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D-glucose Hydrogenation over Ni Based Hypercrosslinked Polyesterene

Alexander Malinovsky^a, Valentina Matveeva^a, Esther Sulman^{a,*}, Valentin Doluda^a, Antonina Stepacheva^a, Evgeny Rebrov^{a,b}

^aTver State Technical University, Dep. Biotechnology and Chemistry, A.Nikitina str. 22, 170026, Tver, Russian Federation

^bUniversity of Warwick, School of Engineering, Coventry, CV4 7AL, UK
 sulman@online.tver.ru

The synthesis of highly selective catalysts for saccharides hydrogenation to sugar alcohols is of great importance in terms of increase in selectivity towards the target products and catalyst stability. In the current work catalytic D-glucose hydrogenation was studied over Ni catalysts based on hypercrosslinked polystyrene in autoclave reactor. Catalysts initial activity of HPS-Ni-25 % was found to be 1.4 kg Glu/(kg Cat*h) at 99.3-99.6 % D-glucose conversion. Process selectivity to sorbitol was equal to 97.6 - 97.8 %. Gluconic acid and maltitol were found in traces amounts during the analysis, while furfural can be considered as the main side products.

1. Introduction

Catalytic processes play the leading role in natural feedstock transformation (Zharova et al., 2015; Palma et al., 2015). Saccharides hydrogenation is one of the synthetic methods for pharmaceuticals, agrochemicals, fuel and food chemicals and other intermediates production (Murzin, 2016). The most important saccharide hydrogenation processes are glucose, xylose, lactose and maltose hydrogenation to the corresponding alcohols. Glucose is a low cost, large-scale product of starch-molasses dairy industry. Glucose hydrogenation is commonly performed batch wise in stirred tank reactors at temperatures ranging from 60 up to 150 °C, pressures of 30-80 bar with sponge nickel (Worstell, 2014) or transition metals supported on oxides. Glucose hydrogenation is characterized by the formation of several side products including D-mannitol (Aho et al., 2015), furfural (Zhang et al., 2013), gluconic acid (Romero et al., 2016). The formation of side products (Figure 1) results in appropriate decrease of the process selectivity.

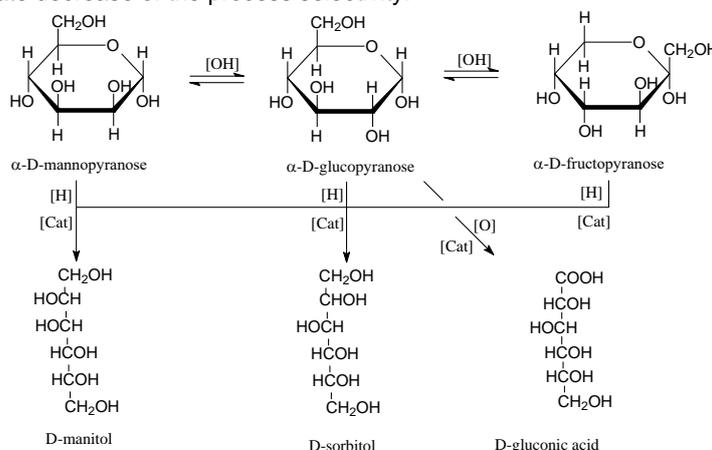


Figure 1: Possible ways of D-glucose hydrogenation

Commonly used sponge Ni catalysts have high selectivity up to 96-98% (Murzin and Simakova, 2013). However, the main problem of this type of catalysts is Ni leaching and fast catalyst deactivation. Hydrogenation over ruthenium supported on MgO, SiO₂, Al₂O₃ and TiO₂ led to increased glucose degradation rate and to extent side products formation, therefore the process selectivity decreases to 20-80% (Zhang et al., 2015). The insight in the catalyst deactivation for D-glucose hydrogenation process can be valuable for the development of new stable catalysts. The results of such study for Ni based catalysts are described in the article.

2. Materials and methods

2.1 Materials

Hypercrosslinked polystyrene (HPS) was purchased from Puralite Int. (U.K.), as Macronet MN 100 (functionalized with amino groups). Nickel acetate (Ni(Ac)₂) (Aurat Ltd., Russia) chemical-grade was used as received. Reagent-grade methanol (MeOH), tetrahydrofurane (THF), acetone and sodium hydrocarbonate (NaHCO₃) were purchased from Sigma-Aldrich (USA) and were used as received. Reagent grade hydrogen of 99.99% purity was received from AGA. Reagent-grade glucose, sorbitol, maltose, maltitol and gluconic acid were purchased from local supplier and were used as received. The distilled water was purified with Elsi-Aqua (Elsico, Russia) water purification system.

2.2 Catalyst synthesis

Prior to the catalyst synthesis HPS samples particles with the diameter 1-2 mm were washed with acetone and water twice and dried under vacuum for 24 hours. Then the particles were grinded and the fraction of 50 µm was taken for catalyst preparation. HPS based catalysts were prepared by the impregnation method of the support with Ni(Ac)₂ solution in complex solvent consisted of 5 mL THF, 1 mL water and 1 mL methanol. In a typical synthesis, the calculated amount of Ni(Ac)₂ was dissolved under nitrogen into 7 mL of a complex solvent, to which 3 g of MN-100 were added. The suspension was continuously stirred for 10 min to allow the adsorption of the solution by the support. After the filtration, Ni-containing polymer was dried at 75 °C for 1 hour. The catalysts were reduced in hydrogen flow (flow rate 100 mL/min) for 3 hours at 300 °C. The obtained samples were designated as HPS-Ni-5%, HPS-Ni-15%, HPS-Ni-25%. The catalysts were analyzed by X-Ray fluorescence analysis (XFA), X-ray photoelectron spectroscopy analysis (XPS), hydrogen chemisorptions, transmission electron microscopy (TEM) and low-temperature nitrogen physisorption as it was described in our previous work (Sulman et al., 2016).

2.3 Glucose hydrogenation methodology

The hydrogenation was conducted batchwise in a shaker type reactor (Figure 2). The reactor was equipped with a heating jacket, a cooling coil, a filter (0.5 µm metal sinter) in a sampling line and a bubbling chamber (for removing dissolved air from the liquid phase and for the saturation of the liquid phase with hydrogen prior to the hydrogenation experiments). The effective liquid volume was 50 mL (total volume 125 mL).

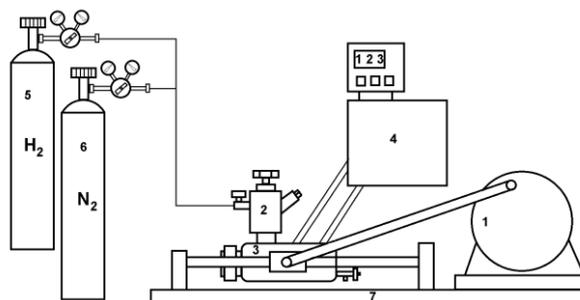


Figure 2: Shaker-type reactor for D-glucose hydrogenation (1 – reciprocating mechanism, 2 - saturation chamber, 3 – reactor, 4 – thermostat, 5 – balloon with hydrogen, 6 – balloon with nitrogen)

In the experiments the suspension of the catalyst in 35 mL of water (catalysts loading 8-70 g/L) was loaded in the reactor, then aqueous glucose solution (15 mL with concentration varied between 0.1 and 0.4 mol/L) saturated with hydrogen in the bubble chamber was rapidly fed into the reactor and the hydrogen pressure (20 - 70 bar) and temperature (110-140 °C) were immediately adjusted to the experimental conditions. The shaking rate was fixed at 174 shakes/min (spm) in all of the kinetic experiments to ensure operation in the kinetically controlled regime. The particle size of HPS based catalysts was below 50 µm. The high shaking rates and small catalyst particles size allow the absence of diffusion limitations. Samples of the reaction mixture were periodically taken for the analysis.

2.4 High performance liquid chromatography (HPLC) analysis

The analysis of the reaction media was performed using Ultimate 3000 HPLC chromatograph (Dionex, USA) equipped with refractive index detector. Reprogel-H column (500 × 10 mm, number of theoretical plates 160,000) was used for ion exchange. H₂SO₄ (1 μM) in deionized water was used as a mobile phase. The flow rate of the eluent was kept constant 0.5 mL/min⁻¹ at column temperature 30 °C. Eluent pressure was maintained 10 MPa. Time of analysis was 120 min (for 1 sample). The concentration of substrate and reaction products was determined using absolute calibration method. Qualitative identification of substances and their assignment to the corresponding peaks in the chromatogram was carried out using of the individual pure substances standards.

3. Results and discussion

3.1 Influence of the stirring rate

The shaking rate influence on glucose hydrogenation was investigated through a correlation between the glucose concentration and the shaking rate, which was varied from 126 c to 218 spm (Figure 3). HPS-Ni-25% was used as the catalyst in the experiments. The catalyst concentration (C_c) was chosen as 8 g/L and the initial substrate concentration (C₀) as 0.4 mol glucose/L, overall system pressure 40 Bar and reaction temperature 140 °C for three experiments. As it can be seen from Figure 3, shaking rate practically does not affect the reaction rate indicating the absence of mass transfer limitations. For all further experiments 174 spm was chosen as shaking rate.

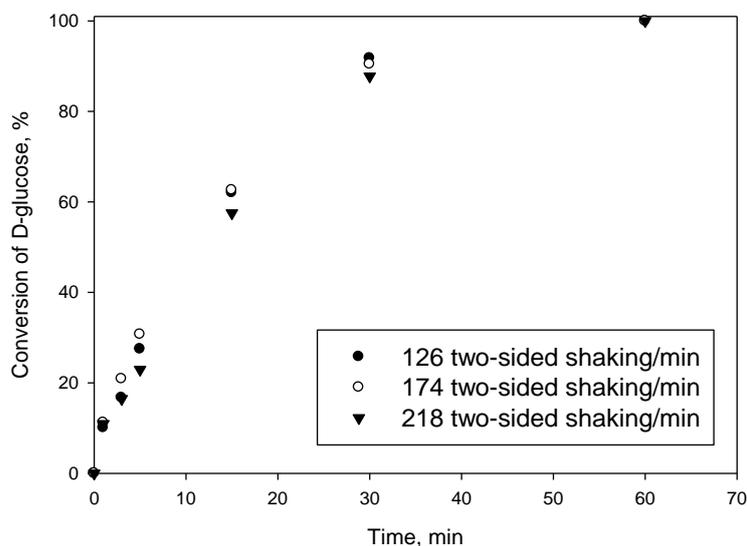


Figure 3: Dependence of glucose conversion on time for different shaking rates (reaction conditions: catalyst HPS-Ni-25%, temperature 140°C, hydrogen partial pressure 40 bar, C_c=8 g/L, C₀= 0.4 mol/L)

3.2 Ni loading effect

The performance of HPS supported nickel catalysts for the hydrogenation of glucose to sorbitol in aqueous solutions (0.4 mol/L) was evaluated at 140 °C and 40 bar of overall pressure with the catalyst concentration equal to 8 g/L. The results obtained for three synthesized samples are presented in Figure 1a. The highest turnover frequency (TOF) was found to be 0.1 s⁻¹ for most active HPS-Ni-25 %. Selectivity towards sorbitol, calculated as a relation of sorbitol quantity to overall glucose conversion, was 97 – 98 % for all studied catalysts is comparable to commonly used industrial sponge Ni catalysts (selectivity up to 96 – 98 %) and higher than that obtained for glucose hydrogenation on ruthenium supported on MgO, silica, alumina and TiO₂ (process selectivity 20 – 80 %). Madon-Boudart test (Figure 1b) shows the absence of internal mass transfer limitations in the glucose hydrogenation process.

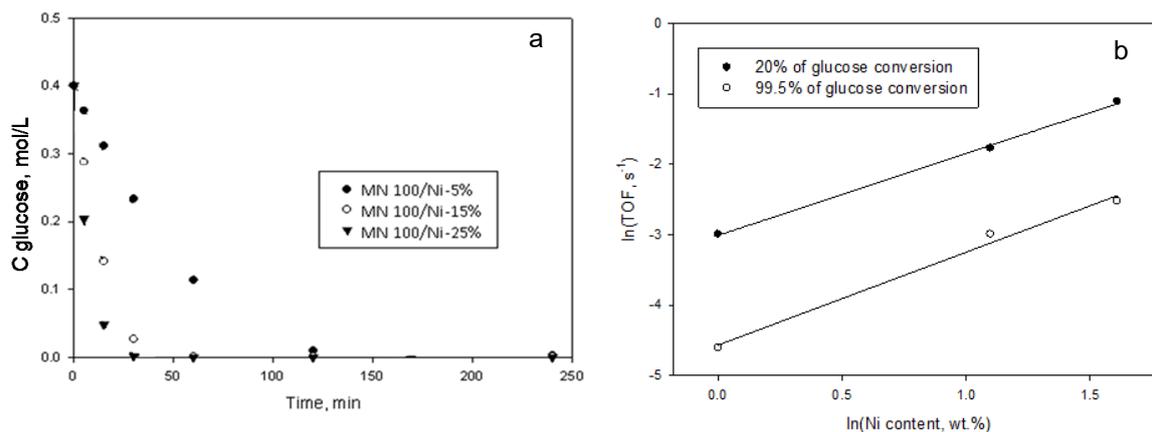


Figure 4: Glucose conversion (a) and Madon-Boudart test curve (b) for Ni supported on hypercrosslinked polystyrene (reaction conditions: temperature 140 °C, hydrogen partial pressure 40 bar, $C_c = 8$ g/L, $C_0 = 0.4$ mol/L)

3.3 Glucose concentration influence

To study the glucose concentration influence the experiments were performed at a temperature 140 °C, 40 bar of overall pressure, catalyst concentration 8 g/L and glucose concentration 0.1 - 0.4 mol/L. Figure 5a shows the dependence of glucose conversion on time. The increase in glucose concentration results in the corresponding increase in the reaction rate. Figure 5b presents the dependence of selectivity towards sorbitol on the degree of glucose conversion for different initial concentrations of the substrate. and the process selectivity for MN100/Ni-25 %. Selectivity towards sorbitol has a character with well-defined maxima (Figure 5b). The analysis of Figure 5 shows that glucose hydrogenation is a complex process with several consecutive and parallel reactions as it is presented in Figure 1. Furfural was found to be the main side product.

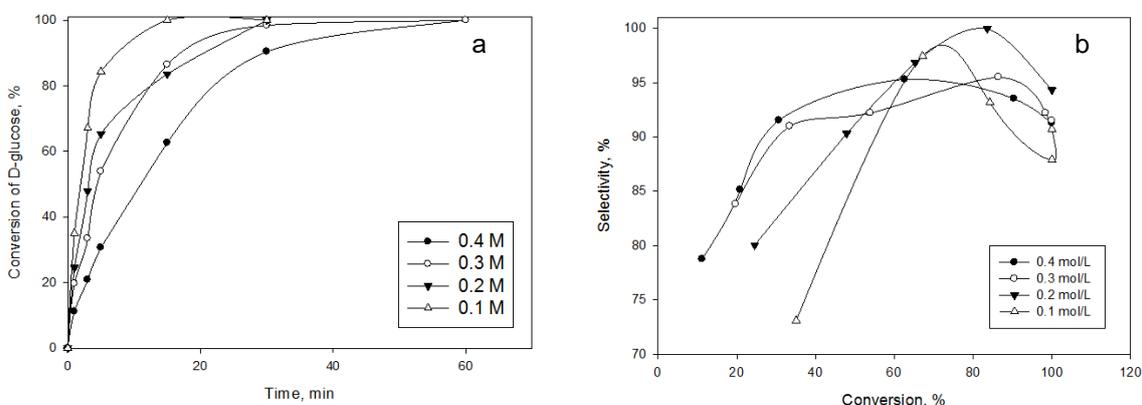


Figure 5: Dependence of (a) glucose conversion on time for different glucose initial concentrations and (b) process selectivity for HPS-Ni-25 % catalyst on D-glucose conversion for different glucose initial concentrations (reaction conditions: temperature 140°C, hydrogen partial pressure 40 bar, $C_c = 8$ g/L)

3.4 Hydrogen pressure influence

Hydrogen pressure influence can be considered as a key factor to obtain high selectivity in glucose hydrogenation reaction. The determination of hydrogen pressure influence was done at the reaction temperature 140°C, $C_c = 8$ g/L, $C_0 = 0.4$ mol/L. Figure 6 represents the glucose transformation dependence on time for HPS-Ni-25% catalyst at different hydrogen pressure. The increase in hydrogen pressure results in the increase in the rate of glucose transformation to sorbitol. The average process selectivity towards sorbitol was found to be 95 %. The highest sorbitol selectivity was observed at 40 bar of hydrogen pressure.

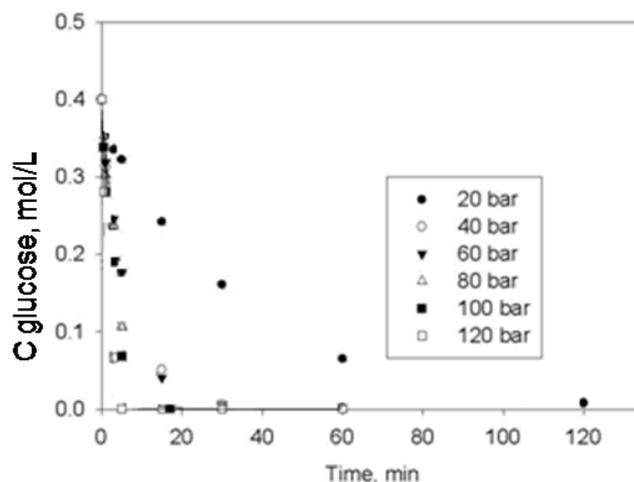


Figure 6: Dependence of glucose concentration on time for HPS-Ni-25 % catalyst (reaction conditions: temperature 140 °C, $C_c=8$ g/L, $C_0=0.4$ mol/L)

3.5 Temperature influence

The study of temperature influence on glucose hydrogenation was evaluated at hydrogen partial pressure 40 bar, $C_c=8$ g/L, $C_0=0.4$ mol/L (Figure 7) for HPS-Ni-25 % catalyst. The increase in reaction temperature from 110 °C to 140 °C results in the increase in glucose hydrogenation rate. Glucose destruction can be considered the main side process at temperatures higher 130 °C, where high concentration of furfural begins to accumulate in the reaction mixture.

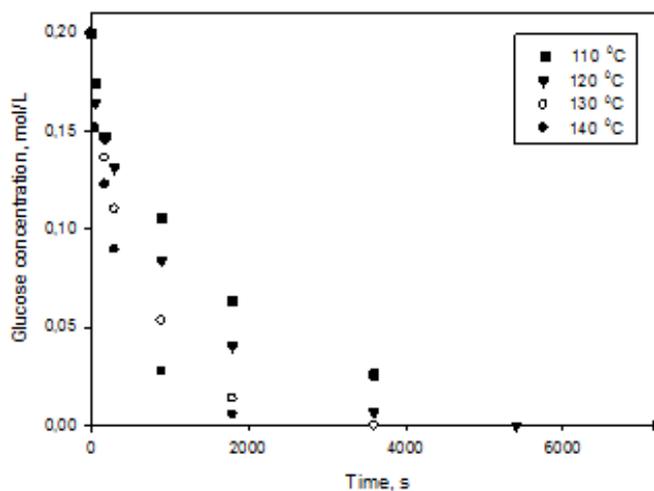


Figure 7: Dependence of glucose concentration on time for HPS-Ni-25 % catalyst at different reaction temperature (reaction conditions: hydrogen partial pressure 40 bar, $C_c=8$ g/L, $C_0=0.4$ mol/L)

The apparent activation energy of glucose hydrogenation process calculated according to the Arrhenius equation was found to be 58 kJ/mol for HPS-Ni-25 % catalyst.

3.6 Repeated D-glucose hydrogenation in a shaker type reactor

HPS-Ni-25% catalyst was studied in 10 consecutive experiments of D-glucose hydrogenation in a shaker type reactor. The results showed the significant decrease in reaction rate from 1.4 kg Glu/(kg Cat*h) to 0.8 kg Glu/(kg Cat*h) at 99.5 - 99.7 % of D-glucose conversion. However, the process selectivity towards sorbitol was maintained about 98.1 -98.2 % for all the experiments. The decrease in the reaction rate can be explained by a metal leaching in the case of a shaker type reactor.

The comparison of initial catalyst sample and the catalyst after ten consecutive cycles was performed using XFA, XPS, hydrogen chemisorption, TEM and low-temperature nitrogen physisorption. According to XPS data Ni species are presented in Ni^{+2} oxide form in both catalyst samples (Table 1). Nitrogen physisorption showed the decrease in catalyst specific surface area compared to the initial catalyst. This can be explained by the

adsorption of substrate and reaction products in the pores of polymeric matrix. According to XFA data 1 % loss in Ni loading was observed after the catalytic experiments that indicates slight metal leaching from the catalyst support. However, this value is less than that obtained for the commercial Ni sponge catalyst (Murzin, 2016). According to hydrogen chemisorptions and TEM analysis slight aggregation of Ni nanoparticles was also observed during glucose hydrogenation.

Table 1: Catalysts characteristics

Catalyst characteristics	HPS-Ni-25 % initial	HPS-Ni-25 % After 10 cycles
Surface area, m ² /g	200	124
Granulometric composition, mm	0.06-0.1	0.06-0.1
Nanoparticles size, nm	3-4	2-5
Ni oxidation state	Ni ⁺²	Ni ⁺²
Ni concentration, wt. %	25	24
Ni dispersion, %	14	12
Sample mass loss, wt. %	-	41

4. Conclusions

A series of catalysts based on NiO nanoparticles incorporated in HPS were synthesized. The glucose hydrogenation to sorbitol on MN100/Ni catalysts in aqueous solutions was studied. The catalytic activity and selectivity for the catalysts synthesized was estimated under a wide variety of reaction conditions in D-glucose hydrogenation process. HPS-Ni-25 % was found to be the most active catalyst. High selectivity to sorbitol (98-99%) can be achieved using HPS-Ni-25 % sample. The formation of negligible amount of side products - D-mannitol, furfural, gluconic acid - was observed. Process selectivity can be improved by the increasing in the hydrogen pressure and by the decreasing in reaction temperature. High temperature increases the rate of glucose destruction, promoting formation of furfural. Gluconic acid as a by-product can be hydrogenated to glucose and sorbitol at a later stage of reaction.

Acknowledgments

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