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Small-angle X-ray scattering experiments and computer simulations to characterise anisotropy of activated carbons prepared from wood

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ABSTRACT

Small-angle scattering was measured from activated carbon monoliths prepared from three different wood species (European beech, Pedunculate oak and Norwegian spruce). Substantial differences were found in the scattering images of axial and tangential slices, attributed to their characteristic phytogenic structures. The decrease in anisotropy in the nanostructured carbon matrix due to the activation process is also different among the three investigated types of wood. For quantitative characterization of the anisotropy and its decrease, the degree of alignment was calculated from the azimuthal scattering curves. A simple numeric model was constructed on the basis of direct information obtained by atomic force microscopy. Scattering patterns calculated from the model were compared with the experimental ones to explain the possible structural changes in the carbon skeleton.

1. Introduction

The functionality and area of application of activated carbons (AC) is based on the properties of their complex pore structure, which is determined by the preparation process and the choice of precursors. It is of great importance to have the means to study – and possibly gain control over – the various parameters of the system. The sizes of the pores in activated carbons and sizes of cellulose nanocrystallites in plain wood are in the nanometer range, which can conveniently be studied using small-angle X-ray scattering (SAXS). Scattering experiments give statistically averaged information which can be further compared with theoretical results from simulations.

Because of its ubiquity and hierarchical micro- and nanostructure, one of the most commonly used precursors for activated carbon is wood. Activated carbons from wood are generally produced by the so-called "physical" activation process, consisting of two steps: carbonization (pyrolysis) and activation (by steam). During carbonization, the skeleton of carbonaceous material is formed with many structural and textural features resembling the original fibrous structure of the wood material. Several studies report details on the pyrolysis process [1]. Although only few of these are concerned with the structural relations of raw and carbonized wood, they agree that distinct features of the product can be attributed to the fibrous structure of the precursor [2–5].

As a biomaterial, wood has to fulfil dual roles of static stabilization and transport of nutrients. Meeting both of these requirements is made possible by the layered structure and arrangement of wood fibres. The structure of wood on the super- and sub-cellular length-scales has been extensively

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studied [6,7]. The wood tissue is composed mostly of elongated cells oriented along the stem axis, enclosing lumina. The origin of the mechanical stability lies in the ultrastructure of the cell wall [8–10]. The wood cell wall consists of cellulose fibrils that are embedded in a hemicellulose-lignin matrix, and wound up along the cell axis in a helical way. With respect to the spiral angle of these helices (also known as the microfibril angle, MFA), the cell wall can be classified into several layers [11]. The thickest one is the so-called "S_2", its average MFA being 5–20°, depending on the species, origin, age and history of the tree. This angle is the primary parameter determining the mechanical strength of wood [10,12].

The typical width of the cellulose microfibrils is reported to be 2.5–3.5 nm, and their length lies in the range of a few millimetres [13–15]. On the packing of the microfibrils, different results are available. Some studies report random orientation of the cell-wall components in the transverse plane of the S_2 layer [16]. Others found the elementary cellulose fibrils to aggregate into larger fibers [17,18]. The typical thickness of these so-called macrofibrils depends strongly on the origin and history of the wood specimen, but usually falls in the range of 10–30 nm [19,20].

The carbon matrix, which is created during carbonization of the fibrous wood, burns off partly in the activation step, giving place for the complex pore structure. The progress of this process determines the development of porosity [21]. First, small crystallites, or single layers of graphene gasify, resulting dominantly in the formation of micropores. Further activation makes whole crystalline groups burn off, while meso- and macropores evolve. Consequently, similarities between structure and texture of pyrolized precursors and ACs originating from anisotropic fibrils can only be observed at the beginning of the activation process.

Even though ACs are produced from different materials, their structures are similar: they are two-phase systems consisting of a carbon skeleton, which is usually composed of turbostratically packed graphene sheets [22], and voids, or pores, which are created mainly during the process of activation. This pore structure is the main cause of the good adsorption properties of activated carbons.

Small-angle X-ray scattering experiments are generally carried out using powdered activated carbon samples, in analogy to powder diffraction. This procedure does not give any information on the anisotropy of the sample. We have already investigated anisotropy of activated carbons originating from different types of wood using small-angle scattering and found that the anisotropy of two-dimensional scattering patterns was characteristic for the fibrous phytogenic structure of the wood precursors [23,24]. Considerable anisotropy was observed in monolith (cube) carbon samples from *Pinus sylvestris*, and the effect of this structure on the adsorption behaviour was examined by using SAXS [25].

In this paper we present measurements and interpretation of anisotropic small-angle scattering images obtained from activated carbons of different origin (European beech, Norwegian spruce and Pedunculate oak). The changes induced by pyrolysis and activation in the anisotropic structure of wood fibres are discussed in detail by means of a simple model consisting of polydisperse spherical units.

2. Materials, methods and preliminary characterization

2.1. *Preparation of the samples*

Activated carbon samples were prepared from three types of wood: European beech (*Fagus sylvatica*), Pedunculate oak (*Quercus robur*) and Norwegian spruce (*Picea abies*). Air-dried slats from trunks of mature trees (Sawmill of Eger Forestry Co., Hungary), where the thickness of early and late wood was less than a millimetre, were cut into small, regular cubes with an edge-length of approx. 10 mm.

These wooden cubes were carbonized at 700 °C (in amounts of 200 g) in a steel reactor flushed with nitrogen gas (flowrate: 50 dm^3/h), for 2 h. During this time, the length of the cube edges shrank by approx. 4 to 6 mm. Only a slight change in the shape of the monoliths was observed, in contrast to the literature [2]. This may be the consequence of the fact, that the wood we have used was matured for years before use and the wooden cubes were dried at 110 °C before the pyrolysis. No significant dimensional changes were observed however due to activation [26]. These carbonized specimens were activated (in amounts of 10 g) in a rotary quartz reactor under steam flow of 18 g/h at 900 °C, diluted by nitrogen in a molar ratio of 1:1 [27]. The time of activation varied between 15 and 90 min, resulting in a wide range of burn-off (conversion of carbonized material), between 10% and 55%. The loss due to mechanical abrasion could be neglected. The change in burn-off among different batches (same wood species and activation time) fluctuated within 1%, while the specific surface (controlled by iodine-number) within 3%, which proves the exceptional stability and controllability of the reactor [23].

The burn-off is shown in Fig. 1, as a function of the time of activation. It increases in a linear way for all types of carbonized wood as activation advances, indicating a pseudo-zero order conversion rate in a wide range of conversion from 0% to 55%. Presumably, the decrease in mass is compensated by the increase in the area of the gas-solid interface due to the activation process. A further feature of the matrix is that

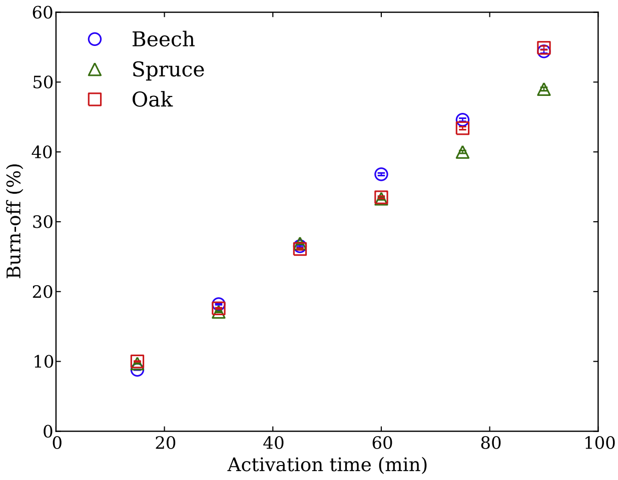

Fig. 1 – Burn-off of different carbon species due to activation. Error bars are smaller than the size of the markers.