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Time-of-flight secondary ion mass spectrometry as a novel method for surface characterization of carbonaceous material formed during thermochemical conversion of cellulose

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ABSTRACT

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was applied for the first time to the surface characterization of carbonaceous material formed during thermochemical conversion of cellulose. Owing to that new information about the composition of solid residue formed in the cellulose pyrolysis was obtained. The use of ToF-SIMS allowed one to demonstrate the differences between the structure of the uppermost layer and subsurface region of the pyrolysed material which were not clear with the use of other analytical methods.

1. Introduction

It is generally known that due to continuous growth of the world energy demand and fast depletion of fossil fuels a development of new efficient methods of energy production from alternative sources is necessary. One of them is the thermochemical conversion of lignocellulose into gaseous and liquid products in the presence of heterogeneous catalysts [1,2]. This kind of biomass is considered to be a very attractive source of renewable energy from both economical and environmental point of view. It is still necessary to optimise the conditions of the aforementioned process, explain its reaction mechanism and develop new, more efficient catalysts. It will however require to not only analyse the reaction products and properties of the catalytic systems, but also study changes in the structure of the raw lignocellulose during the reaction. Carbon deposit that occurs during pyrolysis limits significantly the reaction performance due to its formation both on the cellulose and catalysts surface, therefore understanding of this process is one of the most important issues. The literature data show that different analytical techniques have been applied for this purpose (i.e., TG, FTIR, Raman spectroscopy, XPS and ICP-AES) [3–6]. Nevertheless, these methods give information not only from the surface, but also from the bulk or subsurface region. The use of time-of-flight secondary ion mass spectrometry (ToF-SIMS) is therefore proposed, as it appears that in contrast to other techniques ToF-SIMS allows to obtain analytical data solely from the uppermost layer only of the investigated material [7]. This is especially important due to the fact that changes of the surface composition of the lignocellulose submitted to pyrolysis can decrease the yield of the obtained products.

The aim of this work is to gain new information about the surface of carbonaceous material formed during thermochemical conversion of model biomass – cellulose with and without catalysts. According to our knowledge, this was the first time that ToF-SIMS was successfully applied for this type of measurements.

2. Materials and methods

The experimental part of our studies began with the preparation of 20%Ni/Al_2O_3 model catalysts by the wet impregnation of γ-Al_2O_3 (Merck) with $Ni(NO_3)_2 \cdot 6H_2O$ (Chempur, Piekary Śląskie), following drying in 120 °C overnight, and calcination in air in 500 °C for 4 h. The activity tests were performed in a stirred batch reactor of 250 cm^3, under atmospheric pressure and 15 cm^3/min of argon flow, in the 500–700 °C temperature range for 4 h. Pyrolysis

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of α-cellulose (5 g) as a biomass model was conducted without and in the presence of nickel catalyst (0.2 g).

ToF-SIMS was applied to the characterization of the surface of α-cellulose and residues remaining after the pyrolysis process. In this case the measurements were performed using the ION-TOF GmbH instrument (TOF-SIMS IV) equipped with 25 kV pulsed Bi^+ primary ion gun in the static mode. FTIR measurements were made by transmission analysis on NICOLET 6700 instrument (Thermo Scientific) using the KBr technique. The amount of carbon in the solid residues remaining after the pyrolysis was measured by an automatic carbon analyzer TOC 5000 (Shimadzu) equipped with a solid sample module. The analysis of the reaction products was conducted using GC and GC–MS methods.

3. Results and discussion

The results of the investigation of the distribution of cellulose pyrolysis products showed significant differences in the composition of gaseous phase depending on the reaction temperature and addition of the catalyst (Fig. 1). Similar situation was observed for liquid phase, however in this case a huge number of various chemical compounds has been identified. This indicates that the factors mentioned above may considerably influence the reaction mechanism and the cellulose conversion. In spite of a relatively large number of investigations there are still some doubts in the explanation of this phenomenon [8]. An application of ToF-SIMS to the analysis of the solid residue remaining after the reaction allows for a new look into the processes occurring on the interface between biomass and formed pyrolysis products.

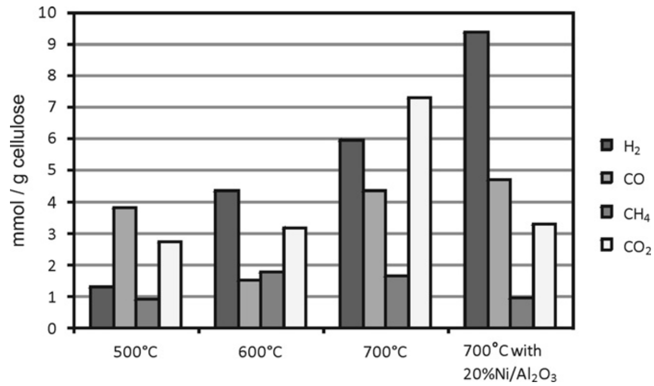

Fig. 1. Distribution of gaseous products of cellulose pyrolysis conducted without catalyst at 500 °C, 600 °C, 700 °C and with the presence of 20%Ni/Al_2O_3 catalyst at 700 °C.

In the first step of ToF-SIMS studies secondary ion mass spectra were collected from the surface of cellulose samples – both fresh and after the pyrolysis. The results showed the presence of signals corresponding to a series of positive and negative ions with the following formulas – $C_xH_yO_z^{\pm}$ and $C_xH_y^{\pm}$ (Figs. 2 and 3). Moreover, the existence of metallic contaminants was observed. A comparison of the mass spectra obtained for untreated and pyrolysed cellulose samples did not reveal any surprising differences in the qualitative composition of the analysed surfaces. However, changes in the intensity of particular ions appeared to be very interesting. In contrast to the results of FTIR measurements (Fig. 4) and literature data

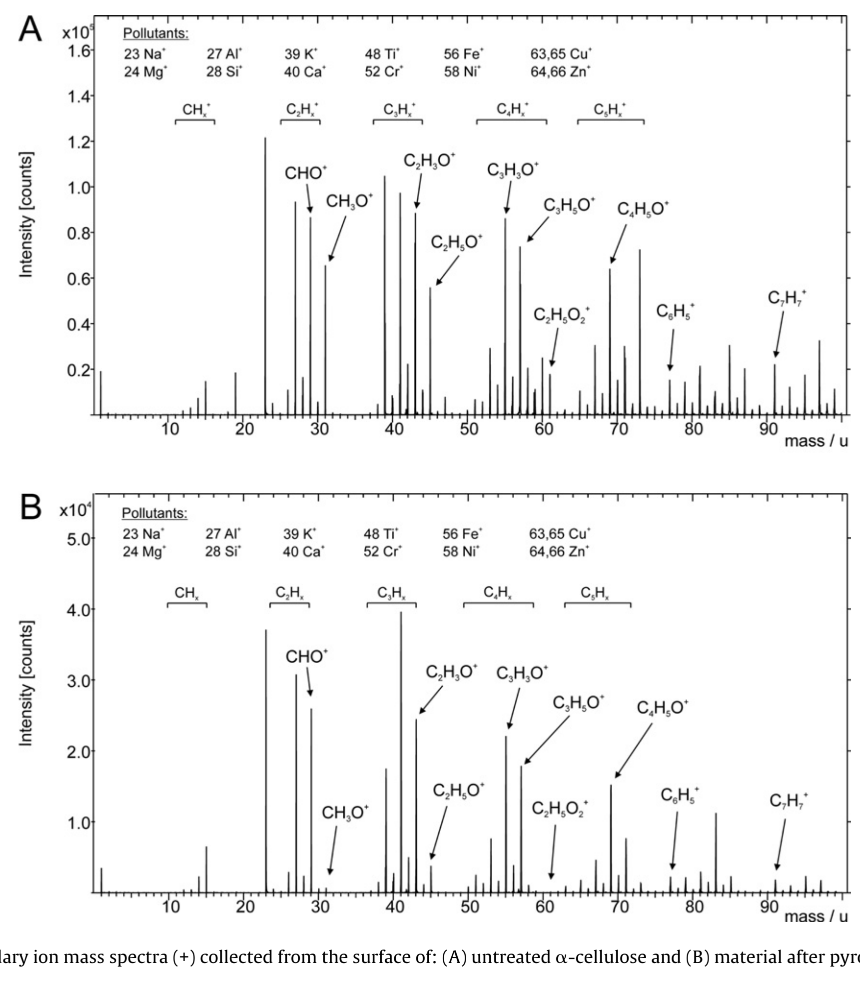

Fig. 2. Secondary ion mass spectra (+) collected from the surface of: (A) untreated α-cellulose and (B) material after pyrolysis at 500 °C.