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# СИНТЕЗ NI ИМПРЕГИРОВАННОГО В СВЕРХСШИТЫЙ ПОЛИСТИРОЛ ДЛЯ КАТАЛИТИЧЕСКОЙ ГИДРОГЕНАЦИИ D-ГЛЮКОЗЫ

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***Разработка эффективных катализаторов находится в центре внимания современной химической технологии для производства тонких химических веществ. D-сорбит, широко использующийся в качестве подсластителя, пищевой добавки и топливного соединения, обычно получают гидрированием D-глюкозы на Ni-катализаторе Ренея. Однако данный катализатор характеризуется недостаточной стабильностью и селективностью к образованию D-сорбита. Описанное исследование посвящено синтезу никельсодержащего сверхсшитого полистирола для процесса гидрирования D-глюкозы. Сверхсшитый полистирол является одним из представителей сшитых полимеров с жесткой матрицей, применимых для синтеза наночастиц металлов. Однако сверхсшитый полистирол характеризуется высокой гидрофобностью поверхности, что препятствует пропитке большим количеством активного металла по его поверхности. Для преодоления этого недостатка гиперсшитый полистирол был модифицирован перекисью водорода, хлором и аммиаком. Был синтезирован ряд никелевых катализаторов, теоретически содержащих 25 мас.% никеля. Модификация сверхсшитого полистирола приводит к соответствующему увеличению поверхностной концентрации активного металла. Синтезированные катализаторы на основе Ni характеризовались сопоставимой загрузкой Ni, варьирующейся от 20,1 до 23,2 мас.%. Некоторое увеличение загрузки Ni может быть связано с наличием поверхностно-активных групп, в случае применения модифицированного гиперсшитого полистирола. Площадь поверхности мезопор в катализаторах на модифицированных носителях уменьшается от 126 до 69 м$^2$/г. Каталитическое гидрирование D-глюкозы на синтезированных Ni-содержащих катализаторах показало значительное увеличение частоты оборота (TOF) для всех образцов по сравнению с обычно используемым никелем типа Ренея. Увеличение TOF может быть связано с соответствующим увеличением поверхностной концентрации активного металла. Кроме того, наблюдалось некоторое увеличение селективности катализатора по отношению к сорбитолу. Значительное улучшение селективности по отношению к сорбитолу может быть объяснено увеличением скорости реакции гидрирования D-глюкозы, в то время как скорость реакции процесса изомеризации D-глюкозы в D-фруктозу остается неизменной. Было установлено, что достигнутый TOF для наиболее активного катализатора составляет 0,27 с$^{-1}$, а селективность катализаторов к D-сорбитолу составляет 98%.***

**Ключевые слова:** Ni-пропитанный гиперсшитый полистирол, Ni-наночастицы, D-глюкоза, D-сорбиотол, гидрирование

# SYNTHEIS OF NI IMPREGNATED HYPERCROSSLINKED POLYSTERENE FOR CATALITIC HYDROGENATION OF D-GLUCOSE

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***Development of efficient catalysts is in focus of modern chemical technology for production of fine chemicals. D-sorbitol is widely used as sweetener, food additive and fuel compound is typically produced by D-glucose hydrogenation over Ni-Reney catalyst. However, this catalyst is characterized by not sufficient stability and selectivity to D-sorbitol formation. The described study is devoted to synthesis of nickel containing hypercrosslinked polystyrene for D-glucose hydrogenation process. Hypercrosslinked polystyrene is one of the representatives of crosslinked polymers with rigid matrix applicable for metal nanoparticles synthesis. However, hypercrosslinked polystyrene is characterized by high surface hydrophobicity that prevent impregnation of high amount of active metal over it surface. To overcome this disadvantage hypercrosslinked polystyrene was modified by hydrogen peroxide, chlorine and ammonia. A series of nickel based catalyst theoretically containing 25wt.% of nickel were synthesized. Modification of hypercrosslinked polystyrene results in appropriate increase in surface concentration of active metal. Synthesized Ni based catalysts were characterized by comparable Ni loading varying from 20.1 wt.% to 23.2 wt.%. Some increase in Ni loading can be subscribed to presence of surface-active groups in a case of modified hypercrosslinked polystyrene application. Mesopores surface area decrease from 126 m$^2$/g to 69 m$^2$/g in case of catalysts on modified hypercrosslinked polystyrene. Catalytic hydrogenation of D-glucose over synthesized Ni-containing catalysts showed considerable increase in turnover frequency (TOF) for all samples compare to commonly used Reney type nickel. Increase in TOF can be subscribed to appropriate increase of active metal surface concentration. Beside, some increase in catalyst selectivity to sorbitol took place. Considerable improvement of selectivity to sorbitol can be explained by increasing of desired D-glucose hydrogenation reaction rate, while reaction rate of D-glucose isomerization process to D-fructose remain the same. The achieved TOF for most active catalyst was found to be 0.27 s$^{-1}$ and catalysts selectivity to D-sorbitol 98%.***

**Key words:** Ni-impregnated hypercrosslinked polystyrene, Ni-nanoparticles, D-glucose, D-sorbiotol, hydrogenation

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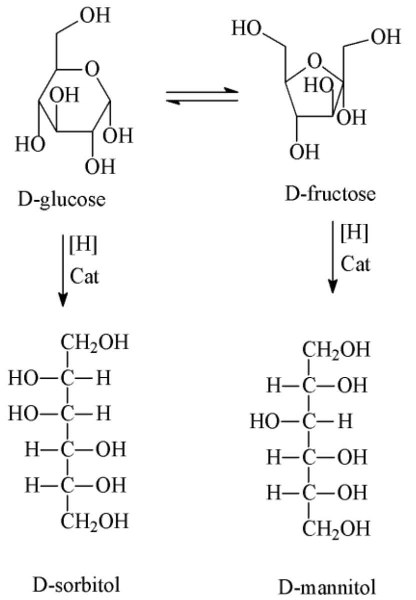
## INTRODUCTION

Catalytic hydrogenation of mono and disaccharides is significant industrial processes used for fine chemicals production [1-7]. D-glucose hydrogenation is one of the most important and typically applies for D-sorbitol synthesis, which is widely used as sweetener, food additive and fuel compound [8-11]. Typically D-glucose transforms in to D-sorbitol (Scheme) with high selectivity [12-15], however formation of mannitol as a side product can take place during hydrogenation process [16]. However, process selectivity strongly depends on reaction conditions and catalysts morphology [1, 12]. Therefore, catalyst properties are in focus of scientific community for this reaction [5, 17].



Scheme. Scheme of D-glucose catalytic hydrogenation
Схема. Схема каталитического гидрирования D-глюкозы

Industrially D-glucose is catalytically hydrogenized over Ni-Reney type catalyst [1, 2, 4, 9, 10, 18], Ni leaching and low catalyst activity and selectivity can be considered as main disadvantage of Reney type catalysts [6, 7, 14, 19]. However, there are a lot of scientific reports on application of modified [1, 2, 7, 19] Ni based catalysts, other transition state metal catalysts [6, 11] and noble metal based catalysts [3, 8, 10, 12, 17, 20-24] for D-glucose selective hydrogenation to D-sorbitol. Wang at. all [24] reported synthesis of Ru–B amorphous alloy deposited on mesoporous silica nanospheres with high active sites densities and tested synthesized samples in D-glucose hydrogenation. Silica nanospheres surface modification with amino groups [24] favor increasing the surface active sites density that results in considerable increase in D-glucose conversion. Romario at. all showed [23] an attempt to synthesize Ru lattice on the surface of Ni nanoparticles impregnated in MCM-48 zeolite. As a result, large Ru lattice was synthesized on the surface of large Ni nanoparticles with mean diameter of 17-20 nm. However, some increase in catalysts activity take place [23]. Perrad et. all [13] reported improving the Pt supported on activated carbon cloth activity in case of partial carbon modification by oxidation, that results in some increase in a metal dispersion. However, partial oxidation of carbon results in appropriate decrease in carbon cloth mechanical properties [13]. Mishra et.all [25] showed direct influence of applied catalysts synthesis methods on Ru dispersion and therefore on catalyst activity in D-glucose hydrogenation process. Synthesis of Ru based catalysts using micro pores zeolite, results in formation of highly dispersed Ru nanoparticles. One more approaches for synthesis of efficient catalysts for D-glucose hydrogenation is to use polymer matrix characterized by high surface area to be a template for active metal nanoparticles formation [16, 26, 27]. Interesting example was reported by Grygoriev at. all [15]. In his work synthesis of Ru nanoparticles for application in D-glucose hydrogenation was performed using hypercrosslinked polystyrene. As a result, sufficient Ru dispersion was achieved. However, theoretical calculations show that active metal dispersion even in this case can be increased at list in two times leading to formation of small nanoparticles with mean diameter of 0.4-0.6 nm.

Therefore, development of efficient catalysts applicable for wide industrial application is of a great value for scientific and engineering community. Development of more efficient catalysis can be based on increasing the active sites densities, synthesis of new more efficient or selective active sites for providing reaction and joint approach. Here a study of Ni impregnated hypercosslinked polystyrene and its testing in D-glucose catalytic hydrogenation is reported. Different methods for increasing the active sites surface densities are discussed.

## EXPERIMENTAL PART

### *Materials and methods*

Catalysts synthesis was provided using following materials: hypercrosslinked polystyrene (HPS) – MN270 (Purolite Inc.), $Ni(Ac)_2$ (reagent grade, 99.5 wt. %), NaCl (reagent grade, 99.9 wt. %), $H_2O_2$ (reagent grade, 20 wt. % water solution), gas phase hydrogen (99.5 wt.%), gas phase ammonia (10 wt.% in nitrogen), glucose monohydrate (96.2 wt.% of glucose) were purchased from local supplier and used as is. Ni-Reney catalysts was purchased from Redkino catalytic plant and used as received. Deionized water was purified using Milli-Q system.

### *Hypercrosslinked polystyrene modification*

To increase hypercrosslinked polystyrene hydrophilic surface properties polymer samples were modified using hydrogen peroxide, chlorine and ammonia.

### *Hypercrosslinked polystyrene modification with hydrogen peroxide*

Hypercrosslinked polystyrene sample of 20 g was suspended in 200 ml of hydrogen peroxide solution at 100 °C in round bottom flask equipped with reflux for five hours. Then suspension was filtered through Shott filter and dried under vacuum. Samples of hydrogen peroxide for modification of hypercrosslinked polystyrene were designated as HPS-Ox.

*Hypercrosslinked polystyrene modification with chlorine*

Chlorination of hypercrosslinked polystyrene sample (20 g) was provided in glass tube heated to 200 °C. Tube was connected to electrolizer, were NaCl solution was hydrolase to obtain chlorine for synthesis. The upper part of glass tube was connected to flask filled with sodium hydroxide solution to neutralize chlorine. Hypercrosslinked polystyrene modification was provided for two hours, then set up was cooled down to ambient temperature. HPS sample was washed at Shott filter and dried under vacuum. Samples of chlorine modified hypercrosslinked polystyrene were designated as HPS-Cl.

*Hypercrosslinked polystyrene modification with ammonia*

To provide hypercrosslinked polystyrene surface modification with ammonia chlorinated sample of hypercrosslinked polystyrene (20 g) was imputed in in glass tube and heated under ammonia to 200 °C. Glass tube was connected to flask filled with sulfuric acid solution to neutralize ammonia. Hypercrosslinked polystyrene modification was provided for two hours, then reaction tube was cooled down to ambient temperature. HPS sample was washed at Shott filter and dried under vacuum. Samples of ammonia modified hypercrosslinked polystyrene were designated as HPS-N.

*Catalysts synthesis*

Ni-based catalysts with theoretical 25 wt.% Ni loading were synthesized using modified and unmodified hypercrosslinked polystyrene. In typical synthesis 10 g of $Ni(Ac)_2$ was dissolved in 200 ml of deionized water and 10 g of hypercrsosslinked polystyrene was added to solution. Suspension was evaporated under vacuum in rotax and was dried under air. After drying samples were reduced by hydrogen in glass tube at 300 °C for six hours, cooled to ambient temperature under nitrogen and stored under nitrogen.

*Physicochemical characterization of synthesized catalyst samples*

Determination of Ni surface concentration and modified HPS surface acidity and basicity was provided using Chemosorber 4580 (Micromerics, USA). In typical analysis 0.5 g of catalyst sample was placed in quartz cuvette, than sample was heated up to 300 °C under hydrogen (10 v.%) in argon, ammonia or carbon dioxide (10 v.%) in argon with gas volumetric flow of 10 ml/min. Then sample was cooled down to ambient temperature, gas flow was switched to argon and sample was again heated up to 300 °C. Hydrogen, ammonia and carbon dioxide desorption curves were recorded by thermal conductivity detector, which data was converted to desorbed gas volume by preliminary made calibration curves.

Specific surface volumes and areas of developed catalysts were calculated using t-plot model using low temperature nitrogen desorption curves by Beckman coulter (USA). For typical analysis, 0.1g of catalyst sample was placed in analytical cell and was flashed with helium for 30 min under heating to 300 °C. After sample cooling nitrogen was input in cell for physisorption. Quantity of adsorbed nitrogen was determined by pressure drop in analytical cell.

Determination of Ni surface oxidation state was performed using X-ray photoelectron spectroscopy (XPS). XPS spectra were collected using ES 2403 M-T electron spectroscope, MgKα (hν = 1253.6 eV) electron source with 200 W power was used for analysis. Electron spectra were collected under vacuum not lower than $10^{-8}$ Pa with preliminary samples degassing.

Ni loading was determined by X-ray fluorescence analysis (XFA) using Spectroscan Max (Spectron, Russia) at 60 kV and 40 mA with a Mo anode, LiF crystal analyzer and SZ detector. Method is based on measuring the intensity of the X-ray fluorescent radiation of the elements. Fluorescent radiation is excited by the primary radiation of an X-ray tube. Intensity of fluorescent radiation is determined by registration system of this. Based on external standards preliminary made calibration curves were used for Ni concentration determination.

*Ni-impregnated samples catalytic properties determination*

A catalyst sample (6 g) was introduced into the autoclave through a side fitting (Fig. 1, point 1), than 50 ml of distilled water was fed through the loading chamber (Fig. 1, point 6). A solution of D-glucose was poured into the loading chamber (Fig. 1, point 6) equipped with the locking needle. The overall volume of the liquid fraction was 62 ml. D-glucose reaction initial concentration was 1.8 mol/l. The reactor was sealed and purged three times with nitrogen and hydrogen. The hydrogen pressure (40 Bar) was controlled by the reducer. Then autoclave was heated with a thermostat to the 160 °C temperature. The resulting excess of hydrogen was carefully vented. Then shaker system of the reactor was switched on for catalyst saturation with hydrogen for one hour. After 1 h catalyst saturation with hydrogen shaker was stopped, the D-glucose solution from the loading chamber (Fig. 1, point 6) was introduced into the autoclave by raising the locking needle. In typical experiments, several samples were taken for analysis. The amount of products formed was determined by HPLC.

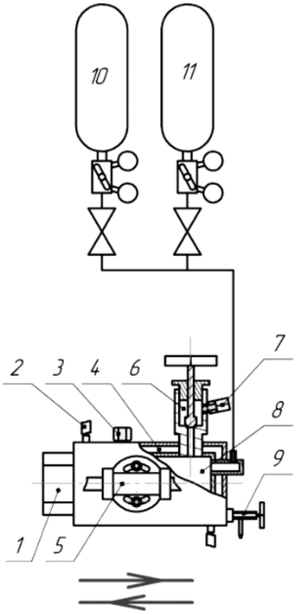


Fig. 1. Reaction set-up for D-glucose catalytic hydrogenation process: 1 – inlet for catalyst input, 2 – fitting for inlet of thermostatic fluid, 3, 7 – purge valve, 4 – thermostat shirt, 5 – attachment unit, 6 – pretreatment chamber, 8 – reaction chamber, 9 – sample valve, 10 – hydrogen tank, 11 – nitrogen tank

Рис. 1. Установка реакции для процесса каталитического гидрирования D-глюкозы: 1-вход для ввода катализатора, 2-фитинг для ввода термостатической жидкости, 3, 7-продувочный клапан, 4-рубашка термостата, 5-узел крепления, 6-камера предварительной обработки, 8-реакционная камера, 9-пробоотборный клапан, 10-бак для водорода, 11-бак для азота

### *Reaction media analysis by high performance liquid chromatography*

Analysis of reaction media for monosaccharides and polyols was performed using high performance liquid chromatograph (HPLC, Chromatech Kristall VGH 2014, Russia) equipped with refractive index detector and column field with Reprogel-H column (Dr. Maisch Gmbh, Germany) characterized by 500 mm lengths, 10 mm diameter and theoretical plates number 40000. Typical analysis was performed under following conditions: eluent – 9 mM solution of $H_2SO_4$, eluent volume flow is 0.5 ml/min, column temperature is 25 °C, eluent pressure is 2MPa, analysis duration is 40 min. Qualitative identification of formed substances was carried out using external standards of pure substances. For HPLC analysis, samples 0.5 ml reaction media was filtered through syringe filter into vial.

## RESULTS AND DISCUSSIONS

Modification of HPS samples with hydrogen peroxide and chlorine results in increase of surface acidity (Fig. 2). Modified HPS samples with hydrogen peroxide and chlorine are characterized by weak chemisorption peaks of ammonia (Fig. 2). HPS sample modified with ammonia is characterized by weak chemisorption peal of carbon dioxide in the range of 130-180 °C. Initial HPS sample shows considerable low surface acidity of 0.02 μmol($NH_3$)/g(HPS), modification of HPS by hydrogen peroxide results in appropriate increase in a surface acidity up to 0.27 μmol($NH_3$)/g(HPS). Modification of HPS by chlorine results in increase of surface acidity up to 0.62 μmol($NH_3$)/g(HPS) (Fig. 2). For HPS modified with ammonia some increase in surface basicity from 0.01 μmol($CO_2$)/g(HPS) up to 1.25 μmol($CO_2$)/g(HPS) was noticed.

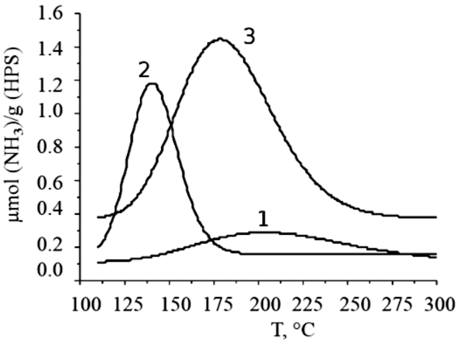


Fig. 2. Ammonia desorption curves for modified and unmodified HPS:1 – initial HPS, 2 – HPS-Ox, 3 – HPS-Cl

Рис. 2. Кривые десорбции аммиака для модифицированного и немодифицированного HPS: 1 - исходный HPS, 2 - HPS-Ox, 3 - HPS-Cl

Synthesized Ni based catalysts are characterized by comparable Ni loading varying from 20.1 wt.% to 23.2 wt.% (Table 1). Some increase in Ni loading can be connected with a presence of surface-active groups in case of modified hypercrosslinked polystyrene application. Mesopores surface area decrease from 126 $m^2$/g to 69 $m^2$/g (table 1) in case of surface modified hypercrosslinked polystyrene.

The same phenomenon is visible for micropores surface area change for modified and unmodified hypercrosslinked polystyrene. Decrees in surface area can be connected with the increase in nanoparticles quantity in a case of HPS surface modification, that can be approved by increase in accessible active metal quantity from 0.064 mmol($H_2$)/g(Cat) up to 0.0121 mmol($H_2$)/g(Cat).

Study of Ni oxidation state showed the partial reduction of nickel acetate in hydrogen atmosphere for all samples. Initial HPS-Ni-25% sample (Fig. 3a) contained nickel acetate in HPS matrix while after reduction of sample with hydrogen (Fig. 3a) presence of nickel oxides, nickel oxyhydroxide and metallic nickel take place.

***Table 1***

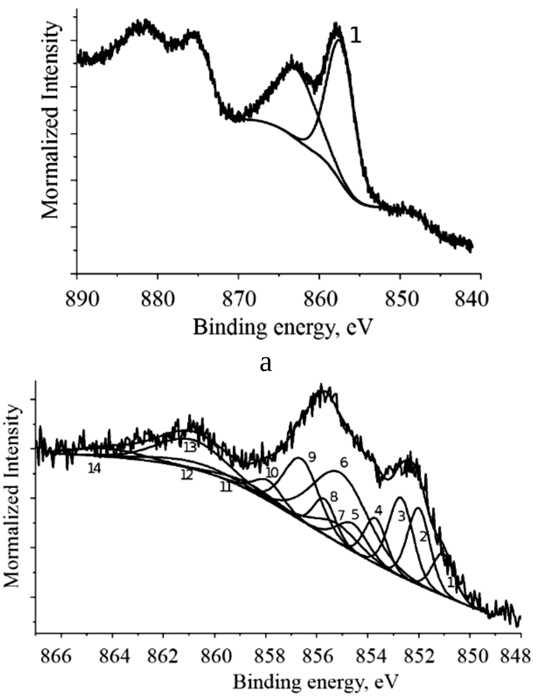
***Physicochemical characteristics of synthesized catalysts***

***Таблица* 1. Физико-химические характеристики синтезированных катализаторов**

| Sample | Ni wt.% | Surface area, $m^2/g^*$ | | $H_2$ chemisorption, $mmol(H_2)/g(Cat)$ |
|---|---|---|---|---|
| | | Mesoporous | micropores | |
| HPS-Ni-25% | 20.1 | 126 | 415 | 0.064 |
| HPS-Ox-Ni-25% | 21.6 | 108 | 386 | 0.087 |
| HPS-Cl-Ni-25% | 22.8 | 84 | 315 | 0.092 |
| HPS-N-Ni-25% | 23.2 | 69 | 224 | 0.121 |

Note: * - t-plot model

Примечание: * t-модель



a

b

Fig. 3. XPS spectra of HPS-Ni-25% sample a) initial, b) after reduction 1,2,3,11 – Ni ; 4,7,12 – NiO; 5,6,8,9 – γ-NiOOH; 10,13,14 – β-NiOOH

Рис. 3. ЕСХА спектры HPS-Ni-25% образца а) исходного, b) после восстановления 1,2,3,11 - Ni; 4,7,12 - NiO; 5,6,8,9 - γ-NiOOH; 10,13,14 - β-NiOOH

Catalytic hydrogenation of D-glucose over synthesized Ni-containing catalysts showed considerable increase in turnover frequency (TOF, Table 2) for all samples compare to commonly used Reney type nickel. Increase in TOF can be connected with the appropriate increase in active metal surface concentration (Table 1). Beside, some increase in a catalyst selectivity to sorbitol took place (Table 2). Considerable improvement of selectivity to sorbitol can be explained by increasing desired D-glucose hydrogenation reaction rate (Scheme 1), while reaction rate of D-glucose isomerization process to D-fructose remain the same.

***Table 2***

**Catalytic properties of synthesized samples in D-glucose hydrogenation***

***Таблица 2.* Каталитические свойства синтезированных образцов при гидрировании D-глюкозы***

| Sample | TOF, $s^{-1}$ | Selectivity to D-sorbitol | Selectivity to D-mannitol |
|---|---|---|---|
| Ni-Reney | 0.09 | 91 | 9 |
| HPS-Ni-25% | 0.10 | 93 | 7 |
| HPS-Ox-Ni-25% | 0.11 | 95 | 5 |
| HPS-Cl-Ni-25% | 0.14 | 96 | 4 |
| HPS-N-Ni-25% | 0.27 | 98 | 2 |

Note: * - t=160 °C, C(D-glucose)=1.8 mol/l, m(Cat)=6 g, $p(H_2)$=40 Bar

Примечание: * - t = 160 °C, C(D-глюкоза) = 1,8 моль/л, m(кат) = 6 г, р ($H_2$) = 40 бар

## CONCLUSIONS

Synthesis of Ni polymer based catalysts characterized by high surface concentration of surface-active metal is described. Typically hypercrosslinked polystyrene is characterized by high hydrophobicity of polymer surface, therefore simple impregnation is inapplicable especially for high concentration of active metal over polymer surface. To solve this problem surface of hypercrosslinked polystyrene was modified by hydrogen peroxide, surface chlorine and ammonia. This modification results in appropriate increase of nickel surface concentration without change in catalyst synthesis methodology. The increase in active metal surface concentration results in the increase of D-glucose catalytic hydrogenation turnover frequency and selectivity to D-sorbitol. The process selectivity to D-sorbitol is tightly connected with reaction rates of D-mannitol side reaction. In the case of high surface concentration of active metal a direct reaction of D-glucose transformation to D-sorbitol is prevail while side reaction of D-mannitol formation is partially suppressed. The achieved TOF for most active catalyst was found to be 0.27 s$^{-1}$ and catalysts selectivity to D-sorbitol 98%.

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