

Promotive Selectivity to C2-C3 Polyols From Alkaline Cellulose Hydrogenated by Ionic Liquid-stablized Ru Nanoparticles

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Abstract

Alkaline cellulose hydrogenolysis on metal catalyst was an effective way to get C2~C3 polyols. The alkaline cellulose was obtained by treating cellulose with 4 wt% NaOH solution. Ionic liquid-stabilized Ru nanoparticles were prepared by reducing metal salt in ionic liquid. The SEM results indicate that the amorphous part of alkaline cellulose is helpful for getting the catalyst into the cavities to have a further hydrogenation reaction. When hydrogenolysis of alkaline cellulose over Ru/[Bmim]BF₄ nanoparticles was conducted at 433 K, 63.78% of the substrate was converted with glycerol, 1,2-propanediol and ethylene glycol as main products of which selectivity was up to 58.91 %, whereas the conversion rate over Ru/C catalyst of alkaline cellulose was 59.23 % and only 26.11 % C2~C3 polyols were detected. Moreover, if the ionic liquid-stabilized Ru nanoparticles were doped with 53.7 % Ni, the selectivity of C2~C3 polyols was promoted to 65.07 %. These results suggested the advantages of the ionic liquid-stabilized Ru nanoparticles, especially doping with Ni, have potentials for promotive selectivity to C2~C3 alcohols. Put forward the plausible mechanism finally.

Introduction

The sustainable utilization of biomass and the high value-added cellulose products have become a major concern because of the worldwide growing environmental awareness (Stöcker 2008; Zhu et al. 2010; Le et al. 2019). Generally, cellulose is difficult to dissolve due to its high crystallinity and a large number of hydrogen bonds, which is not conducive to the catalytic reaction (Binder and Raines, 2009; Deng et al. 2010; [Martínez-Sanz et al. 2016](#)). However, it is well known that the dissolution of cellulose is often the initial step on demand for further material processing and it is more like a challenging task (Klemm et al. 2005; Medronho and Lindman, 2014; Pereira et al. 2018). Previous studies have suggested that cellulose can undergo pretreatment, such as acid treatment (Gavilà et al. 2015; Chimentão et al. 2014), alkali treatment (Hagman et al. 2017), enzymes treatment (Tye et al. 2016; Ying et al. 2018), heat treatment (Tolonen et al. 2011; Hai et al. 2017) and ionic liquids treatment (Pang et al. 2018; Meng et al. 2017), to change the crystal structure before the catalytic reaction, which would make it easier to be conducted in a mild condition ([Pääkkö et al. 2007](#); Asem et al. 2021). Among these treatment methods, the research of alkali treatment of cellulose has gradually attracted great attention in recent years.

It was indicated that microcrystalline cellulose can be stably dispersed at room temperature for two months when it was treated with low concentration of NaOH solution (Hagman et al. 2017). It was also found that Ba(OH)₂ at room temperature can catalyze the conversion of hydrolysis. The yield of lactic acid reacted with glucose and cellulose as substrates for 48 h reached 95 % and 42.2% respectively (Li et al. 2017). However, alkali solvent will corrode the reactor in the strong alkaline aqueous solution system so that people turn their attention to alkaline cellulose which would more easier to hydrolyze (Liu et al. 2012). From the previous research results, it would be mentioned that alkaline cellulose exhibits a new kind of "open" structure, which can absorb some alkaline crystals into the fibers (Palkovits et al. 2010) and enable the cellulose to degrade and convert. On the other hand, nano-catalysts have better catalytic effect, which could make the hydrogenolysis of cellulose much easier. Nanoporous ruthenium catalysts

were prepared from ruthenium and aluminum, and applied to catalyze the reaction of cellulose to methane. The reaction rate was 85.8% at a reaction temperature of 493 K and an initial hydrogen pressure of 0.5 MPa for 8 h, methane selectivity reaches 82.2 % (Lv et al. 2018). It can be seen that the nano-catalyst has a good reference potential in the catalytic conversion of cellulose.

As literatures reported, a great number of intra and intermolecular hydrogen bonds in cellulose can be broken under alkaline conditions and readily make the cellulose turn to the forms of sugars (Balat et al. 2008; SriBala et al. 2016). The high cellulose dissolution potential of alkaline solvent might be due to the ability of the hydroxide ions to interact effectively with its multiple hydroxyl groups. This will promote the catalyze isomerization (Deng et al. 2015) and retro-aldol condensation of carbohydrates (Zhao et al, 2010) during hydrogenation, leading to the cleavage of C-C bonds in cellulose. In addition, alkaline solvents have received particularly attention for their low price and low toxicity (Budtova and Navard, 2016). According to the above, hydrogenation of alkaline cellulose by using efficient catalysts appears to be a favorable way to promote the conversion of cellulose to polyols.

Herein, we envisaged to design an efficient process via hydrogenolysis of alkaline cellulose to C2~C3 polyols by the nanoparticels at mild temperature. Firstly, the conversion of alkaline cellulose to C2~C3 were compared under different catalyst conditions, including commercially Ru/C and Ruthenium nanoparticles coated with various ionic liquids, respectively. Furthermore, the performance of nickel-modified ruthenium nanoparticles and its additive amount were investigated. Comprehensively, by combining the micrographs of the reaction system and the products distribution during the hydrogenolysis time, the mechanism of alkaline cellulose conversion from macromolecular polysaccharide to major polyols was discussed. Combining previous work, this paper aims to show the potential promotive advantages of ionic liquid-stablized Ru nanoparticles in the field of alkaline cellulose hydrogenolysis to polyols under mild conditions, especially in the presence of nickel.

Experimental

Materials and instruments

Cellulose (microcrystalline) which particle size is about 51 μm were provided by Sigma-Aldrich, ruthenium (III) chloride hydrate (RuCl_3 , 42.0 wt% Ru basis), sodium hydroxide (NaOH, 99 wt%) and sodium borohydride (NaBH_4 , 98 wt%) from Sigma-Aldrich were used as received. Ionic liquids (IL) 1-butyl-3-methylimidazolium hexafluorophate ($[\text{Bmim}]\text{PF}_6$) , 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{Bmim}]\text{BF}_4$) , 1-butyl-3-methylimidazolium chloride ($[\text{Bmim}]\text{Cl}$) and 1-(2-hydroxyethyl)-3-methylimidazolium chloride ($[\text{HO-emim}]\text{Cl}$) used in this study were purchased from Henan Lihua Pharmaceutical Co., Ltd. Activated carbon-supported Ru (5 wt% Ru, 45%, w/w, water) catalyst (Ru/C) was purchased from Dalian Tongyonger Chemical Co. Ltd. It needs to be dried in air at 493 K more than 10 hours before used.

Ruthenium (Ru) nanoparticles were prepared by reduction of ruthenium (III) chloride hydrate in liquid (Wei et al. 2011). Ionic liquid (6.00 g) was added to a sodium borohydride solution (20 mL, 0.1139 g NaBH₄). A RuCl₃ solution (20 mL, 0.06g RuCl₃) was dropped slowly and the mixture was stirred at 333 K for 2 hours to reduce the metal ruthenium (III). After reduction reaction, the mixture was dried by rotatory evaporation at 333 K so that the reducing agent was decomposed as the precipitate at the bottom of the flask. Supernatant liquid containing black nanoparticles were centrifuged and then washed by ethanol and deionized water for several times, respectively. The Ru/IL nanoparticles were obtained after being dried under vacuum at 353 K for 24 hours. The nanoparticles were denoted as Ru/[Bmim]PF₆, Ru/[Bmim]BF₄, Ru/[Bmim]Cl and Ru/[HO-emim]Cl. The Ni modified Ru nanoparticles were prepared in the same method by reducing nickel chloride and ruthenium chloride mixture in sodium borohydride solution.

The microstructure of cellulose was assessed by scanning electron microscopy (SEM) that was carried out using a field emission scanning electron microscope (FESEM; S-4800, Hitachi). High-resolution transmission electron microscopy (HRTEM) images were measured on a 200 kV JEM-2100F microscope. Liquid-phase products after hydrogenation were analyzed by high performance liquid chromatography (HPLC) equipped with a refractive index detector (RID) and an ICsep Coregel-87H column at 308 K. H₂SO₄ of 0.005 M was used as the mobile phase flowing at 0.6 mL/min. Phase analysis of catalyst was performed by X-ray diffraction (XRD) using a diffractometer with Cu K radiation at 40 kV and 200 mA (D/MAX-2500, Rigaku, Japan). The samples were scanned and the intensity recorded in a 2θ range from 10° to 90°. The superficial structures of nanoparticles were analyzed by the Fourier transform infrared (FTIR). Their spectroscopy results were recorded on a Bruker Vector-22 FT-IR spectrophotometer. The structures was also detected by Thermogravimetry (TG) at 10 K/min from 293 K to 873 K.

Hydrogenolysis reaction

The Cellulose was soaked in 4 wt% NaOH solution and swelled at room temperature for 2 hours. Then the mixture was washed with ethanol till the pH value was 7. The alkaline cellulose was obtained by centrifugating the mixture and dried at 317 K under vacuum before use. Alkaline cellulose (0.1 g) or cellulose (0.1 g) and catalysts (contented 0.001 g Ru) were combined in a 30 mL stainless steel autoclave equipped with Teflon inserts. Deionized water was added as reaction media. This autoclave was purged with hydrogen several times and finally pressurized to 5 MPa. The hydrogenolysis proceeded at 433 K for 5 hours with continuous stirring. After the reaction time was over, the reactor should be cooled in an ice-water bath. The reaction mixture was centrifuged to separate the catalyst and liquid phase products.

The conversion of cellulose ($X_{cellulose}$) was estimated from the quality changes of cellulose during the reaction. The solid recovered after reaction was containing catalyst, so $m_{cellulose} = m_{solid\ recovered} - m_{solid\ catalyst}$

$$X_{cellulose} = \frac{m_{cellulose_0} - m_{cellulose}}{m_{cellulose_0}} \times 100\%$$

The selectivity of each product was calculated as follow:

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

Finally, based on the standard definition, the yields ($Y_{product}$) are calculated by the theoretical stoichiometric coefficient $v_{substrate}$ and $v_{product}$ as follow:

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

In this formula, the theoretical stoichiometric coefficient $v_{substrate}$ of all C6 compounds would be one, while a C2 product would be accounted for with 6/2, and a C3 with 6/3 and so on, it can get a closed carbon balance by this method for single compound (Palkovits et al. 2010). There is a part of lost carbons, which may be caused by the gas products inevitably lost during liquid sampling.

Results And Discussion

Effect of various catalysts on selectivity of C2~C3 polymers

Ru/IL nanoparticles were prepared through four kinds of ionic liquids. Their properties were all characterized (Supporting Information). Hydrogenolysis reactions were carried out to evaluate the potential for producing polyols over Ru/IL nanoparticles, meanwhile, Ru/C catalysts were chosen to have a comparison. Table 1 shows the effect of various catalysts on selectivity of C2~C3 polymers.

Table 1 Catalytic activity of Ru catalysts on hydrogenolysis conversion of alkaline cellulose ^a

Entry	Catalyst	Conv. ^b (%)	Selectivity				
			XL	EL	GL	1,2-PDO	EG
1	Ru/C ^c	21.97	7.14	2.32	0.00	0.00	0.00
2	Ru/C	59.23	4.65	4.78	1.87	18.08	6.16
3	Ru/[Bmim]PF ₆	65.22	7.27	2.02	1.87	23.51	6.47
4	Ru/[Bmim]BF ₄	63.78	5.90	2.42	18.37	22.55	17.99
5	Ru/[Bmim]Cl	56.65	4.70	2.06	1.96	13.97	1.73
6	Ru/[HO-emim]Cl	61.82	3.56	1.44	1.42	11.24	1.21

^a Reaction condition: alkaline cellulose (0.1 g), Ru/C (0.02 g, 5 wt%) or Ru nanoparticles (0.001 mmol), H₂O (2 mL), H₂ (5 MPa), 433 K and 5h. XL: xylitol; EL: erythritol; GL: glycerol; 1,2-PDO: 1,2-propanediol; EG:

ethylene glycol.

^b Conversion of alkaline cellulose.

^c The substrate was not pre-treated with NaOH solution.

It can be seen from Table 1 that it has the lowest conversion (21.97%) of native cellulose over commercial Ru/C catalyst, and the detected products were mainly xylitol and erythritol, moreover, no C2~C3 polymers were detected. In contrast, the conversion was higher for alkaline cellulose (59.23 %) over the same Ru/C catalyst with 1,2-propanediol in majority. This result suggested that alkaline pretreatment had profound effects to the hydrogenolysis of cellulose to low molecular weight products.

Seen from Table 1(Entry 3-6), Ru/[Bmim]PF₆ nanoparticles showed a much higher conversion of alkaline cellulose (65.22 %) than that on Ru/C catalyst (21.97 %). Furthermore, remarkably high selectivity to C2~C3 polyols (58.91 %) was obtained over Ru/[Bmim]BF₄ catalysts, while only 26.11 % selectivity of C2~C3 polyols was gained from Ru/C catalyst. This may attribute to the small diameter and the high dispersion of nanoparticles which provided larger amounts of active sites. From the molecular point of view, monodisperse ruthenium nanoparticles will make the trend of entering the internal structure of cellulose in the aqueous solution more obvious, thereby improving the conversion of cellulose. Ionic liquid [Bmim]BF₄ has a larger molecular steric hindrance than [Bmim]Cl and [HO-emim]Cl. Meanwhile, considering of anion, it can be seen that the electronegativity of F is greater than that of Cl, so [Bmim]Cl is weaker in the effect of catalytic hydrogenation than that of [Bmim] BF₄. Therefore, [Bmim] BF₄ displays better selectivity for C2~C3 polymers.

To clarify this point further, Fig. 1 were demonstrated that how does the Ru/IL nanoparticle catalyst have high catalytic performance for alkaline cellulose. The amorphous region due to the cleavage of the alkaline cellulose carbon chain makes the nano-sized catalyst easier to enter the interior of the cellulose for basic catalytic reaction, while the carbon-supported catalyst can only react on alkaline cellulose surface to break the chain. It makes a larger area of the amorphous region for Ru/IL nanoparticles to enter the interior. Thus, Ru/C has a lower catalytic efficiency than the nanoparticle catalyst.

Effect of crystalline structure for hydrogenolysis

To investigate the structural changes after hydrogenolysis reaction over different catalysts, the morphology of untreated cellulose and alkaline cellulose before and after hydrogenation are presented in Fig.2(a) and (c). The untreated microfiber cellulose has fine structure and relatively flat surface, while the alkaline cellulose exposes a kind of semi-dissolved amorphous region which is formed of microfiber and tiny cavities. The chemical reactions between cellulose and NaOH cause the rupture of cellulose chains, which reduced their crystallinity and make them easier to be hydrogenated. For this reason, alkaline cellulose appears to a better catalytic activity. In hydrogenation process, the amorphous region of the alkaline cellulose is the main conversion site and metal Ru is playing the main role of hydrogenolysis.

As Ru/C catalyst, the metal Ru is supported on the C atom. During the reaction, the C atom is too large to penetrate into the interior of the cellulose which may not result in a further degradation. Seen from Fig.2(b), because the surficial structure becomes smooth after degradation reaction, Ru/C catalyst is easily to wash away. It shows that the surface of the alkaline cellulose before the reaction has a large number of amorphous regions, so that it forms many open regions, which provides excellent conversion spots for hydro-conversion. When the hydrogenation reaction over Ru/C catalyst is carried out, the active region is converted, so that the crystallized region having a good degree of polymerization is exposed. Ru/C catalyst can only carry out the hydrolysis reaction of the active site of the alkaline cellulose to obtain an intermediate product such as glucose, and catalyze the reaction with the metal Ru on the surface of the C atom in a liquid environment to complete the process of breaking bonds and hydrogenation to form new polyol products.

(a) untreated cellulose; (b) untreated cellulose after hydrogenation on Ru/C ; (c) alkaline cellulose (d) alkaline cellulose after hydrogenation on Ru/C; (e) alkaline cellulose after hydrogenation on Ru/[Bmim]BF₄ nanoparticles.

Ru nanoparticles has the same active sites as Ru/C catalyst, Nonetheless, due to its minisize that Ru nanoparticles could penetrate into the interior of the alkaline cellulose through the small cavities, depressions or scars on the surface. This permeability leads to a further conversion and degradation in alkaline cellulose. It is interesting to note that, the rinse after the reaction does not entirely take away the nanoparticles hidied in the cavies.

Effect of Nickel-doped Ru/IL in hydrogenation

In the same synthetic path, Ni-Ru/ILs was prepared for hydrogenolysis. When Ni was added into Ru nanoparticles as an ameliorant, the catalytic performances were improved (Table 2). The alkaline cellulose conversions over Ni-Ru/IL catalysts were all increased compared to reactions catalyzed with Ru/IL catalysts (Table 1), and the highest conversion was also achieved by the catalyst prepared with [Bmim]PF₆ ionic liquid (67.21%). From the comparison of Table 1 and Table 2, the same growth trending of conversion rate proves again that ionic liquid promotes the conversion of cellulose, and also shows that the conversion rate of hydrophobic ionic liquid to cellulose is better than that of hydrophilic ionic liquid. It should be noted that, contrary to expectation, the selectivity to C2~C3 polyols with Ni-Ru/[Bmim]Cl catalysts was much higher than that catalyzed by other Ni-Ru/IL catalysts. Especially, the selectivity to ethylene glycol is growing up to almost eleven times. The maximum selectivity of C2~C3 polymers of 62.66% was observed in the case of using Ni- Ru/[Bmim]Cl catalyst, which was 3.5 times higher than that from Ru/[Bmim]Cl catalyst. Ni-Ru/[HO-emim]Cl still had a poor preforms that the selectivity of C2~C3 polymers was totally 22.58%.

Table 2 Catalytic activity of Ru catalysts on hydrogenolysis conversion of alkaline cellulose ^a

Entry	Catalyst	Conv. ^b (%)	Selectivity (%)				
			XL	EL	GL	1,2-PDO	EG
1	Ni-Ru/[Bmim]PF ₆	67.21	11.54	3.25	5.43	27.60	7.44
2	Ni-Ru/[Bmim]BF ₄	65.07	3.41	3.60	12.02	24.88	11.71
3	Ni-Ru/[Bmim]Cl	59.67	7.17	3.29	19.52	24.13	19.01
4	Ni-Ru/[HO-emim]Cl	62.41	7.07	1.93	1.53	16.55	4.50

^a Reaction condition: alkaline cellulose (0.1 g), Ni-Ru/IL nanoparticles ($n_{\text{Ni}}:n_{\text{Ru}}=2:1$, $n_{\text{Ru}}=0.001$ mmol), H₂O (2 mL), H₂ (5 MPa), 433 K and 5h. XL: xylitol; EL: erythritol; GL: glycerol; 1,2-PDO: 1,2-propanediol; EG: ethylene glycol.

^b Conversion of alkaline cellulose.

This is because that nickel is a transition metal and has a d-electron orbital which is not full. Due to the holes of the d orbital, the ability to accept external electrons and adsorbed substances to bond with them is enhanced. The addition of nickel enhances the ability of the active metal to adsorb electrons, and plays a positive role in the fracture of C-C bonds. In nickel-doped Ru/IL catalysts, Ni promotes long-chain molecules to further break C-C bonds, so the selectivity to C2~C3 will increase. Comparing Table 1, it can be seen that the conversion of alkaline cellulose is not obvious, and the selectivity to 1,2-propanediol is not greatly improved, but the selectivity to ethylene glycol is increased several times. Despite, ionic liquid [HO-emim]Cl displays a weakness in generating C2~C3 polymers. In ionic liquid [HO-emim]Cl, the lone pair electrons carried by oxygen in the hydroxyl group may form a repulsive force against the lone pair electrons in the hydroxyl groups of cellulose, thereby causing the separation of the active center germanium atoms and reducing the catalytic selectivity.

Left-hand axis: selectivity; right-hand axis: conversion(i). Reaction condition: alkaline cellulose (0.1 g), H₂O (2 mL), H₂ (5 MPa), 433 K and 5 h. Ni-Ru/IL catalyst (the amount of Ru is 0.001 mmol): (a) Ni-Ru/[Bmim]BF₄; (b) Ni-Ru/[Bmim]PF₆; (c) Ni-Ru/[Bmim]Cl; (d) Ni-Ru/[HO-emim]Cl.

Figure 3 illustrates the effect of nickel content for hydrogenolysis of alkaline cellulose pre-treated with 4% NaOH solution. It was clear that the effect of the addition amount of nickel on the catalyst prepared by different ionic liquids has the same effect on the conversion trend, and all have a good conversion rate when the proportion of nickel is 53.7%. On the other hand, the addition of nickel in the catalyst prepared by different ionic liquids has different effects on the selectivity of the products, but in general, erythritol is the main product when Ni/ILs is used alone, and 1,2-propanediol is the main product on Ru/ILs catalysts, and the selectivity of glycerol is relatively higher when the amount of nickel added is 53.7%.

Effect of reaction time in hydrogenolysis

To further understand the process of selective change in the reaction, the effect of reaction time during hydrogenolysis of alkaline cellulose on 53.7 % Ni-Ru/[Bmim]BF₄ catalyst were presented in Figure 4. It is clear that the conversion rate was rapidly increased from 42.9 % to 65.07 %, and barely raised after 5h. The products with selective advantages were mainly 1,2-propanediol and ethylene glycol at 1 h. When the reaction was carried out for 2 h, the selectivity of xylitol was significantly improved from 8.18 % to 12.17 %, and the selectivity of erythritol was slightly decreased, indicating that the cellulose was mostly subjected to hydrolysis to form polyols such as xylitol, and erythritol was catalyzed to degrade that may means a tendency to convert to lower alcohols. When the reaction was carried out for 5 h, the selectivities of glycerol and 1,2-propanediol were significantly improved to 11.71 % and 24.88 %, respectively. The rapid decrease in xylitol selectivity indicated that the polyols such as xylitol were cleaved by C-C bonds and converted to C3. Nevertheless, even the reaction time increased to more than 10 h, the selectivity of C2~C3 polyols decreased slightly. After 24 h, the selectivity to C2~C3 polyol remained unchanged with the slight increase of conversion. Therefore, the study considers that 5 h is the optimum reaction time for alkaline cellulose at 433 K reaction temperature and 5 MPa H₂.

Mechanism

The major polyols detected by HPLC and ESI-MS were xylitol, erythritol, glycerol, 1,2-propanediol and ethylene glycol. Other by-products that can be detected but not significant were glucose, sorbitol, formic acid, glyceraldehyde, methanol and ethanol. The hydrogenolysis process of alkaline cellulose on metal nanoparticle catalysts is described in Scheme 1. Cellulose was firstly hydrolyzed into sugars, mainly glucose, and then converted in the pathway to polyols and aldehyde as intermediates under alkaline conditions (Yin et al. 2011). These intermediates transform through a series of the retro-aldol reaction in the presence of hydroxy ions (Zhao et al., 2010), and finally hydrogenated on metals. In another pathway, the vapors of primary and secondary alcohols can dehydrogenate on the surface of the metal Ni catalyst at high temperature to form aldehydes and ketones, respectively. The intermediates generally contain one or two unsaturated bonds which are too unstable to be hydrogenated in the following steps.

The main pathways to obtain 1,2-propanediol and ethylene glycol are described in scheme 1. Cellulose firstly hydrolysis to glucose, one way is hydrogenation to sorbitol, sorbitol is then hydrocracking to glycerol directly (Pathway III) or dehydrogenated to ketone which will crack and being hydrogenated to ethylene glycol and erythritol (Pathway I) (Knill and Kennedy, 2003). Another straightway is that glucose is hydrocracked to ethylene glycol and erythritol (Pathway IV). The other probable way is that glucose is hydrocracked to xylitol in the first step and then through dehydration of polyols to enols (Montassier et al. 1991). The unstable enol form will change their structures to ketone. In this structure of ketone, the presence of electron-withdrawing group makes adjacent carbon atom become positive, so they are more likely to be dehydrogenated. In this way, during the hydrogenation process, it promotes a retro-aldol reaction, which converts the ketone into 1,2-propanediol and ethylene glycol (Pathway II) (Li and Huber, 2010). Due to the nano-size of metal catalyst which is benefit of increasing the contact area between

catalyst and raw material, the conversion of cellulose was promoted. It is well known that Ru is an effective catalyst for hydrogenation, and Ni has a good performance in C-C bond cleavage.

Compared to the monometal ruthenium catalyst, the selectivity of 1,2-propanediol is higher than that of xylitol in the initial stage of the reaction. It indicates that in the presence of metallic nickel, a-H is more likely to undergo an elimination reaction with b-H, which causes a-C to be changed to a methyl group, and then a bond breaking and hydrogenation reaction occurs to increase the yield of 1,2-propanediol, while long-chain polyols are broken and converted to C2~C3. In Scheme 1, likewise, C3-C6 polyols can undergo a reaction similar to pathway I. Therefore, it can be seen that after the addition of nickel, not only the conversion rate of the reaction is improved, but also the selectivity of the C2-C3 polyol such as 1,2-propanediol can be significantly improved.

Conclusions

In summary, the ionic liquid-stabilized nanoparticle catalyst can effectively improve the conversion of alkaline cellulose in hydrogenolysis reaction and the selectivity to C2~C3 polyols. Especially, Ru/[Bmim]BF₄ allows a better selectivity of C2~C3 sugar alcohols in comparison with that of the Ru/C catalyst. The Ru/IL nanoparticle catalyst doped with Ni can further enhance the selectivity to C2~C3 polyols.

SEM characterization was used to illustrate the structural changes of alkaline cellulose before and after reactions. The SEM micrographs showed that the surfaces of alkaline cellulose were much rougher and exposing many cavities which could make nano-size catalyst pass through. For monometallic catalyst, it surely suggested that Ru/[Bmim]BF₄ was much better for 63.78 % conversion in 5 h was achieved at 433 K with the main products of glycerol, 1,2-propanediol and ethylene glycol, the total selectivity of them was up to 58.91%. Moreover, 53.7 % Ni-Ru/[Bmim]BF₄ could promote the selectivity of C2~C3 polyols to 65.07%. Meanwhile, according to the rule that the product changes with time, the basic path of alkali cellulose hydrolysis can be proposed. Due to excellent catalytic cracking ability of Ni in hydrogenolysis, hydrolyzed cellulose could be directly broken and hydrogenated to form glycerol. At the same time, the hydrolyzate was subjected to retro-aldol reaction to obtain lower molecular alcohols.

In general, using alkaline cellulose combined with ionic liquid-stabilized ruthenium nanoparticles for hydrogenolysis can better promote the degradation of cellulose and convert it into low-molecular polyols. Optimizing the type and loading amount of metal on catalyst can expect better results.

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Availability of data and material

Not applicable

Code availability

Not applicable

Author's contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Scheme

Please see the Supplementary Files for the Scheme 1.

Figures

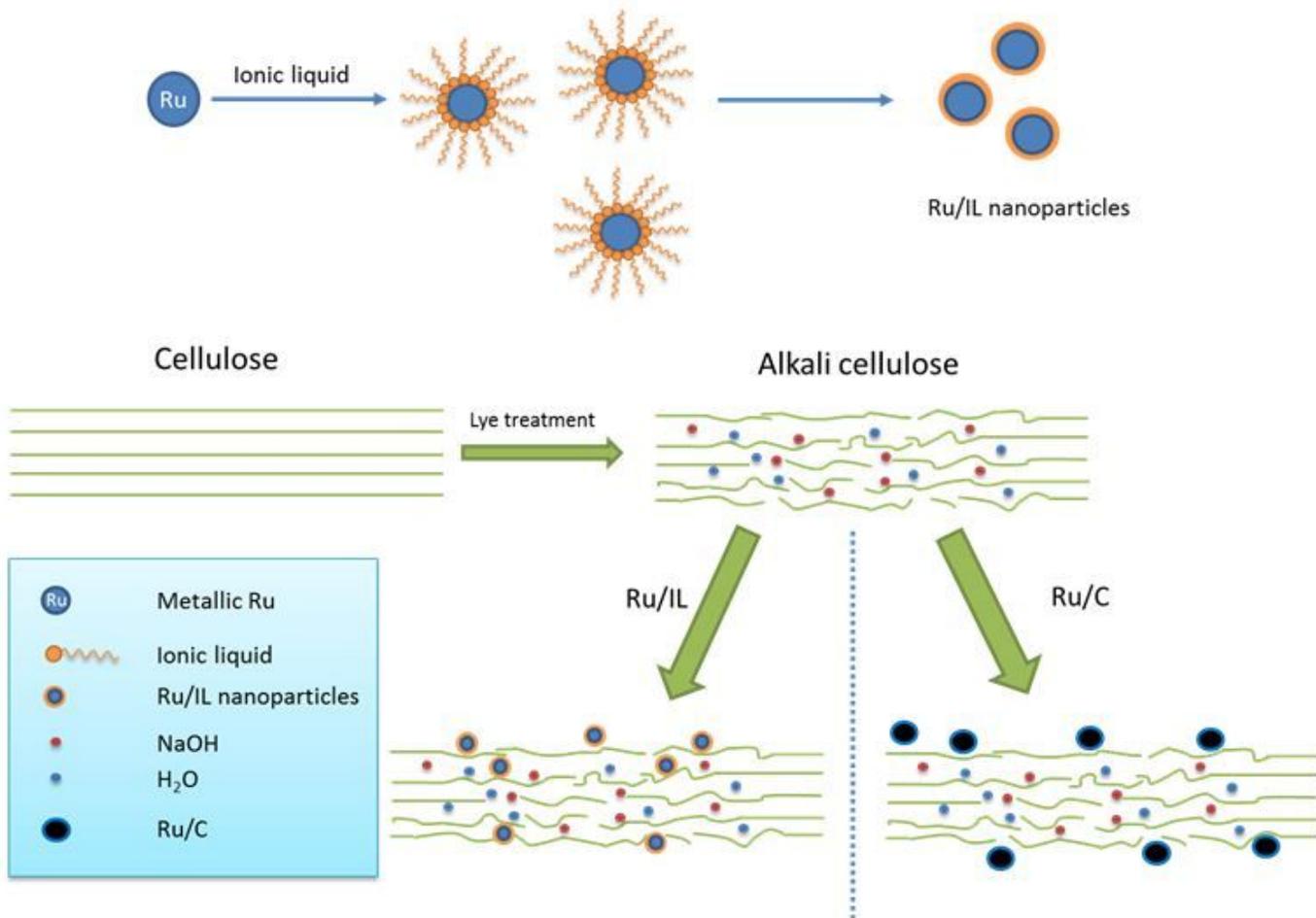


Figure 1

Schematic diagram on synthesis of Ru/IL nanoparticles and catalytic process of alkaline cellulose

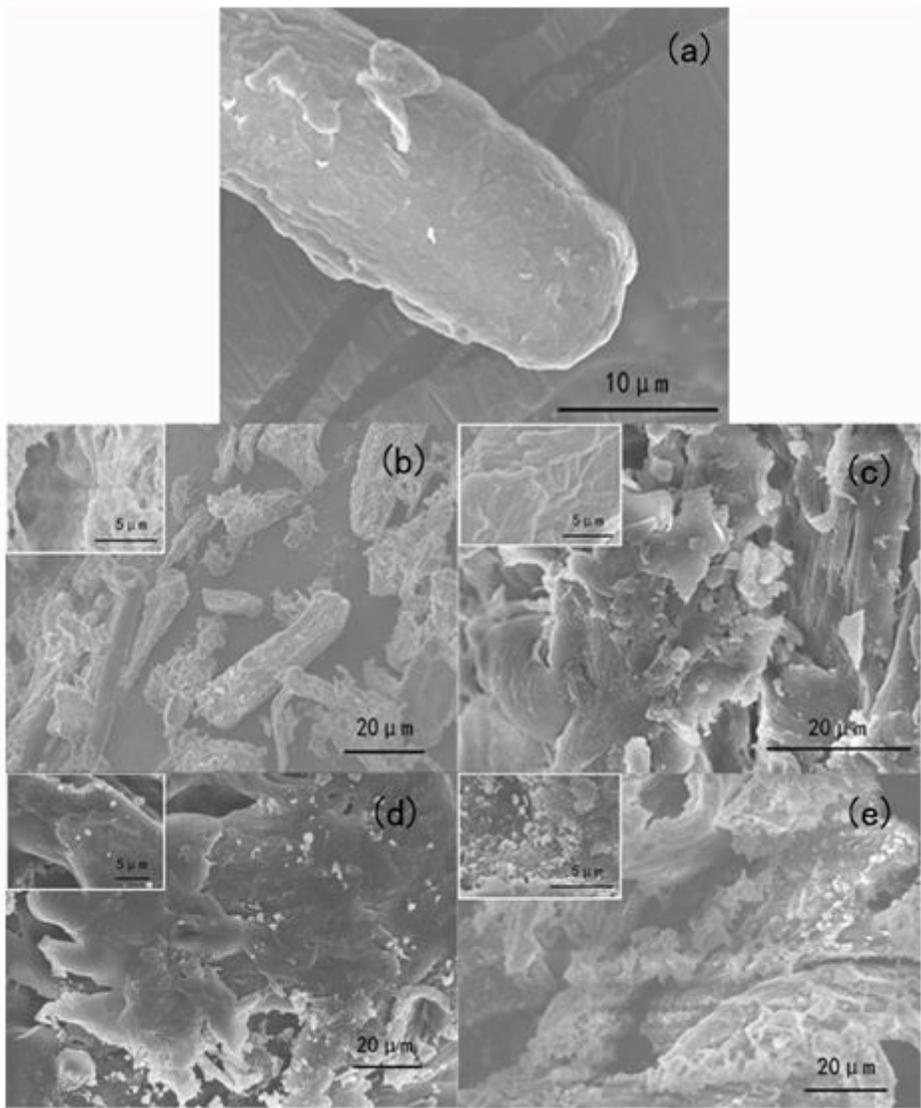


Figure 2

SEM micrographs of cellulose and alkaline cellulose

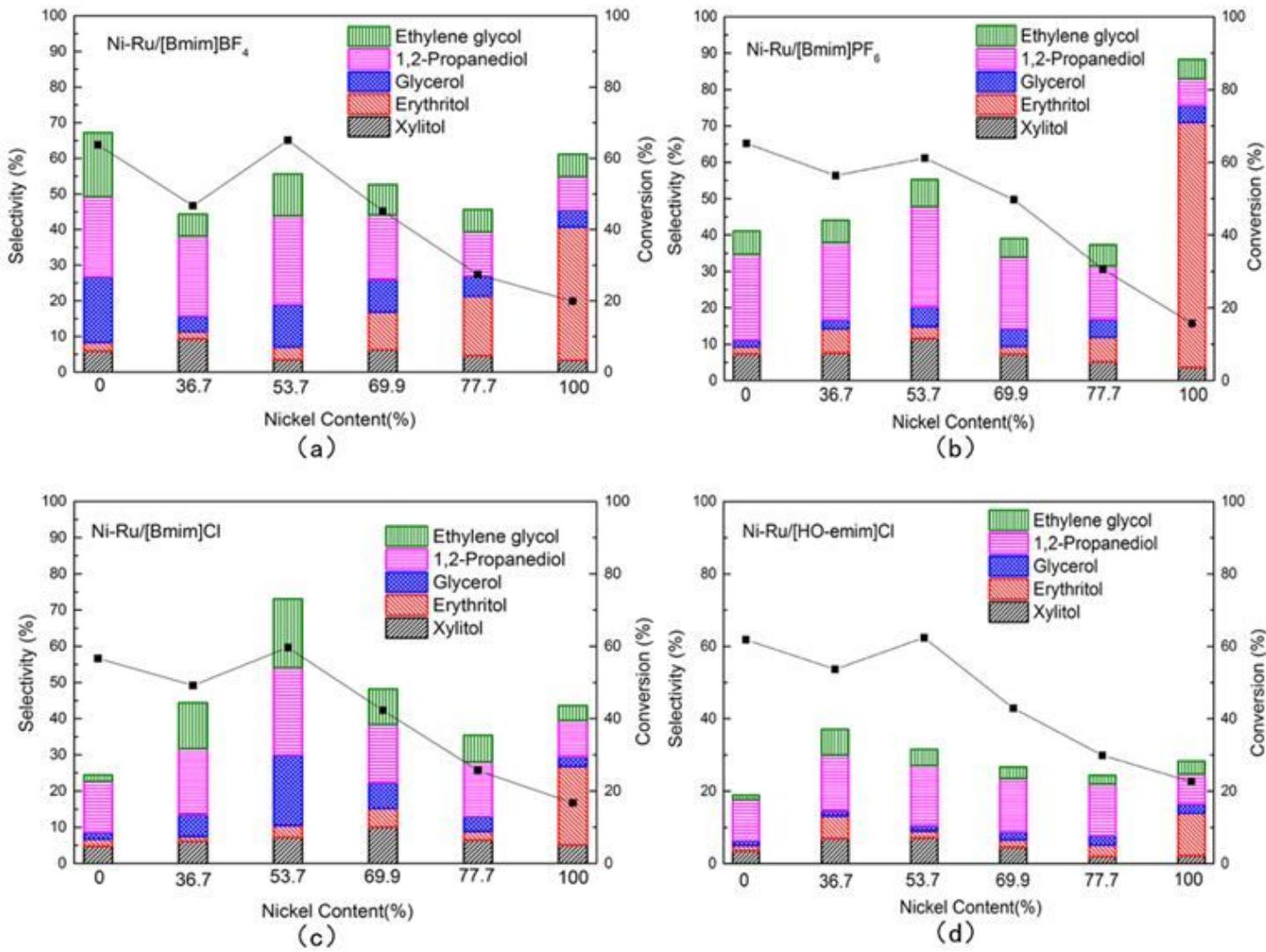


Figure 3

Effect of Nickel content for hydrogenolysis of alkaline cellulose pre-treated with 4% NaOH solution

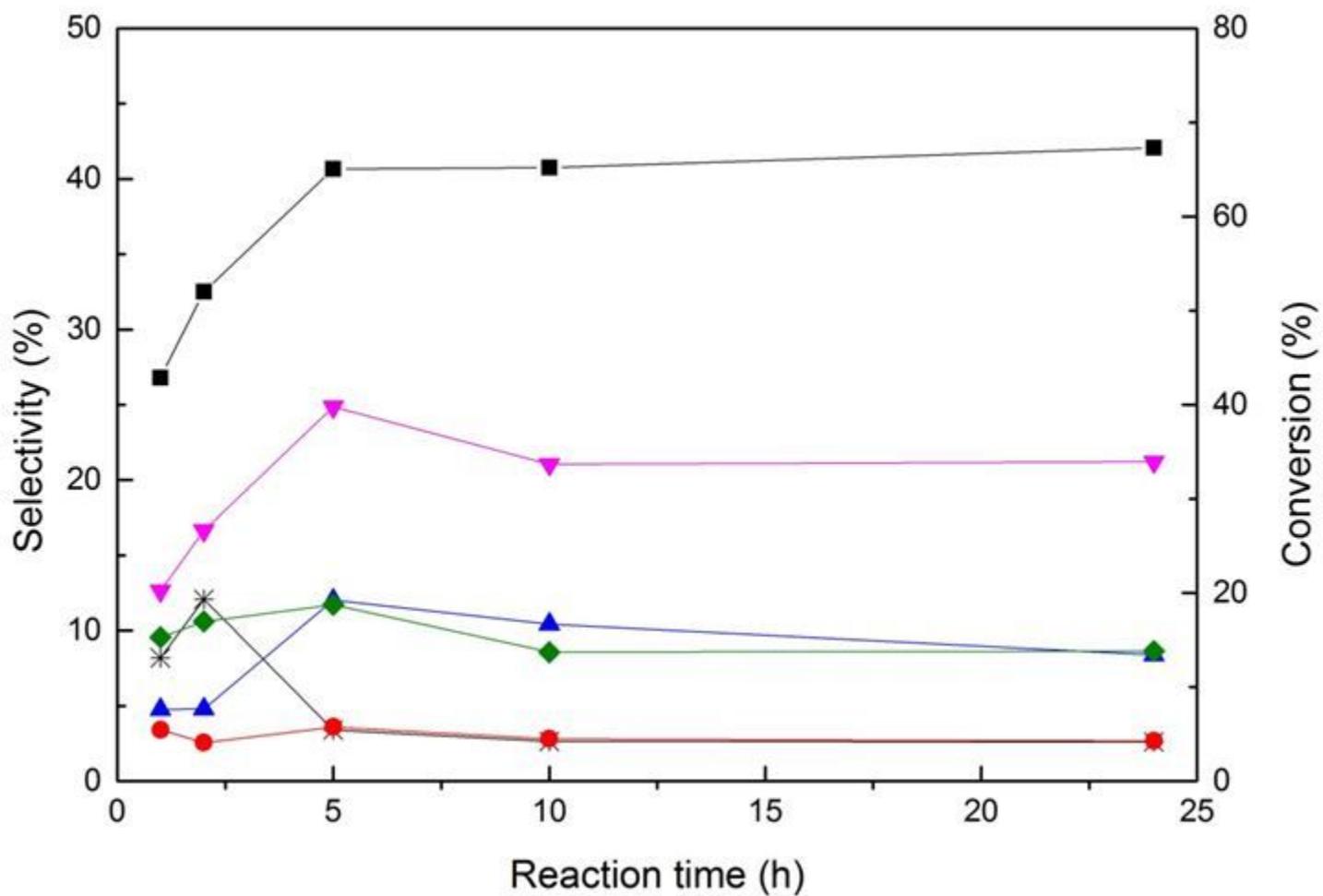


Figure 4

Conversion and selectivities as a function of reaction time at 433 K on 53.7 w% Ni-Ru/[Bmim]BF₄ for cellulose pre-treated with 4% NaOH solution. Left-hand axis: selectivity to xylitol (□); erythritol (◇); glycerol (▲); 1,2-propanediol (▼); ethylene glycol (○); right-hand axis: conversion (■).

Supplementary Files

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- [scheme1.jpg](#)
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