CHEMICAL ENGINEERING TRANSACTIONS

VOL. 52, 2016

A publication of AIDIC

The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Peng-Yen Liew, Jun-Yow Yong, Jiří Jaromír Klemeš, Hon Loong Lam

ISBN 978-88-95608-42-6; **ISSN** 2283-9216

DOI: 10.3303/CET1652113

Ru-containing Catalysts in Hydrogenation of D-glucose in Flow-type Microreactor

Esther M. Sulman*, Valentin Yu. Doluda, Valentina G. Matveeva, Maxim E. Grigorev, Mikhail G. Sulman, Alexey V. Bykov

Tver Technical University, Dep. Biotechnology and Chemistry, A.Nikitina str. 22, 170026, Tver, Russia.
sulman@online.tver.ru

The samples of ruthenium impregnated in hypercrosslinked polystyrene and activated carbon were tested in D-glucose hydrogenation using mini reactror systems. 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 the catalysts stability investigation. A strong influence of the reactor type on the catalysts stability in D-glucose hydrogenation is discussed.

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 (Mishra et al., 2012). Besides 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 (Aho et al., 2015). The catalysts based on active metals incorporated in a different type of carbon supports are more selective compared to the catalysts based on oxide type supports (Aho et al., 2015). However catalytic hydrogenation of D-glucose is characterized by the formation of numerous side products such as D-mannitol, gluconic acid (Figure 1) (Gallezot et al., 2007;). The formation of side products results in appropriate decrease in the process selectivity.

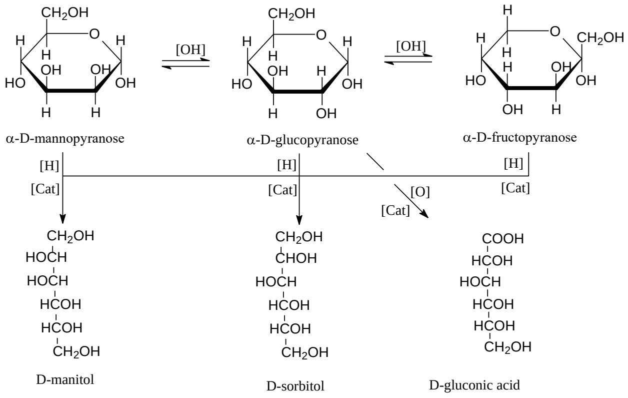

Figure 1: Scheme of the reactions flowing during D-glucose hydrogenation

Catalyst deactivation can be considered a key parameter in D-glucose hydrogenation process (Arena 1992). There are several possible ways of the catalyst deactivation that can be divided into the 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

Please cite this article as: Sulman E. M., Doluda V. Y., Matveeva V. G., Grigorev M. E., Sulman M. G., Bykov A. V., 2016, Ru-containing catalysts in hydrogenation of d-glucose in flow-type microreactor, Chemical Engineering Transactions, 52, 673-678 DOI:10.3303/CET1652113

d) change of the catalysts active phase structure, e) mechanical catalysts abrasion (Worstell 2014). The insight in the catalyst deactivation of 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 paper.

2. Materials and methods

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 ground 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 °C. 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

The hydrogenation was conducted in a specially constructed set up (Figure 2). 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^{-l}. The glucose solution 50 wt. % was purged with nitrogen to decrease oxygen content. The temperatures were maintained at 120±0.5 °C. The reaction media samples were taken once an hour. Catalyst bed height was 10 cm.

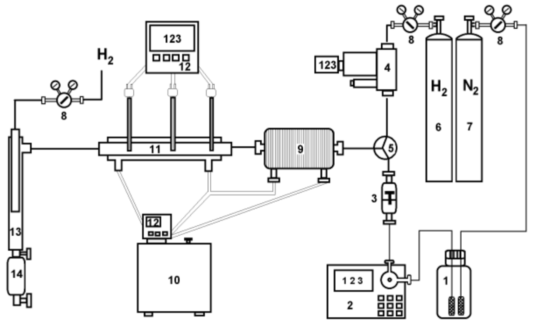

Figure 2: Reactor set-up (1-flasc with glucose solution, 2 – HPLC pump, 3 – back pressure valve, 4 – mass flow controller, 5 – mixer, 6 – balloon with hydrogen, 7 – balloon with nitrogen, 8 – pressure reducer, 9 – preheater, 10 – thermostat, 11 – tube reactor, 12 – thermocontroller, 13 – flow separator, 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 250×4 mm tungsten column produced by Dr. Maish was used for the analysis. H_2SO_4 (1 mM) in deionized water was used as a mobile phase. The flow rate was kept constant at 0.5 $mL\cdot min^{-1}$ 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 CoulterSA 3100 apparatus (Coulter Corporation, USA). Prior to the analysis, samples were degassed in Becman Coulter SA-PREP apparatus for the sample preparation at 120 °C in vacuum for 1 h.

X-ray photoelectron spectroscopy analysis. XPS data were obtained using Mg Kα (*h*ν =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. MicromeriticsAutoChem 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 into the sample and the amount of non-sorbed hydrogen was measured. A ratio of H_2:Ru = 2 was used in the calculations.

*TEM analysis.*TEM of catalysts was performed with a JEOL JEM1010 electron spectroscopic microscope operated at accelerating voltage of 60 kV. Metal-containing HPS powders were embedded in epoxy resin and subsequently microtomed at ambient temperature. Images of the resulting thin sections (*ca*. 50 nm thick) were collected with the Gatan digital camera and analyzed with the Adobe Photoshop software package and the Scion Image Processing Toolkit.

3. Results and Discussion

3.1 Initial catalysts physicochemical 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 catalysts characteristics

Catalyst 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
Mass transfer coefficient, m/s	$0.45*10^{-4}$	$0.32*10^{-4}$

3.2 Investigation of hydrogen pressure influence

Hydrogen pressure influence can be considered a key factor in obtaining high selectivity in glucose hydrogenation. The determination of hydrogen pressure influence was done at a reaction temperature 120 °C and liquid hourly space velocity (LHSV) = 30 h^{-l}. Figure 3 shows the kinetic curves of glucose transformation for HPS-Ru. The increase in hydrogen pressure results in the increase in glucose transformation to sorbitol.

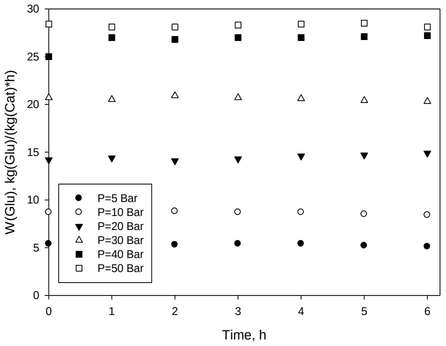

Figure 3: Dependence of glucose conversion rate on reaction pressure

Glucose highest reaction rate was achieved at hydrogen pressure from 10 up to 120 bar, (Figure 3). The average process selectivity to sorbitol is 95 %.

3.3 Investigation of temperature influence

The influence of temperature was studied at hydrogen partial pressure 40 bar, liquid hourly space velocity (LHSV) 30 h^{-l}. The increase in reaction temperature from 110 C up to 150°C results in the increase in glucose hydrogenation (Figure 4). Sorbitol hydrolysis can be considered the main side process at the temperatures higher than 130 °C, when sorbitol begins to accumulate in the reaction mixture.

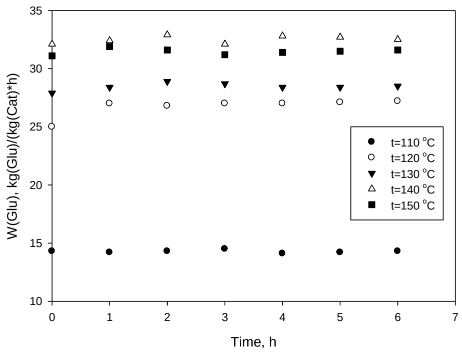

Figure 4: Dependence of glucose conversion rate on the reaction temperature

3.4 Investigation of glucose concentration influence

The study of glucose concentration influence was performed at a temperature 120 °C, P=40 Bar, glucose concentration 0.4-2.4 mol/l. Figure 5 shows the kinetic curves of glucose hydrogenation rate. The increase in glucose concentration results in the corresponding increase in the reaction rate (Figure 5).

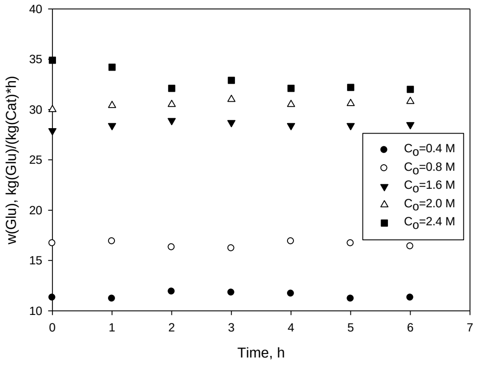

Figure 5: Dependence of glucose conversion rate on initial substrate concentration

3.5 Evaluation of long term stability

The evaluation process in a fixed bed reactor showed that initial D-glucose hydrogenation rate is lower compared to a batch or shaker type reactor (Table 2, Figure 6), this can be attributed to the diffusion limitations (Worstell, 2014). 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 1,008 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% (Figure 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 (Figure 6).

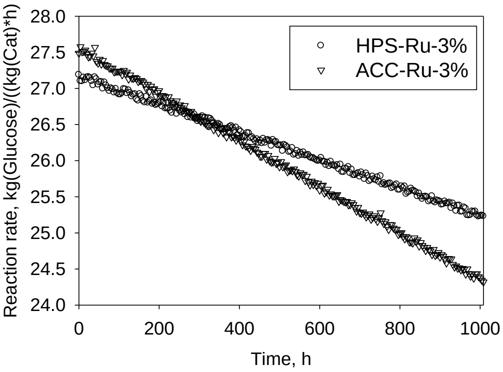

Figure 6: Synthesized catalyst long term stability

It is possible to see the decrease in the catalysts surface area for both catalysts however the decrease in the surface area for HPS-Ru-3% sample is not so high compared to ACC-Ru-3% (Table 2). The decrease in 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 remains the same during D-glucose catalytic hydrogenation.

Table 2: Catalyst 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
Mass transfer coefficient, m/s	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 were found to adsorb on the catalysts surface compared to the catalysts 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 continuous D-glucose hydrogenation in a fixed bed reactor system allows evaluating 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 the initial activity per day for ACC-Ru-3% and 0.17 % of the initial activity per day for HPS-Ru-3%. The main reason for the catalysts deactivation in case of continuous D-glucose hydrogenation was 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.

Acknowledgments

The authors thank the Ministry of Science and Education of the Russian Federation for the financial support.

Reference

Aho A., Roggan S., Simakova O.A., Salmi T., Murzin D.Y., 2015. Structure sensitivity in catalytic hydrogenation of glucose over ruthenium. Catalysis Today, 241(B), 195-199.

Arena B.J., 1992. Deactivation of ruthenium catalysts in continuous glucose hydrogenation. Applied Catalysis A: General, 87, 219-229.

Gallezot P., Cerino P.J., Blanc B., Fleche G., Fuertes P., 1994, Glucose hydrogenation on promoted raney-nickel catalysts. Journal of Catalysis, 146, 93-102.

Mishra D.K., Lee J.-M., Chang J.-S., Hwang J.-S., 2012. Liquid phase hydrogenation of d-glucose to d-sorbitol over the catalyst (Ru/NiO-TiO2) of ruthenium on a NiO-modified TiO2 support. Catalysis Today 185, 104-108.

Worstell J., 2014. Chapter 3 - Catalyst Deactivation(Ed.)^(Eds.), Adiabatic Fixed-Bed Reactors, 35-65. Boston: Butterworth-Heinemann.