



# Influence of the method of activation on the structural and sorption properties of the products of carbonization of sucrose



Nataliya D. Shcherban\*, Pavel S. Yaremov, Vladimir G. Ilyin, Mariya V. Ovcharova

L.V. Piszczek Institute of Physical Chemistry, NAS of Ukraine 31 pr. Nauky, Kyiv 03028, Ukraine

## ARTICLE INFO

### Article history:

Received 4 September 2013

Accepted 20 February 2014

Available online 2 March 2014

### Keywords:

Activation

Activated carbon material

Nanoporous carbon

Hydrogen adsorption

Adsorption potential

## ABSTRACT

The comparative research of bulk carbonization of sucrose at different temperatures (Ar, 400–900 °C) in the presence of activating agents (H<sub>3</sub>PO<sub>4</sub> and ZnCl<sub>2</sub>) and water vapor was carried out. X-ray diffraction, nitrogen and hydrogen adsorption and IR spectroscopy were used for investigating of the structural and sorption characteristics of the obtained materials. It was shown that in conditions of non-catalytic bulk carbonization of sucrose homogeneous microporous carbons were formed; with the increasing of the temperature of carbonization micropore volume and adsorption of hydrogen (up to 1.48 wt.%, 900 °C) were increased. The essential effect of using an activating agent and/or catalytic agent on the porous structure of carbons: in the presence of phosphoric acid carbons with increased micro- and supermicropore volume were obtained. Mainly mesoporous carbons were formed in the presence of zinc chloride. It was established that thermal activation with steam at 800 and 850 °C results in the significant increase of specific surface area of the carbons ( $S_{\text{BET}}$  – up to 2287 m<sup>2</sup>/g) and hydrogen adsorption – up to 1.88 and 1.99 wt.% accordingly.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Among the various methods of hydrogen storage (in cylinders under pressure, in liquefied state, in the form of metalhydrides, etc.) physical reverse adsorption of hydrogen by porous materials, including carbon, with high specific surface area and micropore, supermicropore and small mesopore adsorptive volume remains actual. Bulk carbonization of some organic compounds in combination with activating agent, which will promote the development of porosity of carbon framework can be an effective and affordable way of obtaining of carbon adsorbents of hydrogen. Substances that are easily polymerized or are already polymers preferably branched (sucrose, cellulose, lignin, etc.) can be used as organic precursors of adsorbents, as well as zinc chloride, phosphoric acid, potassium carbonate and potassium hydroxide, water vapor, and others can act as activating agents. Thus significant increase in adsorption characteristics of carbon materials was received by using hydroxides and carbonates of alkali metals (materials from coal and charcoal, lignocelluloses, etc.) [1,2] and potassium carbonate in the processes of synthesis and subsequent carbonization of phenol and urea–formaldehyde resins [3]. Granulated carbon sorbents with high capacity for adsorption, particularly methane

(methane density in micropores reaches 0.25 g/cm<sup>3</sup> at 2.5 MPa) [4] were synthesized by the method of carbonization of lignocelluloses raw materials in the presence of activating agents such as phosphoric acid, zinc chloride, potassium hydroxide. The method [5] of obtaining of highly porous carbon materials ( $S_{\text{BET}}$  is about 2700 m<sup>2</sup>/g,  $V_{\text{micro}} \approx 0.7 \text{ cm}^3/\text{g}$ ) in the result of carbonization of Paulownia wood in the presence of zinc chloride was described. Porous carbon materials, sorption characteristics of which are close to industrial activated carbon adsorbents derived from coal were obtained [6,7] in the result of chemical activation of biomass waste with potassium hydroxide at 550 °C. Effective microporous carbon sorbents for environmental protection from gaseous pollutants were obtained by pyrolysis of waste date stones, containing cellulose and hemicellulose, with the following physical activation of the products of carbonization in the presence of water vapor [8]. Besides, the possibility of obtaining of mainly mesoporous ( $V_{\text{micro+meso}} = 1.0 \text{ cm}^3/\text{g}$ ,  $S_{\text{BET}} \approx 1300 \text{ m}^2/\text{g}$ ) carbon sorbents in the result of pyrolysis of cellulose, xylan and lignin in the presence of phosphoric acid was demonstrated [9]. It was shown [10] that activation of monolithic carbon (disks) obtained from olive stones, with zinc chloride was accompanied by formation of increased micropore volume during carbonization, compared with non-activated samples and decreasing of the content of macropores and voids; thermal activation of the samples in the presence of phosphoric acid leads to decreasing of mesopore volume and micropore size. Activated carbon materials for use as electrodes for supercapacitors

\* Corresponding author. Tel.: +380 445256771.

E-mail address: [nataliyalisenko@ukr.net](mailto:nataliyalisenko@ukr.net) (N.D. Shcherban).

were obtained on the basis of cationic starch using activation with KOH, ZnCl<sub>2</sub> and ZnCl<sub>2</sub>/CO<sub>2</sub> [11]. Correlation between the adsorption of methane and microporosity of chemically activated (ZnCl<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>) carbon materials was found, significant increasing in adsorption of methane in narrow micropores (less than 0.6 nm) was detected, and the impact of the chemical nature of the surface was not observed [12]. Significant development of porosity of the carbon framework [13] was received by sequential activation of the initial carbon with phosphoric acid and potassium hydroxide. As a result of such modification the obtained materials showed high adsorption capacity for hydrogen even at usual temperature – 0.8 wt.% at 298 K and 2 MPa. Mainly microporous materials characterized by high adsorption capacity for hydrogen (2.5 wt.%, 1 atm, 77 K) [14] were obtained by activation of sucrose-derived char with potassium hydroxide. It was shown determining influence of the content of activating agent (KOH) on the porous structure of the samples, carbonization temperature practically does not affect the porosity of the obtained sorbents. O- and N-containing carbon aerogels were synthesized using functionalization (treatment with H<sub>2</sub>O<sub>2</sub> or HNO<sub>3</sub>, reaction with ammonia or melamine) of carbon materials based on cellulose acetate. The obtained materials are characterized by mainly mesoporous structure, low specific surface area (160–300 m<sup>2</sup>/g) and the presence of acid (in the case of oxidative treatments) or basic (due to nitrogen enrichment in the reaction with ammonia or melamine) groups, the relative content of which can be easily regulated [15]. Mesoporous carbon materials (S<sub>BET</sub> up to 892 m<sup>2</sup>/g, pore size ~45 nm) were obtained using nano-CaCO<sub>3</sub> as template and sucrose [16].

As follows from literature data and general considerations, change the parameters of porous structure in the direction of increasing of pore volume and specific surface area of micro- and narrow mesopores, which can significantly affect at high pressures of hydrogen storage is the main approach to increase adsorption capacity of carbon adsorbents, particularly in relation to hydrogen. The above modification of carbon materials can be achieved by postsynthetic treatment and activation, particularly in oxidative media, halogenation, sulfonation, causing of metals dispersions, polymeric coatings, etc. [17]. Removal, burning of the part of frame (defective) and, mostly likely out of frame carbon resulting in release, some expansion of existing and formation of new micro- (mostly) and mesopore, development of the surface, changing of the chemical nature of the surface – formation of carboxyl, phenolic and other surface groups during oxidation, etc. is the result of such treatments.

The aim of our study was to determine the influence of conditions of bulk carbonization of sucrose and methods of activation (water vapor, zinc chloride, phosphoric acid) on structural and sorption properties (nitrogen and hydrogen adsorption), phase composition, peculiarities of the chemical nature of the surface of obtained carbon materials, etc.

Sucrose was used as an organic precursor because its molecules can easily oligo- and polymerized with the formation of cross-linked structures. Besides sucrose, oligo- and polymeric products of its transformations (dextrins, caramelans, etc.) are easily dehydrated during carbonization.

## 2. Materials and methods

### 2.1. Synthesis procedure

For catalytic carbonization an aqueous solution of sulfuric acid (at the rate of 0.112 g H<sub>2</sub>SO<sub>4</sub> per 1 g of sucrose) was added to sucrose (Ecolab, Ukraine), and then the mixture was stirred and dried at 100 °C. The obtained product was heated in a flow of argon at 900 °C for 2.5 h (heating rate 3 °/min). Apparatus for carbonization is

tubular quartz reactor. Number of replicates of the experiment was at least 3 for each type of the sample. The yield of the carbonization is about 0.3 g carbon from 1 g of sucrose.

For non-catalytic pyrolysis a weighted amount of sucrose (1 g) was kept in a flow of argon at 400, 700, 800 or 900 °C for 2.5 h. The obtained samples were indicated as *s-t*, where *t* – temperature of pyrolysis.

Thermal activation of the sample *s-900* with water vapor was carried out by heating in nitrogen up to 800 or 850 °C and followed passing through the sample *s-900* at a given temperature the flow of nitrogen previously saturated with water vapor (transmission of nitrogen through distilled water at ~90 °C). The time of treatment was 2 h. Synthesized samples were marked as *s-H<sub>2</sub>O-800* and *s-H<sub>2</sub>O-850*, respectively.

For chemical activation of carbon materials we used zinc chloride and phosphoric acid. A weighted amount of sucrose was stirred in 60% solution of ZnCl<sub>2</sub> (mass ratio ZnCl<sub>2</sub>/sucrose was ranged from 1 to 7) for 30 min, then was evaporated at 85 °C for 1 h. Then the obtained mixture was heated at 110 °C for 1 day. Then the samples were subjected to pyrolysis in an inert atmosphere (argon) for 3 h at 700 °C (heating rate 3 °C/min). After cooling, the obtained samples were washed with distilled water, then with 1.2 M hydrochloric acid and then with hot (85–90 °C) distilled water until the pH of washing water was ~6–7. The synthesized samples indicated as *s-ZnCl<sub>2</sub>-m-700*, where *m* – mass ratio ZnCl<sub>2</sub>/sucrose.

During the using of phosphoric acid as an activating agent a weighted amount of sucrose was impregnated with 85% water solution of H<sub>3</sub>PO<sub>4</sub> (mass ratio H<sub>3</sub>PO<sub>4</sub>/sucrose was 0.6–0.9), dried in air, and then was subjected to pyrolysis at 400 or 800 °C in an argon atmosphere for 30 min. After carbonization samples were cooled in a stream of argon and washed with hot distilled water to neutral pH in the wash water for removing of excess of H<sub>3</sub>PO<sub>4</sub>. The synthesized samples designated as *s-H<sub>3</sub>PO<sub>4</sub>-m-t*, where *m* – mass ratio H<sub>3</sub>PO<sub>4</sub>/sucrose, *t* – temperature of pyrolysis.

### 2.2. Characterization

Nitrogen and hydrogen adsorption isotherms with a purity of 99.99% were measured by volumetric method at 77 K to atmospheric pressure ( $p \sim 1 \times 10^{-3}$ –760 Torr) on Sorptomatic 1990. Specific surface area S<sub>BET</sub> was estimated by the BET equation [18]. Mesopore size was determined by BJH and DH [19]. Mesopore size was determined by the adsorption branch in the cases where the ad(de)sorption hysteresis on the isotherms ended in the ultimate strength of the meniscus of liquid adsorbate (nitrogen) to break (at  $p/p_0 \sim 0.45$ –0.50). Micropore size was calculated from Horvath–Kavazoe equation [20]. The values of micropore volume were refined with comparative *t*-plot method [18] for porous materials which containing micro- and mesopores in the one structure. IR-spectra were recorded using Fourier spectrometer Perkin Elmer Spectrum One. CHN-analysis was conducted at CHN-analyzer Carlo Erba 1106.

## 3. Results and discussion

### 3.1. Features of bulk non-catalytic pyrolysis of sucrose

Bulk carbonization of sucrose (Ar, 400–900 °C) in the presence of sulfuric acid leads to the formation of dense carbon material with low sorption characteristics, in particular total pore volume does not exceed 0.05 cm<sup>3</sup>/g (nitrogen adsorption isotherm is not present). In this case during the pyrolysis carbon framework is formed by the rapid catalytic dehydration of sucrose and in the absence of porous template (exotemplate in matrix carbonization)

Download English Version:

<https://daneshyari.com/en/article/1198299>

Download Persian Version:

<https://daneshyari.com/article/1198299>

[Daneshyari.com](https://daneshyari.com)