# Magnetically Recoverable Catalysts for Cellulose Conversion into Glycols

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In this paper Ru-containing magnetic catalyst on the basis of $Fe_3O_4$-$SiO_2$ nanoparticles was suggested for the conversion of cellulose into ethylene glycol (EG) and propylene glycol (PG). The use of this catalyst in the process of microcrystalline cellulose hydrogenolysis in subcritical water at 255 °C and hydrogen partial pressure 60 bar in 50 min allows PG and EG selectivities of 23 and 12 %, respectively, at 100 % conversion. The catalyst was stable under hydrothermal conditions of the process and is easily separated from the reaction mixture by means of the external magnetic field.

## 1. Introduction

Ethylene glycol (EG) and propylene glycol (PG) are the important raw materials and are widely used in the production of pharmaceuticals, liquid fuel, emulsifier, surfactants, antifreeze, lubricants and solvents (Ma et al., 2013) as well as for the synthesis of polyester fibres and resins, for example polyethylene terephthalate and polyethylene naphthalate (Köpnick et al., 2005), and biodegradable polylactones (Bayramoglu et al., 2010).

As modern production of these of glycols is based on the use of nonrenewable oil based raw material (Yue et al., 2012), it is essential to develop new effective methods of PG and EG syntheses from cellulose (Sun et al., 2011), the resources of which are rather large and renewable (Huber et al., 2006).

Cellulose conversion into PG and EG can be carried out as one-pot process in subcritical water medium in the presence of heterogeneous catalysts (Verendel et al., 2011). The catalysts on the basis of Ru are the most active in the processes of hydrogenation and hydrogenolysis (Manaenkov et al., 2014) and most research is devoted to the search of the optimal support (Dhepe et al, 2007).

The use of magnetically retrievable catalysts on the basis of magnetic nanoparticles (MNPs) opens up new opportunities (Wang and Astruc, 2014a). MNPs serve as a support for the formation of catalytic complexes or nanoparticles possessing unique catalytic properties due to the large surface area and, consequently, increased number of the active sites (Lu et al., 2007). The catalysts on the basis of MNPs have an important advantage as a result of their easy separation from the reaction mixture by means of the external magnetic field (Adamaki et al., 2016). Nowadays Ru-containing magnetically retrievable catalysts are used in the reactions of olefin metathesis, azide-alkyne cycloaddition, hydrogenation, oxidation and etc. (Wang and Astruc, 2014b).

There are also reports on the use of magnetically retrievable catalysts in the processing of cellulose. In particular, in ref. (Podolean et al., 2014) Ru-MNP catalyst was used for cellulose hydrolysis. The catalyst is shown to be active and selective to glucose. The authors stress the point that this catalyst is stable under hydrothermal conditions, it is easily separated and regenerated. In ref. (Zhang et al., 2013) the magnetic catalyst on the basis of $Fe_3O_4$ MNPs coated with sulfonated carbon was suggested for cellulose hydrolysis.

The catalyst showed high activity. In 12 h at a temperature 140 °C cellulose conversion achieved 48.6 % at 51.2 % selectivity to glucose. The authors also note the catalyst stability and its easy separation from the reaction mixture. The direct conversion of cellulose into sorbitol was carried out using magnetic catalyst $Ni_{4,63}Cu_1Al_{1,82}Fe_{0,79}$ (Zhang et al, 2014). At a temperature 215 °C, hydrogen partial pressure 4 MPa and the duration of the process 3 hours sorbitol yield was 68.07 %. The catalyst showed high activity after being used three, four times.

Thus, the results described in literature prove the benefits of using magnetically retrievable catalysts in the processes of cellulose conversion. In this paper the Ru-containing catalyst on the basis of $Fe_3O_4$ - $SiO_2$ MNPs was suggested for the process of cellulose hydrogenolysis to EG and PG.

## 2. Experimental

### 2.1 Materials

Iron (III) nitrate, mesoporous silica gel (6 nm porosity, 200 - 425 mesh particle size) and ruthenium (III) acetylacetonate ($Ru(acac)_3$, 97 %) were purchased from Sigma-Aldrich and used without purification. Ethylene glycol (99.0 %) and tetrahydrofuran (THF) were purchased from Macron Fine Chemicals and used as received. Ethanol (95 %) was purchased from EMD and used without purification. Cellulose (degree of crystallinity of 75 - 80 %) was purchased from ChimMedService (Russia). The fraction with the particle size <45 μm was used.

### 2.2 The catalyst 5% Ru-$Fe_3O_4$-$SiO_2$ synthesis

To the solution of 2 g of $Fe(NO_3)_3$ dissolved in 10 mL of ethanol, 2.5 g of silica gel was added. The mixture was allowed to stir overnight in air for ethanol evaporation. The sample was then dried in a vacuum oven at room temperature for a minimum of 2 hours. The powder was then stirred with a spatula with 25 drops of ethylene glycol. This sample was then loaded into two porcelain boats and heated in a quartz tube under argon to 250 °C with a heating rate of 2 °C/min. The heating at 250 °C was held for 5 h and then the sample was cooled to room temperature.

$Ru(acac)_3$ (0.495 g) was dissolved in 10 mL of THF and mixed with $Fe_3O_4$-$SiO_2$ prepared in the previous step. The suspension was stirred overnight in air to allow THF evaporation. The sample was then dried in vacuum at room temperature until the sample was entirely dry. The powdered product was then stirred with 25 drops of ethylene glycol. The sample was then loaded into two porcelain boats and heated in a quartz tube in a tube furnace under argon to 300 °C with a heating rate of 2 °C/min followed with 3 h heating at this temperature. After that the product was allowed to cool to room temperature.

Reduction of this sample was carried out before catalytic experiments by hydrogen at 300 °C for 2 h. After cooling the catalyst was stored in a sealed container at room temperature.

### 2.3 Characterization

The TEM images were acquired on a JEOL JEM1010 transmission electron microscope. Images were analyzed with image-processing package ImageJ to estimate nanoparticle diameters. X-ray powder diffraction (XRD) patterns were collected on an Empyrean from PANalytical. Magnetic measurements were performed on a Quantum Design MPMS XL magnetometer using the systems DC measurement capabilities. XPS experiments were performed using PHI Versa Probe II instrument equipped with a monochromatic Al K(alpha) source. Nitrogen adsorption measurements were carried out at liquid nitrogen temperature on a Coulter SA 3100 Surface Area and Pore Size Analyzer (Beckman Coulter). X-ray fluorescence (XRF) measurements to determine the Ru content were performed with a Zeiss Jena VRA-30 spectrometer.

### 2.4 Cellulose hydrogenolysis

The experiments were performed in a steel reactor (50 cm$^3$, Parr Instrument, USA). Microcrystalline cellulose, a catalyst and 30 mL of distilled water were loaded into the reactor. Then reactor was flushed three times with hydrogen under 60 bar pressure. The mixture was heated and stirred at 100 rpm. After reaching the operating temperature 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 was separated by neodymium magnet. The non-hydrolyzed cellulose was separated by filtration.

Hydrogenolysis process studies were carried out at a temperature varying (205 - 260 °C), hydrogen partial pressure varying (40 – 100 bar), the process time varying (0 - 60 min), and varying the ratio of Ru / cellulose, type of catalyst, the percentage of the ruthenium.

The content of the conversion main products was determined by chromatographic methods in liquid phase. For the analysis of a liquid phase highly effective liquid chromatograph UltiMate 3000 (Dionex, USA) was employed.

Cellulose conversion was calculated using the formula: $X = m_c/m_{c0} \cdot 100\ \%$, where $m_c$ is the weight of hydrolyzed cellulose and $m_{c0}$ is the initial weight of cellulose. A selectivity was calculated using the formula $S = m_p/m_c \cdot 100\ \%$, where $m_p$ is the weight of the reaction product.

## 3. Results and discussions

### 3.1 Catalyst characterization

The data of the physicochemical characterization of the catalyst used in this work are presented in Table 1.

*Table 1: Physicochemical characterization data of the 5 % Ru-Fe₃O₄-SiO₂ catalyst*

| Ru loading, wt.% | Content from XPS, at.% | | | Ru content from elemental analysis, wt.% | Ru NP size, nm | BET surface area, m²/g | BET pore volume, cm³/g |
|---|---|---|---|---|---|---|---|
| | Ru | Fe | Si | | | | |
| 5 | 11.0 | 14.7 | 74.3 | 4.0 | 2.0±0.5 | 277.4 | 0.48 |

X-ray diffraction data confirm phase composition of the catalyst that contains amorphous $SiO_2$, Ru nanoparticles and highly crystalline $Fe_3O_4$ particles. XPS data showed that the Ru species are Ru(IV) and Ru(0) at the 1/1 atomic ratio. According to TEM the ruthenium nanoparticle size is 2.0±0.5 nm.

Magnetization curves were obtained for the $Fe_3O_4$-$SiO_2$ sample before the incorporation of Ru-containing NPs. The magnetization curves at 5 K show a hysteresis, while at 300 K no remanence or coercivity was observed, demonstrating superparamagnetic behaviour. To determine the blocking temperature, zero-field cooling (ZFC) and field cooling (FC) susceptibility curves were used. $T_B$ is the point where the two curves merge. The blocking temperature for this sample is about 100 K which is typical for superparamagnetic iron oxide NPs of a comparable size. A low saturation magnetization is due to a small NP size, however, a large number of these NPs allow fast magnetic separation.
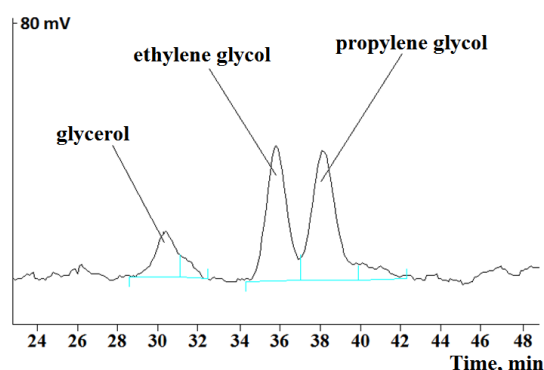




*Figure 1: Chromatogram of liquid phase after the reaction (5% Ru-Fe₃O₄-SiO₂; 0.1167 mmol Ru per 1 g of cellulose; 255 °C; P(H₂) 60 bar; 50 min)*
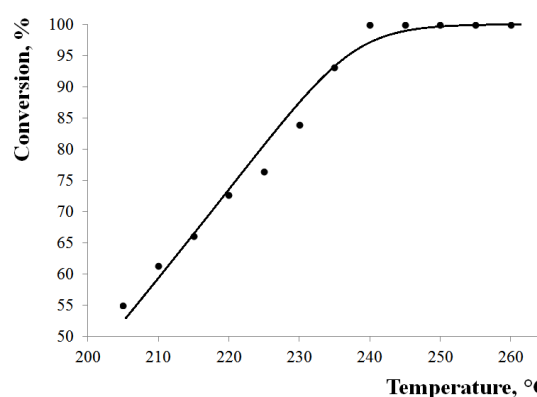
*Figure 2: Cellulose conversion depending on the temperature of the process (0.1167 mmol Ru per 1 g of cellulose; P(H₂) 60 bar; 50 min)*

### 3.2 Cellulose hydrogenolysis

In Figure 1 a typical chromatogram of the liquid phase analysis after the experiment is shown. The main products of cellulose hydrogenolysis are EG, PG and a smaller amount of glycerol. The liquid phase can contain trace amounts (depending on the conditions of the process) of sorbitol, mannitol, 1,4-sorbitan, xylitol, erythritol and also other products of polyol hydrogenolysis. The study of the Ru/cellulose ratio influence shows that the optimal value is 0.1167/1 (mmol Ru as a component of the catalyst per 1 g cellulose). The selectivity to EG and PG is 12 and 23 %, respectively. Lower values of the Ru/cellulose ratio in a liquid phase result in the increase in polyol $C_6$–$C_3$ content with the simultaneous decrease in glycol content. Higher values lead to the decrease in selectivity to glycols, especially to PG (by 6 %); the reason for this is possibly further hydrogenolysis of PG and EG to ethanol, methanol and methane (Maglinao et al., 2012; Wu et al., 2013).

The dependence of cellulose conversion on the process temperature is shown in Figure 2. Maximum selectivity to PG and EG observed at 255 °C (Figure 3) is 23 and 12 %. At the temperatures from 205 °C to 235 °C these values are not high that can be explained by the low intensity of polyol $C_6$–$C_3$ hydrogenolysis as is evidenced by their noticeable content in the liquid phase. In particular, at a temperature 235 °C the selectivity to sorbitol is 4.3 %, to mannitol – 1.2 %, to 1.4 - sorbitan – 1.1 %, to xylitol – 1.3 %, to erythritol – 1.3 %.
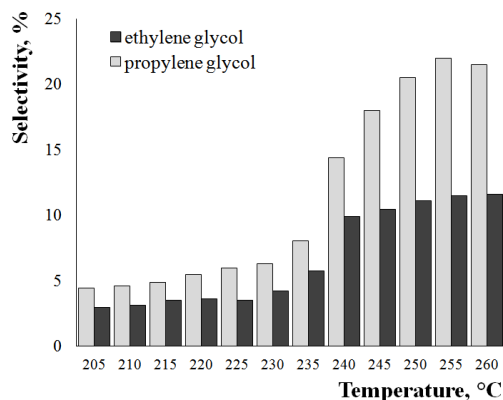
Figure 3: Dependence of EG and PG selectivity on the temperature of the process (0.1167 mmol Ru per 1 g of cellulose; P(H$_2$) 60 bar; 50 min)
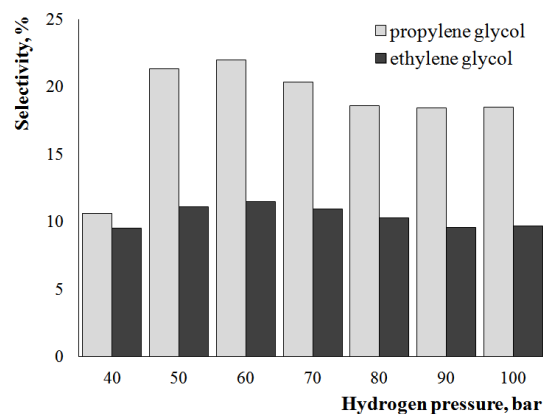
Figure 4: Dependence of EG and PG selectivity on hydrogen pressure (0.1167 mmol Ru per 1 g of cellulose; 255 °C; 50 min)

With the temperature increase the selectivity to PG sharply increases but it decreases smoothly close to 260 °C. The jump of selectivity is not so evident for EG. Besides achieving 10 % at 240 °C, the selectivity to EG continues growing insignificantly, approximately by 0.5 % every 5 °C. The fast increase in selectivity to glycols results from the acceleration of the reaction of cellulose hydrolysis caused by the change in subcritical water properties observed in the temperature range 240 – 260 °C. In particular, at 250 °C pK$_w$ = -log$_{10}$(K$_w$) achieves the value 10.9 (K$_w$ = [H$_3$O$^+$][OH$^-$] is the water ionization constant) (IAPWS, 2007). The concentration of hydroxonium ions, as well as hydroxyl groups, in subcritical water approximately increases by a factor of 35 resulting in the acceleration of acid- and base-catalyzed reactions to which hydrolysis belongs. The acceleration of cellulose hydrolysis at 240 °C leads to the growth of selectivity to sorbitol formed in glucose hydrogenation up to 6.7 %, which is the maximum value observed in this study. However, only its trace amount is found in a liquid phase at a temperature 250 – 260 °C by the 50th min of the process.
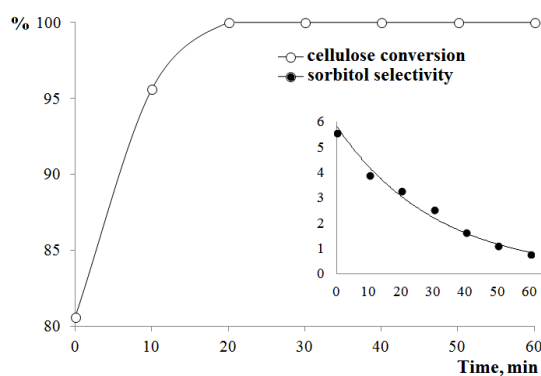


Figure 5: Dependence of cellulose conversion and sorbitol selectivity on the time of the process (0.1167 mmol Ru per 1 g of cellulose; 255 °C; P(H$_2$) 60 bar)
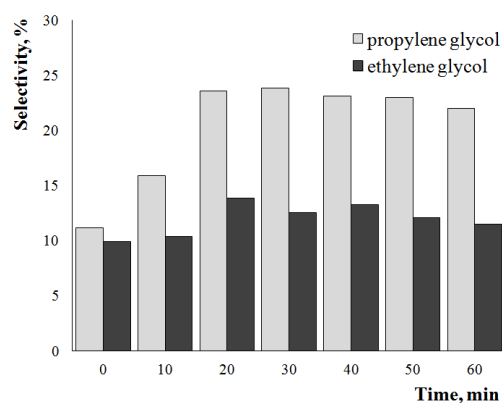
Figure 6: Dependence of EG and PG selectivity on the time of the process (0.1167 mmol Ru per 1 g of cellulose; 255 °C; P(H$_2$) 60 bar)

The results of the experiments to study the influence of hydrogen partial pressure on the process are shown in Figure 4. The optimal pressure 60 bar allows achieving the maximum values of selectivity to EG and PG. At lower pressure the selectivity to glycols decreases while at 40 bar the formation of the brown-colored solutions is observed. This fact indicates to the presence of the products of glucose thermal decomposition in the reaction solution and its partial hydrogenation to sorbitol. At a pressure more than 60 bar a gradual decrease in selectivity to glycols is observed. This decrease can be explained by the following. Firstly, the intensity of sorbitol and mannitol hydrogenolysis lowers as a larger part of the catalyst surface is occupied with H$_2$ molecules preventing hexitol molecules from locating on the catalyst surface. This assumption is proved by

the increase in selectivity to sorbitol up to approximately 3 % at hydrogen pressure 90 - 100 bar. Secondly, glycol hydrogenolysis takes place; glycols molecules are smaller in size and have better opportunity for the contact with the catalyst active sites.

The influence of the time of the process on cellulose conversion and selectivity to the main products was studied. The results obtained are presented in Figure 5 and Figure 6. By the start of the experiment (time 0 min, 255 °C) the cellulose conversion approaches 80 %, and in a liquid phase there is a considerable amount of cello-oligomers, glucose (selectivity 2 %), sorbitol (selectivity 5.6 %) and mannitol (selectivity 1.2 %). The selectivity to PG and EG at this moment is 11 and 10 %, respectively. The maximum values of selectivity to glycols is observed at the 30th minute of the experiment but the optimal duration of the process is considered to be 50 minutes as by this moment trace amounts of polyols $C_6$–$C_3$ remain in a liquid phase and the selectivity to glycols decreases insignificantly. The conversion of 100 % is already observed after 20 min of the reaction.

The stability of the catalyst 5 % $Ru-Fe_3O_4-SiO_2$ was tested in three consecutive reactions (Table 2). Upon the completion of each reaction the catalyst was separated from the reaction medium with the neodymium magnet and fresh cellulose and distilled water were added to it.

*Table 2: Cellulose conversion (X) and the glycol selectivity in the repeated use of 5 % $Ru-Fe_3O_4-SiO_2$*

| Cycle | X, % | Selectivity, % | |
| --- | --- | --- | --- |
| | | Ethylene glycol | Propylene glycol |
| 1 | 100 | 11.7 | 22.8 |
| 2 | 100 | 12.0 | 22.5 |
| 3 | 100 | 11.9 | 22.7 |
| 0.1167 mmol Ru per 1 g of cellulose; 255 °C; P($H_2$) 60 bar; 50 min. | | | |

As is seen from the above data the catalyst is stable under hydrothermal conditions of the process. In all three reactions cellulose conversion is 100 % and the selectivity to EG and PG are practically the same ($\approx$ 12 and 23 %, respectively).

## 4. Conclusions

Ru-containing magnetically retrievable catalysts on the basis of $Fe_3O_4-SiO_2$ MNPs allow converting microcrystalline cellulose into ethylene and propylene glycols with the selectivity 12 and 23 %. The optimal conditions of the process are temperature 255 °C, hydrogen partial pressure 60 bar, the duration of the process 50 min, 0.1167 mmol ruthenium as a component of the catalyst per 1 g of cellulose. Under the above conditions cellulose conversion is 100 %.

The catalyst is stable under hydrothermal conditions of the process, it is easily separated from the liquid phase with the external magnetic field and can be reused. The results of the research prove the advantages of the use of magnetically retrievable catalysts in biomass processing into chemicals and second-generation biofuel.

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