

Characterization of some carbon materials by Raman spectroscopy

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Raman spectroscopy was used to analyze different type of carbon materials: activated carbon (AC), carbonized and green carbon foam (CF), and carbon adsorbents, produced from refuse derived organic fuel (RDF). The Raman spectroscopy allows assessment of surface chemistry, structure and difference in the degree of structure ordering of produced carbon materials. Degree of ordering of carbon structures is based on the identification of the intensity of spectral signals corresponding to the D band, characteristic for the amorphousness of carbon structures and the G band, indicating the ordering of carbon structures. Raman also contributes to identification of carbon structures. This allows studying the changes in the structure and the formation of the porous texture as a result of the physical activation of the carbon materials, which significantly determine their applicability in the purification industry. The results show that carbonized carbon foam possesses more regular structure than “green” carbon foam. The difference in the spectra of the carbonized and activated sample shows that the activation of the sample with water vapor at 700 °C leads to a significant increase of aromatic structures with CH₃ groups and alicyclic compounds.

Key words: Raman spectroscopy; carbon materials; activated carbons

INTRODUCTION

Carbon materials, particularly those classified into the graphite family, have a variety of structures and textures, nanotexture and microtexture. We will focus on several types of carbon materials in our study: activated carbon (AC), carbonized and green carbon foam (CF), and carbon adsorbents, produced from refuse derived organic fuel (RDF). Our choice was guided by their specific structural properties and their applications not only in the various industries but mainly as adsorbents for purifying drinking water.

Activated carbons (AC) are known as promising materials with wide application as adsorbents, catalysts or catalyst supports due to their tunable surface and textural characteristics, which could be easily controlled by the preparation procedure and the precursor used [1-9]. Due to the interest in low-cost activated carbons, it is given special attention to their preparation from various waste materials (biomass, waste polymeric materials, agricultural products, waste organic fuels (RDF), etc.) for applications related to drinking and wastewater treatment [10-14]. There are two fundamental methods for preparing activated carbons: physical and chemical activation. The physical activation method involves: carbonization of raw material and activation at high temperature in carbon dioxide or steam atmosphere [15-17]. Chemical activation is a

well-known method for the preparation of activated carbon, which has been the objective of numerous studies within the last few years, as it presents some advantages compared to the so-called physical activation. In a chemical activation process, the precursor is impregnated with a specific chemical agent and then it is pyrolyzed [18].

Carbon foam is a sponge-like carbon material, representing cellular ligament microstructure, and it is distinguished by certain features, such as light weight, high temperature tolerance in inert atmosphere, high mechanical strength, large external surface area and adjustable thermal and electrical conductivity. As new materials, carbon foams have essential advantages, enhanced structural properties, fire resistance, radar cross-section, corrosion susceptibility. These unique properties, which mainly depend on the precursor features and synthesis conditions, make carbon foams ultra-high performance engineering materials, and determine their many potential applications in numerous industries [19-21].

Raman spectroscopy is ideal for characterization of carbon materials, as it is extremely sensitive to geometric structure and bonding within molecules. It is a simple and non-invasive technique, and it is suitable method, because the carbon atoms are light, the sp² σ bonds are strong, and the π-electron-related optical transitions range from the infrared up to the visible range [22].

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Raman spectroscopy, which is one of the best and most accurate methods for studying carbon materials, was used for physicochemical characterization of the samples. The Raman spectrum is characteristic and can serve for precise identification of the type (by comparison with literature data) and the amount (by the intensity of the bands) of the carbon material. The presence of glassy carbon, graphite, graphene and other carbon structures corresponds to a specific type (close band frequencies, close intensity ratio, etc.) of the Raman spectrum.

Raman spectra of carbon materials like graphene are classically defined by three major bands; these are G-band, D-band, and 2D-band (also known as the G'-band). The G-band appears around 1582cm^{-1} and represents the graphene in-plane sp^2 vibrational mode. This provides an idea for the crystallinity of the material. The peak ratio between the D-band and G-band of sp^2 carbon material is highly significant. Dispersion of the G-band is observed in disordered graphene materials, where the dispersion is proportional to the degree of disorder. The D-band at around 1350cm^{-1} is credited to the structural disorder near the edge of the microcrystalline structure that decreases the symmetry of the structure [23-27].

In this paper we will focus on the characterization of the Raman spectra of different type of carbon materials: activated carbon, carbonized and green carbon foam (CF), and carbon adsorbents, produced from refuse derived organic fuel (RDF) in order to obtain information about surface chemistry, structure and ordering of carbon samples before and after hydrolysis.

EXPERIMENTAL

The sample of carbon adsorbent, produced from RDF was obtained as a linoleum piece (obtain from industry) was heated to a molten state and then concentrated sulfuric acid is added by drops with continuous stirring until solidification. The resulting product is subjected to carbonization in an inert N_2 atmosphere up to $550\text{ }^\circ\text{C}$. The carbonizate is activated with water vapor at a temperature of $700\text{ }^\circ\text{C}$ and a retention time at the final temperature of 60 minutes [28].

Carbon foam (CF) was prepared using the following procedure: coal tar pitch was heated up to $120\text{ }^\circ\text{C}$ till melting conditions. Furfural was heated to the same temperature and added to the pitch with continuous stirring. The obtained mixture was treated at $120\text{--}200\text{ }^\circ\text{C}$ (during the reaction the

temperature rises up to $200\text{ }^\circ\text{C}$) with concentrated H_2SO_4 (98 wt%) or HNO_3 (68 wt%) - drops of acid were added to the mixtures with continuous stirring until solidification. Foaming was carried out in a stainless steel pressure vessel by heating the pitch precursor up to $500\text{ }^\circ\text{C}$ in a N_2 atmosphere at pressure up to 1 MPa. The resultant "green" foams were heated at $1000\text{ }^\circ\text{C}$ in N_2 atmosphere to increase the mechanical strength and to remove the volatiles [29].

The Raman spectroscopy gives spectra containing oscillatory bands corresponding to the normal vibrations of the molecules. The intensity of Raman bands is determined by the change in polarizability during normal vibration. Using this technique, it is possible to determine the crystal form, chemical composition, intermolecular interactions, the degree of ordering, and the spatial distribution of stresses in tested material [24, 25].

Raman spectra were recorded by using Raman Microscope Senterra II (Bruker). Samples were placed onto glass (approximately 10 mg) and analyzed using the vertical 20x objective in an 180° backscattering arrangement. The Raman spectrometer parameters used to analyze the carbon samples include: 532 nm laser wavelength and an exposure time of 100 seconds, resolution was 4 cm^{-1} for all samples, laser power was 6.5 mW.

RESULTS AND DISCUSSION

The analysis of the structure of the studied carbon materials, including the evaluation of the ordering of the crystal structure was possible thanks to research using the Raman spectroscopy. The spectra of the studied carbon materials contain bands directly related to the vibrations of carbon and hydrocarbon structures.

The comparison of the spectra of the carbonized raw material at $600\text{ }^\circ\text{C}$ and the activated carbonizate at $700\text{ }^\circ\text{C}$ is shown on Fig. 1. The analysis of the carbonizate samples shown in Fig. 1 demonstrates the changes occurring in the chemical composition of the different stages of RDF treatment. The difference in the spectra of the carbonized and activated sample (Fig. 1) shows that the activation of the sample with water vapor at $700\text{ }^\circ\text{C}$ leads to a significant increase of aromatic structures with CH_3 groups (1559 cm^{-1}) and the alicyclic compounds (1327 cm^{-1}) in the sample and they become completely predominant.

The chemistry and surface structure of reference and space samples were studied by Raman spectroscopy. In Fig. 1, a band at 1559 cm^{-1} , otherwise known as the G band, is observed. This

band corresponds to stretching vibrations with E_{2g} symmetry. The G band at $1580\text{--}1560\text{ cm}^{-1}$, comes from tensile vibrations of the sp^2 hybridization of the carbon bond pairs occurring in ring structures. An additional band located at the Raman shift at 1327 cm^{-1} characterizes the level of amorphousness of carbon structures and indicates a highly disordered carbon structure. This band is usually called the D (defect) band. D band is usually detected in carbon materials at $1380\text{--}1300\text{ cm}^{-1}$ corresponds to A_{1g} symmetry and is associated with plane imperfections, e.g., defects and heteroatoms [30]. Typical Raman spectrum of graphite contains high frequency line at about 1580 cm^{-1} and a small band around 1350 cm^{-1} (sometimes missing).

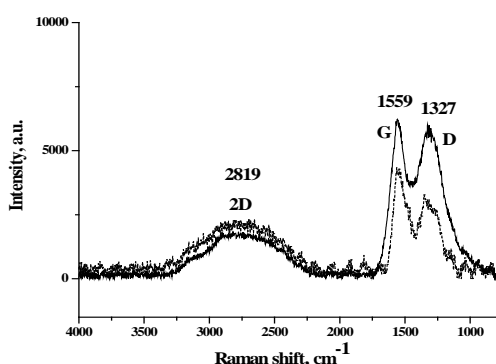


Fig. 1. Raman spectra of the activated carbonizate (black) and carbonizate (dashed) at $700\text{ }^{\circ}\text{C}$.

The analysis of the structure of the obtained carbonized and green carbon foam, including the evaluation of the ordering of the crystal structure, was possible due to research using Raman spectroscopy (Fig. 2 and Fig. 3).

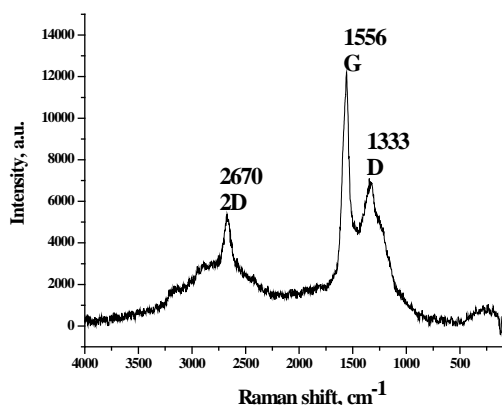


Fig. 2. Raman spectrum of carbonized carbon foam.

In the case of analysis of the Raman spectra obtained for carbon foams, a G bands is observed at 1556 (1574 (Fig. 3)) cm^{-1} . The bands located at the Raman shift at 1333 cm^{-1} (Fig. 2) and 1330 cm^{-1}

(Fig. 3) can be assigned as the so called D band. As we can see in Fig. 2 the intensity of the G band is much higher that one of the D band. The structure is much more ordered then the one of the green carbon foam (Fig. 3).

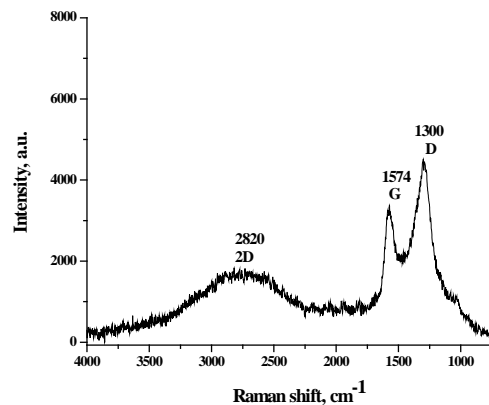


Fig. 3. Raman spectrum of green carbon foam.

In the Raman spectra of green carbon foam (Fig. 3) a great increase of the intensity of the D band can be seen. The increase in the D band can be produced by: (i) an increase in the amount of disordered carbon atoms in CF, corresponding to sp^3 domains; or (ii) a significant reduction in the size of sp^2 domains in the layer. This suggests the coexistence of sp^2 and sp^3 hybridization; i.e., CF contains crystalline and amorphous forms of carbon [31]. The 2D band is also present in the CF samples. The 2D band in the spectrum of the carbonized CF (Fig. 3) it is narrow and sharp. This fact and the very low intensity of the D band indicate a very regular structure compared with the one of the green CF.

CONCLUSION

Raman spectroscopy is suitable method for physicochemical characterization of carbon samples. The Raman spectrum is characteristic and can serve for precise identification of the type (by comparison with literature data) and the amount (by the intensity of the bands) of the carbon material. The presence of glassy carbon, graphite, graphene and other carbon structures corresponds to a specific type (close band frequencies, close intensity ratio, etc.) of the Raman spectrum. The Raman spectroscopy analysis also helps to obtain information about chemistry, surface structure, and difference in the degree of the produced carbon materials structure ordering.

For the obtained samples of carbon materials, two bands are most characteristic: the G band and

the D band. The G band comes from the stretching vibrations of carbon bond pairs of sp² hybridization occurring in ring structures and is closely related to the occurrence of ordered carbon structures. The D band characterizes the level of the amorphousness of carbon structures. The activation with water vapor at 700 °C leads to a significant increase of aromatic structures (1559 cm⁻¹) and alicyclic compounds (1327 cm⁻¹). It was determined that carbonized carbon foam possess more regular structure than green carbon foam.

The obtained results indicate the differences in the physicochemical properties of the synthesized carbon materials and help to identify the areas of their application in the electrochemistry, purification technique, etc.

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