MAGNETICALLY RECOVERABLE POLYMERIC CATALYST FOR CELLULOSE HYDROGENOLYSIS

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A novel catalysts on the base of hypercrosslinked polystyrene (HPS) with magnetic properties are proposed for the one-pot processes of the cellulose conversion into ethylene glycol (EG) and propylene glycol (PG).

HPS-based magnetically recoverable Ru-containing catalysts were synthesized according to the following procedure. First, Fe_3O_4 particles were formed in the polymeric matrix of HPS. 0.3 g of HPS of MN270 type was placed to the 10 mL of EtOH with preliminarily dissolved calculated amounts of $FeCl_3$ and CH_3COONa. The sample of iron-containing HPS was dried at 70 °C, wetted with ethylene glycol and placed in an autoclave. Then, the sample was heated up to 200 °C in argon medium and maintained at this temperature for 5 h. For the synthesis of Ru-Fe_3O_4/HPS catalyst, Fe_3O_4/HPS MN270 was impregnated with the solution of ruthenium (IV) hydroxochloride in a complex solvent consisting of tetrahydrofuran, methanol, and water. Further, the catalyst was dried, treated with solutions of NaOH and H_2O_2, and then washed with water. Then the catalyst was reduced in hydrogen flow (flow rate 100 mL/min) at 300 °C for 2 hours. In this way, Ru-containing system with calculated ruthenium content of 3 wt.% was synthesized.

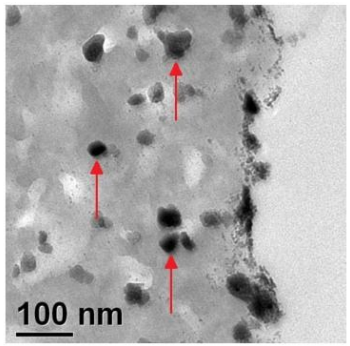

Figure 1: Magnetite nanoparticles with mean diameter 40 ± 5 nm.

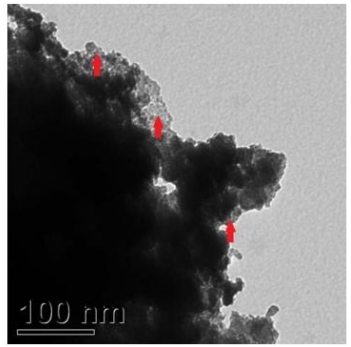

Figure 2: Ru-containing nanoparticles with mean diameter 2.0 ± 0.5 nm.

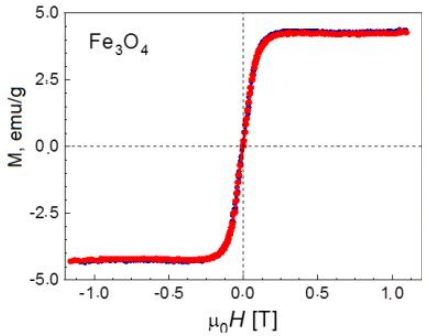

Figure 3: Magnetic properties of Fe_3O_4/HPS MN270.

Figure 4: Fe_3O_4/HPS MN270 before and after magnetic separation.

In Table 1 the results of X-ray fluorescence measurements are presented. From the data presented, it can be seen that the catalyst synthesis procedure provides final ruthenium content in the catalyst close to the Ru loading (3 %). The average iron content is 19.6 %. Table 2 shows the porosity data of the initial HPS MN 270 and Fe_3O_4/HPS MN270 samples and the catalysts obtained from the nitrogen physisorption measurements.

The mean magnetite nanoparticle diameter is 40 ± 5 nm. The mean Ru nanoparticle diameter is 2.0 ± 0.5 nm (Fig. 1, 2).

Testing of the catalyst was carried out in the following conditions : 255 °C, hydrogen partial pressure 60 bar, 50 min, 0.3 g of microcrystalline cellulose (fraction with 0.045-0.063 μm particles size), 0.07 g of 3 % Ru-Fe_3O_4/HPS MN270 catalyst, 30 mL of H_2O, 0.195 mol of $Ca(OH)_2$ per 1 mol of cellulose. Under said experimental conditions, the maximum selectivity for PG and EG were 20.0 % and 22.6 %, respectively. Cellulose conversion in all runs was 100%.

The use of magnetically separable catalysts (MSC) shows many advantages such as convenient separation, efficient recovery (Fig. 3, 4), what is especially important with incomplete biomass conversion.

Table 1: The results of X-ray fluorescence measurements

Sample:	%wt.	
	Fe	Ru
Fe_3O_4/HPS MN270	19.6	-
3 % Ru-Fe_3O_4/HPS MN270	19.6	2.7

Table 2: Porosity data for the initial HPS MN270, Fe_3O_4/HPS MN270 and the catalyst 3 % Ru-Fe_3O_4/HPS MN270

Sample	BET		Langmuir		t-plot		
	S_{BET}, m^2/g	k_{BET}	S_L, m^2/g	k_L	S_t, m^2/g	k_t	V, cm^3/g
HPS MN270	1075	0.99964	1191	0.9996	265[1)]; 807[2)]; 1072	0.99816	0.37
Fe_3O_4/HPS MN270	450	0.99976	480	0.9992	160[1)]; 289[2)]; 449	0.99902	0.13
3 % Ru-Fe_3O_4/HPS MN270	364	0.99982	392	0.9990	175[1)]; 189[2)]; 364	0.99968	0.08

S_L is the specific surface area (Langmuir model); S_{BET} is the specific surface area (BET model); S_t is the specific surface area (t-plot); k_L, k_{BET}, k_t are the correlation coefficients; [1)] specific surface area according to t-plot model; [2)]specific surface area of micropores; V is the micropores volume.

The data in Table 2 show that the selectivity of 3 % Ru-Fe_3O_4/HPS MN270 catalyst was approximately equaled to the selectivity of the magnetically recoverable 5 % Ru-Fe_3O_4-SiO_2 catalyst, which earlier showed good results in the hydrogenolysis of cellulose to glycols. However, due to the lower percentage of ruthenium in the new catalyst, its specific activity was higher by approximately 35% for EG and 20% for PG (Table 2).

Table 2: Catalytic activities for EG and PG with the catalysts tested

Catalyst	Selectivity, %		Specific catalytic activity calculated as a gram of EG or PG per gram of Ru per hour, h^{-1}	
	EG	PG	EG	PG
3 % Ru-Fe_3O_4/HPS MN270	22.6	20.0	39.12	34.62
5 % Ru-Fe_3O_4-SiO_2	19.1	20.9	25.29	27.72

255 °C; 60 bar H_2; 55 min; 0.3 g of cellulose; 0.07 g of catalyst; 30 mL H_2O; 0.195 mol of $Ca(OH)_2$ per 1 mol of cellulose.

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