Thermal behavior of chitosan as a carbon material precursor under IR radiation

A Vasilev\textsuperscript{1,2}, M Efimov\textsuperscript{4}, G Bondarenko\textsuperscript{4}, V Kozlov\textsuperscript{1,2}, E Dzidziguri\textsuperscript{2} and G Karpacheva\textsuperscript{1}

\textsuperscript{1}Chemistry of Polyconjugated Systems Laboratory, \textit{A V Topchiev Institute of Petrochemical Synthesis RAS}, 29 Leninsky Avenue, Moscow 119991, Russian Federation
\textsuperscript{2}Department of Functional Nanosystems and High-Temperature Materials, \textit{National University of Science and Technology “MISiS”}, 4 Leninsky Avenue, Moscow 119991 Russian Federation

\textsuperscript{1,2}E-mail: raver.vasiljev@mail.ru

Abstract. An effective accelerated synthesis procedure of a carbon material based on chitosan via infrared pyrolysis was developed. Infrared radiation heating allows to shorten preparation time significantly. It takes only 2 min of the residence time at 800 °C for complete carbonization of the polymer. The chemical transformations in chitosan during infrared pyrolysis depended on temperature were studied. The formation of C=C–C=N and C=C–C=C conjugated bonds at a low-temperature stage of the carbonization process was demonstrated. It was revealed that the main product of the chitosan pyrolysis at 600-800 °C represents a graphite-like carbon material in the form of carbocyclic structures.

1. Introduction
Carbon supported metal nanoparticles are commonly employed as promising materials for many applications as electrode materials in supercapacitors, gas sensors, carriers for the targeted magnetically-controlled delivery of drugs, and in the designing of new magnetic materials [1-8]. Particularly, carbon supports are perspective in catalysis due to their chemical resistance to aggressive media, thermal stability, electrochemical, catalytic properties, a large specific surface area and a wide variety of carbonaceous precursors.

One of the main methods of obtaining carbon supports is the thermal treatment of carbonaceous materials, for example, woods, seeds, shoots, natural, synthetic polymers, etc [9-11]. Chitosan (CS), a linear polysaccharide produced from chitin shells of shrimp and other crustaceans, attracts researchers’ attention due to their low cost, environmental friendliness, biocompatibility and water solubility. Since CS exhibits fairly high stabilizing and reducing properties for metal nanoparticles, it can be used as a carbon precursor for the preparation of carbon supported metal nanoparticles [12,13].

The main goal of this work was to investigate the chemical transformation of CS at different stages of infrared (IR) pyrolysis in order to determine the possibilities of applying chitosan as an effective precursor of carbon support of metal nanoparticles.
2. Materials and methods

CS flakes (MW = 500 kDa, deacetylation degree - 83 %) purchased from “Bioprogress” (Shchyolkovo, Russia) were used in the present research. The carbonization of the polymer samples was carried out via annealing at the desired temperature for 2 min in a nitrogen atmosphere under IR heating conditions. The preparation temperature range was 150-800 °C. The heat treatment was performed in the laboratory device of incoherent IR annealing. The halogen lamps KG-220 (total power of 24 kW) were applied as a radiation source, which had a maximum emission wavelength in the region of 0.9-1.2 µm. The samples are marked as IR-CS-x, where x is the temperature of IR heat treatment.

Powder X-ray diffraction (XRD) analysis was performed using “Difray-401” diffractometer (Scientific Instruments, Saint Petersburg, Russia) with Bragg-Brentano focusing, using Cr Kα radiation. Raman dispersion spectra were recorded by “Senterra” microscope (Bruker, Billerica, Massachusetts, USA) with 532 nm laser and 0.2 mW of power. A JEM-2100 microscope (JEOL, Tokyo, Japan) were used to examine the surface morphology of the IR pyrolyzed chitosan through transmission electron microscopy (TEM).

Chemical transformation of chitosan was studied via IR spectroscopy. Infrared spectra were recorded in the reflection mode on a HYPERION-2000 IR microscope attached to an IFS-66 v/s FTIR spectrometer (Bruker; crystal – Ge, resolution - 3 cm⁻¹, and region of recording - 600 – 4000 cm⁻¹). X-ray photoelectron spectroscopy (XPS) was conducted using a PHI5500 Versa Probe II instrument (ULVAC-PHI Inc, Chigasaki, Japan) with a monochromatic Al Kα X-ray source.

Thermogravimetry (TG) measurements were carried out in a nitrogen flow at a rate of 50 mL min⁻¹ under non-isothermal conditions from room temperature up to 500 °C at a heating rate of 10 °C min⁻¹ on a Discovery TG instrument (TA Instruments, Newcastle, USA). The device furnace was equipped with four halogen lamps to heat a SiC chamber in the infrared range. The sample was loaded in a platinum crucible and placed into the SiC chamber. The weighing accuracy of the device was 0.1 %, and the accuracy of temperature control was 1 ºC.

Differential scanning calorimetry (DSC) measurements were carried out in a nitrogen flow at a rate of 50 mL min⁻¹ under non-isothermal conditions in the temperature range of 40-500 °C at a heating rate of 10 °C min⁻¹ on a Q20 calorimeter (TA Instruments). The calorimetric precision was 0.1 %, and the sensitivity was 1 µW.

3. Results and discussion

Fourier-transform IR spectroscopy is one of the best methods to study the chemical transformations of polymers. Figure 1 shows the results from the FTIR spectroscopy of the initial CS and the heat-treated samples exposed to IR radiation at different temperatures. For clarity, the spectra were shifted relative to each other along the axis of intensity.

As shown in figure 1, the IR spectra of the initial CS exhibit characteristic bands corresponding to CS structural elements: at 1000-1050 cm⁻¹, the stretching vibrations of C-OH and C-O-C bonds; at 1300-1350 cm⁻¹, the stretching vibrations of C-N bonds; at 1631-1650 cm⁻¹, the bending vibrations of NH₂ groups; at 2800-3000 cm⁻¹, a band attributed to the bonds in -CH₂- groups; at 1150 and 1550 cm⁻¹, bands corresponding to amide groups; and at 3200-3500 cm⁻¹, a broad band corresponding to the associated -OH groups [14].

It was found that the CS structure does not change under IR treatment at 150 °C. The band in the region of 664 cm⁻¹ indicates the keeping of the polymer crystallinity. At the temperature of 200 °C, the crystallinity band disappears, the intensity of the bands from C-O bonds decreases in the region of 1000-1030 cm⁻¹, and a negligible increase in the intensity of the amide groups can be observed. Increasing the temperature of the IR pyrolysis up to 250 °C leads to the formation of conjugated bonds C=C-C=N (166 cm⁻¹) and the rapid vanishing of the amide groups and C-O bonds from the polymer structure. At the temperature of 300 °C, the CS structure changes significantly. All bands characterize the CS structure absence. The position and intensity of two bands at 862 and 1400 cm⁻¹ correspond to the carbonate ion CO₃²⁻. The new broad band at 1260 cm⁻¹ corresponding to C-O-C bonds linked with
adjacent conjugated bonds is revealed as the temperature rises up to 400-500 °C. Further increase in the synthesis temperature up to 600-800 °C provides a reduction of the amount of conjugated bonds C=C=C=N(C) and the change of oxidation degree of the carbon support and formation of different types of C-O-X bonds (X = H, N, O). This can be explained by the intensity decrease of the bands corresponding to the conjugated bonds, growth and shift toward long-wave region of the C-O-C bands as well. The IR spectra of the samples obtained at 600-800 °C have a shoulder in the region of 1050-1500 cm⁻¹, which indicates the remaining of some number of the conjugated bonds.

Figure 1. IR spectra of the initial CS (1) sample and the samples IR-pyrolyzed at temperatures of 150 (2), 200 (3), 250 (4), 300 (5), 400 (6), 500 (7), 600 (8), 700 (9), and 800 °C (10).

Figure 2a demonstrates the TG and DSC curves recorded for the CS. The first endothermic peak can be observed between 40-150 °C, with a minimum at 91 °C. A mass loss of 10 % is associated to this effect, and it is attributed to the evaporation of absorbed water in the polymer. The second effect can be observed between 250-330 °C, with an exothermic peak at 300 °C. This effect can also be associated with a mass loss (40 %), which corresponds to the thermal degradation of polymeric chain with vaporization of volatile compounds. The pyrolysis of polysaccharides structure starts by a random split of the glycosidic bonds, followed by a further decomposition forming acetic and butyric acids and a series of lower fatty acids [15-19]. The energy associated with this second effect was found to be 178.8 J g⁻¹. Finally, the consecutive low-intensity exothermic peaks can be observed up to 500 °C, which corresponds to the residual cross-linked degradation of the CS. The mass loss associated with this effect was found to be about 15 %.

Figure 2. (a) TG and DSC curves of chitosan; (b) Plot for the determination of E and n.
Kinetics of thermal degradation of CS was evaluated from the thermogravimetric analysis. The TG data were applied to the calculation of the activation energy $E$ and the reaction order $n$ of the main transformation in the temperature range of 250-330 °C by the method of Friedman (1) [20].

$$\ln\left(\frac{\alpha}{\alpha_T}\right) = \ln A + n \ln (1 - \alpha) - \frac{E}{RT}$$  

(1)

The activation energy calculated by this method is called effective. The value of the effective activation energy of thermal decomposition is one of the most important indicators that characterizes the resistance of natural and synthetic polymers to high temperatures. Activation energy is also used in the study of the mechanisms of thermal destruction, aging and stabilization of polymeric materials.

Figure 2(b) represents the linearization of the data function $d\alpha/dt = f(T)$ and determination of the activation energy and reaction order. The value of $Y$ intercept is the reaction order, and the slope ratio is equal to the value $(-E/R)$. According to the results, the activation energy and the reaction order of the main stage of the thermos-oxidative degradation of the CS were found to be 71 kJ mol$^{-1}$ and 1, respectively.

XPS is one of the best tools for the study of the surface chemical modification. The results of the chemical composition and the C1s, N1s and O1s spectra of chitosan pyrolyzed at 800 °C are presented in Table 1 and figure 3, consequently. The main asymmetric peak at 284.5 eV (peak 1) and its $\pi$-satellite shifted by 6.0 – 6.1 eV corresponding to carbon with sp$^2$-hybridization, the symmetric peak at 284.9 eV (peak 2) corresponding to carbon with sp$^3$-hybridization including the adsorbed hydrocarbons and also two symmetric peaks in the region of higher energies (peaks 3 and 4) can be revealed by the approximation of the C1s spectrum. The position of the third peak corresponds to carbon-nitrogen and carbon-oxygen bonds (C-N, C-O). The fourth peak is located in a wide range of 288.4-290.1 Ev, which contains different groups with double bonds (C=O) including the carboxylic group. However, a large distribution of the low-intensity bond energies of the fourth peak is associated with a higher measurement error. In order to precisely define function groups, the high-resolution N1s and O1s spectra should be considered.

The analysis of the N1s and O1s spectra revealed the peaks corresponding with single bonds at 533.0 eV (C-O) and 400.6 eV (C-N) and with double bonds at 531.3 eV (C=O) and 398.3 eV (C=N) at the edge of the carbon layers. According to the intensity of the single and double bonds of the N1s and O1s spectra, the carbon bonds with sp$^3$-hybridization are predominant in the pyrolyzed CS.

| Sample     | Chemical composition (at. %) |
|------------|-------------------------------|
|            | C   | N    | O    |
| IR-CS 800 °C | 89.2 | 5.4  | 5.1  |

The XRD analysis showed that the CS IR-pyrolyzed at 400 °C has already a graphite-like structure (figure 4a). XRD patterns 5-7 have graphite reflection peaks located at 2$\theta$ ≈ 37° and 68°. Since the graphite reflection peaks (002) and (101) of the pyrolyzed CS become sharper with rising temperature, it can be concluded that the carbonized structure is more ordered. Similar to IR spectroscopy, it can be seen that the structure of the CS pyrolyzed at 150 °C does not change and at the temperature of 200 °C, the polymer structure became more defective according to the expansion of the main peak at the XRD pattern that means the decrystallization process. At the temperature of 250 °C the CS structure was changed significantly.
Figure 3. XPS spectra of C1s (a), N1s (b) and O1s (c) for the CS IR-pyrolyzed at 800 °C.

Raman spectra of the IR-pyrolyzed CS samples are characterized by the presence of D- and G-bands, which are characteristic of the presence of the carbon with sp$^3$- and sp$^2$-hybridization, accordingly (figure 4b). The Raman spectra of the perfect graphite is characterized by the G-band (1580 cm$^{-1}$). The appearing of the D-band corresponding to the Raman shift of the diamond at 1350 cm$^{-1}$ indicates the oxidized or substituted carbon atoms formation with the sp$^3$-hybridization at the edges of hexagonal carbon layers. Since the intensity ratio $I_D/I_G$ was found to increase with rising temperature, it can be concluded that the amount of the carbon atoms with the sp$^3$-hybridization also increases. This fact was confirmed by the IR-spectroscopy as well. In addition, a wide 2D band can be seen at about 2888 cm$^{-1}$, which indicates the different location of disordered hexagonal layers of carbon, i.e. the amorphous carbon with a low degree of graphitization [21], which was confirmed by the XRD analysis.

The TEM images (figure 5) demonstrate the morphology of the carbonized CS, which is characterized by a homogeneous and layer structure that is typical for most carbon materials. According to the BET-analysis, the specific surface area of the pyrolyzed CS was found to reach approximately 35 m$^2$/g depending on synthesis conditions.
Figure 4. (a) XRD patterns of the initial CS sample (1) and the samples IR-pyrolyzed at 150 (2), 200 (3), 250 (4), 400 (5), 600 (6) and 800 °C (7); (b) Raman spectra of the CS IR-pyrolyzed at 300 (1), 400 (2), 500 (3), 600 (4), 700 (5), and 800 °C (6).

Figure 5. TEM images of the CS IR pyrolyzed at 800 °C.

The previous works have well reported the polysaccharides pyrolysis mechanisms and kinetics [22-25]. It was noted that the main volatile compounds of CS pyrolysis are pyrazines, pyridines, pyrroles and furans. According to the paper [19], the pyrazine compounds are the dominated products among the volatile chemicals of chitosan pyrolysis. However, data about the chemical structure of carbon residue, the main product of chitosan pyrolysis, cannot be observed. Summarizing the research results, the chemical transformation scheme of the CS under IR pyrolysis was proposed (figure 6). At the temperatures of 200-250 °C, the cleavage of the glycosidic bond and the ring-opening from the C1-O bond breaking (as marked in figure 6) takes place. Intra- and intermolecular dehydrogenation leads to the formation of extended chains of the conjugated bonds C=C-C=N. Then, the scheme can be divided into 3 paths: formation of low hydrocarbons (path 1), formation of pyrazine compounds (path 2), and the formation of carbocyclic structures.

The product composition of polysaccharides pyrolysis is complex. For instance, the pyrolysis of cellulose leads to the formation of more than 100 compounds. Along with carbon residue, the polysaccharides pyrolysis characterized by the formation of water and carbon oxides in abundance [18]. Inspired by the ring-opening reactions during the cellulose pyrolysis, the C2-C3 bond in the CS
could be further fractured. As a result, the CS is fragmented into aminoacetaldehyde and other low hydrocarbons (path 1 in figure 6). According to path 2, the bimolecular nucleophilic addition reaction occurs leading to the formation of pyrazine compounds. It can be assumed that the carbon residue formation proceeds through dehydration, decarboxylation, aromatization, and intramolecular condensation to form the carbocyclic structures (path 3 in figure 6) [18,26]. The results of the IR-, Raman and X-ray photoelectron spectroscopy showed that the CS pyrolysis at 600-800 °C provides the formation of graphite-like carbon structure. The other above mentioned products of pyrolysis either are volatilize or their amount is very low.

Figure 6. The proposed scheme of the CS decomposition.
4. Conclusion
CS possesses the potential to be a precursor of carbon-supported metal nanoparticles. It was revealed that during the thermal decomposition, especially at 300 °C, a lot of volatile products were released. Some of them (CO, H₂) have reducing properties, thereby making the CS an attractive precursor in terms of the reducing agent. It was shown that during the IR pyrolysis, the CS structure undergoes strong changes up to 800 °C. At relatively low temperatures (200-500 °C), the formation of C=C–C=N and C=C–C=C conjugated bonds was observed. Starting from 500 °C, the length of the polycyclic system and the number of conjugated bonds was found to decrease due to the carbocyclic structures formation which, probably, begins at 300 – 350 °C. Thus, the CS can be effectively applied as a metal reducer and stabilizing support that hinders the agglomeration of nanoparticles.

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