

## Preparation of Copper-Modified Porous Carbon Materials from Plant Polymers

BORIS N. KUZNETSOV, NIKOLAY V. CHESNOKOV, NADEZHDA M. MIKOVA, LILIA V. NAIMUSHINA, NINA I. PAVLENKO and GENNADY E. SELYUTIN

<sup>1</sup>*Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Ul. K. Marxa 42, Krasnoyarsk 660049 (Russia)*

*E-mail: cnv@icct.ru*

(Received November 19, 2001; in revised form December 7, 2001)

### Abstract

The parameters of the pyrolysis of copper-modified sulphite cellulose and aspen wood have been chosen to provide obtaining of copper-containing porous carbon materials. Dependencies connecting the yield of carbonized product and its specific surface area with pyrolysis conditions and the method of sample modifying were obtained. Transformations of metal-containing cellulose under thermal treatment and textural characteristics of carbon products were investigated by FTIR (DRIFT)-spectroscopy, ESR spectroscopy, electron microscopy, thermogravimetry and BET techniques. Decreasing of the start of intensive thermal decomposition process for copper-containing cellulose on 40–50 °C and for aspen wood – 15 °C in comparison with non-modified samples has been found. Preliminary treatment of cellulose with H<sub>2</sub>O<sub>2</sub> decreases its structural ordering and leads to the additional formation of C–O–C bonds. Thermal treatment of cellulose at 500–700 °C is accompanied by breaking of C–O–C ether bonds and by the formation of polyconjugated carbon structures.

### INTRODUCTION

Porous carbon materials (PCM) are widely used as adsorbents [1–3], supports for catalysts [4–6], carbon molecular sieves [7, 8]. Various application areas require PCM with definite texture and specified composition of the surface functional groups [9]. Because of this, the development of methods to prepare new types of modified PCMs is a very urgent problem.

Chemical modification of plant polymers is widely used to vary the structure and properties of carbon sorbents. In particular, the treatment of lignocellulosic materials with various chemical reagents, such as acids (H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>BO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>) [10–12], alkalis (KOH, *etc.*) [13], metal chlorides (ZnCl<sub>2</sub>, AlCl<sub>3</sub>, *etc.*) [14, 15] allows one to regulate the yield of carbon product and its texture.

The promising direction in designing PCMs with new properties is the modification of plant polymers by transition metals compounds with

following carbonization of the modified raw materials [8, 16]. The transformation of celluloses modified by metal ions is known [16–19]. The pyrolysis of metal-substituted cellulosic materials is simultaneously accompanied by the carbonization of cellulose and by the chemical transformation of the added metal.

It is known that during the cellulose treatment with such oxidizers as KMnO<sub>4</sub>, HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, *etc.*, the functional groups are formed in the cellulose macromolecule. Due to these groups, cellulose gets new properties [20]. In order to achieve the better interaction of cellulosic material with supported metal compound and to obtain its uniform distribution into cellulose matrix, it is reasonable to introduce a metal in the initial raw material using methods of chemical binding with reactive function groups of cellulose. For example, carboxylic groups are known to be able to bind Ca, Cu, Al cations [21, 22] and some others due to the ion exchange interaction.

To characterize carbon products, in particular obtained by the pyrolysis of wood raw material, as well as to perform the qualitative and semiquantitative analysis of the surface functional groups of the initial plant polymers, IR and ESR spectroscopy is widely used [23–25]. Within the recent years, Fourier Transform IR spectroscopy (FTIR), as well as the Diffuse Reflectance (DRIFT) version, make it possible to record the spectra of light-tightness samples of carbonaceous materials [26–28].

In the present work the process of copper compounds supporting on cellulose and aspen wood sawdust and the process of copper-containing materials pyrolysis were investigated. The purpose of the work is to study the physical and chemical transformations which take place during preparation and carbonization of these materials, as well as to investigate their textural characteristics and the state of the introduced copper.

## EXPERIMENTAL

The sulphite cellulose from the Krasnoyarsk Pulp-and-Paper Plant and aspen wood sawdust were used as initial materials. The composition of aspen wood (% mass): cellulose, 46; hemicellulose, 24; lignin, 22; extractives, 7.5; ash content, 0.3 (the ash contains 0.2 % Ca, 0.1 % Mg, Si, S, P, Cu, Fe). The composition of sulphite cellulose (% mass): cellulose, 90; lignin, 9; ash content, 0.9 (the ash contains 0.3 % Ca, Mg and S). The initial cellulose was crushed before using into particles of the size of  $2 \times 5$  mm, with thickness 1–2 mm. The fraction of aspen wood sawdust  $\leq 2$  mm was used. In some cases, cellulose was pretreated by hydrogen peroxide for producing an additional number of carboxylic groups, which are able to interact chemically with metal ions.

In order to introduce metal ions into plant polymer, cellulose and aspen samples were impregnated with aqueous solutions of  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{CH}_3\text{COO})_2$ ,  $\text{Cu}(\text{NH}_3)_n(\text{OH})_2$  ( $n = 2, 4$ ) of different concentration. Copper content in solutions was varied from 0.08 to 13 %. The excess of solution was removed by filtering; the samples were air-dried by alternating vacuum and atmospheric pressure. Additional drying till the

constant mass was performed at 104–105 °C directly before experiments on pyrolysis.

The initial and copper-modified samples were carbonized in a quartz reactor 30 cm long with a diameter of 16 cm in the flow of inert gas ( $\text{N}_2$  or Ar) in a programmable heating regime. The following parameters of pyrolysis were used: heating rate, 5 °C/min; gas flow rate, 2.5 l/h; exposure at final temperature, 2 h.

The specific surface area of carbon products was measured by BET method using argon adsorption at  $-196$  °C followed by desorption at room temperature.

The IR spectra of the initial and carbonized samples were recorded with the Fourier Transform IR spectrometer Vector 22 (Bruker); the number of scans was 150, and resolution  $4 \text{ cm}^{-1}$ . The concentration of sample in KBr matrix was 0.8 %. The treatment of spectroscopic data was performed using the Opus/IR software, version 2.2. The DRIFT spectra were recorded with a Bio-Rad FTS 165 spectrometer equipped with the Graseby-specac “Selector” optical accessory; the number of scans was 256, resolution  $2 \text{ cm}^{-1}$ .

Electron microscopic data were obtained with electronic microscope Jeol-JSM 820; the magnification was 300. EPR-spectroscopy study was carried out on spectrometer ER-1307 at room temperature. Thermal decomposition of cellulose samples was studied by thermogravimetric technique with the use of derivatograph of Paulic-Paulic-Erdey system of the Hungarian MOM company at the heating rate of 20 °C/s.

The reaction of  $\alpha$ -pinene hydrogenation was studied in a pulse microreactor with volume  $1.35 \text{ cm}^3$  at temperatures 250–270 °C and hydrogen space velocity  $10^2$ – $10^3 \text{ h}^{-1}$ . The catalyst loading in the reactor 0.2–0.3 g, the volume of the introduced pulses 0.3–1.0  $\mu\text{l}$ .

## RESULTS AND DISCUSSION

### *Investigation of modified plant polymers*

The IR absorption spectra of initial cellulose and aspen wood samples are shown in Fig. 1. They have the main absorption maximum at  $3390 \text{ cm}^{-1}$ , related to the stretching vibrations

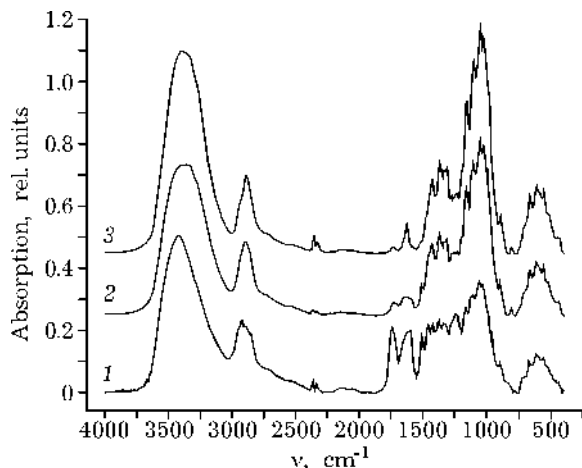


Fig. 1. IR spectra of aspen wood (1), sulphite cellulose (2), and sulphite cellulose treated with  $\text{H}_2\text{O}_2$  (3).

of OH groups. Rather broad half-width of this absorption band and of some additional maxima in the region  $3500\text{--}3050\text{ cm}^{-1}$  indicate the presence of OH groups of the different nature. The IR spectra of these samples contain a group of weakly resolved absorption bands in the regions  $2900\text{--}2800$  and  $1450\text{--}1380\text{ cm}^{-1}$ , related to stretching and bending vibrations of  $\text{CH}_2$ - and  $\text{CH}_3$ -groups, respectively [29, 30]. This indicates the presence of the saturated aliphatic fragments in cellulose and in aspen wood. The possibility of the presence of aromatic structures in the investigated samples is confirmed by the absorbance in spectral regions  $800\text{--}400$ ,  $1600$ , and  $1500\text{--}1450\text{ cm}^{-1}$ .

The presence of absorption bands within the region  $1250\text{--}1050\text{ cm}^{-1}$  is likely to be due to the vibrations of C-O groups of ethers and esters, including glycoside bonds of cellulose, observed at around  $1000\text{ cm}^{-1}$ . Within this spectral region, the deformation vibrations of phenolic and alcoholic OH groups can also be appeared [29]. Within the region  $880\text{--}600\text{ cm}^{-1}$ , bands of lower intensity are recorded; they are likely to belong to C-H vibrations in aromatic rings, as well as in pyranose cycles. In the IR spectrum of aspen wood (see Fig. 1, curve 1) two middle-intensity bands are present: at  $1625$  and at  $1740\text{ cm}^{-1}$ , which can be attributed to aromatic fragments containing C=O groups. Their noticeable intensity may be due to the presence of high-molecular lignin com-

ponents in aspen wood; they are absent in the case of pure cellulose.

The IR spectrum of sulphite cellulose treated with hydrogen peroxide is shown in Fig. 1 (curve 3). The comparison of spectra samples before and after treatment of cellulose by  $\text{H}_2\text{O}_2$  (curves 2, 3) shows that the oxidative treatment of cellulose by hydrogen peroxide increases the intensity of absorption bands in the region  $1250\text{--}910\text{ cm}^{-1}$ , as well as in the region of stretching and bending vibrations of OH groups, indicating the additional formation of new C-O-C bonds, without the change of the general character of spectra. At the same time, in the spectrum of the oxidized cellulose the intensity of absorption band in the region of the vibrations of carboxylic groups  $\nu_{\text{CO}}$  was slightly increased.

We determined previously [31] that the IR spectra of cellulose in the studied region ( $4000\text{--}400\text{ cm}^{-1}$ ) did not changed significantly after its treatment with copper solutions with metal concentration not higher than 4 %. The treatment of cellulose with more concentrated solutions of  $\text{Cu}(\text{CH}_3\text{COO})_2$  and  $\text{Cu}(\text{NO}_3)_2$  ( $\geq 4\%$ ) results only in the insignificant increase of the intensity of absorption bands corresponding to  $\nu_{\text{OH}}$  vibrations and to the increase of the intensity of bands related to the symmetrical and antisymmetric vibrations of the  $\text{COO}^-$  group ( $1604$  and  $1435\text{ cm}^{-1}$ ), and  $\text{NO}_3^-$  anion ( $1387\text{--}1350$  and  $830\text{ cm}^{-1}$ ). The intensity of these bands correlates with a concentration of the corresponding copper compounds. The high-frequency band of copper acetate ( $1604\text{ cm}^{-1}$ ) overlaps with the absorption band of the stretching vibrations of C=C group of aromatic ring.

For cellulose samples with low copper content (not higher than 4 %), ESR spectra with the magnetic parameters typical for  $\text{Cu}^{2+}$  -  $\text{Cu}^{2+}$  ( $g_z = 2.37$  and  $A_z = 0.0147\text{ cm}^{-1}$ ) are registered. These parameters are in good agreement with the ESR spectra described in literature for the doublet of copper ions in copper acetate ( $g_z = 2.34$ ,  $A_z = 0.0152\text{ cm}^{-1}$ ) [32]. The analysis of the observed ESR spectra of the modified cellulose samples allows us to attribute them to the isolated  $\text{Cu}^{2+}$  ions bound with oxygen ligands. It is possible that the oxygen ions in

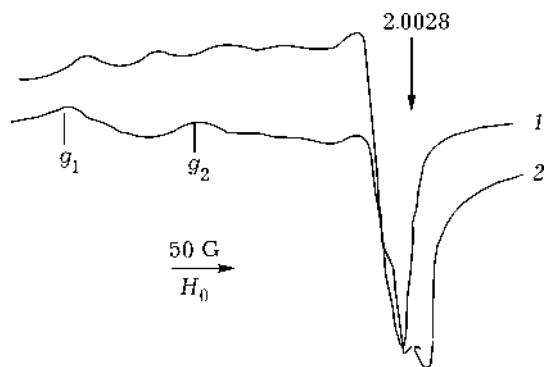


Fig. 2. ESR spectra of copper-modified cellulose samples: 1 - 4 %  $\text{Cu}(\text{CH}_3\text{COO})_2/\text{sulphite cellulose}$  treated by  $\text{H}_2\text{O}_2$ , 2 - 7 %  $\text{Cu}(\text{NH}_3)_4(\text{OH})_2/\text{sulphite cellulose}$ .

the first coordination sphere of  $\text{Cu}^{2+}$  belong to water molecules, while the charge of metal cations is compensated by the anions of the second coordination sphere.

The increase of concentration of  $\text{Cu}^{2+}$  ions in cellulose to 7 % leads to the appearance of additional replicate transitions in the ESR spectra (Fig. 2, curve 2) in area  $g_1 = 2.6$  and  $g_2 = 2.34$ . This signal can be conditioned by electronic exchange and dipole-dipole interactions of closely located  $\text{Cu}^{2+}$  ions. The estimations indicate that the Cu-Cu inter-ion distance is about 10 Å. Further increase of the copper concentration in cellulose sample leads to the appearance of the spectrum of exchange interaction between  $\text{Cu}^{2+}$  ions.

#### *Transformations of copper-containing plant polymers during their pyrolysis*

Thermal transformations of copper-substituted cellulose were investigated at the pyrolysis temperature region 250–650 °C. It was found that the thermal treatment at 250 °C did not significantly change the IR spectra of the modified cellulose. Only the small increase of intensity of absorption bands at 1710 and 1620  $\text{cm}^{-1}$  which belongs to carbonyl C=O groups and unsaturated C=C bonds was observed in carbonaceous samples in comparison with spectra of initial cellulose. The pyrolysis of initial and modified cellulose samples at 500 °C leads to the substantial changes in their IR spectra.

The following general regularities were revealed from the spectra of pyrolyzed samples, shown in Fig. 3. The destruction of ether

bonds C-O-C occurs, accompanied by nearly complete disappearance of absorption bands in the region 1250–800  $\text{cm}^{-1}$ . At the same time, the hydroxyl group content decreases substantially, which is evidenced by the decrease of the intensity of absorption bands of the stretching and bending vibrations of  $\nu_{\text{OH}}$  modes. The presence of intensive bands at 1586 and 1420  $\text{cm}^{-1}$ , as well as at 3030  $\text{cm}^{-1}$ , is a very probable indication of the formation of conjugated polyaromatic structures [29]. The observed triplet of absorption band in the region 700–900  $\text{cm}^{-1}$  in pyrolyzed samples, by analogy with [28, 33], can be attributed to out-of-plane deformation vibrations of the aromatic C-H groups. The absorption bands of low intensity at 2924 and 2336  $\text{cm}^{-1}$  are most likely related to the vibrations of  $\text{CO}_2$  adsorbed on the surface of the carbonized product.

The increase of pyrolysis temperature of copper-substituted cellulose up to 650–700 °C has only slight effect on the IR spectrum; only some redistribution of the band intensities is observed in the regions ~1586, 1426, ~875 and 816  $\text{cm}^{-1}$ , indicating the increased contribution from the conjugated polyaromatic structures. Assignment of these absorption bands to aromatic fragments is not quite unambiguous, because the cyclization processes that occur during the pyrolysis of cellulose can lead to the formation of aromatic structures included in the conjugation system of non-aromatic char-

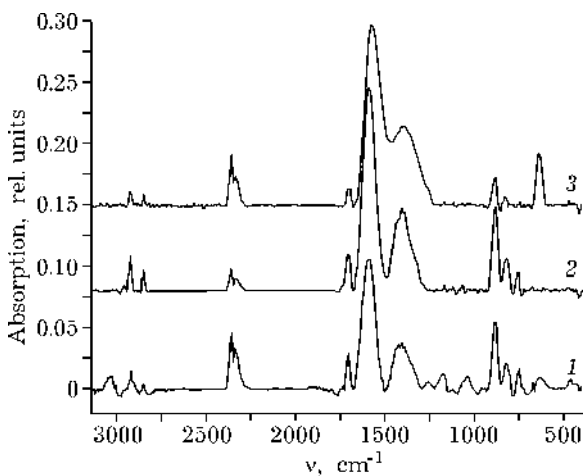


Fig. 3. IR spectra of copper-substituted cellulose samples pyrolyzed at 600 °C: 1 - 7 %  $\text{Cu}(\text{CH}_3\text{COO})_2/\text{sulphite cellulose}$  treated with  $\text{H}_2\text{O}_2$ , 2 - 4 %  $\text{Cu}(\text{NH}_3)_4(\text{OH})_2/\text{sulphite cellulose}$ , 3 - 13 %  $\text{Cu}(\text{NO}_3)_2/\text{sulphite cellulose}$ .

acter. However, the high degree of aromatization of carbonized products is confirmed by the intensive absorption in the region 900–700  $\text{cm}^{-1}$ , since it is known [28, 34] that the compounds in which aromatic fragments prevail exhibit high intensity of absorption bands in the mentioned region.

The IR spectra of the samples containing not more than 4 % copper, pyrolyzed at 600 °C, generally coincide with the spectrum of the pyrolyzed sample of initial cellulose. In the spectra of pyrolyzed samples, containing  $\geq 7$  % copper (see Fig. 3, curves 1, 3), the absorption band at  $\sim 635 \text{ cm}^{-1}$  is present; it is likely to belong to  $\nu_{\text{Cu-O}}$  of copper (I) oxide. An increase of the intensity of this band with the increase of copper content in the carbonized products, and the presence of a similar band in the spectrum of the individual  $\text{Cu}_2\text{O}$  confirm this assumption.

EPR spectra of copper-containing pyrolyzed samples have no signals indicating the presence of paramagnetic  $\text{Cu}^{+2}$  ions. By analogy with [10] it is possible to propose that in studied samples the copper is present in the metallic state and as  $\text{Cu}^{+1}$  ions. The ESR spectra of copper-containing celluloses pyrolyzed at 500 and 600 °C have a narrow signal with  $g = 2.0028$  and line width  $\Delta H = 7.5 \text{ Gs}$ . The singlet character of the ESR signal, shape of the line and  $g$ -factor value are the evidence of the similarity of obtained ESR spectra and those recorded for the fossil coal. The observed spectrum can indicate the presence of polyconjugated structures in carbon matrix.

As follows from the analysis of the IR and ESR spectra the treatment of cellulose with hydrogen peroxide leads to the loosening of cellulose structure. A similar effect was observed after cellulose treatment with a copper-ammonia complex resulting in a partial dissolution of cellulose fibers [20, 22]. The decrease of structural ordering of cellulose treated with hydrogen peroxide is appeared both as the increase of resolution of the IR spectrum at 1500  $\text{cm}^{-1}$  (see Fig. 3, curves 1, 2), and as the additional increase of the width of ESR signals of the pyrolyzed samples. With increasing the pyrolysis temperature up to 700 °C, the further more profound changes occur in the

structure of the pyrolyzed cellulose, increasing its electronic conductivity substantially.

Thus, the set of data obtained by of IR and ESR spectroscopy suggests that the pyrolysis of studied cellulose samples is accompanied by breaking of C–O–C bonds and by condensation of fragments of cellulose destruction with the formation of polycondensed carbon structures. A conclusion about deep rearrangement of the initial structure of the cellulosic material is confirmed by an increase of the C/H ratio in the pyrolysis products by 3–5 times in comparison with the initial cellulose (Table. 1). The C/H ratio in studied products increases with increasing the pyrolysis temperature that is an indirect confirmation of the high degree of final product carbonization.

Additional data on thermal transformations of cellulose and aspen wood samples are obtained by thermogravimetric analysis. The DTA curves of cellulose samples (Fig. 4) have weak endoeffect at 95–150 °C which corresponds to the removal of physically adsorbed water within this temperature range. The mass loss at this region is approximately 4–5 % for the samples of the initial and modified cellulose. The DTA curves of the initial cellulose and aspen wood (see Figs. 4, 5) have two exoeffects within temperature ranges 380–400 and 480–510 °C, accompanied by the major mass loss. In the case of cellulose, these peaks are most clearly ob-

TABLE 1  
C/H ratio in the initial cellulose samples and those pyrolyzed at 600 °C

| Sample  | C/H ratio, % mass |                 |
|---|-------------------|-----------------|
|   | before pyrolysis  | after pyrolysis |
| Sulphite cellulose (SC)                           | 8.71              | 25.07           |
| SC treated with $\text{H}_2\text{O}_2$ (SC*)      | 6.35              | 27.84           |
| 1 % $\text{Cu}(\text{NO}_3)_2/\text{SC}$          | 6.43              | 25.87           |
| 13 % $\text{Cu}(\text{NO}_3)_2/\text{SC}$         | 5.28              | 26.56           |
| $\text{Cu}(\text{CH}_3\text{COO})_2/\text{SC}$    | 6.45              | 25.06           |
| $\text{Cu}(\text{NH}_3)_n(\text{OH})_2/\text{SC}$ | 6.55              | 26.04           |
| $\text{Cu}(\text{CH}_3\text{COO})_2/\text{SC}^*$  | 6.39              | 29.07           |
| Aspen wood  | 6.92              | 23.08           |

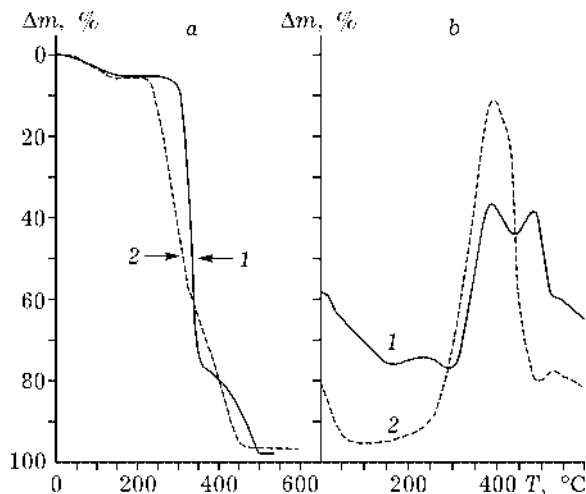


Fig. 4. TG (a) and DTA (b) curves of sulphite cellulose (1) and  $\text{Cu}(\text{CH}_3\text{COO})_2/\text{sulphite cellulose}$  treated with  $\text{H}_2\text{O}_2$  (2).

served; the first one of them, with mass loss of 52 %, is characterized by the maximum at 395 °C; most likely, it is connected with the processes of intensive depolymerization and carbonization of cellulose macromolecules (see Fig. 4). The second exothermal peak with the maximum at 490 °C begins to start while the first one is over (450 °C) and it goes to finish at 520 °C. The presence of second peak may be due to the further carbonization of cellulose with the mass loss 24.6 %. The occurrence of a substantial endoeffect at 450 °C, which is probably connected with the structural rearrangements in the matrix of the carbon material is the specific feature of this system.

The main processes of aspen wood destruction begin to start at higher temperature (see Fig. 5) and they go to finish at a temperature of about 600 °C owing to the higher thermal stability of lignin in comparison with cellulose.

Modification of cellulose and aspen wood by copper compounds (see Figs. 4, 5, curve 2) leads to evening-out of the observed exoeffects. The intensive mass loss due to the removal of gaseous products of decomposition starts at the temperature of 230 °C for  $\text{Cu}(\text{CH}_3\text{COO})_2/\text{SC}$  and  $\text{Cu}(\text{CH}_3\text{COO})_2/\text{SC}^*$  samples, while the intensive mass loss of the initial cellulose – only at 280 °C. The modification of aspen wood with copper compounds does not result to such noticeable effect as in the case of cellulose.

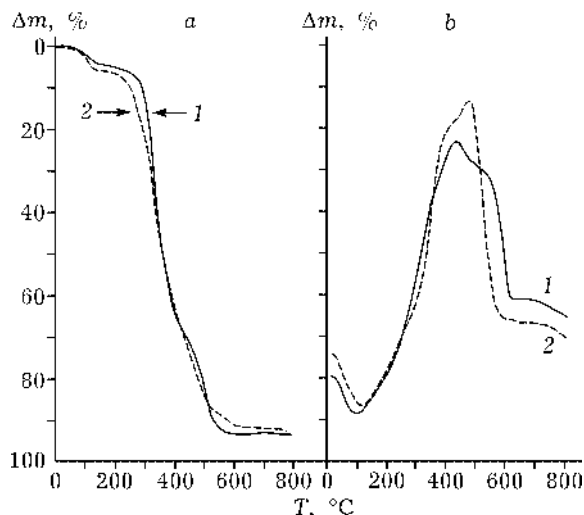


Fig. 5. TG (a) and DTA (b) curves of aspen wood (1) and  $\text{Cu}(\text{CH}_3\text{COO})_2/\text{aspen wood}$  (2) samples.

The performed termogravimetric studies have confirmed previously described facts that the presence of metal ions in cellulose matter shifts of the start of intensive thermal decomposition process to the lower temperature region [16, 19, 35]. This shift was about 15 °C in case of copper-containing aspen wood and about 50 °C – for cellulose treated by copper acetate.

#### FEATURES OF THE STRUCTURE OF CARBONACEOUS PRODUCTS

According to the literature data [36–38] one should expect that the fibrous structure of cellulose remains after its pyrolysis. The samples of modified cellulose and products of its pyrolysis were investigated by scanning electron microscopy. The obtained data show that the pyrolyzed cellulose samples have the fibrous structure. The comparison of the electron micrographs of initial, modified by copper acetate and pyrolysed samples (Fig. 6) allows us to conclude that the morphological structure of the initial cellulose fibers remains in the resulting carbon products.

On the basis of preliminary experiments with sulphite cellulose, the optimum parameters of pyrolysis process were selected for obtaining of porous carbon materials. For this purpose the influence of the pyrolysis temperature, method of temperature increase and

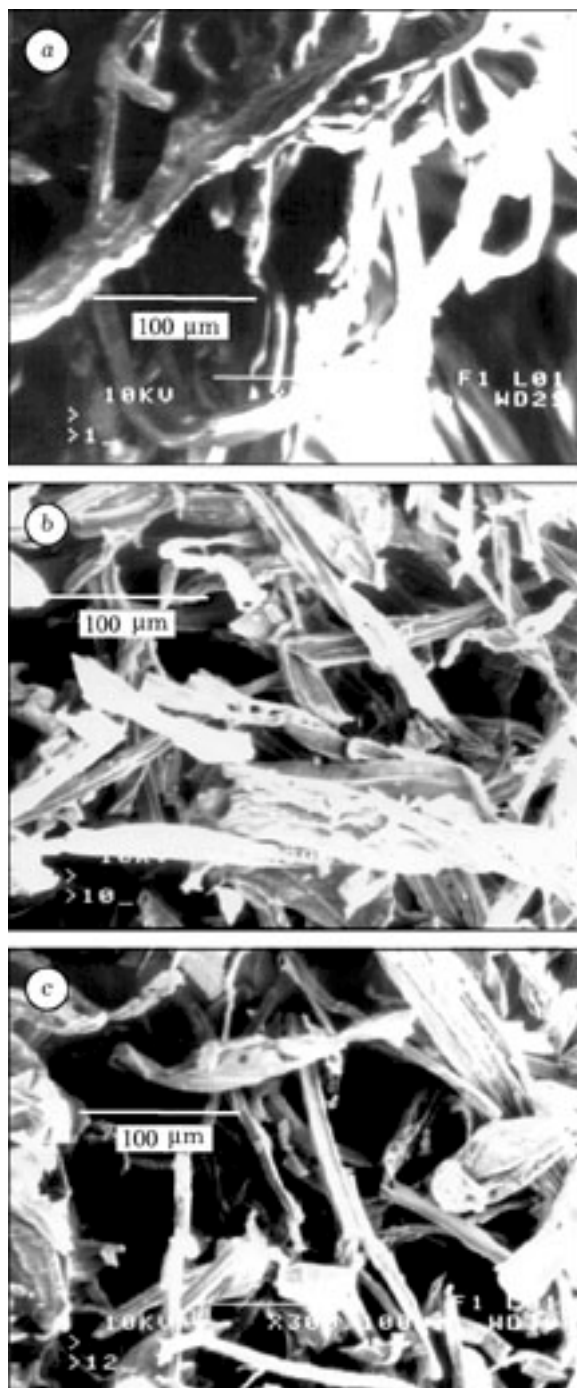


Fig. 6. Electron microscopic images of the sulphite cellulose (a), cellulose modified with  $\text{Cu}(\text{CH}_3\text{COO})_2$  (b), sample  $\text{Cu}(\text{CH}_3\text{COO})_2/\text{cellulose}$  treated by  $\text{H}_2\text{O}_2$  and pyrolyzed at  $600\text{ }^\circ\text{C}$  (c).

time of exposure at the final temperature on the specific surface area of resulting carbon products were studied. It was found that the increase of pyrolysis temperature up to  $700\text{ }^\circ\text{C}$ , and the increase of the flow rate of carrier gas from  $150$  to  $200\text{ h}^{-1}$  lead to the increase of

the specific surface area determined by BET method at the insignificant decrease of the yield of porous carbon product. On the basis of data obtained the parameters of pyrolysis process described in the Experimental section were chosen.

The comparison of specific surface areas (determined by BET method) of the chars obtained by carbonization of initial and copper-modified cellulose samples shows that the metal promotes the development of the porous structure of the carbon material. The pyrolyzed samples  $\text{Cu}(\text{NO}_3)_2/\text{SC}$  and  $\text{Cu}(\text{Ac})_2/\text{SC}^*$  have the largest surface area (see Table 2).

Various factors can be responsible for the high porosity of carbon products obtained by carbonization of copper-modified plant polymers. The molecules of metal compound are able to penetrate into the interlayer spacing of cellulose macromolecules resulting in a more developed surface of the polymer due to its swelling [39]. Finally, this facilitates the emission of volatile compounds during modified cellulose thermal destruction and promotes the formation of macro- and mesopores in carbonized product. In addition, metal salts and complexes introduced into plant polymers can act as catalysts in depolymerization and gasification processes that occur during thermal transformations of the biomass and they promote the formation of a more developed porous structure in the carbon product [8, 17, 40–42]. To specify the mechanism of this action, additional systematic investigations are required.

The influence of the nature of the initial cellulosic material on the yield of carbon product and its specific surface area was investigated with sulphite cellulose and aspen wood samples modified by copper acetate (Figs. 7, 8). The most substantial differences in the yield of carbon products and in their specific surface area were detected at the pyrolysis temperatures of  $500\text{--}600\text{ }^\circ\text{C}$ . At these temperatures both the yield and the specific surface area of pyrolyzed samples of modified aspen wood are higher than those of modified cellulose. The observed phenomenon is connected with the presence of lignin in aspen wood. Being the most thermally stable component of wood, lignin undergoes less degradation than cellulose under the pyrolysis at increased

TABLE 2

Specific surface area (BET) of carbonaceous products obtained by the pyrolysis of copper-containing plant polymers at different temperatures,  $\text{m}^2/\text{g}$

| Sample  | Pyrolysis temperature, °C |     |     |
|---|---------------------------|-----|-----|
|   | 500                       | 600 | 700 |
| Sulphite cellulose (SC)                                   | 50                        | 330 | 480 |
| SC treated with $\text{H}_2\text{O}_2$ (SC*)              | 250                       | 380 | 430 |
| $\text{Cu}(\text{NH}_3)_4(\text{OH})_2/\text{SC}$         | 82                        | 140 | 180 |
| 4 % $\text{Cu}(\text{CH}_3\text{COO})_2/\text{SC}$        | 86                        | 250 | 470 |
| 13 % $\text{Cu}(\text{NO}_3)_2/\text{SC}$                 | 80                        | 250 | 280 |
| 1 % $\text{Cu}(\text{NO}_3)_2/\text{SC}$                  | 100                       | 460 | 580 |
| 4 % $\text{Cu}(\text{CH}_3\text{COO})_2/\text{SC}^*$      | 200                       | 470 | 600 |
| $\text{Cu}(\text{NH}_3)_4(\text{OH})_2/\text{aspen wood}$ | 42                        | 100 | 285 |

temperatures. Furthermore, it is known [43, 44] that the fragments of thermal destruction of lignin are able to enter into condensation reactions which increase the yield of carbon product. The increase of pyrolysis temperature up to 700 °C levels out the difference in the yield of carbon products (see Fig. 8).

It is known that the copper-modified porous carbon materials catalyse some hydrogenation reactions [45, 46]. The catalytic properties of copper-containing carbons obtained by pyrolysis at 500 °C of  $\text{Cu}(\text{NH}_3)_4(\text{OH})_2/\text{SC}$  and  $\text{Cu}(\text{NO}_3)_2/\text{SC}$  samples were tested in reaction of  $\alpha$ -pinene hydrogenation. Preliminary experiments demonstrate that the degree of  $\alpha$ -pinene conversion to pinane on these catalysts reaches 50–70 % at the reaction temperature 270 °C. The obtained copper-modified carbon materials have perspectives of their use as catalysts for the industrially important hydrogenation processes. The fibrous structure of

these samples opens new possibilities for the reduction of hydraulic resistance of the catalyst loaded in industrial reactor.

## CONCLUSIONS

The information about thermal transformations of copper-modified celluloses pyrolyzed at 250–700 °C was obtained by using of IR and ESR spectroscopy and DTA methods. The thermal treatment at temperature of 250 °C gives no substantial changes in the cellulose structure. The increase of pyrolysis temperature up to 500–700 °C leads to the destruction of C–O–C bonds and to the generation of polyaromatic systems with further formation of carbon matrix with the ordered structure.

The variation of introduced metal state from  $\text{Cu}^{2+}$  for initial samples of modified cellulose to  $\text{Cu}^0$  and  $\text{Cu}^{1+}$  ions for pyrolyzed sam-

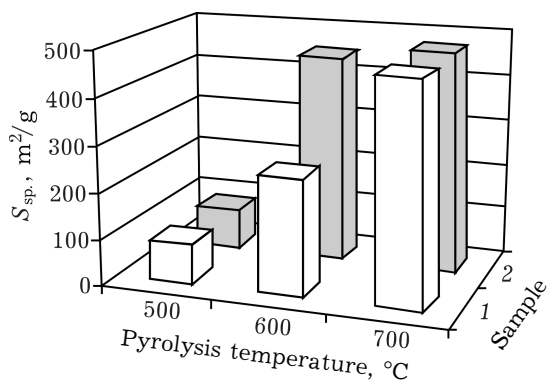


Fig. 7. Specific surface area of carbonic products obtained by the pyrolysis of modified  $\text{Cu}(\text{CH}_3\text{COO})_2$  samples of sulphite cellulose (1) and aspen wood (2).

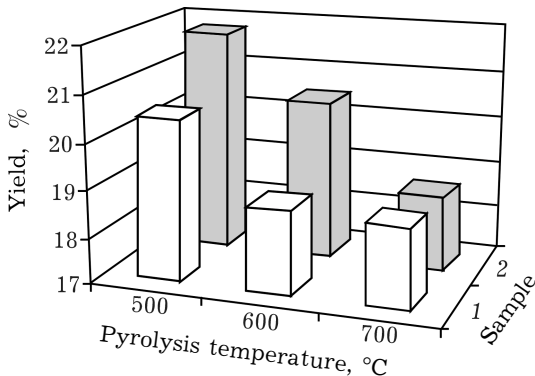


Fig. 8. The yield of carbon products obtained by the pyrolysis of modified  $\text{Cu}(\text{CH}_3\text{COO})_2$  samples of sulphite cellulose (1) and aspen wood (2).



ples has been detected. The information about the influence of copper additives on the process of plant polymer pyrolysis was obtained. The decrease of the start of thermal decomposition process on 40–50 °C for copper-containing samples in comparison with non-modified cellulose has been found. For copper-containing aspen wood this shift was about 15 °C.

It was shown that the char yield for modified aspen wood samples at the pyrolysis temperature of 500–600 °C is higher than that for cellulose samples. This fact can be explained by the higher thermal stability of wood lignin in comparison with cellulose. Data of SEM study indicate that the carbonized copper-modified samples remain the fibrous structure of the initial cellulose.

The conditions of cellulose and aspen wood modification and the parameters of Cu-modified samples pyrolysis resulting in the formation of porous carbon materials with high specific surface area (up to 600 m<sup>2</sup>/g) were selected. The obtained copper-containing carbons are catalytically active in  $\alpha$ -pinene hydrogenation reaction.

## Acknowledgements

The investigation has been supported by the European Commission within the framework of the Inco-Copernicus program (Grant No. ERBIC 15 CT98-0804).

## REFERENCES

- 1 L. Sorum, M. G. Gronli, J. E. Hustad, *Fuel*, 80 (2001) 1217.
- 2 V. F. Olontsev, *Khim. prom-st'*, 11 (1997) 31.
- 3 B. N. Kuznetsov, *Sorosovskiy obrazovatel'ny zhurn.*, 12 (1999) 29.
- 4 V. A. Likholobov, *Ibid.*, 5 (1997) 35.
- 5 V. A. Likholobov, V. B. Fenelonov, L. G. Okkel, *React. Kinet. Catal. Lett.*, 54 (1995) 381.
- 6 N. S. Polyakov, G. A. Petukhov, V. F. Surovikin, *Izv. AN. Ser. khim.*, 8 (1993) 1377.
- 7 Z. Hu, E. F. Wansant, *Carbon*, 33 (1995) 561.
- 8 Jia Guo, Aik Chong Lua, *Ibid.*, 38 (2000) 1985.
- 9 V. B. Fenelonov, *Poristy uglerod, izd. In-ta kataliza SO RAN, Novosibirsk*, 1995.
- 10 J.-S. Yu, S. B. Yoon, G. S. Chai, *Carbon*, 39 (2001) 1421.
- 11 H. Benaddi, T. J. Bandoz, J. Jagiello *et al.*, *Ibid.*, 38 (2000) 669.
- 12 G. E. Domburg, T. N. Skripachenko, G. A. Rossinskaya, *Khimiya drevesiny*, 3 (1982) 76.
- 13 C. Moreno-Castilla, F. Carrasco-Marin, M. V. Lopez-Ramon, M. A. Alvarez-Merino, *Carbon*, 39 (2001) 1425.
- 14 F. Caturla, M. Molina-Sabio, F. Rodriguez-Reinoso, *Ibid.*, 29 (1991) 999.
- 15 A. Ahmadpour, D. D. Do, *Ibid.*, 35 (1997) 1723.
- 16 Yu. G. Kryazhev, A. T. Kalashnik, G. P. Khokhlova, I. Yu. Petrov, *Khimiya tv. topliva*, 3 (1998) 28.
- 17 M. C. M. Alvim Ferraz, *Fuel*, 67 (1988) 1237.
- 18 M. C. M. Alvim Ferraz, G. L. Cabral Monteiro, *Ibid.*, 79 (2000) 645.
- 19 T. V. Chubar', V. N. Vysotskaya, Yu. I. Khimchenko *et al.*, *Ukr. khim. zhurn.*, 53 (1987) 243.
- 20 Tsellyuloza i eye proizvodnye, in N. Bickles and L. Segal (Eds.), Mir, Moscow, 1974, vol. 1, part 4.
- 21 I. A. Tarkovskaya, S. S. Stavitskaya, *Ros. khim. zhurn.*, 39 (1995) 44.
- 22 V. M. Nikitin, A. V. Obolenskaya, V. P. Shchegolev, *Khimiya drevesiny i tsellulozy, Lesn. prom-st'*, Moscow, 1978.
- 23 I. R. Moliner, J. L. Miranda, R. Cypres, *Fuel*, 67 (1988) 464.
- 24 O. Ito, H. Seki and M. Iino, *Ibid.*, 67 (1988) 573.
- 25 S. W. Dack, D. M. Hobday, T. D. Smith and J. R. Pilbrow, *Ibid.*, 64 (1985) 219.
- 26 C. Q. Yang and J. R. Simms, *Ibid.*, 74 (1995) 543.
- 27 G. Mul, F. Capteijn, J. A. Moulijn, *Carbon*, 37 (1999) 401.
- 28 A. Koch, A. Krzton, G. Fingueneisel *et al.*, *Fuel*, 77 (1988) 563.
- 29 L. G. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1975.
- 30 K. H. Michaelian and W. I. Friesen, *Fuel*, 69 (1990) 1271.
- 31 N. V. Chesnokov, N. M. Mikova, L. V. Naimushina *et al.*, in B. N. Kuznetsov and R. Gruber (Eds.), Proc. of 4th Intern. Symp. "Catalytic and Thermochemical Conversions of Natural Organic Polymers", Krasnoyarsk, 2000, pp. 150–157.
- 32 G. F. Kokoszka, H. C. Allen, *J. Chem. Phys.*, 42, 10 (1965) 3693.
- 33 T. Zerlia, *Fuel*, 64 (1985) 1310.
- 34 N. D. Rusyanova, *Uglekhimiya, Nauka, Moscow*, 2000.
- 35 Yu. F. Patrakov, I. Y. Petrov, E. S. Kotlyarova, Yu. G. Kryazhev, Proc. of Intern. Conf. "Eurocarbon'98", Strasbourg, 1998, Vol. 1, pp. 195–196.
- 36 J. B. Donnet, R. C. Bansal, *Carbon Fibers*, Dekker, New York, 1990.
- 37 C. E. Byrne, D. C. Nagle, *Carbon* 35 (1997) 267.
- 38 S. Kubo, Y. Uraki, Y. Sano, *Ibid.*, 36 (1998) 1119.
- 39 C. A. Zaror, I. S. Hutchings, D. L. Pyle, R. Kandioti, *Fuel*, 64 (1985) 990.
- 40 B. N. Kuznetsov, *Kataliz khimicheskikh prevrashcheny uglya i biomassy, Nauka, Novosibirsk*, 1990.
- 41 J. J. Freeman, F. G. R. Gimblett, *Carbon*, 26 (1988) 501.
- 42 O. Ito, H. Seki, M. Iino, *Fuel*, 67 (1988) 573.
- 43 D. Fengel, G. Vegener, *Wood (Chemistry, Ultrastructure, Reactions)*, Walter de Gruyter, Berlin *etc.*, 1984.
- 44 G. G. Jernigan and G. A. Somorjai, *J. Catal.*, 147 (1994) 567.
- 45 R. Rao, A. Dandekar, R. T. K. Baker and M. A. Van- nance, *Ibid.*, 171 (1997) 406.
- 46 X. Hu, L. Lei, H. P. Chu, P. L. Yue, *Carbon*, 36 (1998) 631.