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Polymeric Catalysts for Oxidation of Cellobiose into Gluconic Acid in Aqueous Medium

Oleg V. Manaenkov*, Olga V. Kislitsa, Ekaterina A. Ratkevich, Yuriy Yu. Kosivtsov

Tver State Technical University, Af. Nikitina, 26, Tver, Russia.
ovman@yandex.ru

In this work, a polymer heterogeneous Pt-containing catalyst based on a mesoporous matrix of hypercrosslinked polystyrene (HPS) is proposed for the process of hydrolytic oxidation of cellobiose. Studies of the processes of hydrolytic oxidation of disaccharides are the first step towards the development of technologies for the direct conversion of plant polysaccharides, primarily cellulose, into aldonic and aldaric acids, which are widely used in chemical synthesis and various industries. It was shown that the use of Pt-containing catalytic systems based on a polymer matrix of hypercrosslinked polystyrene in the process of hydrolytic oxidation of cellobiose to gluconic and glucaric acids is promising. The yield of gluconic and glucaric acids reaches 21.6 and 63.4%, respectively.

1. Introduction

Gluconic acid is widely used in a wide variety of industries. The annual world volume of its production is about 60-65 thousand tons. Gluconic acid is formulated in many food, pharmaceutical and hygiene products; used in the textile and metallurgical industry (Ramachandran et al., 2006). Basically, gluconic acid is obtained by glucose oxidation, which can be carried out by electrochemical, biochemical, bioelectrochemical methods (Tan et al., 2009). However, at the moment, the most preferable is the biotechnological method (Anastassiadis et al., 2005), or the use of immobilised enzymes (Sulman et al., 2019). At the same time, all these methods have one common drawback - the starting substance in all variants of gluconic acid synthesis is glucose, which is a valuable raw material and has a high nutritional value. The biotechnological method is also associated with a long fermentation time (15-24 hours) and high operating costs (air pressure 4 bar, stirring, etc.) (Zhang et al., 2017).

Glucaric acid, a product of deeper oxidation of glucose, is also an important compound with broad prospects for use in the food industry, medicine, in the manufacture of detergents, etc. For example, according to the analytical portal (Reports and Data, 2020), by 2027 the global market for glucaric acid will reach 1.46 billion US dollars. The calcium salt of glucaric acid is used therapeutically to lower cholesterol (Walaszek et al., 1996) and in cancer chemotherapy (Singh et al., 2007). By the Pacific Northwest National Laboratory and the National Renewable Energy Laboratory, funded by the US Department of Energy, glucaric acid has been identified as the “highest added value chemical derived from biomass” (Werpy et al., 2004). Laboratory reports, in particular, indicate that glucaric acid has been successfully used to synthesize hydroxylated nylon, which opens up possibilities for the production of biodegradable fiber (Kiely et al., 1994). At present, glucaric acid is produced by chemical oxidation of glucose, a nonselective, expensive and environmentally unsafe process using nitric acid as an oxidizing agent (Werpy et al., 2004).

Thus, the relevance of the search for new methods for the synthesis of gluconic and glucaric acids from cheap and accessible raw materials such as cellulose is obvious. In particular, there are works that report the direct conversion of cellulose to gluconic acid in a homogeneous medium using high concentration $FeCl_3$ solutions (Liu et al., 2018). Despite the fairly good yield of the target product, the process is complicated by the need to purify it from ferric chloride. Most researchers are focused on the search for new heterogeneous catalysts for the process under study, since, provided that subcritical water is used as a reaction medium, the final product will be an aqueous solution of acids with greater industrial potential. Thus, in the work of An et al., (2012), the process of direct conversion of cellobiose and cellulose to gluconic acid in water in the presence of O_2,

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catalyzed by Au nanoparticles on insoluble polyoxometallates of the composition $Cs_xH_{3-x}PW_{12}O_{40}$, was studied. The authors have shown that the acid sites of the catalyst and the average size of Au nanoparticles are of decisive importance for the effective conversion of the starting substrates into gluconic acid. The former catalyze the hydrolysis of cellobiose and cellulose with the formation of glucose; Au nanoparticles catalyze glucose oxidation. However, as the authors note, the developed catalytic systems turned out to be unstable under hydrothermal conditions with repeated use. In the work of Onda, (2012), a Pt-containing catalyst based on sulfonated carbon (Pt/AC-SO_3H) was proposed for the direct conversion of polysaccharides into gluconic acid. The combination of acidic properties and a metal active phase makes it possible to obtain a yield of gluconic acid up to 46% when starch, maltose, pullulan and cellobiose are used as substrates. However, there are suggestions that when using cellulose as a raw material, the yield of gluconic acid will be lower.

Thus, analyzing the current state of research, it can be stated that the problem of direct catalytic transformation of carbohydrate substrates into aldonic and aldaric acids has not been satisfactorily solved and remains interesting and relevant both from the point of view of fundamental science and from the point of view of the chemical industry.

The aim of this work is to study the process of hydrolytic oxidation of cellobiose to gluconic and glucaric acids in the presence of a Pt-containing catalyst based on a mesoporous matrix of hypercrosslinked polystyrene (HPS) – 3 % Pt/HPS MN270. Ni-containing catalysts based on HPS have previously shown excellent results in the oxidation of glucose to gluconic acid (Malinovsky et al, 2017).

2. Experimental

2.1 The catalyst synthesis

The 3 % Pt/HPS MN270 catalyst was synthesised as follows. The initial sample of HPS brand MN270 (Purolite®, Great Britain) was washed five times with distilled water heated to 40 °C, acetone and dried to constant weight at 50 °C. The dried HPS was ground by means of a vertical cutting mill and separated into fractions by particle size using a vibrating sieve analyzer. For the synthesis of the catalyst, an HPS fraction with a particle size of 45 - 63 μm was used. The dried polymer was impregnated according to moisture capacity with a solution of the calculated amount of hydrogen hexachloroplatinate (IV) ($H_2[PtCl]_6$) in tetrahydrofuran. The sample was dried at 70 °C, treated with hot (80 °C) Na_2CO_3 solution, dried, and washed with distilled water. The washed catalyst was dried at 80 °C. The reduction of the catalyst was carried out with hydrogen gas at atmospheric pressure and a temperature of 300 °C for 2 hours, cooled in an atmosphere of nitrogen gas and stored in a sealed container.

2.2 Characterisation

The specific surface area and porosity of the catalyst and the initial HPS sample were determined by low-temperature nitrogen adsorption using a Beckman Coulter SA 3100 surface analyzer (Coulter Corporation, USA). The texture characteristics of the samples were calculated by mathematical processing of nitrogen adsorption isotherms in accordance with the Brunauer-Emmett-Teller (BET), Langmuir, and de Boer-Lipens (t-plot) models.

TEM images were obtained at an accelerating voltage of 80 kV using a JEOL JEM1010 electron microscope. ImageJ software was used to estimate the size of the nanoparticles.

Elemental analysis of the catalyst was performed on a VRA-30 analytical X-ray spectrometer (Zeiss Jena, Germany).

2.3 Cellobiose hydrolytic oxidation

Experiments on the hydrolytic oxidation of cellobiose (> 98%, Roth, Germany) were carried out in a 50 cm^3 high-pressure steel reactor (Parr Instrument, USA) with a PARR 4843 controller. The reactor was loaded with cellobiose, catalyst, and distilled water. After three times purging the reactor with oxygen at a pressure of 5 bar, heating and stirring were switched on at a rate of ≈100 rpm to prevent the formation of local overheating zones and saturation of the catalyst surface with oxygen. After reaching the operating temperature, the stirrer speed was increased to 600 rpm to transfer the reaction to the kinetic region. This moment served as the beginning of the countdown of the experiment. At the end of the experiment, the reactor was quickly cooled, the catalyst was separated by filtration through a paper filter, and the catalyzate was diluted to 50 cm^3 in a volumetric flask.

The analysis of the liquid phase of the catalyzate was carried out by the method of capillary zone electrophoresis under the following conditions: the leading electrolyte is an aqueous solution of tryptophan (5 mM) and NaOH (50 mM); analysis temperature 20 °C; detector wavelength 280 nm (indirect detection); voltage +20 kV; inner diameter of the capillary is 50 μm; capillary length up to the detector 50 cm; hydrodynamic sample injection for 3 s at a pressure of 30 mbar.

3. Results and discussion

Table 1 shows the values of the specific surface area of the samples of the HPS used in the work and the catalyst based on it. As can be seen from the data in the table, the samples are predominantly mesoporous with a highly developed inner surface. For 3 % Pt/HPS MN270, a decrease in the surface area and specific volume of both micropores and small mesopores is observed, which indicates the formation of platinum nanoclusters in them.

Table 1: Results of the study of the initial sample of the HPS and the catalyst by the method of low-temperature nitrogen adsorption

Sample	BET	Langmuir	t-plot	
	S_{BET}, м^2/г	S_L, м^2/г	S_t, м^2/г	V, cm^3/g
HPS MN270	1484	1616	731[1]; 792[2]; 1523[3]	0.36651
3 % Pt/HPS MN270	1015	1248	470[1]; 650[2]; 1120[3]	0.13728

[1] - specific surface area as calculated by the t-plot model; [2] - specific surface area of micropores; [3] is the total specific surface area; S_L - specific surface area (Langmuir model); S_{BET} - specific surface area (BET model); S_t - specific surface area (t-plot); V is the volume of micropores.

According to the results of X-ray fluorescence analysis, the average content of platinum in the catalyst was 2.91 %, which practically corresponds to the calculated theoretical value and speaks of the optimal method for the synthesis of the catalyst.

In the course of studying the catalyst by transmission electron microscopy (TEM), photographs of metal clusters were obtained (Figure 1a). The histogram of the particle size distribution is shown in Figure 1b. The average size of platinum clusters was 2.8 nm. According to the results of the study, it can be concluded that platinum nanoparticles are uniformly distributed in the volume of the granules, and there is no metal crust on the polymer surface.

In the course of the work, the influence of the temperature of the process of hydrolytic oxidation of cellobiose on the degree of conversion of the substrate and the yield of the reaction products was investigated. The experiments were carried out in the temperature range from 110 to 150 °C. In Figure 2 shows electropherograms for the analysis of the liquid phase of catalysts obtained at different temperatures. Based on the obtained results of a qualitative and quantitative nature, a reaction scheme for the conversion of cellobiose into gluconic and glucaric acids was proposed under these conditions in the presence of a 3 % Pt/HPS MN270 catalyst (Figure 3). In the work of Armstrong et al. (2019), it was shown that the oxidation of D-glucose on platinum catalysts to gluconic and glucaric acids proceeds with the formation of various lactones, which are not determined by chromatographic methods. It is very likely that in our study the peaks of gluconic and glucaric acids on the electrophoretogram correspond to a mixture of these acids and their lactones.

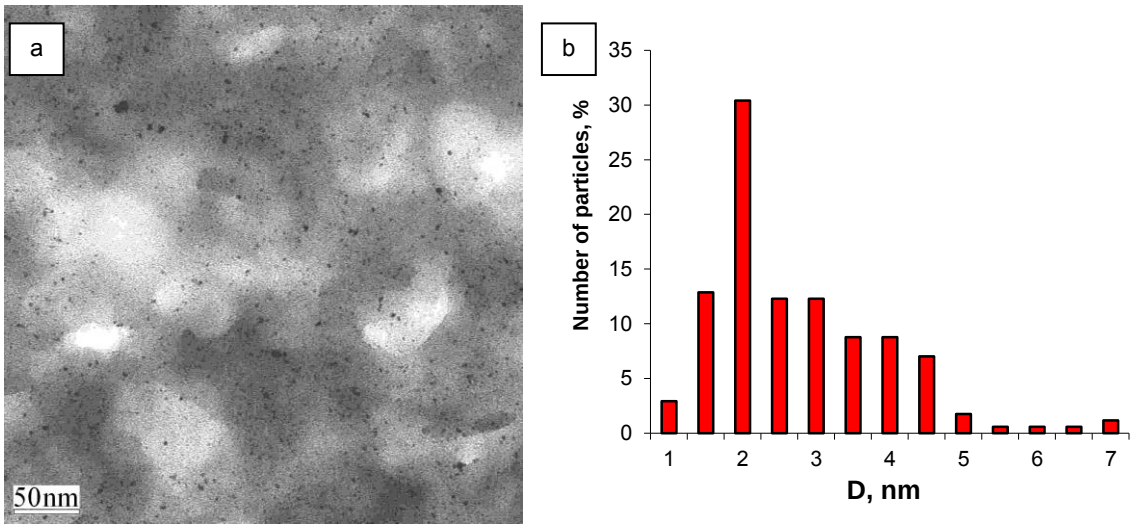

Figure 1: TEM photograph of a sample of 3% Pt / SPS MN270 (a); histogram of the size distribution of platinum nanoclusters (b)

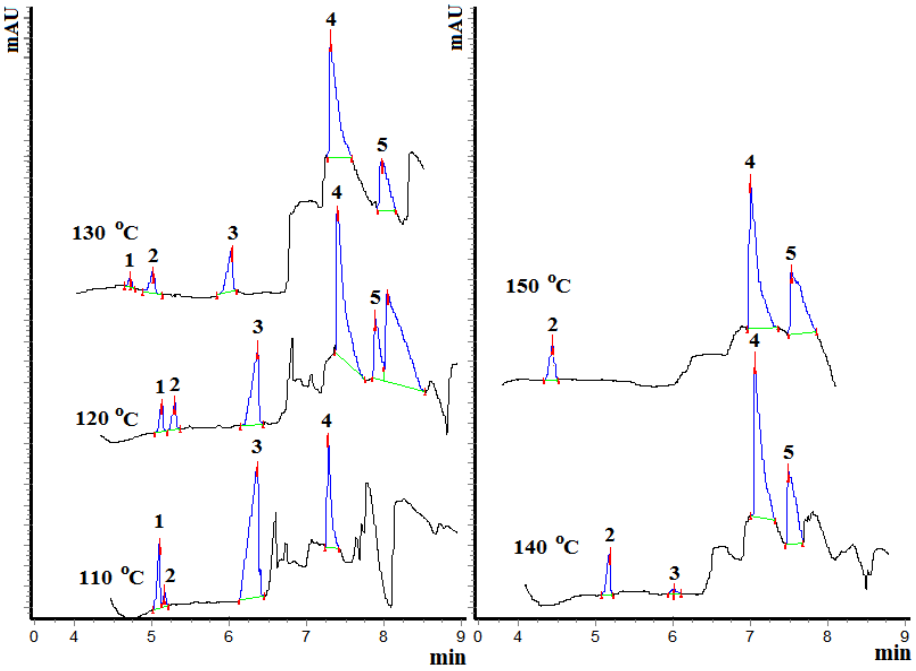

Figure 2: Results of the analysis of the reaction mixture at different temperatures of the experiment: 1 - cellobiose; 2 - glucose; 3 - cellobionic acid; 4 - gluconic acid; 5 - glucaric acid (cellobiose 0.5 g; 3 % Pt/HPS MN270 0.1 g; H_2O 20 mL; O_2 5 bar; 3 h)

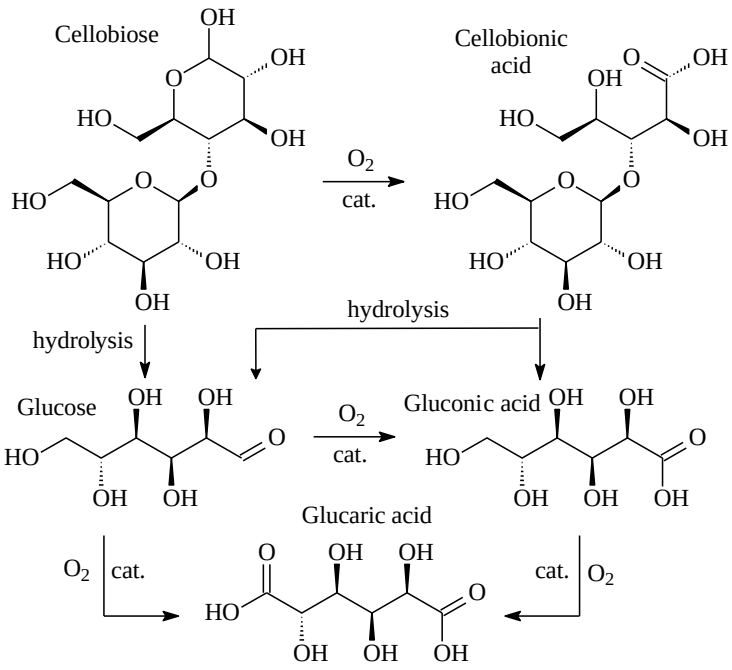

Figure 3: Proposed scheme for the conversion of cellobiose to gluconic and glucaric acids in the presence of a 3 % Pt/HPS MN270 catalyst

According to the data obtained, at a reaction temperature of 110 °C, cellobionic acid is mainly accumulated in the reaction mixture (yield up to 65 %, see Figure 4), the hydrolysis of which, like the initial cellobiose, proceeds slowly. The conversion of cellobiose is quite high and amounts to 87 %, and the yield of gluconic acid does not exceed 3.5 %.

With an increase in temperature, the rate of hydrolysis of the β-glycosidic bond in cellobiose and cellobionic acid molecules increases, and at 130 °C the conversion of cellobiose reaches 100 %, and the yield of cellobionic acid decreases to 13 %. At 140 °C, cellobionic acid is present in the catalysis in trace amounts (Figure 2). Acceleration of hydrolysis leads to the accumulation of glucose in the reaction mass (up to 6%). Moreover, at temperatures of 130 - 150 °C, the presence of glucose is due exclusively to the breakdown of cellobionic acid. It is characteristic that a noticeable increase in the yields of gluconic (from 8.7 % to 12 %) and, especially, glucaric (from 8.7 % to 24 %) acids is observed precisely in the interval 130 - 140 °C, when the accelerated decomposition of cellobionic acid forms an additional amount of gluconic acid, which is rapidly oxidised at high temperatures to glucaric acid.

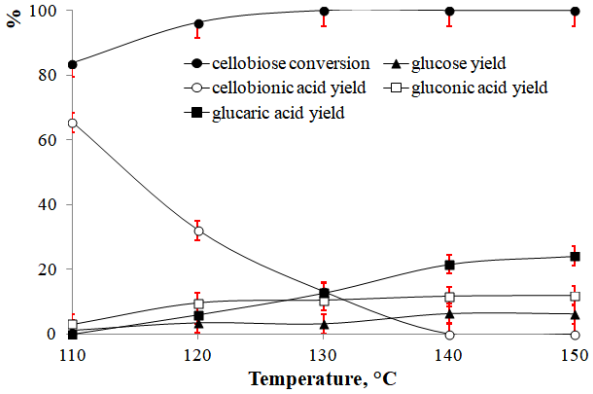

Figure 4: Dependence of the conversion of cellobiose and the yields of the main products on the reaction temperature (cellobiose 0.5 g; 3 % Pt/HPS MN270 0.1 g; H_2O 20 mL; O_2 5 bar; 3 h)

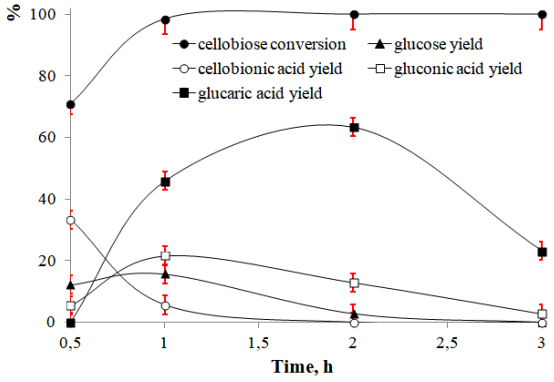

Figure 5: Dependence of the conversion of cellobiose and the yields of the main products on the reaction time (cellobiose 0.2 g; 3 % Pt/HPS MN270 0.05 g; H_2O 20 mL; O_2 5 bar; t 145 °C)

A further increase in temperature leads to the formation of brown solutions with a characteristic odor, indicating the presence of glucose caramelization products in the catalysis, which, in turn, indicates the limiting nature of the glucose oxidation reaction under these conditions. In this regard, in further experiments, the substrate / catalyst ratio was optimised to reduce the load on the catalytic system. The optimum weight ratio of cellobiose/3 % Pt/HPS MN270 was 4/1. At these values, the resulting solutions were transparent, and the smell characteristic of the products of thermal degradation of glucose was absent.

The study also optimised the process duration. It was shown (Figure 5) that the maximum yield of gluconic acid is 21.6 % with a reaction time of 1 h. At the same time, if the target product is glucaric acid, then the optimal reaction time is 2 h. The yield of acid in this case reaches 63.4 %.

The synthesised catalyst proved to be stable under the hydrothermal conditions of the process and was used for at least three successive cycles of use, without noticeable loss of activity.

4. Conclusions

Thus, in the course of the work, it was shown that it is promising to use Pt-containing catalytic systems based on a polymer matrix of hypercrosslinked polystyrene in the process of hydrolytic oxidation of cellobiose to gluconic and glucaric acids. At a temperature of 145 °C, an O_2 pressure of 5 bar, a substrate/catalyst weight ratio of 4/1, the yield of gluconic and glucaric acids reaches 21.6 and 63.4 %, respectively.

The results obtained in the future can be used to create a technology for the catalytic conversion of plant polysaccharides, primarily cellulose, into aldonic and aldaric acids, which are widely used in chemical synthesis, food, pharmaceutical and other industries.

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