

## Cellulose hydrolytic hydrogenation in subcritical water with the use of the new type of the catalysts

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**Abstract:** The study presents the results of cellulose hydrolytic hydrogenation process in subcritical water in the presence of Ru-containing catalyst based on hypercrosslinked polystyrene (HPS) and its functionalized analogues. It was shown that the replacement of the traditional support (carbon) by HPS increases the yield of the main cellulose conversion products – polyols – important intermediates for the chemical industry. The catalysts were characterized using transmission electron microscopy (TEM), high resolution TEM, and porosity measurements. Catalytic studies demonstrated that the catalyst containing 1.0% Ru and based on MN-270 is the most active. The total yield of sorbitol and mannitol was 50% on the average at 85% cellulose conversion.

**Key-Words:** cellulose, heterogeneous catalysis, hypercrosslinked polystyrene, hydrolytic hydrogenation, sorbitol

### 1 Introduction

Cellulose is one of the most wide-spread organic materials on the earth. It has been estimated that  $10^{11}$ – $10^{12}$  tons of cellulose are synthesized in nature annually. It is mostly combined with hemicelluloses and lignin in the plant cell walls [1].

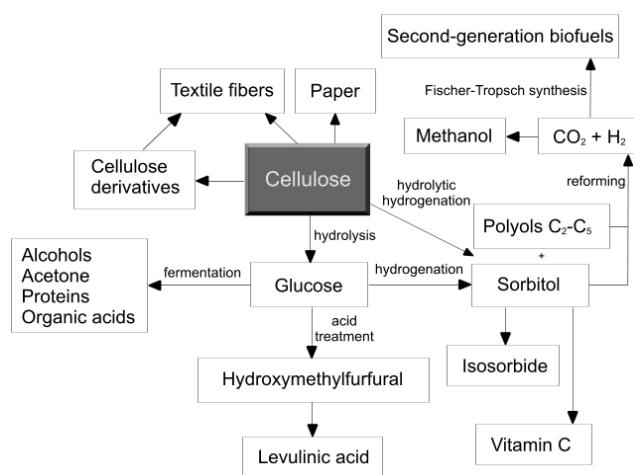


Fig. 1. Conversion of cellulose to chemicals and biofuels.

Lignocellulosic biomass is considered a likely alternative to fossil fuels as its renewable resources can provide the production of raw materials for the

chemical industry and second-generation biofuels on a large scale [2 - 6]. Moreover, at present, taking into consideration constantly increasing expenses on hydrocarbon fossil fuel mining, chemicals obtained from biomass can be much cheaper than those obtained from oil [7]. The scheme of cellulose conversion to chemicals and biofuels is based on two processes: hydrolysis and hydrolytic hydrogenation (Fig. 1).

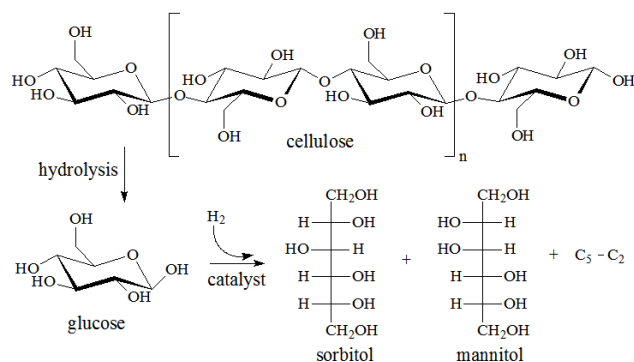


Fig. 2. Hydrolytic hydrogenation of cellulose to polyols.

A large number of hydroxyl groups in cellulose allow for its conversion to polyols [8, 9]. First, cellulose is hydrolyzed to glucose which is then hydrogenated under hydrogen pressure  $> 2$  MPa in

the presence of a catalyst to form sorbitol (for the most part), mannitol and some amount of C<sub>2</sub> – C<sub>5</sub> polyols (Fig 2). The first study of combined hydrolysis and hydrogenation processes was published by A.A. Balandin and his colleagues [10, 11]. They conducted hydrolytic hydrogenation of cellulose in the presence of 1.0% of H<sub>3</sub>PO<sub>4</sub> and Ru/C catalysts at 160 – 200 °C and hydrogen pressure 8 – 10 MPa.

Palkovits R. et al studied the process of cellulose joint hydrolysis and hydrogenation in the presence of diluted mineral acids [12 – 14]. In [14] the process was conducted at the following conditions: hydrogen pressure 50 bar, temperature 160 °C, reaction time 1 or 5 hours. In the work the catalysts containing 5% Pt, Pd and Ru on carbon in the presence of 0,5 % and 2,5 % sulphuric or phosphorus acid were used. The maximum yield of sorbitol (33 %) was obtained when Ru/C was used as a catalyst in the presence of 2.5 % sulphuric acid; the reaction time was 1 hour. In [15] the authors used only trace amount of a mineral acid and a double-effect catalyst – ruthenium on the basis of zeolite. Zeolites were tested in the reactions with low-strength chlorohydric acid (35 ppm, constant concentration). The most yield of hexitols (63 %) was obtained in the case of using USY group zeolites with aluminum-silicon ratio > 15.

The catalytic systems with mineral acids show high activity and selectivity and their use leads to the fast cellulose conversion into polyols but these systems application is limited by acids corrosive properties and by the necessity of the waste neutralization.

The alternative method of cellulose hydrolysis is the use of heteropoly acids (HPA) [16-19]. According to [18, 19] heteropoly acids are highly selective to glucose in cellulose and cellobiose hydrolysis. The use of heteropoly acids in combination with ruthenium catalyst on carbon (Ru/C) for the conversion of cellulose into sugar alcohols was studied in [16]. The maximum yield of sorbitol was approximately 30 % when using H<sub>3</sub>PW acid with the concentration 17.4 mmol/L in combination with Ru/C (5 % Ru).

In spite of good catalytic properties it is rather difficult to separate liquid acids from the solution and to reuse them [20]. Besides, these catalysts can't be used on an industrial scale because of the difficulty and long time of their preparation.

Solid acid catalysts have a number of positive properties: high activity and selectivity, long catalyst cycle life, easy reduction and reuse. Hara et al. [21-24] developed a new type of a solid acid on

the carbon base with a high density of Broensted acidic sites (SO<sub>3</sub>H и COOH) using pyrolytic carbonatization of such sugars as glucose, saccharose or cellulose with the following sulphonation of the carbons obtained. These sulphonated carbon materials have high activity in the process of microcrystalline cellulose hydrolysis for the obtaining of water-soluble saccharides even at a low temperature of the reaction (100 °C). This result cannot be achieved when using solid strong acid catalysts such as niobic acid, H-mordenite, Nafion и Amberlyst-15 [22].

The use of sulphonated silicon-carbon nanocomposites provide up to 50% yield of glucose at 61% of cellulose conversion [25]. Besides it is reported in [26] that the use of sulphonated mesoporous carbon SMK-3 results in the increase in glucose yield up to 75 % and cellulose conversion 94 %. Solid acids make the process ecologically friendly but it is impractical to use them for cellulose conversion into mannitol because of comparatively low yield [27].

In [28-30] ionic liquids are used as a medium for the conversion. High yield of hexitols (80-90 %) was obtained but the main disadvantage of this method is the complexity of the ionic liquids and the reaction products separation.

From the beginning of the 21<sup>st</sup> century there were several studies discussing the possibilities of cellulose hydrolytic hydrogenation in subcritical water at 180 – 260°C and 5-6 MPa [9, 31]. It allowed exclusion of mineral acids from the process, thus eliminating their disposal and the corrosion of the equipment. Subcritical water is an effective medium for the rapid hydrolysis of cellulose to glucose [32, 33]. The reason for this is that specifically at 250 °C subcritical water pK<sub>w</sub> has the minimum value and is equal to 11.2 (Table 1). Ions H<sub>3</sub>O<sup>+</sup> or OH<sup>-</sup> concentration of it thereafter is 25 times more than that of the water under standard conditions (SATP) that makes subcritical water an effective medium for acid- and base-catalyzed reactions. The decrease in viscosity from 0.89 mPa·s (SATP) to 0,11 mPa·s (at a temperature 250 °C) contributes to the elimination of the problems of external mass transfer of the reagents. Besides, the decrease in the value of dielectric permittivity (ε) results in the better solubility of gases and hydrophobic substances in water. The interest in these problems accounts for a large number of the current research on chemical and extraction processes in subcritical water [34 - 38].

Table 1. Physical chemical properties of water as a function of temperature and pressure

| Value:               | SATP  | Subcritical water | Supercritical water |
|----------------------|-------|-------------------|---------------------|
| t, °C                | 25    | <b>250</b>        | 400                 |
| P, MPa               | 0.1   | <b>4</b>          | 25                  |
| pK <sub>w</sub>      | 14.0  | <b>11.2</b>       | 19.4                |
| ρ, g/cm <sup>3</sup> | 0.997 | <b>0.80</b>       | 0.17                |
| ε                    | 78.5  | <b>27.1</b>       | 5.9                 |
| η, mPa·s             | 0.89  | <b>0.11</b>       | 0.03                |

As the cellulose hydrolysis in subcritical water is very rapid, it is necessary to provide immediate hydrogenation of glucose formed in hydrolysis because it degrades under the process conditions. In this case the efficiency of the catalyst is of primary importance. Ru-containing catalysts are known to be the most active in the glucose hydrogenation to sorbitol [1, 9, 31, 39, 40]. However the question of a suitable carrier of the active phase is under discussion. Thus, the major trend nowadays is to develop new or optimize the existing supports. Carbon supports or aluminum oxide are used for this purpose [9, 41 - 44]. However, the catalysts based on these supports are characterized by a comparatively low yield of hexitols (30-40%) so they require modification. For example, functionalization of carbon with sulfate groups (Ru/AC-SO<sub>3</sub>H) allows increasing a hexitol yield up to 55-60% [45]. Good results were obtained when using soot particles (Black Pearl, BP, 2000). For example, in the presence of Pt/BP 2000 the hexitol yield was 57.7% and for Ru/BP 2000, it was 49.6% [39]. Addition of a small amount of hydrochloric acid (from 35 to 177 ppm) to the Ru-containing catalyst based on a zeolite (Ru/H-USY) allowed similar results: hexitol yield of 30-60% depending on the amount of the catalyst and the duration of the process [46]. The catalysts based on carbon nanotubes (CNT) and nanofibers (CNF) showed excellent results. The authors [47] demonstrated the hexitol yield of 70-75% with the CNT catalyst containing 1.0% of Ru. Nickel nanoparticles stabilized on carbon nanofibers (Ni/CNF) provided the hexitol yield of 60-75% [48, 49]. The essential disadvantage of these catalysts is the complicated methods of their preparation.

In this paper a new type of Ru-containing catalysts based on non-functionalized and functionalized hypercrosslinked polystyrene (HPS) is proposed for cellulose hydrolytic hydrogenation. HPS is characterized by ultra-high porosity and

excellent sorption properties and was successfully used as a support for nanocomposite catalysts. Active transformations of substrates occur due to their fast concentrating in the pores of HPS [50 - 52]. As HPS can swell in any solvent, thus the access to catalytic sites is possible in all reaction media including water [40].

## 2 Experimental

### 2.1 Materials

HPS Macronet MN-270 (without functional groups), MN-100 (amino groups), and MN-500 (sulfate groups) were purchased from Purolite Int., U.K. and purified by rinsing with water and drying in vacuum. Distilled water, gaseous pure hydrogen, microcrystalline cellulose (degree of crystallinity 75-80%, Chimmeservice, Russia), and ruthenium (IV) hydroxochloride (pure, OJSC Aurat, Russia) were used as received.

The industrial catalyst 5.0 % Ru/C (J. Matthey, Materials Technology, U.K.) was used for the comparison.

### 2.2 Catalyst preparation

HPS granules were washed with water, acetone, methylic alcohol and dried at 70 °C during the night. Washed and dried HPS samples were ground in the mill and fractionated with the help of the vibrating screen. The fractions with the particle size less than 60 μm were used for the catalysts preparation.

HPS (MN-270, MN-100, or MN-500) was impregnated according to moisture absorption capacity with the solution of the calculated amount of ruthenium (IV) hydroxochloride in a complex solvent consisting of tetrahydrofuran, methanol, and water at a volume ratio 4:1:1 at room temperature. Further, the catalyst was dried at 70 °C, consecutively treated with solutions of NaOH and H<sub>2</sub>O<sub>2</sub>, and then washed with water until the absence of chloride anions in the washing water. The catalyst purified was dried at 85 °C. Then the catalyst was reduced with hydrogen at 300 °C and atmospheric pressure for 2 hours, cooled in nitrogen and kept under air. The catalyst particle size was controlled by sieving (mesh size 60 μm) the initial powdered support.

### 2.3 Characterization

Low-temperature nitrogen adsorption was carried out with the surface analyzer Beckman Coulter SA 3100 to determine specific surface areas and porosity of the catalysts and the initial HPS samples. Before the analysis the samples were degassed at

120°C in vacuum for 1 hour using the device for preliminary preparation of the samples (Coulter Corporation, USA).

Transmission electron microscopy was performed with a Techai G<sup>2</sup> 30S-TWIN (FEI, USA) operated at accelerating voltage of 300 kV. Ru-containing HPS powders were embedded in epoxy resin and subsequently microtomed at ambient temperature. Images of the resulting thin sections (*ca.* 50 nm thick) were collected with the Gatan digital camera and analyzed with the Adobe Photoshop software package and the Scion Image Processing Toolkit.

## 2.4 Method of cellulose hydrolytic hydrogenation

Cellulose conversion to polyols was carried out in subcritical water under the following conditions: temperature 245 °C, hydrogen partial pressure 6 MPa, propeller stirrer speed 600 rpm. The experiments were performed in a steel reactor (50 cm<sup>3</sup>, Parr Instrument, USA). Microcrystalline cellulose (0.5 g), a catalyst (0.07 g) and 30 mL of distilled water were loaded into the steel reactor (PARR Instrument, USA, 50 mL). Then reactor was flushed three times with hydrogen under pressure. The mixture was heated and stirred ( $\approx$ 100 rpm) to prevent the formation of local hot spots and the catalyst surface was saturated with hydrogen. After reaching 245 °C the stirrer speed was increased up to 600 rpm. This moment was chosen as the reaction starting time. At the end of the experiment the catalyst and non-hydrolyzed cellulose were separated by filtration. The weight of the non-hydrolyzed cellulose was determined as the difference between the weight of the residue on the filter and the catalyst weight. The content of the conversion main products was determined by chromatographic methods in liquid and gas phases. For the analysis of a gas phase, gas chromatograph Crystallux-4000M (MetaKhrom, Russia) was used, while for the liquid phase, highly effective liquid chromatograph UltiMate 3000 (Dionex, USA) was employed.

Mass spectrometer GCMS-QP2010S (SHIMADZU, Japan) was used for the chromatography-mass spectrometric analysis of the liquid phase.

The test for the ruthenium content of the liquid phase was carried out using atomic absorption spectrometer MGA-915 (“Lumex”, Russia).

Thermogravimetric analysis of the samples of hypercrosslinked polystyrene MN 270, MN 100, MN 500 was done using thermogravimetric analyzer TG 209 IRIS, equipped with differential scanning

equipped with differential scanning calorimeter DSC 204 PHOENIX (NETZSCH, Germany).

Cellulose conversion was calculated using the formula:  $X = m_c/m_{c0} \cdot 100\%$ , where  $m_c$  is the weight of non-hydrolyzed cellulose and  $m_{c0}$  is the initial weight of cellulose. A hexitol yield was calculated using the formula  $\eta_{hex.} = m_{hex.}/m_{c0} \cdot 100\%$ , where  $m_{hex.}$  is the weight of sorbitol (or mannitol) formed. The selectivity was calculated using the formula  $S = m_p/(m_{c0} - m_c) \cdot 100\%$ , where  $m_p$  is the weight of the reaction product.

## 3 Results and discussion

We studied the influence of the Ru content, Ru/cellulose ratio, and the type of HPS on the catalytic properties in cellulose hydrolytic hydrogenation. The highest yields of hexitol ( $\eta_{hex.}$ ) were obtained with the catalysts containing 1 wt.% of Ru in HPS (Table 2). Moreover, in this case, the cellulose conversion ( $X$ ) also increases. In addition, for these catalysts, the decrease of the ratio Ru/cellulose (mmol/g) results in the increase of hexitol total yield (Table 2). Thus, further studies were carried out with the HPS catalysts containing 1.0 wt.% of Ru and the Ru/cellulose ratio of 0.028/1 (mmol/g).

Table 2. Dependence of  $X$  and  $\eta_{hex.}$  on Ru percentage of the catalyst and its amount per cellulose unit weight

| Variable parameter value:                    | $X$ , % | $\eta_{hex.}$ , % |
|--|---------|-------------------|
| Ru percentage of the catalyst <sup>a</sup> : |         |                   |
| 3.0 %  | 70.0    | 39.5              |
| 2.0 %  | 81.3    | 36.6              |
| 1.0%   | 91.4    | 41.0              |
| 0.5 %  | 61.0    | 4.1               |
| Ratio Ru/ cellulose (mmol/g) <sup>b</sup> :  |         |                   |
| 0.042/1                                      | 91.4    | 41.0              |
| 0.028/1                                      | 84.3    | 50.4              |

<sup>a</sup> 245 °C, 6 MPa H<sub>2</sub>, 30 mL water, Ru/ MN-270 (0.042 mmol Ru), 1 g cellulose, 600 rpm, process duration 5 min; <sup>b</sup> The same conditions as in (a) but different Ru/cellulose ratios.

Table 3. Porosity data for the HPS samples and the catalysts

| Sample | Surface area                   |         |                                    |             |                                |         |
|--------|--------------------------------|---------|------------------------------------|-------------|--------------------------------|---------|
|        | Langmuir                       |         | BET                                |             | t-plot                         |         |
|        | $S_L^a$ ,<br>m <sup>2</sup> /g | $k_L^c$ | $S_{BET}^b$ ,<br>m <sup>2</sup> /g | $k_{BET}^c$ | $S_t^c$ ,<br>m <sup>2</sup> /g | $k_t^d$ |

|              |      |        |      |         |                                       |         |
|--------------|------|--------|------|---------|---------------------------------------|---------|
| MN-270       | 1500 | 0.9995 | 1420 | 0.99962 | 295 <sup>e</sup><br>1140 <sup>f</sup> | 0.99667 |
| MN-100       | 840  | 0.9998 | 730  | 0.99954 | 200 <sup>e</sup><br>590 <sup>f</sup>  | 0.99981 |
| MN-500       | 650  | 0.9999 | 540  | 0.99943 | 150 <sup>e</sup><br>450 <sup>f</sup>  | 0.99996 |
| 1% Ru/MN-270 | 1270 | 0.9994 | 1180 | 0.99957 | 250 <sup>e</sup><br>990 <sup>f</sup>  | 0.99787 |
| 1% Ru/MN-100 | 890  | 0.9999 | 740  | 0.99938 | 195 <sup>e</sup><br>600 <sup>f</sup>  | 0.99974 |
| 1% Ru/MN-500 | 120  | 0.9985 | 90   | 0.99994 | 80 <sup>e</sup><br>15 <sup>f</sup>    | 0.99879 |
| 5% Ru/C      | 665  | 0.999  | 613  | 0.99975 | 290 <sup>e</sup><br>337 <sup>f</sup>  | 0.99898 |

<sup>a</sup>S<sub>L</sub> is the specific surface area (Langmuir model);  
<sup>b</sup>S<sub>BET</sub> is the specific surface area (BET model); <sup>c</sup>S<sub>t</sub> is the specific surface area (t-plot); <sup>d</sup>k<sub>L</sub>, k<sub>BET</sub>, k<sub>t</sub> are the correlation coefficients; <sup>e</sup>specific surface area according to a t-plot model; <sup>f</sup>specific surface area of micropores

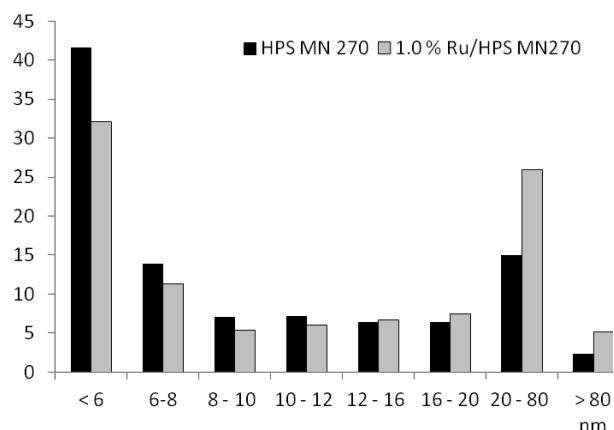


Fig. 3. Pore size distributions for MN-270 and 1.0% Ru/MN-270.

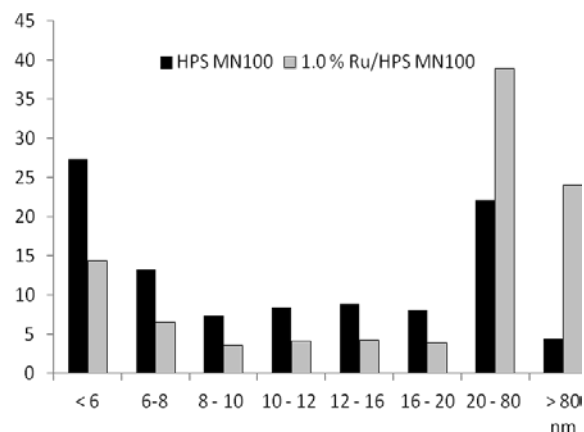


Fig. 4. Pore size distributions for MN-100 and 1.0 % Ru/MN-100.

Table 3 and Fig. 3-6 show the porosity data of the initial HPS samples and the catalysts obtained from the nitrogen physisorption measurements. As shown in Table 3, MN-270 has the highest surface area as well as the specific surface area of micropores compared to the other supports. Pore size distributions presented in Fig. 3 - 6 reveal that for all the catalysts, pores of < 6 nm in diameter dominate the total pore volume. It is mostly pronounced for the catalyst based on MN-270. The presence of such pores is important because they can control catalytic nanoparticle formation by controlling the volume of the precursor material inside the pores. After the reduction the particle sizes decreases. Fig. 7 shows a histogram of the Ru particle size distribution for 1% Ru/MN-270 obtained from the TEM data. The mean Ru nanoparticle diameter is  $1.4 \pm 0.3$  nm. The HRTEM image and FFT pattern shown in the inset of Figure 7 demonstrate that Ru nanoparticles are single crystals.

The specific surface areas of the catalysts based on MN-270 and MN-500 are lower than those of the initial supports. In the case of MN-270 where the decrease does not exceed 15%, this is easily understood as Ru nanoparticles fill the pores and the matrix can shrink because the reduction by hydrogen is carried out at 300 °C. However, for MN-500 and 1% Ru/MN-500, the surface area decreases by a factor of 5. This fact is explained by desulfurization of MN-500 which takes place at 100 - 150 °C [53] and results in the change of the HPS structure.

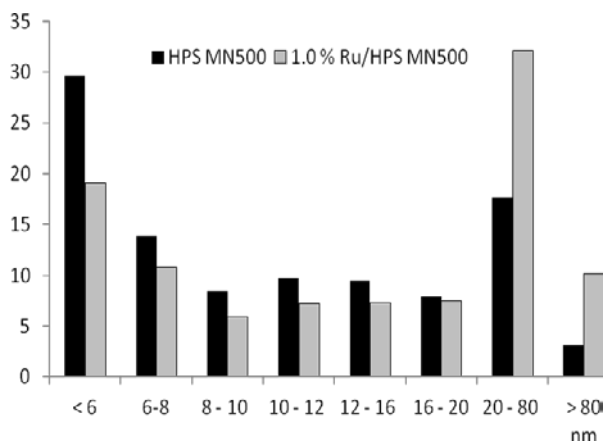


Fig. 5. Pore size distribution for MN-500 and 1.0% Ru/MN-500.

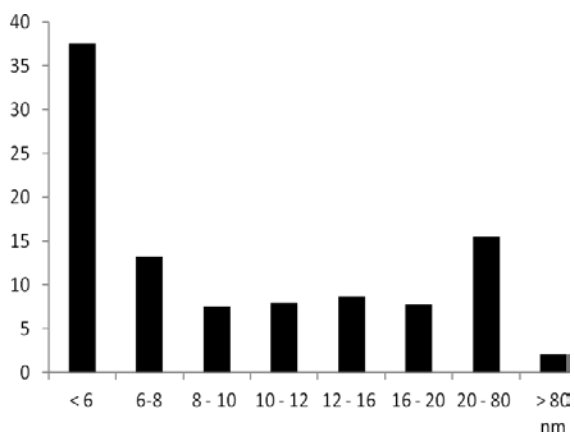


Fig. 6. Pore size distribution for 5.0% Ru/C.

This assumption was confirmed by the results of thermogravimetric analysis of the initial samples of hypercrosslinked polystyrene (Fig. 8). As it is shown in Fig. 8a the intensive, multi-stage (probably, resulting from the break of the methylene cross links) destruction of HPS MN 270 starts at a temperature of about 450 °C (TG line). At this temperature the polymer weight loss rate is maximum – 10 %/min (DTG line). The resulting weight loss was approximately 55 %. These facts prove the possibility of the reduction of the catalyst on the basis of HPS MN 270 with the gaseous hydrogen at a temperature 300 °C.

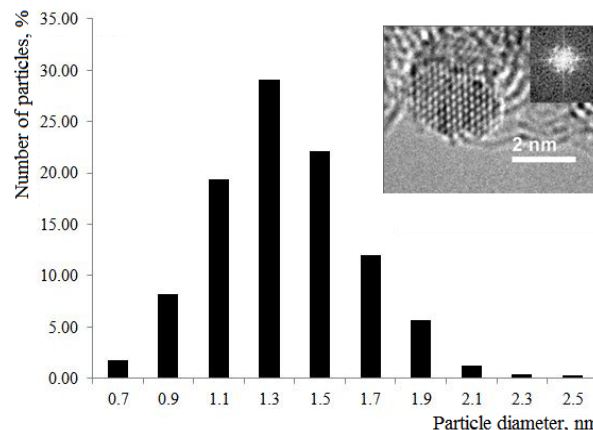


Fig. 7. Histogram of the Ru particle size distribution for the 1% Ru/MN-270 catalyst. Inset shows a HRTEM image and Fast Fourier Transform pattern.

A similar picture is observed in case of HPS MN 100. The intensive destruction of a polymer also starts at a temperature 450 °C. However, Fig.8b demonstrates that the maximum rate of the weight loss in this case is higher and makes 15 %/min. HPS MN 100 breaks up faster, possibly, because of NH<sub>2</sub>-groups removal. The resulting weight loss was 45 %.

HPS MN 500 is the least thermostable (Fig. 8c). Being heated the polymer loses weight fast and constantly. The destruction already starts at a temperature < 100 °C. At the temperatures ranging from 100 to 250 °C the polymer desulfurization and further destruction of SO<sub>3</sub>H-groups at > 250 °C take place. The resulting weight loss was maximum compared to the other samples and was approximately 58 %. These facts indicate that the catalysts on the basis of sulphonated HPS cannot be used in the process of cellulose hydrolytic hydrogenation.

Table 4 shows the results of the cellulose hydrogenolysis in subcritical water in the presence of the catalysts synthesized. Fig. 9 presents typical chromatographs of the liquid and gas phases obtained after the reaction with 1% Ru/MN-270. The main products of cellulose hydrolytic hydrogenation are sorbitol (S), mannitol (M), as well as 1,4-sorbitan (1,4-S), xylitol (X), erythritol (E), glycerol (G), propylene glycol (PG), ethylene glycol (EG) and some glucose which has not been hydrogenated (Fig. 9a). Chromatography-mass spectrometric analysis also shows trace amounts of cellobiose, hexane-1,2,5,6-tetrols, hexane-1,2,3,4,5-pentol and other products of glucose and sorbitol hydrogenolysis in a liquid phase. In a gas phase there are methane and trace amounts of ethane, propane, and isobutane (Fig. 9b).

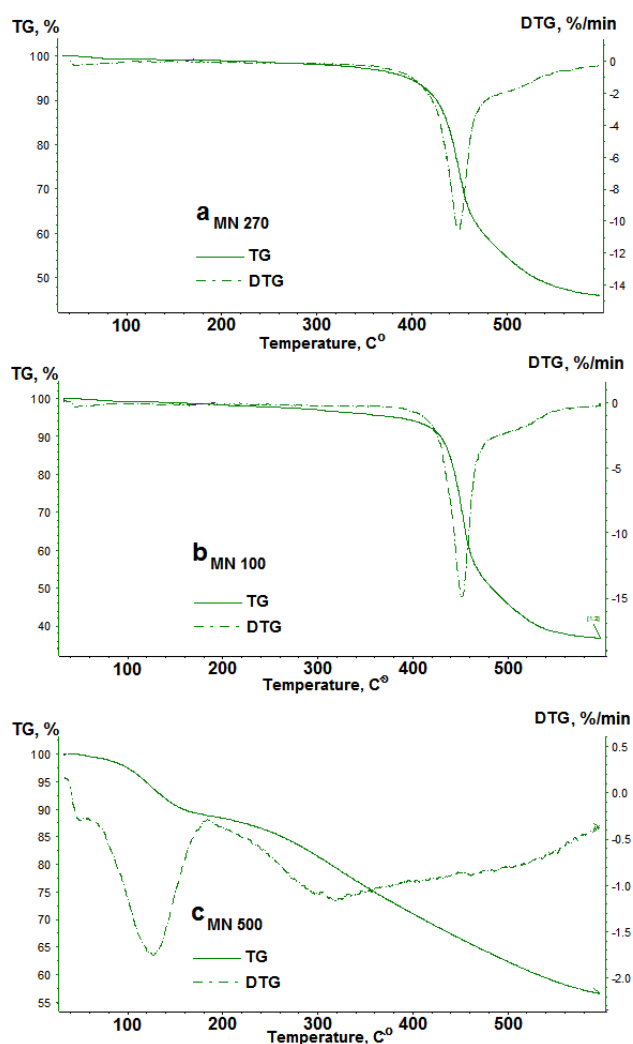


Fig. 8. Results of thermogravimetric analysis of HPS MN 270 (a), MN 100 (b) and MN 500 (c).

When the 1% Ru/MN-500 catalyst was used in cellulose hydrolytic hydrogenation, darkening of the solution after the reaction was observed which is characteristic of the glucose degradation products. In addition, the catalyst was inactive which can be explained by the poisoning of the catalyst due to the MN-500 desulfurization. The 1% Ru/MN-100 catalyst showed a slightly better result. At the almost equal  $X$  values the hexitol yield increased by 10%. At the same time, for both catalysts, the yields of lower polyols and methane are high.

The industrial catalyst 5,0 % Ru/C turned out to be inefficient. It is characterized by the  $X$  least value, 19,3 % total yield of hexitol and high selectivity to propylene glycol and ethylene glycol.

In the experiments without a catalyst, the brown solutions containing the products of glucose caramelization were also obtained. The  $X$  value in such experiments decreased to 55%. This fact

proves that in the presence of the catalyst both hydrolysis and hydrogenolysis of cellulose take place, which is not the case, when the catalyst is absent.

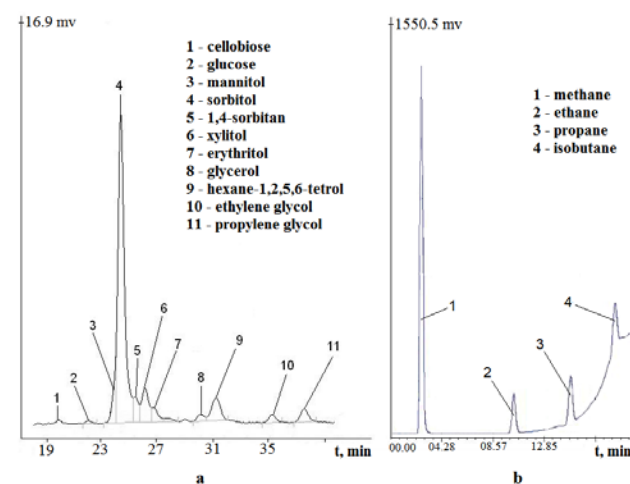


Fig. 9. Chromatograms of liquid (a) and gas (b) phases after the reaction (245 °C, 6 MPa H<sub>2</sub>, 30 mL water, 600 rpm, 1 % Ru/MN-270, 0.028 mmol Ru on 1 g cellulose, process duration 5 min.)

Table 5. Cellulose conversion and the total yield of hexitols in the repeated use of 1% Ru/MN-270

| Cycle | $X$ , % | $\eta_{hex.}$ , % |
|-------|---------|-------------------|
| 1     | 84.3    | 50.4              |
| 2     | 84.5    | 49.5              |
| 3     | 85.2    | 48.4              |

245°C, 6 MPa H<sub>2</sub>, 30 mL water, 600 rpm, 0.028 mmol Ru on 1 g cellulose, 1% Ru /MN-270, process duration 5 min.

The best results were obtained for 1% Ru/MN-270. This catalyst demonstrates the highest hexitol yield and the lowest yield of other products. Most likely the high efficiency of this catalyst is due to the combination of the high specific surface area, narrow pore size distribution, and small, monodisperse Ru nanoparticles. To evaluate stability of this catalyst, after the completion of the reaction, the catalyst was separated and used again with fresh cellulose. The results show that the repeated use of the 1% Ru/MN-270 catalyst in three consecutive reaction cycles leads to only a slight decrease of its activity (Table 5) which can be explained by a loss of some amount of the catalyst during the filtration. The analysis of the liquid phase by atomic absorption spectroscopy showed no Ru leaching.

Table 4. Dependences of the cellulose conversion, total yield of hexitols and selectivity on the catalyst type<sup>a</sup>

| Catalyst               | X, % | $\eta_{hex.}$ , % | Selectivity, % |     |       |     |     |     |     |     |                 |                |
|------------------------|------|-------------------|----------------|-----|-------|-----|-----|-----|-----|-----|-----------------|----------------|
|                        |      |                   | S              | M   | 1,4-S | X   | E   | G   | PG  | EG  | CH <sub>4</sub> | - <sup>b</sup> |
| 1.0 %<br>Ru/<br>MN-270 | 84.3 | 50.4              | 50.5           | 6.1 | 6.2   | 4.7 | 3.3 | 2.1 | 2.9 | 2.2 | 3.2             | 18.8           |
| 1.0 %<br>Ru/<br>MN-100 | 77.0 | 12.7              | 12.7           | 1.6 | 2.0   | 3.3 | 2.3 | 1.7 | 5.2 | 5.2 | 5.6             | 60.4           |
| 1.0 %<br>Ru/<br>MN-500 | 80.6 | 1.8               | 1.8            | 0.2 | 0.5   | 1.0 | 1.1 | 0.3 | 7.8 | 5.3 | 8.1             | 73.9           |
| 5.0 %<br>Ru/C          | 76.1 | 19.3              | 19.0           | 2.8 | 2.3   | 3.5 | 2.3 | 1.9 | 3.5 | 4.0 | 6.7             | 54.0           |
| Without a<br>catalyst  | 55.6 | 0.5               | 0.6            | -   | -     | -   | -   | -   | -   | -   | -               | 99.4           |

<sup>a</sup> 245°C, 6 MPa H<sub>2</sub>, 30 mL water, 600 rpm, 0.028 mmol Ru on 1 g cellulose, process duration 5 min;

<sup>b</sup>Secondary and hard to identify products of glucose hydrogenolysis and decomposition.

#### 4 Conclusions

Ru-containing catalysts based on HPS were studied in hydrolytic hydrogenation of cellulose. We demonstrated that only the catalysts based on non-functionalized MN-270 provide high efficiency and selectivity towards hexitols due to stability of the HPS framework resulting in high surface areas of the catalysts and well-defined Ru nanoparticles. The catalysts based on functional analogues of MN-270, i.e., MN-100 and MN-500, were practically inactive in this process.

The use of the 1.0% Ru/MN-270 catalyst allows achieving the total sorbitol and mannitol yield about 50% at the ~85% conversion that is comparable with the results obtained with more complex and expensive catalytic systems. Moreover, preliminary studies show that the temperature decrease and the increase of the process duration result in the increase of the hexitol yield up to 60 – 70%. This catalyst is also highly stable in the repeated use making it promising for cellulosic biomass conversion to feedstock for chemical synthesis and industrial production of second-generation biofuel.

The further investigation will be aimed at the increase in cellulose conversion and hexitols yield by means of preliminary mechanochemical treatment of the initial cellulose.

The development of the catalytic systems on the basis of HPS and the optimization of the conditions of the reaction of cellulose hydrolytic hydrogenation are planned to obtain maximum yield of lower polyols (ethylene- and propyleneglycol) which can

be easily converted into hydrogen using reforming in liquid.

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