Microporous and Mesoporous Materials 130 (2010) 7–13

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Carbon xerogels: Nano- and adsorption textures, chemical nature of the surface and gas chromatography properties

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ARTICLE INFO

Article history:
Received 22 May 2009
Received in revised form 5 October 2009
Accepted 5 October 2009
Available online 11 November 2009

Keywords:
Carbon xerogels
Nanostructures
Adsorption textures
Gas chromatography properties
Catalytic reaction products

ABSTRACT

Nano- and adsorption textures, gas chromatography features of carbon xerogels obtained by carbonization of phenol–formaldehyde resins have been studied. The properties of carbon xerogels were compared with those of carbon-containing and silica–alumina adsorbents. Depending on carbonization, they have properties typical of carbons or carbons combined with silica–alumina materials. The application of carbon xerogels in practical gas chromatography has been exemplified.

1. Introduction

Carbon xerogels as one more type of technical carbons attract attention of specialists in catalysis due to their properties intended for preparation of new catalysts [1] and fuel cells [2]. They can be obtained by carbonization of xerogels of different resins (phenol-, resorcinol- and cresol formaldehydes) [3]. Varying the conditions of the preparation and carbonization of resins, one may change the ratio of micro-, meso- and macropores and accordingly their specific surface areas over a wide range [4,5]. Moreover these carbon-containing materials are characterized by large mechanical strength and can be easily formed as thin films, powders, microspheres of any required form and sizes, etc. The developed porous structure and high specific surface area make then promising materials for adsorption, including gas chromatography. Furthermore, some data on adsorption and application of activated charcoal based on phenol–formaldehyde resin (AChPhFR) as an adsorbent to concentrate the impurities of light hydrocarbons have been published [6]. But these data are very limited and insufficient. In addition, it was interesting to know their place among carbons and carbon-containing materials such as activated charcoals [7–9], carbon sieves [10–12], graphitized carbon blacks [13–17], carbon fibers [18,19] and nanotubes [20,21], carbonized alumina [22] and zeolite [23] which are used in gas chromatography.

Our report is devoted to the study of these carbon xerogels by X-ray phase analysis, microscopy, adsorption and gas chromatography. We investigated the influence of the preparation methods on the nano- and adsorption textures of xerogels carbonized as well as their chromatographic properties.

Their adsorption, structural and gas chromatography properties are compared with those of various chromatographic materials, carbon-containing and aluminum silicate.

2. Experimental

2.1. Preparation of porous phenol–formaldehyde resins and their carbonization

We investigated the samples of microporous technical carbon material (MTCM) [3] obtained according to the techniques described below.

In order to prepare carbon material of MTCM-1, we used phenol–formaldehyde resin of SFZh-302 by OAO "Karbolit" (Orekhovo-Zuevo). SFZh-302 resin was pretreated to obtain porous texture. The building of the porous system with diameter more than 10 nm was attained by introducing a blowing agent. It was the solution of ethane diacid ($COOHCOOH{\cdot}6H_2O$) in glycerine. The first component was taken in 30 g quantity and the second one was 100 g. The mixture obtained (after intimate mixing) was transferred into the mould and was hardened in the baker at 70 °C (from 20 min up to 90 min). The ratio of the components (SFZh-302: blowing agent) in the prepared sample was 1:2.

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1387-1811/$ - see front matter © 2009 Published by Elsevier Inc.
doi:10.1016/j.micromeso.2009.10.002

Cured a sample of porous phenol–formaldehyde resin was carbonized without air in steel container at a steady gradient of temperature at 6 °C min^{-1}up to 900 °C. Holding-temperature time at 900 °C was not less 30 min. Then container with the sample was taken out from the baker and it was cooled without air.

Microporous carbon materials MTCM-2 were obtained using preliminary nitrated porous phenol–formaldehyde resin. We carried out the nitration of this resin by impregnating it with 33 wt.% nitric acid followed by the 24-h storage at ambient temperature. Then the sample was washed from excess acid by distilled water and dried at 110 °C. Nitrated phenol–formaldehyde resin was further oxygenized by nitrogroups in the regime of self-propagating high-temperature synthesis in absence of air followed by its carbonization.

2.2. Instrumentation and systems used

Nanostructure of carbon-containing materials has been established by X-ray diffraction and electron microscopy.

The X-ray phase analysis was performed using a HZG 4/C X-ray diffractometer (FEB Freiberger Precision Mechanics) with Cu-anode and graphic plane reflected beam monochromator. X-ray diagrams were registered by the scanning point by point within the angle interval of $2\theta = 10°–75°$. The scanning pitch was 0.05°, storage time at each point was 3 s.

We determined the interplanar space (d_{002}) from the location of the 002 diffraction peak on the X-ray diagram. The d_{002} means the distance between the carbon layers 002 in the carbon crystal structure whose value for graphite (d_{graph}) equals 0.336 nm. Moreover, we evaluated the graphitization degree, g, or the three-dimensional ordering degree. It determines the part of the hexagonal carbon layers packed like their packing in graphite crystal whose value for graphite is equal to 1 [24]:

$$g = (d_{\text{disord}} - d_{002})/(d_{\text{disord}} - d_{\text{graph}}), \tag{1}$$

where $d_{\text{disord.}} = 0.385$ nm is the interplanar space of disordered carbon structure, which we used in our calculations.

Electron microscopic images were obtained using a JEM-2010 electron microscope (JEOL, Japan) with a lattice-fringe resolution of 0.14 nm at an accelerating voltage of 200 kV. Samples to be examined by electron microscopy were prepared on a perforated carbon film mounted on a copper grid.

The adsorption characteristics of carbon-containing materials were examined by measuring low-temperature nitrogen adsorption isotherms with an automated ASAP-2400 instrument (Micromeritics, USA). Thus, specific surface area of the sample (S^{BET}_{specif}) was formally determined by the BET-method. The total volume of the pores (V_{total}) was calculated from their maximum filling point. The volume of the micropores (V_{μ}) was determined by comparative method [25].

Gas chromatography investigations of our samples were carried out using a Tsvet gas chromatograph equipped with flame ionization (FID) and thermal conductivity detectors (TCD).

The carrier gas was helium. To improve its purity we used filters to remove water and oxygen traces. The carrier gas flow rate was 30 $\text{cm}^3\ \text{min}^{-1}$. The column temperature was varied from 50 to 200 °C.

Each adsorbent (0.25–0.5 mm fraction) was packed into a stainless steel chromatographic column. It was conditioned in a special thermostat for 8 h in the argon stream.

Light saturated and unsaturated hydrocarbons and gases (hydrogen, nitrogen, oxygen and carbon oxides) were taken as adsorbate molecules. The basis for this choice was connected with peculiarities of the studied materials and mainly with their high specific surface areas (about 500 $\text{m}^2\ \text{g}^{-1}$). In addition, the elution order of adsorbates often allows one to make conclusions about the chemical nature of the studied adsorbent surface.

2.3. Evaluation of the retention data

The retention data of adsorbates, retention time (t_R) and specific retention volume (V_g) were evaluated according to the following relationship [26]:

$$V_g = (t_R - t_M) \cdot F_0 \cdot (T_c/T_0) \cdot j/W \tag{2}$$

where
t_R – retention time of the investigated sorbate (min);
t_M – retention time of an unretained sorbate (hydrogen or air when we used TCD as well as methane for FID) (min);
F_0 – volumetric flow rate of the carrier gas (helium) at column outlet and ambient temperature ($\text{cm}^3\ \text{min}^{-1}$);
Tc – column temperature (deg K);
T_0 – ambient temperature (deg K);
W– mass of the adsorbent in the chromatographic column (g);

$$j\text{— compressibility correction factor,}\quad j = \frac{3}{2} \cdot \frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \tag{3}$$

where p_i and p_o – carrier gas pressure at the inlet and outlet of the chromatographic column, respectively (mm Hg).

Note, hydrogen was used as a not retained sorbate when we studied carbon xerogels, aktilen-1, initial and carbonized zeolites with TCD. In this case hydrogen was eluted before air. Moreover, air that is commonly used as the gas for the determination of the hold-up time was separated, for example, by carbonized zeolite giving two peaks on the chromatogram (oxygen and nitrogen).

Nano- and adsorption textures and gas chromatography properties of carbon xerogels were compared with those of other adsorbents: graphitized thermal carbon black (GTCB) [13,14,17], carbon sieves (carbosphere) (Alltech Associates) [12,27], carbon fibers (aktilene-1) [17,18], filamentous carbon (C/Fe), obtained via hydrocarbon decomposition [17,27,28], alumina and carbonized alumina [17,22], zeolite 13X and zeolite 13X modified with 5.0 wt.% C [17,23] as well as activated charcoal based on phenol–formaldehyde resin [6].

3. Results and discussion

3.1. Investigation of nano- and adsorption textures of carbon xerogels

Substructure characteristics of the studied samples and their adsorption textures are presented in Table 1. Here one can see analogous data of other adsorbents including graphite-like carbons and aluminum silicate materials studied by us. The data in Table 1 show the carbon materials to be characterized by various graphitization degrees. So, the graphitized thermal carbon black has the highest (after graphite) value of g equal to 0.94 (sample 2).

Catalytic carbon C/Fe (sample 3) has graphitization degree close to that of GTCB ($g = 0.92$). Like the graphitized thermal carbon black, the surface of C/Fe carbon consists mainly of the basal graphite crystal structure faces [17,27]. Interplanar spaces in their carbon structures are practically equal (cf. $d_{002} = 0.339$ nm for GTCB and $d_{002} = 0.340$ nm for C/Fe). Also they are close to that of graphite ($d_{002} = 0.336$).

SKT activated charcoal (sample 9) has the most disordered structure because it has the lowest value of $g = 0.1$. It is well-known that activated charcoal is X-ray amorphous ($g = 0$). The value of SKT interplanar space (0.380 nm) is significantly larger than that of graphite structure.