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Ni Impregnated into Hypercrosslinked Polystyrene for N-Methyl-D-Glucosamine Synthesis

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D-glucose simultaneous catalytic hydro condensation with methylamine can be considered a promising way of N-methyl-D-glucosamine synthesis. In the current work, the use of novel polymeric nickel-based catalyst is proposed for the production of N-methyl-D-glucosamine in one step through reductive amination. The one-step N-Methyl-D-glucosamine synthesis was performed in a batch reactor using heterogeneous catalyst based on the polymeric matrix of hypercrosslinked polystyrene. The experiments on varying of temperature (80 – 140 °C), Ni loading (10 – 25 wt. %), D-glucose initial concentration (0.8 – 1.6 mol/L), and hydrogen pressure (40 – 60 bar) were performed in order to find optimal reaction conditions. The initial catalyst activity was found to be 1.3 kg(Glu)/(kg(Cat)*h). Catalysts activity after 10 cycles of D-glucose transformation showed a little slowdown and was calculated to be 1.1 kg(Glu)/(kg(Cat)*h) at 99.4 – 99.5 % D-glucose conversion.

1. Introduction

Amines are one of the key intermediates for a synthesis of different substances and polymers. Typically, amines can be synthesized by the direct amination of alcylhalogenides. Another way to produce amines is the direct amination of alcohols (Froidevaux et al., 2016). However, these methods involve the oil- or natural gas-based substrates for the amination.

The modern tendencies in the use of bio-derived feedstock for the synthesis of amines are of great interest. Chitosan is one of the most important biopolymers which can be used for the synthesis of amines. However, the limitation of the chitosan resources makes the problem of a search of novel routes for the production of bio-based amines (Froidevaux et al., 2016). Among the different bio-based feedstock for amine synthesis, the sugar derivatives are the most promising. There are two main routes for the conversion of sugars into bio-based amines: (i) reductive amination of carbonyl compounds, and (ii) amination of sugar alcohols (Pelckmans et al., 2017).

There are some researches devoted to the conversion of sugars and their derivatives into amines. Pera-Titus and Shi (2014) reported the application of ruthenium and iridium catalysts for the amination of sugar alcohols. Another research was done by Pingen et al. (2013) which used Ru/C catalyst for direct amination of bio-based polyols into the primary amines at high temperature. An alternative way to produce bio-based amines was proposed by Sieber et al. (2010) in order to produce aminated isosorbide. This way was based on the reductive amination was also performed by Montgomery and Wiggins (1946).

Reductive amination involves the transformation of C=O bonds into C-N bonds and is typically conducted in two steps. First, the imine is formed from the sugar and ammonia or primary amine. Then, the resulted imine is reduced by molecular hydrogen or hydrogen donors (Hutchins and Hutchins, 1991). This step is performed in the presence of hydrogenation catalysts (Gomez et al., 2002).

Catalytic D-glucose hydro condensation with methylamine can be used for methyl-glucosamine synthesis (Shumate et al., 1992). Methylamine reacts with reducing sugars in methanol to prepare N-alkylpolyhydroxyimines. Glucose is reacted with methylamine and the resulting adduct is hydrogenated to yield N-methylglucamine. The production of N-methylglucamine as early as 1935 was patented by American

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scientists Robert B. Flint and Paul L. Salsberg, the rightful owner is the large chemical company E. I. du Pont de Nemours & Company (Scheibel et al., 1992). The reaction for the production of N-methylglucamine by reductive amination proceeds in one or two steps (Figure 1).

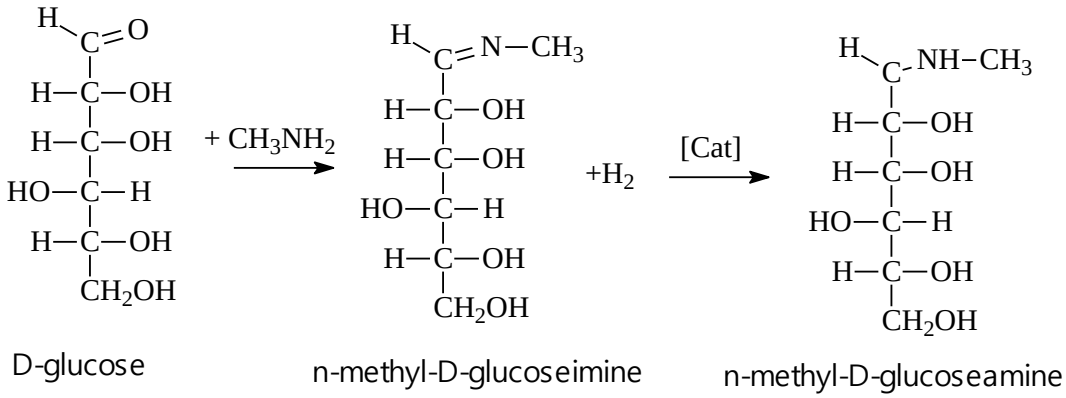

Figure 1: Scheme of N-methyl-D-glucosamine synthesis

As can be seen, there is a limited amount of the researches for the production of bio-based amines. These studies practically do not provide any information about the yield of the amines. Moreover, in the hydrogenation step, Ru is the most frequently used catalyst. As Ru is quite expensive, the search of the cheaper metal for the hydrogenation catalyst is one of the key tasks for the reductive amination of bio-based molecules. In the current work, the use of novel polymeric nickel-based catalyst is proposed for the production of N-methyl-D-glucosamine in one step.

2. Materials and methods

2.1 D-glucose transformation reaction in a batch reactor

Figure 2 shows a high-pressure vessel produces by Parr Instrument Inc., USA. for the catalytic transformation of D-glucose into N-methyl-D-glucosamine. Typically 30 g of D-glucose places in the reactor vessel, and then 150 mL of methanol and 13 mL of 40 wt. % methylamine and 10 g of catalyst were feed into the reactor. Then reactor flushed with nitrogen three times and heated to 120 °C with further purging of the reactor with hydrogen. The experiments on varying of temperature (80 – 140 °C), Ni loading (10 – 25 wt. %), D-glucose initial concentration (0.8 – 1.6 mol/L), and hydrogen pressure (40 – 60 bar) were performed in order to find optimal reaction conditions.

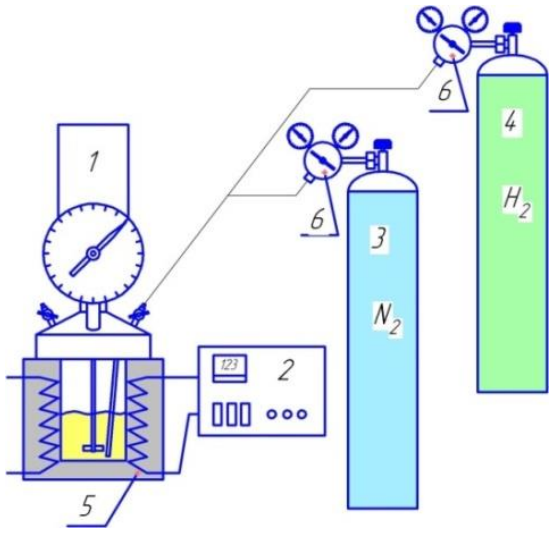

Figure 2: Reaction vessel for D-glucose transformation to N-methyl-D-glucosamine. 1 – Parr instrument high-pressure reactor, 2 – controller, 3 – tank for nitrogen, 4 – tank for hydrogen, 5 – heater, 6 – pressure reducer.

Samples of the reaction mixture were taken during the reaction and were analyzed using thin layer plate chromatography followed by UV visualization.

2.2 Catalysts synthesis

Samples of 10, 15, 25 wt % nickel supported hypercrosslinked polystyrene (HPS) were synthesized as the following: pre-calculated amount of $Ni(CH_3COO)_2$ was added to 250 mL of distilled water under a constant stirring, then 30 g of HPS (MN-100) was added partially to the solution of $Ni(CH_3COO)_2$. Samples were treated using the ultrasonic bath at 80 °C with further drying at 105°C. Before using the catalysts were reduced with hydrogen in the tube furnace at 300 °C for 6 h. In order to prevent oxidation, the catalysts were transferred to the reactor in argon.

2.3 Hydrogen chemisorption

Determination of catalyst metal active sites quantity was based on the measurement of the amount of hydrogen adsorbed on the catalyst surface. The Chemosorb 4580 gas chemisorption analyzer (Micromeritics, USA) was used for the study. The sample was placed in a quartz cuvette and blown with helium at a temperature of 300 °C, after cooling the sample to a temperature of 50 °C gas mixture of hydrogen and helium was adsorbed over catalysts surface. Further desorption of hydrogen was provided at a temperature increasing up to 300 °C with a heating rate 10 °C/min. The amount of adsorbed hydrogen was determined using a thermal conductive detector and a previously made calibration line.

2.4 Determination of the catalyst surface area

Determination of the catalyst surface area was performed by low-temperature nitrogen sorption. The nitrogen adsorption isotherm was made using the volumetric method implemented in the Beckman Coulter gas sorption analyzer (Coulter Corporation, USA). The surface area of the micro and mesoporous catalysts was calculated using the t-plot model.

2.5 X-ray photoelectron spectroscopy of catalysts

XPS spectra were obtained using a spectrometer ES 2403 M-T modified with analyzer PHOIBOS 100 (SPECS, Germany). For photoelectron extraction, the characteristic MgK-α line was used (hv = 1253.6 eV). The data analysis was performed by CasaXPS. Mathematical modeling of the Ni 2p sublevel was performed using Shirley-Marcward equation.

3. Results and Discussions

Investigation of synthesized catalysts activity Ni - 10 wt. % - HPS, Ni - 15 wt. % - HPS and Ni - 25 wt. % - HPS is presented in Figure 3. The increase of nickel loading results in an appropriate increase of methylglucimine and methylglucamine formation rate. The sample Ni - 25 wt. % - HPS showed the highest activity therefor all further experiments were provided using this sample.

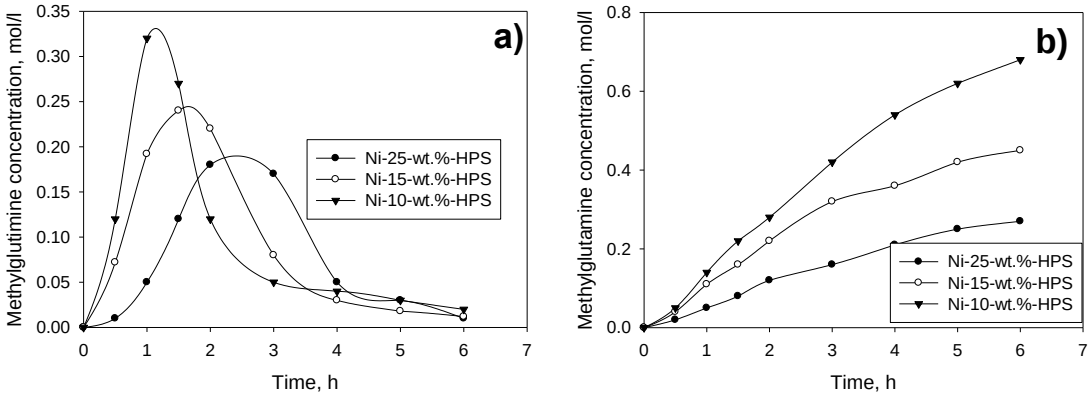

Figure 3: Investigation of synthesized catalysts activity for a) N-methyl-D-glucosimine, b) N-methyl-D-glucosamine yield.

During the experiments N-methyl-D-glucoseimine, N-methyl-D-glucosamine were found in the reaction media and can be considered as main products, sorbitol was found as a main side product. Investigation of temperature influence on N-methyl-D-glucosimine and N-methyl-D-glucosamine yield is presented in Figure 4. Increase in

the reaction temperature results in an appropriate increase in N-methyl-D-glucosimine and N-methyl-D-glucosamine yield (Figure 4a and 4b).

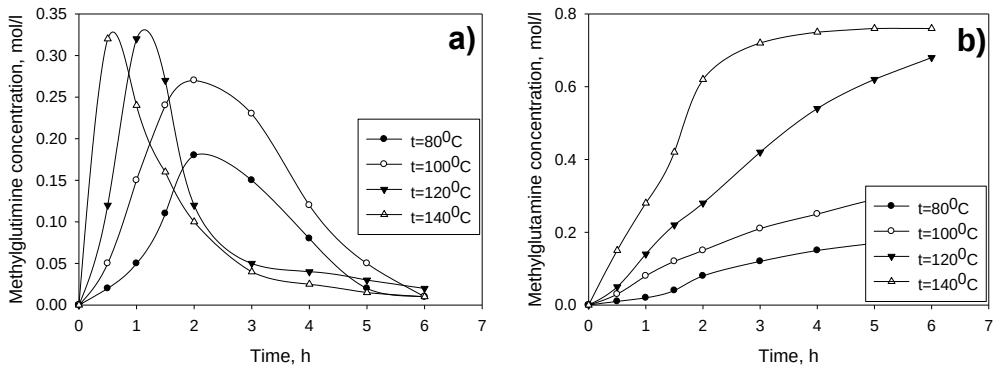

Figure 4: Temperature influence on a) N-methyl-D-glucosimine, b) N-methyl-D-glucosamine yield.

For determination of the processes activation energies Arrhenius equation plot was made (Figure 5). Determined specific activation energies were found to be 39±7 kJ/mol and 30±9 kJ/mol for N-methyl-D-glucosimine and N-methyl-D-glucosamine synthesis process.

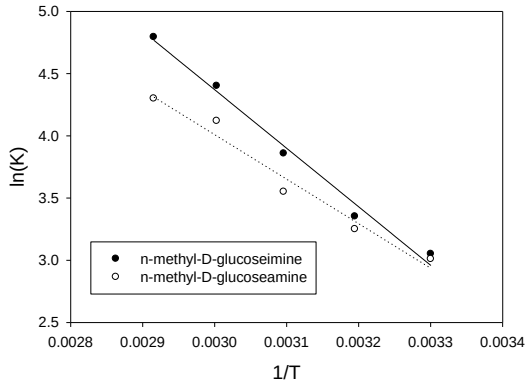

Figure 5: Arrhenius plot for N-methyl-D-glucosimine and N-methyl-D-glucosamine formation.

Influence of D-glucose concentration on N-methyl-D-glucosimine and N-methyl-D-glucosamine yield is presented in Figure 6. Increasing of D-glucose initial concentration from 0.8 mol/L to 1.6 mol/L results in increasing of N-methyl-D-glucosimine and N-methyl-D-glucosamine formation rates.

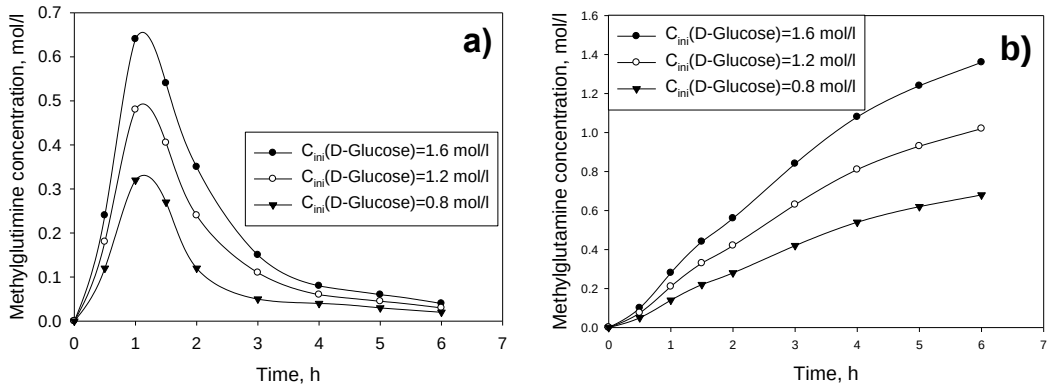

Figure 6: D-glucose initial concentration influence on a) N-methyl-D-glucosimine, b) N-methyl-D-glucosamine yield.

Influence of hydrogen pressure on N-methyl-D-glucosimine and N-methyl-D-glucosamine yield is presented in Figure 7. Increase in hydrogen partial pressure from 40 to 60 bar results in an increase in N-methyl-D-glucosimine and N-methyl-D-glucosamine formation rates.

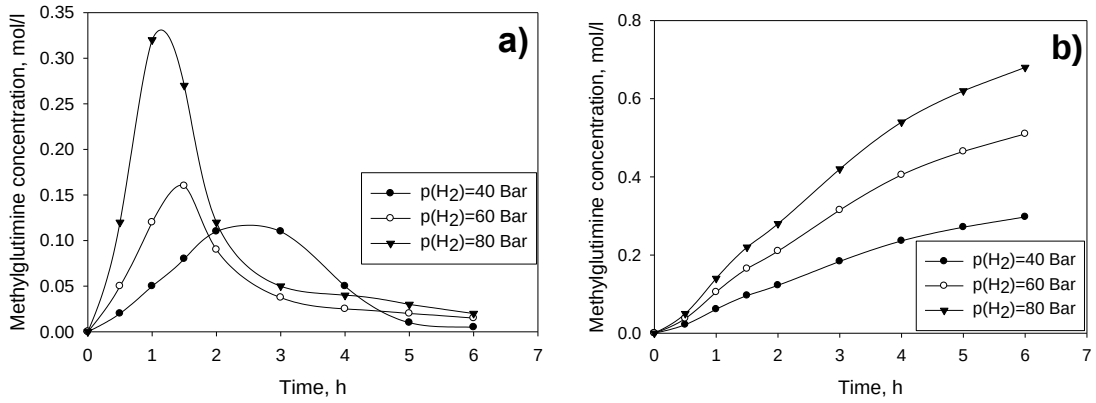

Figure 7: Hydrogen pressure influence on a) N-methyl-D-glucosimine, b) N-methyl-D-glucosamine yield.

Determination of reaction order of N-methyl-D-glucosamine synthesis on hydrogen and D-glucose was provided using kinetic curves of the logarithm of reaction rate vs logarithm of D-glucose concentration and logarithm of hydrogen pressure (Figure 8). Founded partial reactions order was near to one that suggests monomolecular surface reaction.

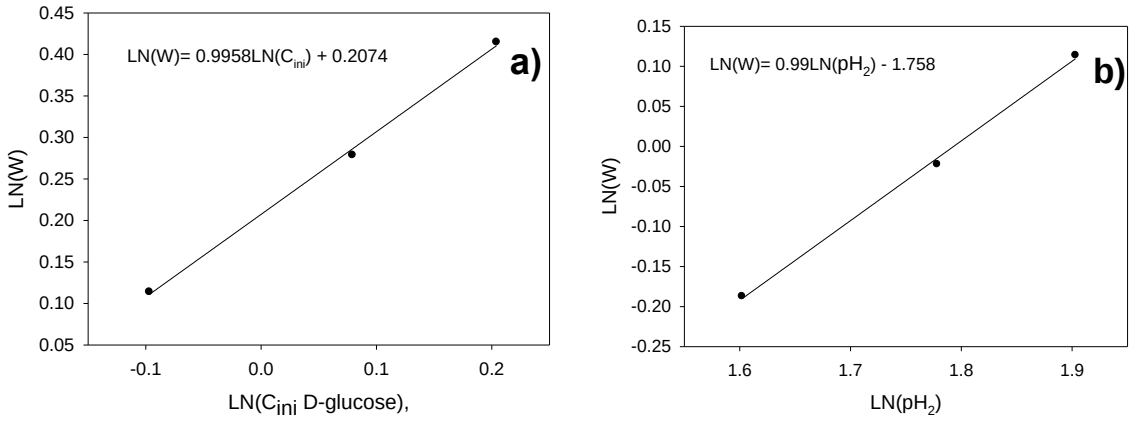

Figure 8: Determination of partial apparent reaction order for N-methyl-D-glucosamine synthesis for (a) D-glucose, (b) hydrogen.

The investigation of the catalysts long term stability showed that after 10 reaction cycles of 6 hours hydrogenation the HPS-Ni catalyst was ground by a reactor mixer, therefore, catalysts particles diameter becomes smaller than 0.01 – 0.07 mm compare to the initial (Table 1). Besides the catalysts mechanical losses were calculated to be 78 %, the catalyst weight losses can be attributed to the catalysts particles grinding and losses during the centrifugation and separation. The catalysts activity after 10 cycles of D-glucose transformation showed a little slowdown and was calculated to be for 1.1 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 Ni dispersion is noticed that can be also explained by the catalyst particles grinding and particles transformation during the reaction. The oxidation state of an active metal according to XPS data remains +2 and Ni is mainly presented in the oxide form.

Table 1 Catalysts characteristics of the used catalyst

Catalyst characteristics	Before synthesis	After synthesis
Surface area, m^2/g	240	187
Granulometric composition, mm	0.1-0.12	0.1-0.14
Nanoparticles size, nm	4-16	4-12
Ni oxidation state	0, +2	+2
Ni concentration, wt. %	2.3	2.4
Ni dispersion, %	25	27
Sample mass losses, wt. %	27	12

4. Conclusions

D-glucose simultaneous catalytic hydro condensation with methylamine can be considered a promising way of methylglucamine synthesis. Amines such as methylamine are reacted with materials such as reducing sugars in hydroxy solvents such as methanol to prepare N-alkyl polyhydroxy amines. Accordingly, glucose is reacted with methylamine and the resulting adduct is hydrogenated to N-methylglucamine. Catalysts initial activity of Ni impregnated in hypercrosslinked polystyrene was found to be 1.3 kg(Glu)/(kg(Cat)*h) at 99.3 – 99.6 % D-glucose conversion. Process selectivity to N-methyl-d-glucosamine was 97.6 – 97.8 %. Sorbitol was found in traces during the analysis and can be considered the main side products. Some losses of catalysts activity can be attributed to metal leaching. However, some increase in Ni dispersion is noticed that can be also explained by the catalyst particles grinding and particles transformation during the reaction. The oxidation state of an active metal according to XPS data remains +2 and Ni is mainly presented in the oxide form.

Acknowledgments

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