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Enhanced hydrogenolysis conversion of cellulose to C2–C3 polyols via alkaline pretreatment

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ABSTRACT

Alkaline pretreatment was applied to enhance hydrogenolysis conversion of cellulose to C2–C3 polyols. The alkali cellulose was obtained by treating cellulose with different concentration of NaOH solution. The scanning electron microscopy (SEM) and X-ray diffraction (XRD) results indicate that the cleavage of cellulose chains occurs and the amorphous part is increased after alkaline treatment, which means the alkali cellulose has more accessible structure. Moreover, the absorbed NaOH crystal in alkali cellulose could make the further reaction perform in weak basic condition. When hydrogenolysis of alkali cellulose over Ru/C was conducted at 433 K, 59.23% of the substrate was converted with 1,2-propanediol and ethylene glycol as main products, whereas the corresponding conversion rate of untreated cellulose was 25.05% and no C2–C3 polyols were detected. These preliminary results suggested the advantages of activating the cellulose by alkaline pretreatment and potentials for efficient conversion of cellulose. Finally the plausible mechanism was also discussed.

1. Introduction

It is generally accepted that the declining fossil fuel reserves, combined with the increasing price of fossil fuel, has prompted researches towards novel ways to develop alternative resources for renewable fuels and chemicals (Klaas & Schöne, 2009). Cellulose, the most abundant biomass in nature, has been regarded as a promising renewable resource (Binder & Raines, 2009). However, it is not easy for cellulose to degrade under mild conditions due to its highly crystalline structure and resistant microfibrils network with extensive intra- and inter-molecular hydrogen bonds (Deng, Sun, & Liu, 2010). A key challenge for the next decades is to develop effective, safe, environmental friendly and economic technologies to convert biomass into target molecules.

Up to now, the main methods of cellulose hydrolysis involve the use of acids (Kobayashi et al., 2011; Suganuma et al., 2008), enzymes (Kim et al., 2011; Pala, Mota, & Gama, 2007), hot-compressed water (Kumar & Gupta, 2008; Tolonen et al., 2011) and ionic liquids (Amarasekara & Wiredu, 2011; Ignatyev, Doorslaer, Mertens, Binnemans, & Vos, 2010). Only little information can be found in the literature concerning controlled hydrolysis of cellulose in alkaline medium. However, basic treatment at elevated temperature is often used to enhance the reactivity of the crystalline cellulose through decreasing DP (degrees of polymerization) and increasing accessibility of cellulose (Hendriks & Zeeman, 2009; Kumar, Barrett, Delwiche, & Stroeve, 2011). It faintly reminds us of a capable solution to transfer resistance between solid catalyst and insoluble or partially soluble cellulose in water, which significantly restrict the catalytic activity. Meanwhile as literatures reported, hydroxide ions can not only readily break the hydrogen bonds in cellulose to finally form sugars (Kuo & Hong, 2005), but also catalyze isomerization (Moreau, Durand, Roux, & Tichit, 2000) and retro-aldol condensation of carbohydrates (Maris & Davis, 2007), leading to their C–C bond cleavage and degradation. In view of the above, hydrogenolysis of cellulose combining alkaline and hydrogenation catalysts appears to be an attractive way to obtain reduced compounds.

As far as we know, the unsatisfied results with 38.3% conversion at 473 K were reported among literatures concerning cellulose conversion over hydrogenation catalysts in solid bases solution (Cabiac et al., 2011; Deng et al., 2010; Jollet et al., 2009; Rinaldi & Schüth, 2009) which is much lower than that of acid catalysts. Poorer activities could be explained by the dependence of cellulose reactivity in alkaline medium on reaction temperature. When cellulose is treated with sodium hydroxide at temperatures above 443 K, a detectable fall in DP is observed due to random scissions of glycosidic bond (Kumar et al., 2011). Therefore, activating the cellulose might be a good compromise to meet the severe requirement for high temperature. One can consider the use of alkali as a pretreatment step before hydrolysis or hydrogenolysis. The crystalline cellulosic structure is disrupted by swelling in the alkaline medium. Once swelled, cellulose is more reactive and further reactions can be performed more easily, meaning at lower temperature.

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Furthermore, regarding the cellulose conversion to low molecular polyols, the role of pH has been highly emphasized in literatures. Deng's research (Deng et al., 2010) found that the selectivity of ethylene glycol and propylene glycol are relatively better at pH 8 on Ru/C catalyst in aqueous basic solution. In addition, Maris and Davis (Maris & Davis, 2007) investigated the importance of solution pH through the addition of basic promoters such as NaOH and CaO, which indicated that the basic solution is also beneficial to hydrogenolysis of glycerol to ethylene glycol and propylene glycol. For that matter, it should be mentioned that alkali cellulose not only shows a new transformational "open" structure but also might absorb a few alkaline crystals (Palkovits, Tajvidi, Procelewska, Rinaldi, & Ruppert, 2010), which may be at work in situ as the alternative to the basic solution.

Herein, we envisaged to realize an efficient hydrogenolysis of cellulose to polyols by the combination of alkaline pretreatment at room temperature and heterogeneous metallic catalysis at low temperature. The first step is to transform cellulose to a more reactive solid by dilute NaOH solution. In the second step, the alkali cellulose is converted into polyols in presence of commercially Ru/C, especially producing C2–C3 polyols. To our knowledge, no similar work has been yet reported. Therefore, this work aims to show the potential advantages of alkaline pretreatment for cellulose hydrogenolysis to polyols at mild conditions.

2. Experimental

2.1. Alkaline pretreatment of cellulose

Cellulose and sodium hydroxide (NaOH) were purchased from Sigma–Aldrich. Activated carbon-supported Ru (5 wt% Ru, 45%, w/w, water) catalyst was obtained from Dalian Tongyonger Chemical Co. Ltd. The Ru/C catalyst was dried in air at 493 K overnight before use.

Pretreatment was carried out in a plastic beaker (50 mL) with plastic wrap. An amount of dry cellulose powder was soaked into NaOH solution by continuous stirring at room temperature. After being held at target conditions, the insoluble residue was extensively washed with ethanol for several times until pH of the supernatant liquor was neutral. The slurry was then centrifuged. The retained solid was dried at 317 K under vacuum. Finally the alkali cellulose was obtained. The NaOH concentration was adjusted from 2 wt% to 18 wt%.

The untreated and alkali cellulose were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Each sample was mounted on a stub and sputter-coated with gold prior to imaging with a field emission scanning electron microscope (FESEM; S-4800, Hitachi) using 5.0 kV accelerating voltage. XRD patterns were recorded on an X'pert Pro diffractometer (D/MAX-2500, Rigaku Corporation) with Cu-Kα radiation in the 2θ range from 6° to 50°.

2.2. Hydrogenolysis reaction

The native and pretreated cellulose were used as substrates respectively. In a typical experiment, alkali cellulose (0.1 g), Ru/C (0.02 g) catalyst and deionized water (2 mL) were combined in a stainless steel (30 mL) autoclave reactor equipped with Teflon inserts. The reactor was sealed and flushed with hydrogen for several times and finally pressurized to 5 MPa hydrogen pressure. The reactions were carried out at 433 K for 5 h with vigorous stirring. After reaction, the reactor was cooled down to room temperature in ice-water bath. After the gas was released, the reaction mixture was centrifuged. The obtained liquid was analyzed by high performance liquid chromatography (HPLC) equipped with an ICSep ICE-Coregel 87H3 column and RID detector. The HPLC column was retained at 308 K, with a mobile phase of H_2SO_4 (5 mM) solution flowing at 0.6 mL/min. The unknown constituents were further identified by ESI-MS.

The conversion of cellulose ($X_{\text{cellulose}}$) was determined by the change in the weight of cellulose loaded before ($m_{\text{cellulose0}}$) and after the reactions ($m_{\text{cellulose}}$). The solid recovered after reaction had the fraction of solid catalyst, so $m_{\text{cellulose}} = m_{\text{solid recovered}} - m_{\text{solid catalyst}}$.

$$X_{\text{cellulose}} = \frac{m_{\text{cellulose0}} - m_{\text{cellulose}}}{m_{\text{cellulose0}}} \times 100\%$$

The selectivity of each product was calculated as follow:

$$S_{\text{product}} = \frac{Y_{\text{product}}}{X_{\text{cellulose}}} \times 100\%$$

Then the yields (Y_{product}) are calculated based on the standard definition. However, the amount of carbon in reaction system was lost, it can be explained by the loss of gas products inevitably lost during liquid sampling. Thus, Y_{product} can be described with the theoretical stoichiometric coefficient $\nu_{\text{substrate}}$ and ν_{product} as follows:

$$Y_{\text{product}} = \frac{n_{\text{product}}}{n_{\text{substrate}}} \frac{\nu_{\text{substrate}}}{\nu_{\text{product}}} \times 100\%$$

In this formula, the theoretical stoichiometric coefficient $\nu_{\text{substrate}}$ would be one for all C6 compounds, while a C5 product would be accounted for with 6/5, and a C4 with 6/4 and so on, in this way it can get a closed carbon balance for every single compound (Palkovits et al., 2010).

3. Results and discussion

3.1. Crystalline structure changes of the alkali cellulose

A comparison of the morphology of untreated cellulose and alkali cellulose is presented in Fig. 1. The micrographs reveal the fiber surface characteristics and fine structure of the cellulose. The microfibril surface of the untreated cellulose is relatively smooth (Fig. 1a). For the alkali cellulose, the more microfibril aggregates are visible, showing a much rougher and more wrinkled surface with the enhancement of NaOH concentration (Fig. 1b–f). What is more, the image of Fig. 1f indicated that the structure change of cellulose treated with 4 wt% NaOH for 24 h is more dramatic than that in case of 2 h. It suggested that both the NaOH concentration and the treating time could affect the level of reducing the crystallinity of cellulose. As literature reported (Warwicker & Wright, 1967; Yin, Chen, & Ha, 2005; Porro et al., 2007), cellulose can be activated with alkali, and the structure transformation of cellulose was caused by some chemical reactions between cellulose and alkali. This kind of reaction led to the cleavage of cellulose chains and the degradation of the crystallinity of cellulose (Nlewem & Thrash, 2010). The amorphous part of cellulose is found to be more reactive to hydrolysis than crystalline one (Kumar et al., 2011).

To investigate the crystal structures of the cellulose before and after the pretreatment, the XRD patterns were measured for these samples as shown in Fig. 2. The XRD spectrum of the native cellulose showed three significant peaks corresponding to (1 0 1), (2 0 0) and (0 4 0) lattice planes of crystalline cellulose I polymorph (Zuluaga et al., 2009). With the enhancement of alkali concentration, the XRD spectra of alkali cellulose showed a more obvious reduction in intensities of these three peaks. Especially, when the concentration reached 18 wt%, the intensities of peaks corresponding to (1 0 1) and (0 4 0) lattice planes were greatly reduced to an almost undetectable level, and the remaining peak was broader and shifted. The changes of these peaks indicated that the different extent of

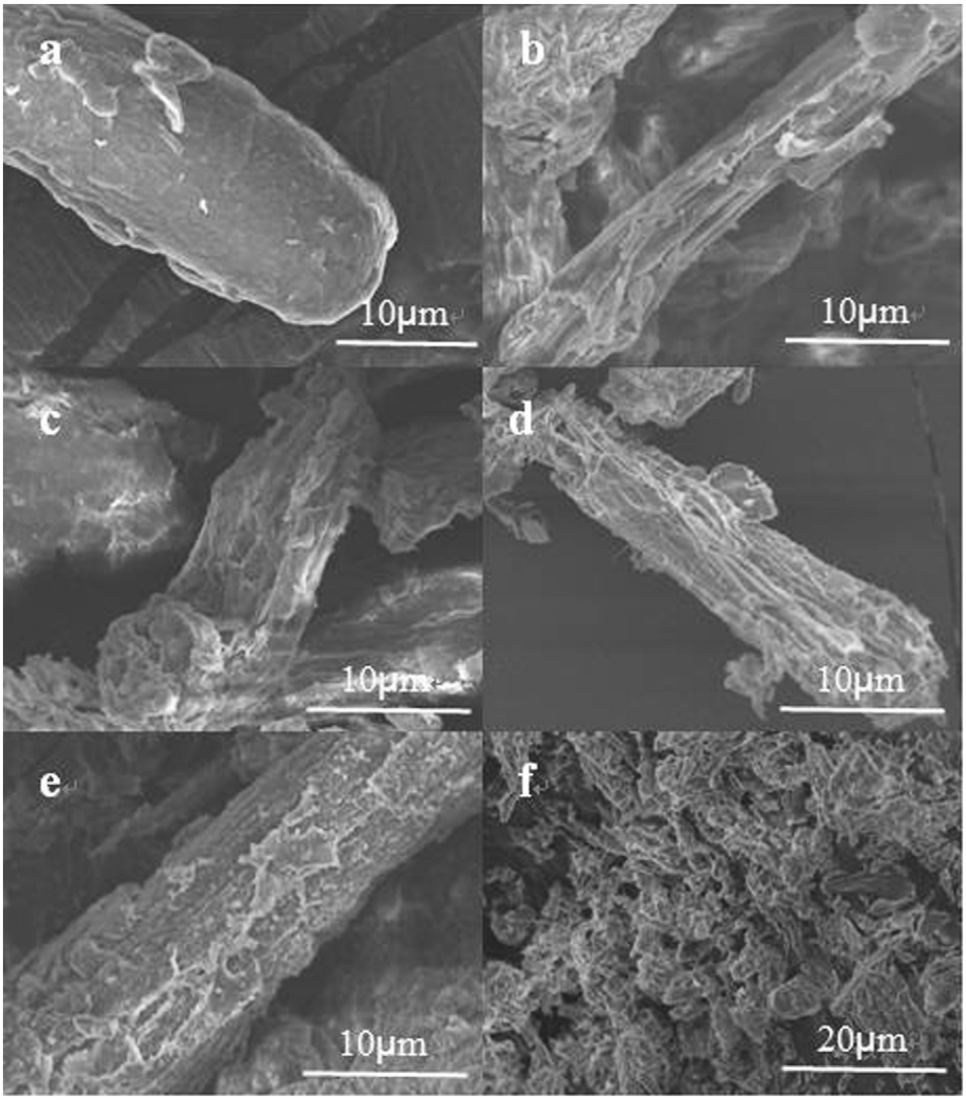


Fig. 1. SEM micrographs of cellulose and alkali cellulose: (a) untreated; (b) treated with 2 wt% NaOH for 2 h; (c) treated with 4 wt% NaOH for 2 h; (d) treated with 6 wt% NaOH for 2 h; (e) treated with 18 wt% NaOH for 2 h; (f) treated with 4 wt% NaOH for 24 h.

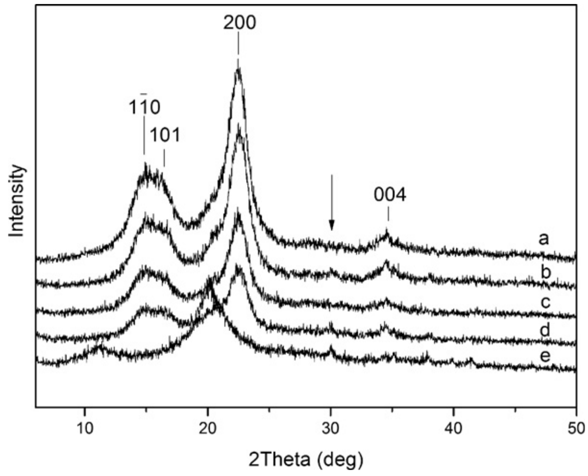


Fig. 2. X-ray diffraction of cellulose: (1) untreated; (2) treated by 2 wt% NaOH for 2 h; (3) treated by 4 wt% NaOH for 2 h; (4) treated by 6 wt% NaOH for 2 h; (5) treated by 18 wt% NaOH for 2 h.

crystallinity degradation of cellulose. In basic solution, hydrogen bonds between and inside the cellulose were broken, and the structure of cellulose transformed (Eronen, Österberg, & Jääskeläinen, 2009). Meanwhile, it is to be noted that there are several small peaks from 28° to 40°, which have been proved as the characteristic peaks of NaOH crystal (Warwicker & Wright, 1967). As the NaOH concentration increased, the peaks tended to be apparent. The cellulose with new structure absorbed NaOH crystals, and the amount of absorbed NaOH could increase with the increasing concentration of NaOH solutions (Yin et al., 2005).

3.2. *Effect of pretreatment NaOH concentration in hydrogenolysis*

Hydrogenolysis reactions were conducted to evaluate the potential for producing polyols. Table 1 shows the effect of pretreatment NaOH concentrations on the cellulose conversion and product selectivities. In Table 1, it can be seen that conversion from native cellulose was the lowest and the detected products were mainly xylitol and erythritol (Entry 1). The conversion of alkali cellulose initially increased then decreased as the NaOH pretreatment concentration increased (Table 1, Entries 2–8). The maximum conversion of 67.02% was observed in the case of 6 wt% NaOH, which

Table 1
Summary of conversion and product selectivities during alkali cellulose hydrogenolysis.[a]

Entry	NaOH concentration (wt%)	pH[b]	pH[c]	Conversion (%)	Selectivity (%)				
		Initial	Last		XL	EL	GL	1,2-PDO	EG
1	None	7.0	7.0	21.97	7.14	2.32	0.00	0.00	0.00
2	2.0	8.0	7.8	49.20	8.19	6.25	3.40	11.03	4.42
3	4.0	8.3	8.0	59.23	4.65	4.78	1.87	18.08	6.16
4	6.0	8.7	8.3	67.02	4.76	3.90	2.41	8.79	3.39
5	8.5	9.0	8.7	50.85	5.41	7.08	2.93	6.35	2.74
6	12.0	9.5	9.3	47.14	5.29	8.60	2.82	7.50	2.68
7	16.0	9.7	9.5	46.52	5.47	7.04	2.41	9.38	3.56
8	18.0	10	9.7	42.14	6.04	6.24	2.42	10.06	4.02
9	None	8.0	7.0	25.05	15.19	0.00	0.00	0.00	0.00

[a] Reaction condition: alkali cellulose (0.1 g), Ru/C (0.02 g, 5 wt%), H_2O (2 mL), H_2 (5 MPa), 433 K and 5 h. XL: xylitol; EL: erythritol; GL: glycerol; 1,2-PDO: 1,2-propanediol; EG: ethylene glycol.
[b] pH value of reaction mixture at the beginning.
[c] pH value of reaction mixture at the end of reaction.

was 3 times higher than that from the native cellulose. These results demonstrate clearly that the alkaline pretreatment can improve the cellulose hydrolysis through swelling cellulose to modify the crystalline structure and to increase the accessibility to chemicals. Meanwhile, it should be noted that some adsorbed NaOH crystal on cellulose in pretreatment was dissolved during reaction, which benefits alkaline hydrolysis of cellulose to some extent (Zhao, Zhou, Sui, & Zhou, 2010). Although the underlying reason is not clear for the decrease of cellulose conversion as the NaOH concentration overran 8.5% (Table 1, Entry 5), the difference of initial pH value in reaction (Table 1) may give a clue. It had been reported that the cellulose conversion would be enhanced with the increasing pH value to some extent, and when pH value was over 9.0, the conversion evidently decreased (Deng et al., 2010; Yin et al., 2005).

It also can be seen from Table 1 that the selectivities of C2–C3 polyols were relatively high for the alkali cellulose (Entries 2–8), because the C–C bonds of xylitol, erythritol and glycerol are easy to be splitted to form ethylene glycol and 1,2-propanediol in weak basic condition (Maris & Davis, 2007). Further shown in Table 1, the selectivity of ethylene glycol and 1,2-propanediol increased with increasing NaOH concentration up to 4 wt% and a sharp decrease at 6 wt%. In Deng's study (Deng et al., 2010), it was also reported the yield of ethylene glycol will reach the maximum at pH 8. Increasing the base concentration can accelerate the retro-aldol condensation, but high base concentration also can enhance the reversible aldol scrambling reactions, which could lead to the decline of cellulose conversion and selectivity amongst the hydrocracked products (Kumar & Gupta, 2008). Only in weak basic condition cellulose could have a high conversion and selectivities to C2–C3 polyols. In this work, when cellulose was pre-treated with 4 wt% NaOH solution, the amount of adsorbed NaOH in alkali cellulose is appropriate to make the reaction mixture at pH 8.3–8.0, which is surely beneficial for producing 1,2-propanediol and ethylene glycol.

To further understand the importance of activating the cellulose by alkaline pretreatment, the hydrogenolysis reaction of native cellulose in NaOH solution at pH 8.0 was conducted (Table 1, Entry 9). The cellulose conversion was only 25.05%, which was much lower than that of alkali cellulose, and the products were mainly xylitol. Consequently, alkaline pretreatment is of profound significance for efficient hydrogenolysis of cellulose to valuable chemicals.

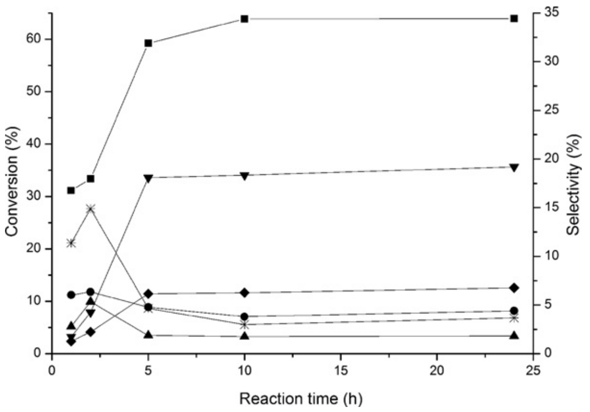


Fig. 3. Conversions and selectivities as a function of reaction time at 433 K on Ru/C catalyst for cellulose pre-treated with 4 wt% NaOH solution. Left-hand axis: conversion (■); right-hand axis: selectivity to xylitol (∗); erythritol (●); glycerol (▲); 1,2-propanediol (▼); ethylene glycol (♦).

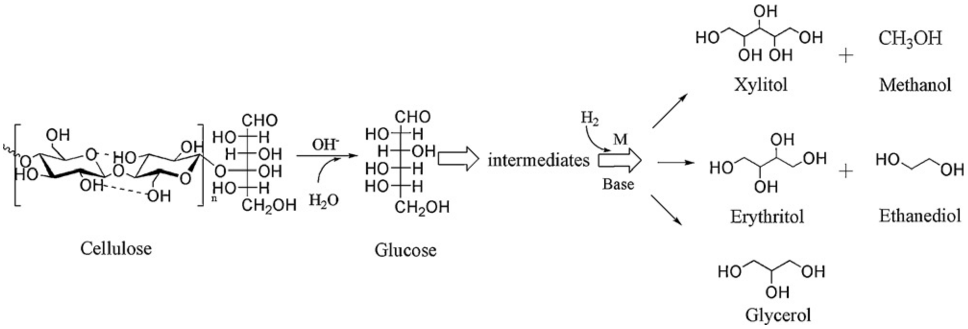
3.3. *Effect of reaction temperature in hydrogenolysis*

Hydrogenolysis reactions of alkali cellulose in the range of 393–473 K were conducted for investigating the effects of reaction temperature. As shown in Table 2, the cellulose conversion straightly went up from 26.59% to 86.00% when the temperature increased from 393 K to 473 K. It can be illustrated that high temperature promotes the hydrolysis process. Meanwhile the results in Table 2 indicated reaction temperature also have obvious effects on the products distribution. At the temperature of 393 K (Table 2, Entry 1), C4∼C6 products took the majority, especially the selectivity of xylitol was up to 26.61%, contrasted to 0.97% selectivities totally of ethylene glycol and 1,2-propanediol.

Table 2
Summary of reaction temperature for alkali cellulose hydrogenolysis.[a]

Entry	Temperature	Conversion	Selectivity (%)				
	(K)	(%)	XL	EL	GL	1,2-PDO	EG
1	393	26.59	26.61	5.66	5.33	0.14	0.83
2	433	59.23	4.65	4.78	1.87	18.08	6.16
3	453	75.08	4.26	4.37	2.44	14.69	6.05
4	473	86.00	4.35	4.73	4.59	13.41	6.36

[a] Reaction condition: alkali cellulose (0.1 g), Ru/C (0.02 g, 5 wt%), H_2O (2 mL), H_2 (5 MPa) and 5 h. XL: xylitol; EL: erythritol; GL: glycerol; 1,2-PDO: 1,2-propanediol; EG: ethylene glycol.



Scheme 1. Reaction scheme of the hydrogenolysis of cellulose after pretreatment with the major products.

When the temperature increased to 433 K (Table 2, Entry 2), the product distribution was changed tremendously. The selectivity of xylitol declined from 26.61% to 4.65%. However, the selectivity increased to 18.08% and 6.16% for 1,2-propanediol and ethylene glycol, respectively. While the temperature rose to 453 K or 473 K (Table 2, Entry 2 and Entry 3), the selectivity of 1,2-propanediol and ethylene glycol did not change distinctly.

3.4. Effect of reaction time in hydrogenolysis

Fig. 3 illustrates the effect of reaction time on hydrogenolysis of alkali cellulose. It was clear that the conversion rate and products distribution are strongly dependent on reaction time within 10 h. When the reaction proceeded from 1 h to 10 h, the cellulose conversion changed from 31.14% to 63.89%. Moreover, it is interesting to note that the selectivity of xylitol was at a relatively high level after 1 h while that of 1,2-propanediol, ethylene glycol, and glycerol were very low. As time went by, the selectivities to all the products were increasing. But 5 h later, the selectivity of xylitol came to its lowest level. The selectivities of 1,2-propanediol and ethylene glycol increased dramatically from 4.42% to 18.08% and 2.23% to 6.16%, respectively.

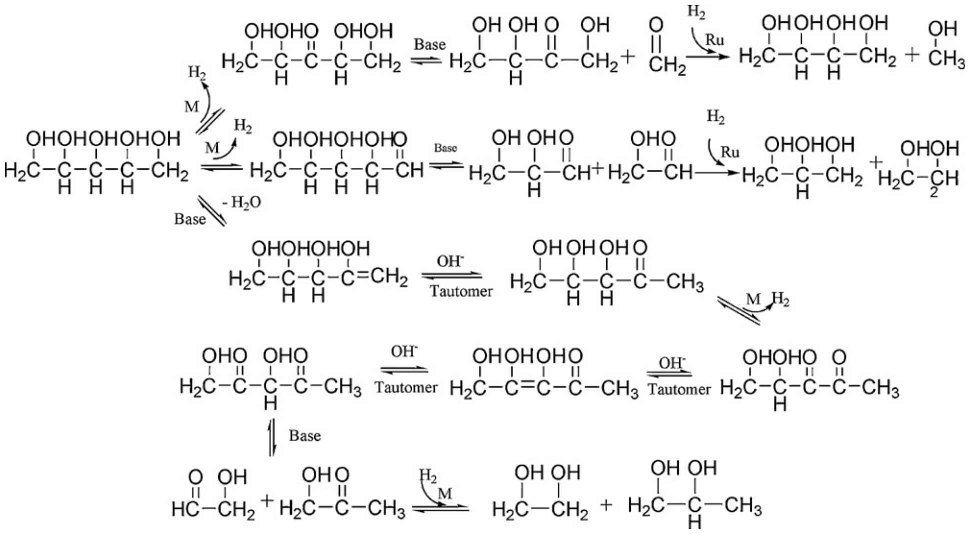
In contrast to above, without Ru/C catalyst, only 23.82% of alkali cellulose could be conversed for 1 h in hydrolysis reaction. It can be inferred that the hydrolysis products were consumed for the hydrogenolysis in the presence of Ru/C, which could promote the cellulose conversion (Palkovits et al., 2010). Subsequently, when the time added to 5 h, the conversion was 59.23%, which was almost two times higher than that of 1 h. However, when the time was more than 5 h, the conversion would change a little. Even when the reaction lasted for 24 h, the conversion was up to 63.93%. The selectivities to the main products remained even after 10 h.

3.5. Reaction pathways and mechanism

The major valuable polyols observed were xylitol, erythritol, glycerol, 1,2-propanediol and ethylene glycol. Other by-products detected in trace amount by HPLC and ESI-MS included sorbitol, formic acid, glyceraldehyde, methanol and ethanol.

The hydrogenolysis reaction of alkali cellulose is illustrated in Scheme 1 . Cellulose was firstly degraded through hydrolysis path to sugars and then converted in alkaline pathway to some intermediates (Yin, Mehrotra, & Tan, 2011). Through the diverse elimination reactions, glucose transformed to a series of compounds with one or two unsaturated bonds. These unsaturated bonds will be hydrogenated in the following step. In alkaline conditions, the C–C cleavages happened by means of the retro-aldol reaction in the presence of hydroxy ions (Zhao, Zhang, & Liu, 2010).

Scheme 2 described the conversion of xylitol to 1,2-propanediol and ethylene glycol (Montassier, Menezo, Hoang, Renaud, & Barbier, 1991). One pathway is the dehydrogenation of polyols over the transition metal catalyst to form aldehyde or ketone intermediates (Knill & Kennedy, 2003). It might be enhanced by the presence of base. Due to an electron-withdrawing group of the ketone, the adjacent carbon atom becomes positive and tends to be dehydrogenated. The other is the dehydration of polyols to enols. The enol form is not stable, so its structure will change to ketone.



Scheme 2. The pathway of xylitol hydrogenolysis on Ru/C catalyst in basic medium.

Then through a retro-aldol reaction and hydrogenation in sequence, the ketone conversed to 1,2-propanediol and ethylene glycol (Li & Huber, 2010). Because Ru is an effective catalyst for C–C bond cleavage, xylitol would converse to glycerol and ethylene glycol directly. This mechanism was also supposed to be applicable to glucose, erythritol and glycerol (Maris & Davis, 2007).

4. Conclusion

In summary, combination of alkaline pretreatment of cellulose at room temperature and heterogeneous Ru/C catalysis at low reaction temperature allows a better conversion of cellulose and selectivity of C2–C3 sugar alcohols in comparison with that of the untreated cellulose.

SEM and XRD characterization were used to illustrate the structural changes of alkali cellulose. The SEM micrographs showed that a much rougher and more wrinkled surface of cellulose with the enhancement of NaOH concentration. The XRD spectra indicated the crystallinity degradation after pretreatment. It surely suggested that the cellulose was transformed to a more accessible structure. Moreover, the absorbed NaOH crystal in alkali cellulose could make the further reaction perform in weak basic condition. Therein, for the cellulose pre-treated with 4 wt% NaOH solution, 59.23% conversion in 5 h was achieved at 433 K with the main products of 1,2-propanediol and ethylene glycol. Meanwhile based on the products profile with time, the mechanism of hydrogenolysis in alkaline medium was proposed. Cellulose was firstly degrade by base hydrolysis to sugars, and then alkaline hydrogenolysis occurred to produce C2–C3 polyols.

Overall, using the alkali cellulose as the substrate of hydrogenolysis presents an attractive approach for an efficient conversion of cellulose into the low molecular polyols. The better results would be realized by the improvement of the catalysts.

Acknowledgments

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