

Conversion of cellulose with the use of catalysts based on hypercrosslinked polystyrene

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Abstract: - The study presents the results of cellulose hydrolytic hydrogenation process in subcritical water in the presence of Ni, Fe, Pt, Pd, Au and Ru-containing catalysts based on hypercrosslinked polystyrene (HPS) MN-270 and its functionalized analogues: NH₂-HPS (MN-100) and SO₃H-HPS (MN-500). Nonfunctionalized HPS was shown to be the optimal carrier for these catalysts, and Ru-containing catalysts are the most active in the process of cellulose conversion into polyols. In this case the total yield of sorbitol and mannitol was 50% on the average at 85% cellulose conversion. On the basis of the experimental and computed data the pathway of hydrolytic hydrogenation of cellulose was suggested.

Key-Words: - cellulose, hydrolytic hydrogenation, subcritical water, hypercrosslinked polystyrene, sorbitol.

1 Introduction

Cellulose is one of the mostly wide-spread organic materials on the earth. It has been estimated that 10¹¹–10¹² tons of cellulose are synthesized in nature annually. It is mostly combined with hemicelluloses and lignin in the plant cell walls [1]. Cellulose 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]. Moreover, at present, taking into consideration constantly increasing expenses on hydrocarbon fossil fuel mining, chemicals obtained from cellulose biomass can be much cheaper than those obtained from oil [3].

A large number of hydroxyl groups in cellulose allow for its conversion to polyols [3, 4] (Figure 1). 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 C₂ – C₅ polyols. The first study of combined hydrolysis and hydrogenation processes was published by A.A. Balandin and his colleagues [5, 6]. They conducted hydrolytic hydrogenation of cellulose in the

presence of 1.0 % of H₃PO₄ and Ru/C catalysts at 160 – 200 °C and hydrogen pressure 8 – 10 MPa.

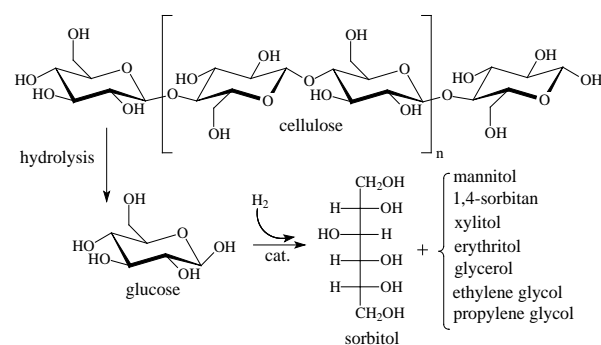


Fig. 1. Hydrolytic hydrogenation of cellulose to polyols.

From the beginning of the 21st century there were several studies discussing the possibilities of cellulose hydrolytic hydrogenation in subcritical water at 180 – 260 °C and 5-6 MPa [4, 7 - 9]. 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 a rapid hydrolysis of cellulose to

glucose [4, 7 - 9]. One of its advantages is the increase in gas solubility, which in turn contributes to the diffusion of hydrogen from the gas phase to the catalyst surface, thus accelerating catalytic processes of hydrogenation and hydrogenolysis. Another important advantage is the process is environmentally friendly.

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, 4, 7, 10, 11]. 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 [4, 12-15]. 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-SO₃H) allows increasing a hexitol yield up to 55-60 % [16]. 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 % [10]. 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 [17]. The catalysts based on carbon nanotubes (CNT) and nanofibers (CNF) showed excellent results. The authors [18] 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 % [19, 20]. 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 [21-23]. As HPS can swell in any solvent, thus the access to catalytic sites is possible in all reaction media including water [11].

2 Experimental

Hypercrosslinked polystyrene 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 %, Chimmedservice, Russia), and ruthenium (IV) hydroxochloride (pure, OJSC Aurat, Russia) were used as received.

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 (THF), 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 H₂O₂, 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.

Table 1. HPS based catalysts

Active metal:	Catalyst:
Ni	5.0 % Ni/MN 270
Fe	5.0 % Fe/MN 270
Pt	3.0 % Pt/MN 270
Pd/Au	3.0 % Pd – 1.0 % Au/MN 270

The other catalysts were prepared by impregnation of MN-270 with H₂[PtCl₆], Na₂[PdCl₄], H[AuCl₄], Fe(Ac)₃, Ni(Ac) in a solution containing THF, methanol and distilled water. In a typical procedure, a precursor sample was dissolved under nitrogen in 7 mL of the solvent mixture consisting of 5 mL of THF, 1 mL of water and 1 mL of methanol, to which 3 g of MN 100 were added. The suspension was continuously stirred for 10 min to allow absorption of the solution by the polymer granules. Then the sample was treated with Na₂CO₃ solution (0.845 g of Na₂CO₃ in 7 mL of H₂O), and after 10 min stirring, it was dried at 70 °C for 1 h. After that the catalyst was washed with water at pH=6.4-7.0 and dried at 70°C. The metal content was calculated according to loading. The catalysts prepared are presented in Table 1.

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. Transmission electron microscopy was performed with a Techai G² 30S-TWIN (FEI, USA) operated at accelerating voltage of 300 kV.

Cellulose conversion to polyols was carried out in a 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 cm³, Parr Instrument, USA). Microcrystalline cellulose (0.5 g), a catalyst (0.07 g) and 30 mL of distilled water were loaded into the reactor. 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 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, CLIA) was employed.

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

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 (η_{hex}) were obtained with the catalysts containing 1 wt.% of Ru in HPS (Table 1). 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 η_{hex} on Ru percentage of the catalyst and its amount per cellulose unit weight

Variable parameter value:	X , %	η_{hex} , %
Ru percentage of the catalyst ^a :		
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) ^b :		
0.042/1	91.4	41.0
0.028/1	84.3	50.4

^a 245 °C, 6 MPa H₂, 30 mL water, Ru/ MN-270 (0.042 mmol Ru), 1 g cellulose, 600 rpm, process duration 5 min. ^b The same conditions as in (a) but different Ru/cellulose ratios.

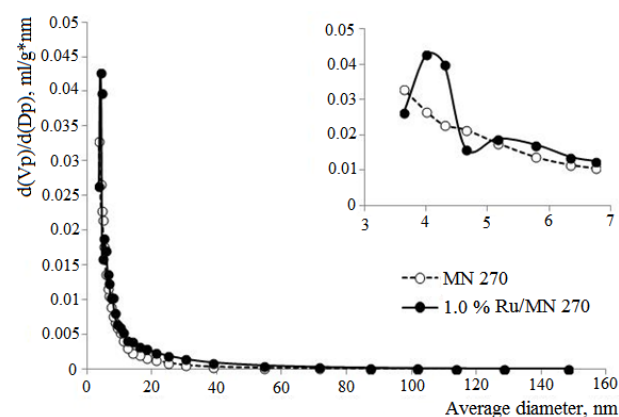


Fig. 2. Pore size distributions for MN-270 and 1.0% Ru/MN-270.

Table 3 and Figures 2 - 4 shows the porosity data of the initial HPS samples and the catalysts obtained from the nitrogen physisorption measurements. As shown in Table 2, 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 Figures 2 - 4 reveal that for all the catalysts, pores of 4.0 - 4.5 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. Figure 5 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 ± 0.3 nm. The HRTEM image and FFT pattern shown in the inset of Figure 6 demonstrate that Ru nanoparticles are single crystals.

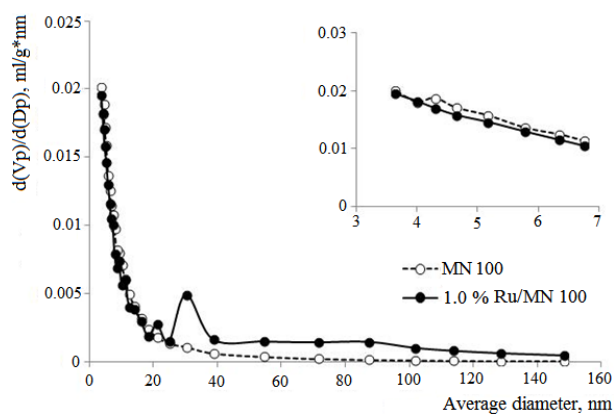


Fig. 3. Pore size distributions for MN-100 and 1.0 % Ru/MN-100.

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 200 - 300 °C [24] and results in the change of the HPS structure.

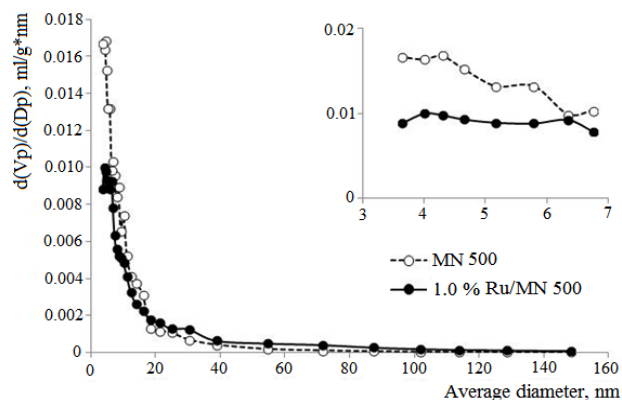


Fig. 4. Pore size distribution for MN-500 and 1.0 % Ru/MN-500.

Table 4 shows results of the cellulose hydrogenolysis in subcritical water in the presence of the catalysts synthesized. Figure 6 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. 6a). 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. 6b).

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

Sample	Surface area		
	Langmuir	BET	t-plot
	$S_L^a, m^2/g$	$S_{BET}^b, m^2/g$	$S_t^c, m^2/g$
MN-270	1500	1420	295 ^d 1140 ^e
MN-100	840	730	200 ^d 590 ^e
MN-500	650	540	150 ^d 450 ^e
1% Ru/MN-270	1270	1180	250 ^d 990 ^e
1% Ru/MN-100	890	740	195 ^d 600 ^e
1% Ru/MN-500	120	90	80 ^d 15 ^e

^a S_L is the specific surface area (Langmuir model); ^b S_{BET} is the specific surface area (BET model); ^c S_t is the specific surface area (t-plot); ^dspecific surface area according to a t-plot model; ^especific surface area of micropores.

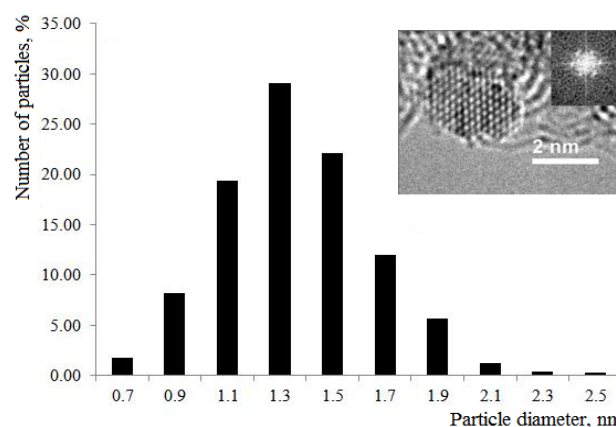


Fig. 5. Histogram of the Ru particle size distribution for the 1% Ru/MN-270 catalyst. Inset shows a HRTEM image and Fast Fourier Transform pattern.

Table 4. Dependences of the cellulose conversion and total yield of hexitols on the catalyst type

Catalyst	X, %	$\eta_{hex.}$ %
1.0 % Ru/MN-270	84.3	50.4
1.0 % Ru/MN-100	77.0	12.7
1.0 % Ru/MN-500	80.6	1.8
Without a catalyst	55.6	0.5

245 °C, 6 MPa H₂, 30 mL water, 600 rpm, 0.028 mmol Ru on 1 g cellulose, process duration 5 min.

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. 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.

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 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 filtration. The analysis of the liquid phase by atomic absorption spectroscopy showed no Ru leaching.

Table 6 shows the results of the study of hydrolytic hydrogenation of cellulose in the presence of the catalysts based on HPS MN 270 with different active phase. It is possible to see that all the catalysts are less efficient in this process compared to Ru-containing catalysts. The solutions after the reaction were colored due to the presence of glucose thermal degradation products.

The best result among the investigated catalysts was observed for 3% Pt/MN 270 catalyst. This

catalyst showed high conversion of cellulose (A) but the total yield of hexitol was about 5%. The intensity of the color of the liquid phase was less pronounced. Thus, one can say that when used as a substrate HPS MN 270 Ru-containing catalyst is the most effective.

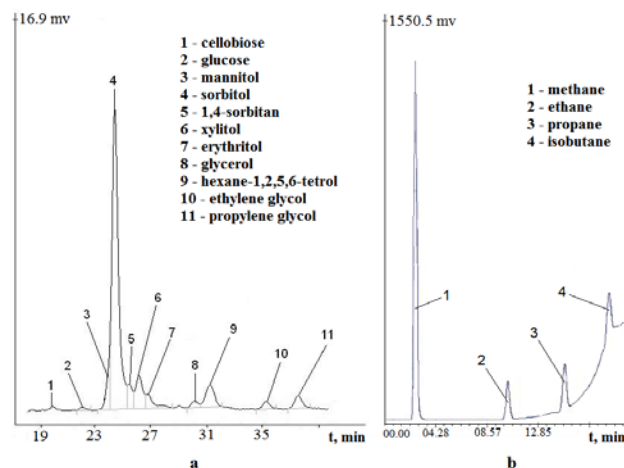


Fig. 7. Chromatograms of liquid (a) and gas (b) phases after the reaction (245 °C, 6 MPa H₂, 30 mL water, 600 rpm, 1 % Ru/MN-270, 0.028 mmol Ru on 1 g cellulose, process duration 5 min.)

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 H₂, 30 mL water, 600 rpm, 0.028 mmol Ru on 1 g cellulose, 1% Ru /MN-270, process duration 5 min.

Table 6. Dependences of the cellulose conversion, total yield of hexitols and selectivity on the catalyst type.

Catalyst	X, %	$\eta_{hex.}$ %
5.0 % Ni/MN 270	66.6	1.5
5.0 % Fe/MN 270	64.6	2.1
3.0 % Pt/MN 270	67.2	5.0
3 % Pd - 1 % Au/MN 270	78.5	3.0

^a 245 °C, 6 MPa H₂, 30 mL water, 600 rpm, process duration 5 min.

To suggest the hypothesis on the mechanism of hydrolytic hydrogenation the fact that the process runs in two steps was taken into consideration. First, cellulose is hydrolyzed to glucose and then its hydrogenolysis to polyols follows. It was proved experimentally that the limiting stage of all the

process is glucose hydrogenolysis, thus the kinetics of this stage was studied.

To study the kinetics of glucose hydrogenolysis the experiments were carried out at varying the following parameters: reaction time, hydrogen partial pressure and temperature. The dependence of $\ln k$ on $\ln P$ (Figure 6) was plotted and the reaction order with respect to hydrogen was calculated (0.028). So, it is conceivable that the order with respect to hydrogen is pseudo-zero. Such order of reaction indicates that hydrogen partial pressure does not influence the process of glucose hydrogenolysis. It is explained by the excess amount of hydrogen which is present in the reaction.

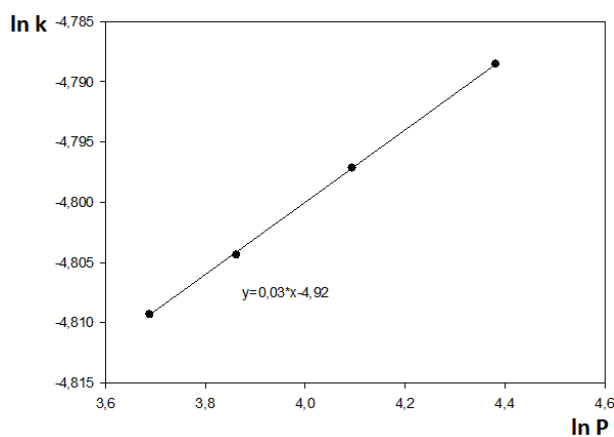


Fig.6. Dependence of $\ln k$ on $\ln P$ at varying pressure

The kinetic dependences of the change of glucose concentration on time at various temperatures of the process of glucose hydrogenation were obtained. Glucose hydrogenolysis runs most intensively at a temperature 508 K. To estimate the change of the substrate consumption rate the degree of glucose conversion was chosen at a point in time 300 s. On the basis of the data presented the apparent activation energy was calculated. It was 45 ± 5 kJ/(mol·K).

To choose the kinetic model describing adequately the experimental data various pathways of the reaction flow were analyzed. Additionally, the hydrogenolysis processes of such pure substances as sorbitol, xylitol, erythritol, ethylene glycol, glycerol, propylene glycol were studied. On the basis of the experimental data the possible ways of cellulose transformation and the scheme of its hydrogenolysis were suggested (Figure 7).

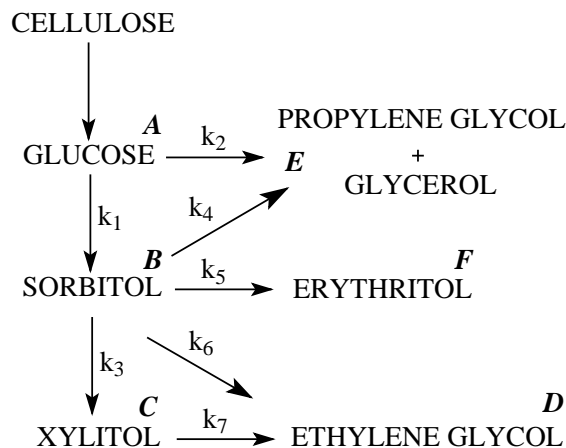


Fig. 7. Mechanism of cellulose hydrogenolysis on Ru-containing catalysts

Formal kinetic description of the process mechanism in Fig. 7 leads to the equation system:

$$W_A = \frac{-K_1[A] - K_2[A]}{Z}$$

$$W_B = \frac{K_1[A] - K_3[B] - K_4[B] - K_5[B] - K_6[B]}{Z}$$

$$W_C = \frac{K_3[B] - K_7[C]}{Z}$$

$$W_D = \frac{K_6[B] + K_7[C]}{Z}$$

$$W_E = \frac{K_2[A] + K_4[B]}{Z}$$

$$W_F = \frac{K_5[B]}{Z}$$

Where W_i – the rate of hydrogenolysis reaction at the single initial concentration of the substrate $C_0 = 1$ mol/L and the single concentration of the catalyst $C_k = 1$ mol/L, Z – denominator of the kinetic equation reflecting reagents adsorption on the solid phase

At varying the right parts of the equations (denominators), several mathematical models were constructed. The inverse solution and models equations verification were carried out using explicit integral method.

The kinetic model which describes well the experimental data is based on the assumption about the absence of adsorption (or coordination) interactions. Thus it is expected that on the catalyst surface the substrate adsorption does not take place

during glucose hydrogenolysis process. This fact was proved by the results of IR-spectroscopy.

To estimate the parameters of Arrhenius equation the kinetic parameters of glucose hydrogenolysis were calculated. The calculations were done for different temperatures on the basis of the model chosen and the experimental data. The rate constant (K , $(\text{mol/mol})^n \cdot \text{c}^{-1}$), preexponential factor (K_0) and apparent activation energy (E_{app} , kJ/mol) calculated on the basis of the temperature dependence agree with the results of the inverse solution. This fact proves again the right choice of the kinetic model (Table 7).

Table 7 - Kinetic parameters of glucose hydrogenation calculated on the basis of the model chosen

T, K	K $(\text{mol/mol})^n \cdot \text{c}^{-1}$	E_{app} , kJ/mol	K_0
478	0.102713	45±5	8.92•10 ⁶
*478	0.103125	45±5	8.67•10 ⁶
K - kinetic parameter. K_0 - preexponential factor. * - calculated data on the basis of the model.			

4 Conclusion

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 adequate kinetic model of the process of cellulose hydrogenolysis was chosen. The kinetic parameters for this model were calculated:

activation energy ($E_{app} = 45 \text{ kJ/mol}$, preexponential factor $K_0 = 8.92 \cdot 10^6$, the reaction rate constant $K = 0.102713 (\text{mol/mol})^n \cdot \text{c}^{-1}$. On the basis of the experimental data the reaction order with respect to hydrogen was determined as near zero. Physical chemical study proved the validity of the reaction mechanism suggested.

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