Evaluation of D-glucose hydrogenation catalysts stability in different reactor systems

V. DOLUDA[1], M. GRIGOREV[1], V. MATVEEVA[1], E. SULMAN[1], M. SULMAN[1], N. LAKINA[1],
V. MOLCHANOV[1], E.V. REBROV[1,2]
[1]Department of biotechnology and chemistry
Tver State Technical University
A.Nikitin Str., 22, 170026, Tver
RUSSIA
[2]School of Engineering
University of Warwick
Coventry CV4 7AL
UK
* matveeva@science.tver.ru

Abstract: D-glucose catalytic hydrogenation to D-sorbitol can be considered a promising step in cellulose feedstock transformation technology to fuel components and valuable chemicals. Traditionally D-glucose is hydrogenated in bath reactor systems using Ru, Ni, Pd impregnated over different organic and inorganic supports. The samples of ruthenium impregnated in hypercrosslinked polystyrene and activated carbon were tested in D-glucose hydrogenation using butch reactor, shaker type reactor and fix bed reactor system to evaluate catalysts long term stability. Catalysts were characterized by nitrogen physisorption, X-Ray photoelectron spectroscopy, hydrogen chemisorption, X-Ray fluorescence analysis. Physicochemical changes of the studied catalysts are shown during catalysts stability investigation. A strong influence of the reactor type on catalysts stability in D-glucose hydrogenation is discussed.

Key-Words: glucose, sorbitol, hypercrosslinked polystyrene, Ru, stability

1 Introduction

D-glucose catalytic hydrogenation to D-sorbitol can be considered a promising step in cellulose feedstock transformation technology to fuel components and valuable chemicals [1-3]. Beside D-sorbitol has wide application in food, nutrition and chemical industries. Traditionally D-glucose is hydrogenated in bath reactor systems using Ru, Ni, Pd impregnated over different organic and inorganic supports [2-13]. Catalysts based on active metals incorporated in different type of carbon supports are more are selective compare to catalysts based on oxide type supports [5, 14-16]. However catalytic hydrogenation of D-glucose is characterized by the formation of numerous side products such a D-mannitol, gluconic acid (Fig. 1)[3, 4, 10, 14, 17, 18]. The formation of side products results in appropriate decrease of the process selectivity.

Catalyst deactivation can be considered as a key parameter for D-glucose hydrogenation process[6]. There are several possible ways for catalyst deactivation that can be divided into following groups: a) blockage of the catalyst active surface with different adsorbed substances (carbon, polymers, carbon monoxide and dioxide etc.), b) leaching of the catalysts active phase, c) active phase sintering and migration d) change of the catalysts active phase structure, e) mechanical catalysts abrasion [19]. 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 Ru based catalysts are described in the article.

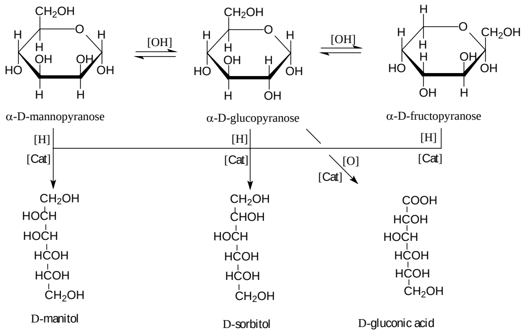


Fig. 1 Scheme of the reactions flowing during D-glucose hydrogenation

2 Experimental

2.1 Materials

Reagent grade hydrogen of 99.99% purity, sodium hydrogen carbonate ($NaHCO_3$), reagent-grade THF, methanol activated carbon (designated as ACC), glucose, sorbitol, maltose, maltitol, gluconic acid, acetone were purchased from local supplier and were used as received. Ruthenium hydroxychloride ($Ru(OH)Cl_3$) was purchased from Aurat Ltd (Moscow, Russia). The distilled water was purified with Aqua post water purification system. Hypercrosslinked polystyrene (HPS) was purchased from Purolite Int. (U.K.), as Macronet MN 100. 1-2 mm polymer and ACC granules were washed with acetone and water twice and dried under vacuum for 24 h.

2.2 Catalyst synthesis

Prior to the catalyst synthesis ACC and HPS samples were grinded and fraction 0.12 mm was taken for preparation. Carbon and HPS based catalysts were prepared by the impregnation of supports with ruthenium hydroxychloride in a complex solution. The complex solution consisted of 5 mL of THF, 1 mL of water and 1 mL of methanol. In a typical synthesis, 0.21 g $Ru(OH)Cl_3$ was dissolved under nitrogen into 7 mL of a complex solvent, to which 3 g of ACC or MN-100 were added. The suspension was continuously stirred for 10 min to allow the adsorption of the solution by the support, which was then dried at 75 °C for 1 h. The catalysts were reduced in hydrogen for 3 hours at 300^0C. Ru content was found to be 2.9 and 2.85 wt % for ACC and HPS based catalysts by XRF elemental analysis. Samples were designated as HPS-Ru-3%, ACC-Ru-3% (Table 1).

2.3 Glucose hydrogenation methodology

D-glucose hydrogenation in batch reactor equipped with impeller mixer.

The hydrogenation was conducted batchwise in Parr 4561 autoclave (Fig 2). The reactor was equipped with a heating jacket and a bubbling chamber (for the removal of the dissolved air from the liquid phase and for the saturation of the liquid phases with hydrogen prior to hydrogenation experiments).

The effective liquid volume was 50 ml (total volume 75 ml). The reactor was equipped with impeller to ensure efficient mixing and gas dispersion into the liquid phase. The reactor was operated at hydrogen pressure 4 MPa and temperature 120 °C. The catalysts concentration was 2 g/l. The glucose concentration was 50 wt%. The suspension of the catalyst (5 mL) prepared at a predetermined concentration was placed in the reactor. A glucose solution (45 mL) saturated with hydrogen in the bubble chamber was rapidly fed into the reactor and the hydrogen pressure and reactor temperature were immediately adjusted to the experimental conditions. The impeller rate was fixed at 600 rpm in all of kinetic experiments to ensure operation in the kinetically controlled regime. The median particle size of HPS based catalyst was 1-2 mm as well as for activated carbon catalysts. After the reaction the substrate was centrifuged from the catalysts and then were washed with water and weighted.

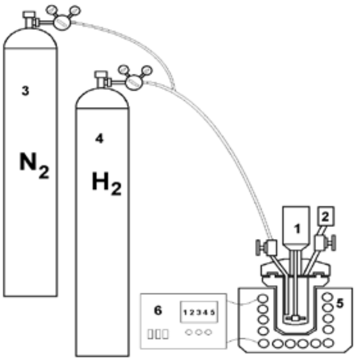


Fig. 2. Reactor set up for D-glucose hydrogenation in a batch reactor equipped with an impeller mixer. (1 – reactor, 2 - bubbling chamber, 3 – balloon with nitrogen, 4 – balloon with oxygen, 5 - a heating jacket, 6 – thermocontroller)

D-glucose hydrogenation in a shaker type reactor.

The periodic catalytic tests of D-glucose hydrogenation were provided in a thermostatic reactor autoclave (Fig. 3) installed over the reciprocating mechanism equipped with electric motor and electronic system for maintaining the shaking rate. The rector consists of the main chamber, saturation chamber, heating jacket, sampling valves, and gas inlet unit. The overall main chamber volume was 100 cm^3, the volume of saturation chamber was 25 cm^3. The catalyst suspension of 10 ml in water is flashed with nitrogen four times and then the catalyst is reduced by hydrogen for 2 hours at 120^0C and 4 MPa of hydrogen. D-glucose solution is placed in to the saturation chamber, flashed with nitrogen four times and then with hydrogen. The saturation is provided at 120^0C and 40 MPa of hydrogen for two hours. After finishing the catalysts reduction and D-glucose solution saturation the bypass valve is opened and two chambers are connected to each other. The mixing rate of 300 double two side shakings is maintained during the reaction. After the reaction the catalysts suspension was taken to the centrifugation for the catalysts regeneration. The rotor speed was maintained 6000 rpm, and the centrifugation was provided for 30 minutes.

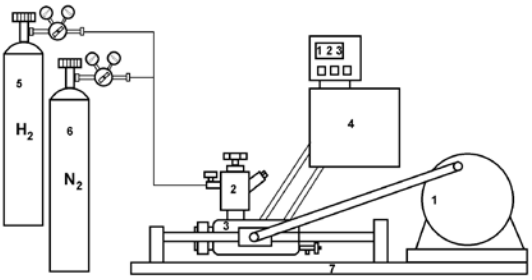


Fig. 3. Reactor set up for D-glucose hydrogenation in a shaker reactor. (1 – reciprocating mechanism, 2 - saturation chamber, 3 – reactor, 4 – thermostat, 5 – balloon with hydrogen, 6 – balloon with nitrogen)

D-glucose hydrogenation in a fix bed reactor.

The hydrogenation was conducted in a specially constructed set up (Fig. 4). The set up consists of 2 cm^3 fix bed stainless tube reactor with liquid preheater, gas-liquid mixer, liquid pump and gas-liquid separator. The reactor was heated with thermostat. Hydrogen pressure was maintained with reducer at 4 MPa. The reactor was operated in down flow, fixed bed regime, liquid hourly space velocity (LHSV) = 30 h^{-1}. The glucose solution 50 wt% was purged with nitrogen to decrease oxygen content. The temperatures were maintained at 120±0.5^{0}C. The reaction media samples were taken once an hour. Catalyst bed height was 10 cm.

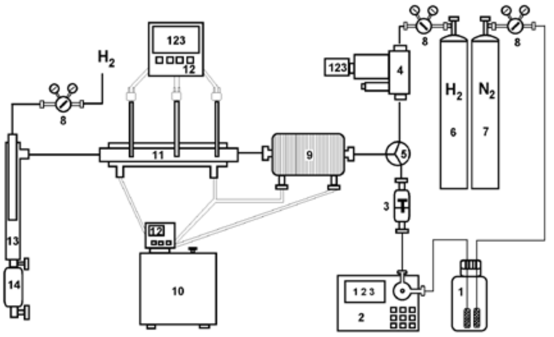


Fig. 4. Reactor set up (1-flasc with glucose solution, 2 – HPLC pump, 3 – back pressure valve, 4 – mass flow controller, 5 – mixer, 6 – balloon with hydrogen, 7 – balloon with nitrogen, 8 – pressure reducer, 9 – preheater, 10 – thermostat, 11 – tube reactor, 12 – thermocontroller, 13 – flow separator, 14 – sample tube)

2.4 Analysis

HPLC analysis

The analysis of the reaction media was performed using ULTIMATE 3000 HPLC chromatograph equipped with an IR detector. Ion exchange a 250×4 mm tungsten column produced by Dr. Maish was used for analysis. H_2SO_4 (1 mM) in deionized water was used as a mobile phase. The flow rate was kept constant at 0.5 $mL.min^{-1}$ at 30 °C. The concentrations of glucose, sorbitol, maltitol, gluconic acid were determined using standards and calibration curves.

X-Ray fluorescence analysis

XFA measurements were done to determine Ru concentration using Spectroscan – Maks – GF1E spectrometer (Spectron, St-Petersburg, Russia) equipped with Mo anode, LiF crystal analyzer and SZ detector. The analyses were based on the Co Kα line. A series of Ru standards was prepared by mixing 0.1-0.2 g of matrix with 10-20 mg of standard Ru compounds.

Liquid nitrogen physisorption

Nitrogen physisorption analysis was conducted at the normal boiling point of liquid nitrogen using Beckman Coulter SA 3100 apparatus (Coulter Corporation, USA). Prior to the analysis, samples were degassed in Becman Coulter SA-PREP apparatus for sample preparation at 120 °C in vacuum for 1h.

X-ray photoelectron spectroscopy analysis

XPS data were obtained using Mg Kα ($h\nu$ =1253.6 eV) radiation with ES-2403 spectrometer modified with analyzer PHOIBOS 100 produced by SPECS (Germany). All the data were obtained at an X-ray power of 200 W and an energy step of 0.1 eV. The samples were allowed to outgas for 180 min before the analysis and were sufficiently stable during the examination. The data analysis was performed by CasaXPS. Deconvolution of Ru based catalysts was made by simultaneous fitting of Ru 3p and C1s+Ru 3d energy levels.

Chemisorption

The dispersion and the mean diameter of the ruthenium nanoparticles were measured by hydrogen chemisorption. Micromeritics AutoChem 2910 was used in the measurements. Prior to the analysis the samples were purged in-situ at 300 °C for 2 h in a continuous flow of Ar. Thereafter the temperature was decreased to 25 °C. Pulses of hydrogen (10% H_2 in Ar) were introduced in to the sample and the amount of non-sorbed hydrogen was measured. A ratio of H_2:Ru = 2 was used in the calculations.

3 Results and discussion

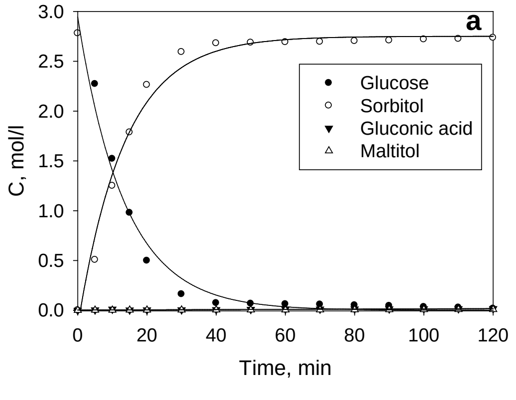
Initial catalysts characterization results. The synthesized catalysts are characterized by large surface areas typical for micro-mesoporous materials (Table 1). Active metal dispersion is 32% and 28% for ACC-Ru-3% and HPS-Ru-3% samples. The dispersion values correspond to particle sizes between 2-5 nm for ACC-Ru-3% and 2-8 nm for HPS-Ru-3%. Ru is mainly presented in the +4 oxidation state in the form of ruthenium oxide.

Table 1 Initial catalyst characteristics

Catalysts characteristics	ACC-Ru-3%	HPS-Ru-3%
Surface area, m^2/g	720	810
Granulometric composition, mm	0.1-0.14	0.1-0.14
Nanoparticles size, nm	2-5	2-8
Ru oxidation state	Ru^{+4}	Ru^{+4}
Ru concentration, w %	2.9	2.85
Ru dispersion, %	32	28

D-glucose hydrogenation in batch reactor equipped with impeller mixer

Initial catalysts activity for HPS-Ru-3% and ACC-Ru-3% samples was very similar and found to be 120 and 125 kg(Glu)/(kg(Cat)*h) at 99.3-99.6% D-glucose conversion, process selectivity to sorbitol was found to be 97.6-97.8% for both catalysts (Fig. 5). Gluconic acid and maltitol are found in traces during the analysis and can be considered as main side products (Fig. 5).



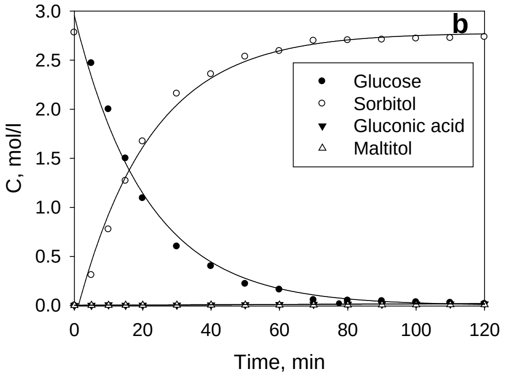


Fig. 5. D-glucose catalytic hydrogenation curve over a) ACC-Ru-3%, b) HPS-Ru-3% (t=120^0C, p(H_2)=4 MPa, C(Glu)=50 wt%, C(Cat)=2 g/l)

The investigation of the catalysts long term stability showed that after 10 reaction cycles of 2 hours hydrogenation the ACC-Ru-3% and HPS-Ru-3% catalysts were ground by a reactor mixer therefore catalysts particles diameter becomes smaller than 0.01-0.07 mm and 0.1-0.11 mm (Table 2). Besides the catalysts mechanical losses were calculated to be 78% and 44% for ACC-Ru-3% and HPS-Ru-3% samples, the catalyst weight losses can be attributed to the catalysts particles grinding and losses during the centrifugation and separation [20]. The catalysts activity after 10 cycles of D-glucose hydrogenation showed a little slow down and was calculated to be for HPS-Ru-3% and ACC-Ru-3% samples 110 and 112 kg(Glu)/(kg(Cat)*h) at 99.4-99.5% D-glucose conversion. Some losses of catalysts activity can be attributed to metal leaching. However some increase in Ru dispersion is noticed that can be also explained to the catalyst particles grinding and particles transformation during D-glucose hydrogenation. The oxidation state of active metal according to XPS data remains +4 and Ru is mainly presented in the oxide form. It should be noted that providing D-glucose hydrogenation in the reactor equipped with impeller mixer results in high mechanical losses therefore the catalysts overall time on steam was only 20 h, that is insufficient for the study of metal leaching, poising and nanoparticles transformation.

Table 2 Catalysts characteristics after 10 repeated reaction cycles in batch reactor equipped with an impeller mixer

Catalyst characteristics	ACC-Ru-3%	HPS-Ru-3%
Surface area, m^2/g	800	920
Granulometric composition, mm	0.01-0.07	0.1-0.11
Nanoparticles size, nm	2-4	2-7

Ru oxidation state	Ru^{+4}	Ru^{+4}
Ru concentration, w %	2.89	2.84
Ru dispersion, %	33	30
Sample mass losses, %	78	44

D-glucose hydrogenation in a shaker type reactor

D-glucose hydrogenation over HPS-Ru-3% and ACC-Ru-3% samples in a shaker type reactor results in the increase in the of reaction rate up to 135 and 139 kg(Glu)/(kg(Cat)*h) at 99.5-99.7% D-glucose conversion, process selectivity to sorbitol was higher and was found to be 98.1-98.2% for both catalysts. The gluconic acid and maltitol were noticed in traces, however the concentration of side products are lower compared to the reaction conducted in the batch reactor equipped with impeller mixer. The increase in the reaction rate can be explained by a better mass transfer in case of a shaker type reactor. Nitrogen physisorption showed that some catalysts surface area increase (Table 3). D-glucose hydrogenation in a shaker type reactor compare to D-glucose hydrogenation in a bath reactor with an impeller mixer results in lower catalysts mass losses and lower catalysts grinding. According to XPS data Ru species are presented in Ru^{+4} oxide form.

Table 3 Catalysts characteristics after 10 repeated reaction cycles in a shaker type reactor

Catalyst characteristics	ACC-Ru-3%	HPS-Ru-3%
Surface area, m^2/g	782	915
Granulometric composition, mm	0.06-0.1	0.1-0.12
Nanoparticles size, nm	2-5	2-8
Ru oxidation state	Ru^{+4}	Ru^{+4}
Ru concentration, w %	2.9	2.84
Ru dispersion, %	32	29
Sample mass losses, %	52	31

D-glucose hydrogenation in a fix bed reactor.

The evaluation process in a fixed bed reactor showed that initial D-glucose hydrogenation rate is lower compared to batch or shaker type reactor (Table 2-3, Fig. 6), this can be attributed to diffusion limitations [19]. Initial D-glucose hydrogenation rate over HPS-Ru-3% and ACC-Ru-3% was found to be 27.2 and 27.5 kg(Glu)/(kg(Cat)*h) at 99.7% D-glucose conversion, the process selectivity to sorbitol was higher and was found to be 98.6% for both catalysts. However catalysts showed rather high stability, overall time on steam was 1008 hours, deactivation rate was found to be 0.31% of the initial activity per day for ACC-Ru-3% and 0.17% of the initial activity per day for HPS-Ru-3% (Fig. 6). It should be noted that the catalysts activity becomes the same at 300th h on steam for both catalysts due to lower deactivation rate of HPS-Ru-3% sample. Afterwards HPS-Ru-3 shows higher activity compared to ACC-Ru-3% sample (Fig. 6).

It is possible to see the decrease of the catalysts surface area for both catalysts however the decrease of the surface area for HPS-Ru-3% sample is not so high compared to ACC-Ru-3% (Table 4). The decrease of the surface area can be attributed to the pores blockage with oligosaccharides that can be formed during the reaction. The granulometric composition of the studied catalysts decreased a little during D-glucose catalytic hydrogenation. This decrease can be explained by the catalyst granules self-grinding, however self-grinding rate is rather low compared to the catalysts ground by a reactor impeller mixer. This also explains rather small catalysts mass losses that are only 27% and 12% for ACC-Ru-3% and HPS-Ru-3% samples.

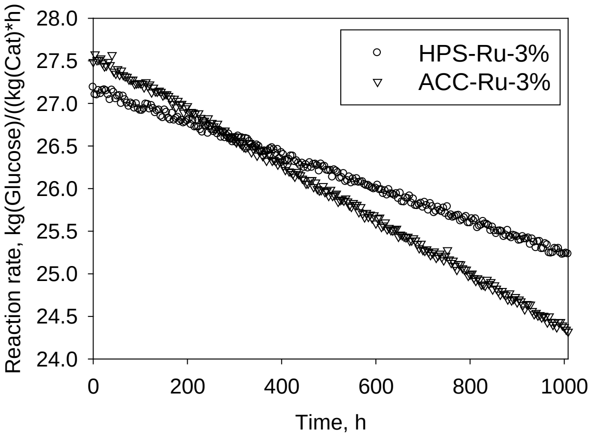


Fig. 6 Synthesized catalysts long term stability

Table 4 Catalysts characteristics of D-glucose hydrogenation in a fixed bed reactor

Catalyst characteristics	ACC-Ru-3%	HPS-Ru-3%
Surface area, m^2/g	610	711
Granulometric composition, mm	0.01-0.12	0.1-0.14
Nanoparticles size, nm	4-16	4-12
Ru oxidation state	Ru^{+4}	Ru^{+4}
Ru concentration, w %	2.3	2.4
Ru dispersion, %	25	27
Sample mass losses, %	27	12

However there is some decrease in the active metal concentration, Ru dispersion and nanoparticle size that can be explained by the active metal leaching and nanoparticles sintering. XPS data showed that Ru remained mainly in the form of ruthenium oxide, meanwhile 0.1 at% of Fe^{+3} and traces of S^{+6} ions was found to adsorbed on the catalysts surface compared to the catalyst before the reaction. The appearance of iron on the catalysts surface can be explained by iron leaching from the reactor surface and the appearance of sulfur can be explained by its adsorption from the reaction solution.

4 Conclusions

The investigation of HPS-Ru-3%, ACC-Ru-3% catalysts stability in different reactor systems shows that the use of common batch and shaker type reactor systems results in high losses of the initial catalysts, due to catalysts grinding on the reactor impeller and reactor walls and during the catalysts separation and washing. Besides providing D-glucose hydrogenation in periodic batch or shaker type reactors results in some decrease in process selectivity due to gluconic acid formation because of oxygen traces. However the initial D-glucose hydrogenation rate in periodic reactor systems is higher compared to a continuous process in a fixed bed reactor, that can be explained by better mass transfer in this systems. D-glucose hydrogenation rate was found to be 110-135 and 112-139 kg(Glu)/(kg(Cat)*h) for over HPS-Ru-3% and ACC-Ru-3% in batch and shaker at 99.5-99.7% D-glucose conversion, the achieved process selectivity to sorbitol was found to be 97-98% for both catalysts. HPS-Ru-3% sample showed lower weight losses in a periodic D-glucose hydrogenation process that can be explained by better mechanical properties of hypercrosslinked polystyrene compare to activated carbon. A continuous D-glucose hydrogenation in fixed bed reactor systems allows to evaluate catalysts long term deactivation. The studied catalysts initial mass losses were very low due to the absence of the milling parts in a reactor system. The calculated deactivation rate was found to be 0.31% of initial activity per day for ACC-Ru-3% and 0.17% of initial activity per day for HPS-Ru-3%. The main reason for the catalysts deactivation in case of continuous D-glucose hydrogenation was found to be leaching of an active phase and adsorption of iron and sulfur ions over the catalysts surface. HPS-Ru-3% sample showed rather high stability during testing compared to ACC-Ru-3% sample.

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