of asphaltene is characterized both by separate reflections at 11.5, 18.5, 22.5 and 27°, and by a broad halo within 2θ angle range from 22 to 28°.

Processing of the diffraction patterns by means of full-profile analysis [20] using TOPAS software allowed us to determine the degree of ordering of particle structure, the structural parameters of turbostratic packets of asphaltene molecules, and to carry out identification of the structure using the powder diffraction card file [21].

The crystallographic parameters of turbostratic carbon structures were calculated from the positions, intensities and width of diffraction maxima within 2θ angle range from 22 to 28°. The average diameter of the packets was determined to be  $L_a \approx 0.66$  nm, with the thickness of  $L_c \approx 1.30$  nm, the distance between separate layers was  $d_{002} \approx 0.34$  nm, the average number of layers in packets was 5–7. It was established that the degree of crystallinity is only weakly dependent on precipitation conditions. For instance, the degree of crystallinity of asphaltene having the spherical particle shape is about 21 %, while for the polyhedral shape it is 28 %. It may be assumed

from the comparison between the recorded diffraction patterns and the diffraction patterns of various carbon structures that the peaks at  $2\theta = 11.5, 18.5, 22.5$  and  $27^\circ$  are close to reflections characteristic of fullerenes (see Fig. 2). The presence of fullerenes in the asphaltene powders is quite expectable, and it was demonstrated previously, for example in [22]. It is also known that fullerenes may be synthesized from natural high-molecular hydrocarbons of coal tar pitch or resin [23–25] and extracted from the reaction medium by toluene. Taking into account the fact that the obtained asphaltene powders were isolated from coal tar pitch with toluene, we cannot exclude the extraction of fullerenes from initial raw material. However, this assumption requires further investigation.

## CONCLUSION

The shape of asphaltene particles is almost neglected in scientific publications; there is a notion of the nearly spherical shape of particles (colloid micelles) in disperse medium. However, it is known [19, 26] that the size and shape of particles during precipitation are affected by a number of factors including hydrodynamic conditions in the system. Our studies showed that the shape and dispersity of asphaltene particles depend on precipitation conditions. Intensification of mixing in the system in combination with the use of ultrasound leads to precipitation of smaller particles, a simultaneous increase in the polydispersity of the system, and the appearance of polyhedral particles, which is likely to be due to a decrease in the concentration of adsorbed petrolenes providing the colloid stability of asphaltene nuclei.

X-ray phase analysis of the resulting asphaltene revealed a weak dependence of the structural properties of precipitated asphaltene particles on precipitation conditions. Powders mainly contain turbostratic carbon structures. However, along with them, more ordered carbon forms are detected. Additional studies are necessary to reveal their nature.

The results obtained in the present work allow us to consider CTP asphaltene as a promising precursor of graphitized carbon materials with low content of heteroatoms, especially S, and mineral microimpurities.

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