CELLULOSE CHEMISTRY AND TECHNOLOGY

HYDROLYTIC HYDROGENATION OF CELLULOSE TO SUGAR ALCOHOLS BY NICKEL SALTS

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Direct and selective hydrolytic hydrogenation of cellulose was carried out over catalytic amounts of nickel salt. C4-C6 polyols were obtained with an 87.9% yield in a neutral aqueous solution without an aid of liquid phase acid at the temperature of 150 °C in the presence of $NiSO_4$.

Keywords: cellulose, hydrolytic, hydrogenation, polyols

INTRODUCTION

As the most abundant biomass, cellulose has been regarded as a promising alternative to fossil fuels for sustainable production of biofuels and biochemicals.[1] Unlike starch, cellulose is insoluble in water and not digestible by humans, because of the semicrystalline structure composed of β-1,4-glycoside bonded glucose monomers. One of the most promising routes for cellulose utilization is catalytic conversion of cellulose into useful chemicals.[2] Catalytic conversion of cellulose consists in hydrolysis under the acid catalyst, followed by a fast metal-catalyzed hydrogenation of the formed glucose to hexitols. Several authors have reported on the catalytic conversion of cellulose diluted in water. Ding[5] described the use of less expensive bifunctional nickel phosphide catalysts for selective transformation of cellulose into sorbitol. Sels[6] demonstrated the quantitative transformation of cellulose to the sugar alcohols (85%) and sorbitan (15%), using $H_4SiW_{12}O_{40}$ and Ru/C. The conversion of α-cellulose at 433 K over H_2SO_4 or H_3PO_4 combined with carbon-supported noble metal catalysts (Pt, Pd and Ru) has been investigated.[7] With regard to the product distribution for reactions over Ru/C, the main identified products were sorbitol, sorbitan, isosorbide, and xylitol, with selectivities of up to 83%. Whereas small amounts of glycerol and methanol were detected when high sulfuric acid concentrations were used, eritritol was formed when using phosphoric acid. Liu[8] presented a green approach to an efficient conversion of cellulose into hexitols, together with other lighter polyols through two steps: cellulose hydrolysis to glucose by acids, which are reversibly formed *in situ* from hot water, and subsequent glucose hydrogenation by supported Ru clusters. Zhu *et al.*[9,10] evolved the methodology using Ru nano-particles and [BMIM]Cl to the colloidal Ru-boron binding agent-[BMIM]Cl system for the synthesis of sorbitol using 1MPa of H_2, but the stoichiometry is not accurately represented in that report. Zhao *et al.*[11] suggested that the rate ratio of the hydrolysis to the hydrogenation is a key factor to inhibit both the decomposition of glucose and the further hydrogenolysis of sugar alcohols, resulting in high yields of sugar alcohols. The main advantage of the bifunctional catalytic approach is the fast removal of unstable glucose avoiding its degradation into caramel, tars. Since the formed hexitols have a higher thermal stability than the corresponding hexoses, higher process temperatures and cellulose concentrations are feasible than in classic cellulose hydrolysis.[3,4] The biggest drawback of the above process is its high cost, due to using noble metal catalysts.

Nickel catalysts are well-known for glucose hydrogenation. In this work, we have tried to depolymerize cellulose by using only catalytic amounts of nickel salts and hydrogenation of hydrolysis products by nickel. The low acid concentration avoids corrosion and allows the use of minor quantities of neutralizing agent.

EXPERIMENTAL

Materials

The cellulose (microcrystalline) was supplied by Merck. All chemicals employed were of analytical grade and were purchased from commercial sources in China.

Hydrogenation reactions of cellulose

The cellulose hydrogenation reactions were carried out in a stainless steel autoclave reactor. 6.4 g of microcrystalline cellulose, 2.0 g of the nickel salt, and 800 mL of water were introduced into the reactor, and the reactor was purged with hydrogen gas. Then, the reactor was heated to setting temperature with stirring at 450 rpm. After the reaction, the product solution was centrifuged, and the supernatants were filtered.

Product analysis

The liquid product mixture was analyzed by Waters Alliance 2695 HPLC system, equipped with a refractive index detector. The separation of the product mixture was achieved using an AminexHPX-87H column at 40 °C; 0.005 mol/L H_2SO_4 solution was used as mobile phase at a flow rate of 1 mL/min and a typical analysis run lasted 25 min.

RESULTS AND DISCUSSION

In the reaction, the glucose and xylose resulting from the hydrolysis of cellulose and hemicelluloses are hydrogenated to sorbitol and xylitol, respectively. Additionally, further dehydration and hydrogenolysis may yield sorbitan and isosorbide, as well as eritritol, glycerol, propylene or ethylene glycol and methanol. The reaction results for the conversion of cellulose into polyols over nickel salt are summarized in Table 1.

Table 1
Cellulose conversion over different nickel salt catalysts

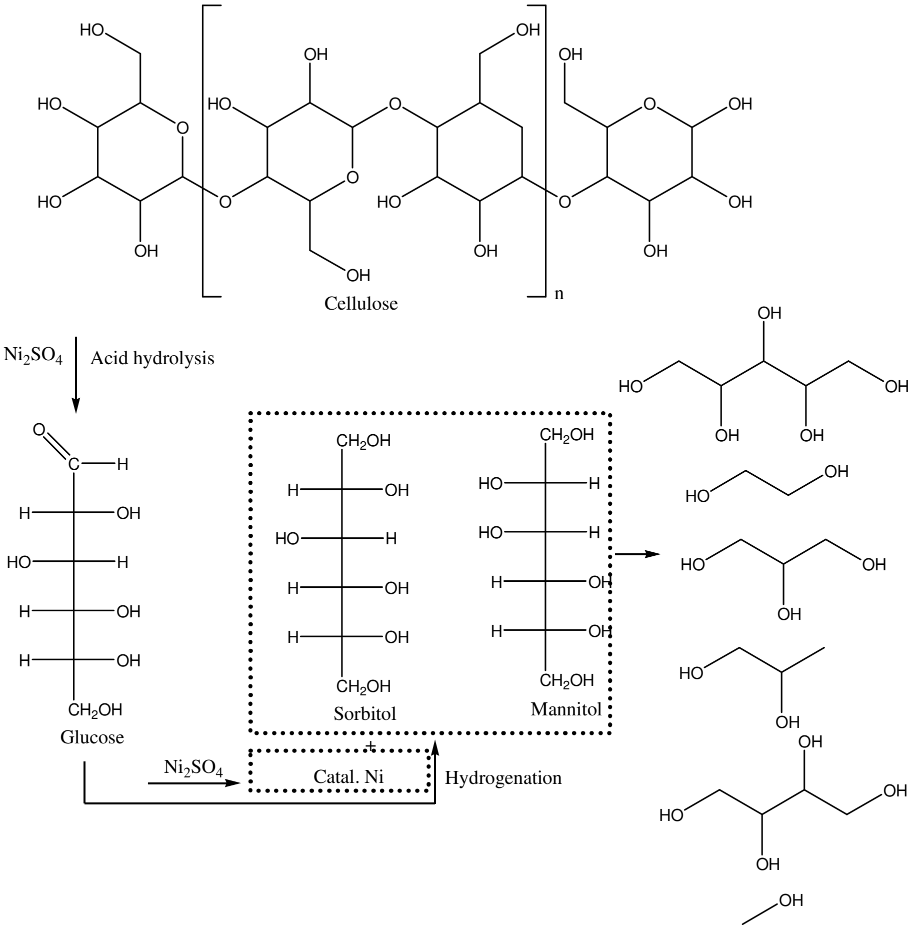
Entry	Catalyst	Pressure, MPa	Temperature, °C	Conversion, %	Yield, % C4-C6	Yield, % C1-C3	Yield, % Glucose
1	$NiSO_4$	8	150	96	87.9	4.5	2
2	$NiSO_4$	10	200	100	85.1	4.7	<5
3	$NiSO_4$	12	250	100	83.6	7.2	<5
4	$Ni(NO_3)_2$	8	200	100	74.2	15.6	<5
5	$Ni(NO_3)_2$	10	250	100	73.4	16.4	<5
6	$Ni(NO_3)_2$	12	150	94	83.4	6.7	2
7	$NiCl_2$	8	250	100	75.1	13.7	<5
8	$NiCl_2$	10	150	95	73.0	14.6	3
9	$NiCl_2$	12	200	100	74.6	15.7	<5

Obviously, various nickel salts were used to reach reasonable conversion of cellulose. However, the observed product distributions are rather different (Table 1). By using $NiSO_4$ as catalyst, the percent of conversion cellulose obtained was above 95% (Table 1, entries 1-3). The main products are C5 and C6 sugar alcohols with a selectivity up to 83%, while no sugars can be detected. In contrast, a low yield of C4–C6 sugar alcohols is observed with $Ni(NO_3)_2$ as catalyst, significant amounts of C1-C3 remain, probably due to the fact that $Ni(NO_3)_2$ is more acidic (Table 1, entries 4-6). But at a lower temperature (150 °C), an 83.4% yield of C4-C6 sugar alcohols can obtained.

Studies indicate the rate of cellulose hydrolysis to be strongly dependent on acid concentration. Since $NiCl_2$ is more acidic than $Ni(NO_3)_2$, our results emphasize an increasing conversion of cellulose at higher H_3O^+ concentrations, respectively. Additionally, further dehydration of sorbitol to sorbitan and isosorbide, together with the formation of smaller polyols, appear. According to the reaction mechanisms discussed in the literature,[12] C–C and C–O cleavage may occur via retro-aldol and dehydration reactions. Thereby, dehydrogenation to a β-hydroxyl carbonyl occurs, followed by retro-aldol condensation or dehydration and final rehydrogenation. Possible products include C1-C6 polyols, whereby the extent of C–C cleavage and remaining hydroxyl groups appear to depend on the balance of metal and acid catalyst.

The reason of hydrolytic hydrogenation cellulose by nickel salts is determined because nickel salts could be reduced by glucose. Nickel catalysts are well-known for their hydrogenation reactivity. Upon promotion with a small amount of nickel, the hydrogenation ability was improved substantially, thus leading to a large enhancement of the sugar alcohols yield.

As shown in Scheme 1, the hydrolysis of cellulose to glucose under acid conditions takes place firstly, and then glucose restores nickel salts as nickel. Secondly, the hydrogenation of glucose to C4–C6 sugar alcohols under nickel catalyst is produced.



Scheme 1: Reaction scheme for cellulose conversion to hexitols

CONCLUSION

Nickel salts are effective homogeneous catalysts for the selective hydrolysis of cellobiose and cellulose to sugar alcohols. We have shown that nickel salt catalysts allow the direct transformation of cellulose into sugar alcohols with a yield of 87.9% and carbon efficiency above 90%. For the hydrolytic hydrogenation of cellulose, $NiSO_4$

offered a higher yield, in comparison with $Ni(NO_3)_2$ and $NiCl_2$. Additionally, this approach may even be applied to other feedstocks.

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