Enhanced Sugar Alcohol Production from Cellulose by Pretreatment with Mixed Ball-Milling and Solid Acids

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Efficient pretreatment is the key step in catalytic biomass conversion. Herein, a mixed ball-milling method was used to pretreat cellulose with a solid catalyst. The method was tested with solid acid and commercial 5 wt% Ru/C in water, and the effect of pretreatment on yield was measured by the hydrolytic-hydrogenation of cellulose to sugar alcohols, which are the platform compounds for the production of gasoline and fine chemicals. The influence of ball-milling mode, time, and reaction parameters was studied. The properties of cellulose and the catalyst were also analyzed before and after treatment. The yield of sugar alcohols reached 90.3% at 463 K with amorphous zirconium phosphate (ZrP) and Ru/C and a mixed ball-milling time of 2 h. The high sugar alcohol yield was achieved 12 times faster than with the single ball-milling method under the same reaction conditions for 24 h. This effect is ascribed to the enhanced contact between cellulose and catalyst, which promotes the rate-determined cellulose depolymerization to obtain high sugar alcohols yield.

Keywords: Cellulose; Sugar alcohols; Hydrolytic-hydrogenation; Solid acid; Mixed ball-milling

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INTRODUCTION

Lignocellulosic biomass is a renewable resource that has attracted increasing attention in recent years. As it comprises 30% to 50% of lignocellulosic biomass, cellulose represents a greater proportion of this material than hemicellulose or lignin (McKendry 2002). Cellulose is formed by the linkage of β-1,4-glucosidic bonds between glucose units and contains numerous inter- and intra-molecular hydrogen bonds (Klemm *et al.* 2005). It can be converted into platform compounds such as glucose, levulinic acid, 5-hydroxymethylfurfural, lactic acid, and polyols (Fukuoka and Dhepe 2006; Li *et al.* 2008; Zhang *et al.* 2009; Rackemann and Doherty 2011; Deng *et al.* 2013; Dusselier *et al.* 2013; Huang *et al.* 2013; van Putten *et al.* 2013; Mäki-Arvela *et al.* 2014). Of these compounds, sugar alcohols (sorbitol and mannitol) can be converted to liquid fuel (bio-gasoline) through aqueous phase hydrodeoxygenation (Kunkes *et al.* 2008). They also have many applications in chemistry, medicine, the food industry, *etc*. (Bozell and Petersen 2010; Zhang *et al.* 2013). For example, isosorbide, the dehydration product of sorbitol, is a versatile chemical that can be used for synthesizing biopolymers (Op de Beeck *et al.* 2013).

One-pot conversion of cellulose to sugar alcohols is a continuous two-step reaction involving the depolymerization of cellulose to sugars and *in-situ* hydrogenation of soluble sugars to sugar alcohols. Depolymerization of cellulose is the rate-limiting step in this process (Kobayashi *et al.* 2011). However, cellulose depolymerization is hampered by the inaccessibility of the catalyst because of its crystallinity and insolubility in traditional solvents. Liquid acids are more efficient because the contact between cellulose and catalyst is improved, but the recovery and corrosive nature of liquid acids are impediments to bioconversion. Tailor-made solid catalysts can be used to degrade cellulose. They are advantageous because the catalyst is easily recycled, and liquid waste from the reaction does not require neutralization. Despite these advantages, solid catalysts require severe conditions or cellulose pretreatment to achieve high yields from bioconversion. The yield of sugar alcohols is reduced at high temperatures (*e.g.,* higher than 463 K) because of significant side reactions such as hydrogenolysis and dehydration (Luo *et al.* 2007). Additionally, cellulose depolymerization by solid catalysts is a solid-solid phase reaction, and the degradation rate is limited by the inability of catalyst to interact with cellulose surfaces. Therefore, enhancing the contact between cellulose and solid catalyst, which subsequently reduces the reaction temperature and time, is essential for cellulose valorization by heterogeneous catalysis (Shuai and Pan 2012).

Traditional ball-milling has been extensively used in chemical and enzymatic processes to improve the reactivity of cellulose with biocatalysts. The primary aim of mechanical pretreatment is to render cellulose amorphous, thus improving its depolymerization rate. However, this process takes a long time (*e.g.*, 24 h). Hick *et al.* (2010) have developed a mechano-catalytic process for cellulose deploymerization in the presence of solid acids; the ball-milling method obtains 84% cellulose conversion by layered mineral delaminated kaolinite. This approach greatly reduces the energy required for the cleavage of glycosidic bonds, but the selectivity and yield of specific products (glucose, fructose, or levoglucosan) is very low. The mechano-catalytic depolymerization of cellulose is an attractive and efficient method (Zhang and Jérôme 2013). The oligomerization of *in situ*-produced glucose is responsible for the remarkably enhanced selectivity. However, the acidic solution promotes side reactions during steel ball milling (Kobayashi *et al.* 2013). In addition, the mixed ball-milling of activated carbons and cellulose promotes cellulose depolymerization, and this process combined with HCl efficiently convert cellulose to glucose (Kamiya *et al.* 2004).

In this study, a series of solid acid catalysts were blended with cellulose during ball milling. After mixed ball-milling, the mixture of cellulose and solid acid catalyst underwent the hydrolytic-hydrogenation of cellulose to sugar alcohols in the presence of 5 wt% Ru/C. The influence of ball-milling mode, time, and reaction parameters was investigated, and the characteristics of cellulose and the catalyst before and after mixed ball-milling were monitored. Interestingly, this mixed ball-milling technology obtained more than 90% sugar alcohol yield under mild reaction conditions.

EXPERIMENTAL

Materials

Microcrystalline cellulose (Avicel® PH101) was purchased from Sigma-Aldrich and dried at 343 K for 12 h prior to use. $ZrOCl_2 \bullet 8H_2O$ was obtained from Sinopharm Chemical Reagent, China. $NH_4H_2PO_4$ was obtained from Tianjin Fu Chen Chemical Reagents Factory, China. $Na_2SiO_3 \bullet 9H_2O$, $NH_3 \bullet H_2O$, and NH_4NO_3 were purchased from Guangzhou Chemical Reagent Factory, China. Unless otherwise indicated, all chemicals were used without further treatment. The 5 wt% Ru/C was obtained from Aladdin

Industrial Inc., China. HZSM-5 (Si/Al=38), HMOR (Si/Al=10), and Hβ (Si/Al=25) were purchased from the Catalyst Plant of Nankai University, China and were calcined at 773 K in air for 4 h prior to use. Kaolinite was obtained from Tianjin Damao Chemical Reagents Factory, China and calcined at 673 K in air for 4 h. ZrO_2 was purchased from Aladdin Industrial Inc., China and calcined at 773 K in air for 4 h.

Catalyst Preparation

The amorphous zirconium phosphate (ZrP) catalyst was prepared as previously described (Geboers *et al.* 2010). Briefly, ZPA was precipitated from $NH_4H_2PO_4$ (1.0 M, 200 mL) with $ZrOCl_2•8H_2O$ (1.0 M, 100 mL) at the mole ratio of P/Zr=2. The solution was vigorously stirred for 1 h and then filtered. The filter cake was dried at 373 K for 12 h and calcined at 673 K for 4 h in air.

The SiO_2-ZrO_2 composite oxide was prepared as follows. $Zr(OH)_4$ was obtained by adding $NH_3•H_2O$ into the $ZrOCl_2•8H_2O$ solution with continuous agitation until the solution reached pH 8. $Si(OH)_4$ was prepared by the same method but with Na_2SiO_3 as the input solution and NH_4NO_3 saturated solution as the precipitator. $Zr(OH)_4$ and $Si(OH)_4$ were blended with vigorous stirring at a mole ratio of Si/Zr=3. The mixed precipitate was incubated overnight at 348 K. The precipitate was filtered, washed with water to remove chloride ions completely, and dried at 393 K overnight. Before the reaction, SiO_2-ZrO_2 was calcined at 773 K in air for 5 h.

Ball-milling Treatment of Cellulose

Ball-milling of cellulose was conducted using a planetary ball mill (QM-3SP04, Nanjing NanDa Instrument Plant) at room temperature. For single ball-milling, microcrystalline cellulose was charged in a 100-mL ZrO_2 container, and the ball-milling was carried out at a speed of 500 rpm with ZrO_2 balls (15 balls, Φ=7 mm) for 0-4 h. For mixed ball-milling, microcrystalline cellulose and the solid acid catalyst were charged in a 100-mL ZrO_2 container, and the ball-milling was carried out at a speed of 500 rpm with ZrO_2 balls (15 balls, Φ=7 mm) for 0-4 h. To avoid thermal degradation of the microcrystalline cellulose, the temperature was not higher than 333 K.

Hydrolytic-Hydrogenation of Cellulose to Sugar Alcohols

The conversion of ball-milled cellulose was conducted in a 100-mL stainless steel autoclave (316 L) equipped with magnetic agitation. In a typical reaction, solid acid catalyst with commercial 5 wt% Ru/C, ball-milled cellulose, and H_2O were charged in the autoclave and pressured with H_2 to 6 MPa at room temperature. The residual air was removed by several hydrogen purges. The reactor was heated to a given temperature with stirring and held at this temperature for 2.5 h. After the reaction, the system was quickly cooled with water. The aqueous products and solid residue were separated by filtration and decantation. The aqueous products were analyzed by high-performance liquid chromatography (HPLC).

Characterization

The cellulose particle size distribution was measured using a Zetasizer Nano ZS (Malvern Instruments Ltd., UK). The ^{13}C CP/MAS NMR analysis was conducted on an AVANCE III 300 WB spectrometer (7.05 T; Bruker, USA). X-ray powder diffraction (XRD) patterns were measured by an X-ray diffractometer (X'PERT Pro MPD, Philips, Netherlands) with Cu Kα radiation (λ=0.154 nm) operated at 40 kV and 100 mA. The

BET specific surface area and average pore diameter were measured by N_2 isothermal adsorption-desorption profiles at 77 K using a QUADRASORB PoreMaster 33 analyzer, USA. Ammonia-temperature programmed desorption (NH_3-TPD) was conducted in a U-tube quartz reactor using an ASIQACIV200-2 automatic physical/chemical adsorption analyzer (Quantachrome, USA). Scanning electron microscopy (SEM) images were monitored using a Hitachi S-4800 instrument operated at 10 kV.

The solubility of cellulose after ball-milling was monitored gravimetrically. The water-soluble intermediates were observed by stirring the mixed ball-milled sample in 50 mL of water. The solution was passed through a Millipore filter with a pore size of 0.22 μm. The residue was dried at 343 K overnight and then weighed.

Product Analysis

The aqueous products were detected by high performance liquid chromatography (HPLC; Waters e2695, USA) by a refractive index detector. An Inertsustain C_{18} column was used to analyze the polyols, and water was used as the mobile phase. An external standard method was used for quantification.

Cellulose conversion was quantified by the difference in cellulose weight before and after the reaction, as given by:

$$\text{Conversion (\%)} = \frac{m_{\text{cellulose,0}} - m_{\text{cellulose}}}{m_{\text{cellulose,0}}} \times 100\% \tag{1}$$

where $m_{\text{cellulose,0}}$ is the weight of cellulose charged in the reactor and $m_{\text{cellulose}}$ is the weight of residual cellulose after the reaction. $m_{\text{cellulose}}$ was calculated as follows:

$$m_{\text{cellulose}} = m_{\text{residue}} - m_{\text{catalyst}} \tag{2}$$

where m_{residue} is the weight of residual solid after the reaction and m_{catalyst} is the weight of solid catalysts (solid acid catalyst and Ru/C).

The yield of sugar alcohols was determined by the carbon moles in sugar alcohols and carbon moles in the cellulose charged in the reactor. The yield ($Y_{\text{sugar alcohols}}$) was calculated as

$$Y_{\text{sugar alchols}} = \frac{C_{\text{sugar alcohols}}}{C_{\text{cellulose,0}}} \times 100\% \tag{3}$$

where $C_{\text{sugar alcohols}}$ is the carbon moles of sugar alcohols and $C_{\text{cellulose,0}}$ is the carbon moles of cellulose charged in the reactor, which was calculated as follows:

$$C_{\text{cellulose,0}} = \frac{m_{\text{cellulose,0}}}{M(C_6H_{10}O_5)} \times 6 \tag{4}$$

where $m_{\text{cellulose,0}}$ is the weight of cellulose charged in the reactor and $M(C_6H_{10}O_5)$ is the molecular weight of anhydroglucose units.

The selectivity of product was calculated by the following equation:

$$S_{\text{sugar alcohols}} = \frac{Y_{\text{sugar alcohols}}}{\text{Conversion}} \times 100\% \tag{5}$$

where $Y_{\text{sugar alcohols}}$ is the yield.

The concentration of sugar alcohols was determined by the following equation:

$$\text{Concentration}_{\text{sugar alcohols}} = \frac{Y_{\text{sugar alcohols}} \times C_{\text{cellulose,o}} \times 182}{6 \times V_{\text{liquid}}} \times 100\% \tag{6}$$

RESULTS AND DISCUSSION

Comparison of Ball-Milling Modes

Several solid acid catalysts combined with 5 wt% Ru/C were tested in hydrolytic-hydrogenation of single and mixed ball-milled cellulose under the same reaction conditions (Table 1). Solid acid catalyst was important for cellulose transformation because the conversion of cellulose and the yield of sugar alcohol were 16.8% and 1.5%, respectively, with only Ru/C added (entry 1). Conversion of cellulose with mixed ball-milling was higher than with single ball-milling, which illustrated that blending cellulose and solid acid catalyst during ball-milling promoted cellulose transformation (entry 2 to 8) to the target product. During this process, cellulose is firstly hydrolyzed to glucose over acidic catalyst and then hydrogenated to sugar alcohols by the Ru/C catalyst. Apart from the above mentioned route for producing sugar alcohols, side products such as glycerol, propanediols and ethylene glycol, could be also obtained by hydrogenolysis of intermediate glucose and final sugar alcohols. The mix ball-milling possibly improves contact between cellulose and solid acid catalyst and is thus favorable for the rate-determined cellulose hydrolysis to glucose, followed by hydrogenation to obtain the significantly enhanced sugar alcohols yield. Generally, hydrogenation of glucose and hydrogenolysis of glucose/sugar alcohols occur simultaneously at the surface of Ru/C. Comparing to hydrogenolysis of glucose/sugar alcohols, glucose hydrogenation to sugar alcohols is preferable due to the lower activation energy. Indeed, the yield of hydrogenolysis products was lower than 5% over all of the combined solid catalysts by the two ball-milling models, indicating that such kind of side products were suppressed.

Cellulose conversion was influenced noticeably by different solid acid catalysts (Table 1). For single ball-milled cellulose, less than 40% conversion was achieved with Kaolinite, ZrO_2, and SiO_2-ZrO_2. In contrast, 75% to 78% conversion was obtained by H-MOR, Hβ, HZSM-5, and ZrP. These differences probably reflect intrinsic properties of the catalysts.

Table 2 shows the textual and acidic properties of solid acid catalysts. Generally, the solid acids with larger surface area and acidic amount presented higher cellulose conversion and sugar alcohols selectivity due to enhanced cellulose hydrolysis (Table 1), but there were no obvious relationship for volume and pore size. Comparing to ZrP, SiO_2-ZrO_2 showed large surface area but only obtained the activity of below 50% for both ball-milling models, possibly due to its weak acidity. Although the microporous zeolite HMOR, Hβ, and HZSM-5 showed larger surface area than ZrP, their performance was inferior based on cellulose conversion and sugar alcohols yield under mixed ball-milling condition. This is possibly attributed to the acidic sites within the micropores of zeolites limited contact by the large molecular cellulose, resulting in the reduced hydrolysis efficiency, besides possessing less acidic sites comparing to ZrP. Among the catalysts tested, ZrP presented the superior performance with enhanced cellulose conversion and sugar alcohol yield. Therefore, ZrP was selected as the solid acid for the subsequent experiments.

Table 1. Conversion of Cellulose to Sugar Alcohols by Solid Catalysts Combined with Ru/C [a]

Entry	Solid Acid Catalyst	Cellulose Conversion (%)		Sugar Alcohol Yield (%)		Sugar Alcohols Selectivity (%)	
		Single Ball-Milling	Mixed Ball-Milling	Single Ball-Milling	Mixed Ball-Milling	Single Ball-Milling	Mixed Ball-Milling
1[b]	-	16.8	-	1.5	-	8.9	-
2	Kaolinite	23.4	30.0	0.03	3.7	0.13	12.3
3	ZrO_2	21.8	31.1	1.0	4.7	4.6	14.8
4	SiO_2-ZrO_2	39.8	50.1	4.1	8.3	10.3	16.6
5	H-MOR	75.6	81.5	35.8	40.0	47.4	49.1
6	Hβ	77.1	85.1	41.5	51.5	53.8	60.5
7	HZSM-5	78.2	86.9	41.7	48.9	53.3	56.3
8	ZrP	77.6	100.0	65.1	90.3	83.9	90.3

[a] Reaction conditions: cellulose, 1 g, solid acid catalyst, 0.9 g, 5 wt% Ru/C, 0.075 g, H_2O, 50 mL, 463 K, H_2, 6 MPa, reaction time, 2.5 h

[b] No solid acid catalyst used

Table 2. Textural Properties and Acid Densities of the Solid Acid Catalysts

Entry	Catalyst	Surface Area[a] (m^2/g)	Volume[b] (cm^3/g)	Average Pore Diameter[b] (nm)	Acid Density (mmol/g)
1	Kaolinite	9	0.07	26.12	0.11
2	ZrO_2	5	0.05	27.49	0.42
3	SiO_2-ZrO_2	253	0.91	7.88	0.82
4	HMOR	574	0.21	0.61	1.15
5	Hβ	541	0.19	0.49	1.24
6	HZSM-5	320	0.22	2.75	1.19
7	ZrP	127	0.31	4.83	1.80
8	Ru/C	1176	0.28	3.82	–

[a] surface area, calculated by BET method; [b] volume and average pore diameter, calculated from desorption branch by BJH method.

Next, the influence of ball-milling time on cellulose transformation by ZrP was examined (Fig. 1). Cellulose conversion increased from 34% for microcrystalline cellulose (no ball-milling, 0 h) to 87% and 63% after 1 h of mixed and single ball-milling, respectively. The overall time (the sum for reaction and ball-milling time) for ball-milled cellulose (3.5 h) was shorter than for microcrystalline cellulose (4.5 h).

For the single ball-milling, cellulose conversion and sugar alcohol yield gradually increased with ball-milling time. After 4 h, 90.3% cellulose conversion and 70.7% sugar alcohol yield were obtained. Comparatively, the mixed ball-milled cellulose was completely converted after 2 h, and the highest sugar alcohol yield reached 90.3% at this time point. This yield was the highest obtained in this study. Moreover, the total ball-milling and reaction time (4.5 h) was remarkably shortened by this optimized process compared with previously published methods where the overall time was greater than 24 h (Park *et al.* 2013). This result demonstrated that mixed ball-milling of cellulose and solid acid catalyst is highly effective in promoting cellulose conversion. Although these reactions required higher reaction temperatures, there was no need to neutralize the products or used acid solution. Thus, the method is both eco-friendly and beneficial for suppressing the side reactions of sugar alcohols, for example, sorbitans by dehydration and small glycerol, propanediols and ethylene glycol by hydrogenolysis. As the highest sugar alcohol yield was obtained at the ball-milling time of 2 h, this time was chosen to study the influence of other reaction parameters.

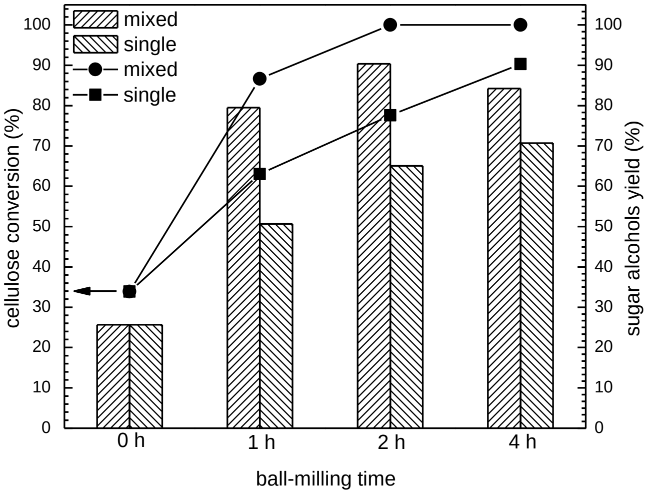

Fig. 1. The influence of ball-milling time on hydrolytic-hydrogenation of cellulose to sugar alcohols Reaction conditions: cellulose 1 g, ZrP 0.9 g, 5 wt% Ru/C 0.075 g, H_2O 50 mL, 463 K, H_2 6 MPa, reaction time 2.5 h. For 0 h, the reaction time was 4.5 h. Bars indicates sugar alcohol yield; data points and lines represent cellulose conversion.

The Effect of Reaction Time and Temperature

The effect of reaction temperature on mixed ball-milled cellulose transformation was studied (Fig. 2(a)). Cellulose conversion increased with increasing reaction temperature, and cellulose was completely converted at 463 K. As the reaction temperature increased, the sugar alcohol yield also gradually increased to the highest yield (90.3%) at 463 K. However, as the temperature further increased to 473 K, the sugar alcohol yield decreased to 82%. This reduction was likely due to side products such as sorbitans and small molecular polyols produced from sugar alcohols dehydration and hydrogenolysis, respectively.

The effect of reaction time on the mixed ball-milled cellulose conversion was also investigated (Fig. 2(b)). Compared with reaction temperature, reaction time showed a moderate effect on cellulose conversion and sugar alcohol yield. When cellulose conversion was lower than 100%, the yield of sugar alcohols experienced the slightly increase.

When cellulose conversion was 100%, the target product yield decreased with prolonging the reaction time because the produced sugar alcohols were converted to the byproducts as mentioned above. To ascertain whether the solid cellulose was degraded to water-soluble intermediates during mixed ball-milling, as previously reported (Hick *et al.* 2010), the solubility of cellulose was tested after mixed ball-milling. The detectable soluble intermediates were no more than 1%, which contrasted with results from the mechano-catalytic depolymerization of cellulose (Hick *et al.* 2010). Water is essential for the disruption of the β-O-4 bond of cellulose. The trace water-soluble intermediates after mixed ball-milling is possibly attributed to residual water after cellulose drying at 343 K.

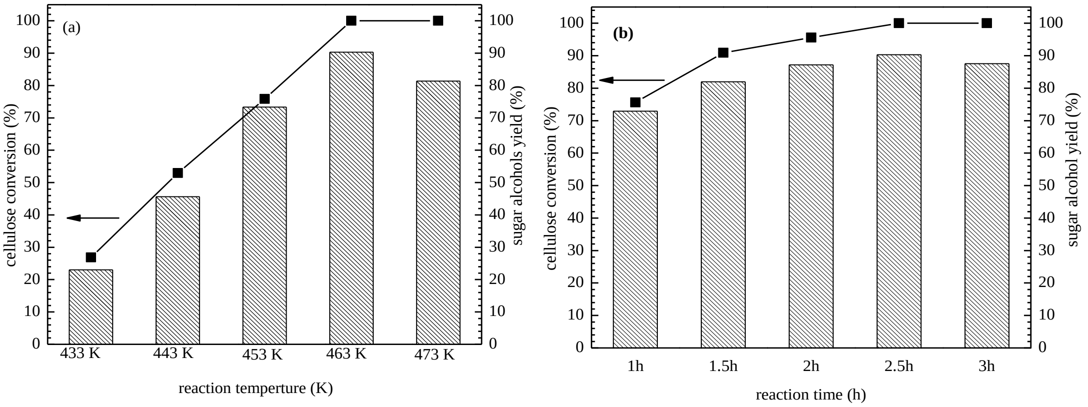

Fig. 2. The effect of reaction temperature (a) and time (b) on hydrolytic-hydrogenation of mixed ball-milled cellulose to sugar alcohols. Reaction conditions: cellulose, 1 g, ZrP, 0.9 g, 5 wt% Ru/C, 0.075 g, H_2O, 50 mL, H_2, 6 MPa, (a) reaction time, 2.5 h, (b) reaction temperature 463 K. Bars indicates sugar alcohol yield; data points and lines represent cellulose conversion.

Characterization of Cellulose and ZrP

To further understand the mixed ball-milling process, the crystallinity of the microcrystalline, single, and mixed ball-milled cellulose were determined by solid state ^{13}C NMR.

As shown in Fig. 3, the peaks between 60 and 110 ppm represented the C_1-C_6 carbons of the cellulose pyranose ring (Kono *et al.* 2002). The signal peak from 86 to 92 ppm was assigned to the C_4 carbon from the crystalline part of cellulose, whereas the field peak at 82 to 86 ppm corresponded to the amorphous part of cellulose. The peaks representing the crystalline part of cellulose clearly decreased after ball-milling, and the single and mixed ball-milled cellulose had similar structures. These results indicated that both ball-milling modes reduces the crystallinity of cellulose.

The particle size distribution of cellulose was also investigated (Fig. 4). The average particle size of microcrystalline cellulose was around 20 μm. Surprisingly, regardless of ball-milling modes, the average particle size of cellulose was not largely changed; both the single and mixed ball-milled cellulose particles were approximately 22 μm.

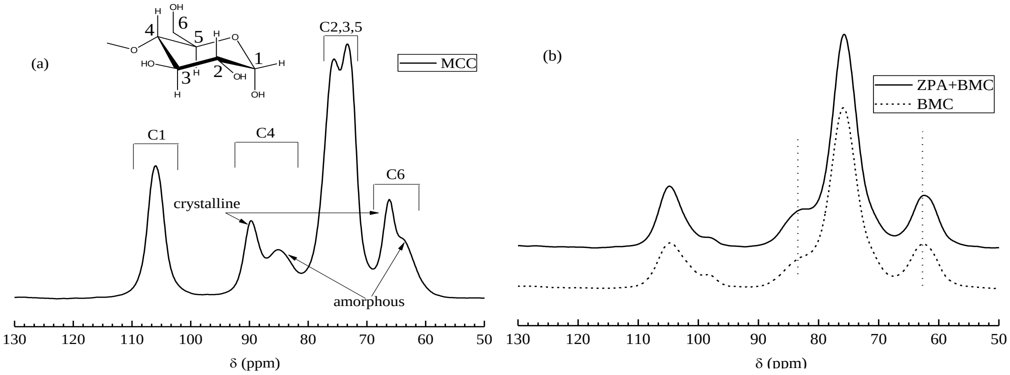

Fig. 3. ^{13}C CP/MAS NMR spectra of MCC (a) and mixed and single ball-milled cellulose (b). MCC: microcrystalline cellulose; BMC: single ball-milled cellulose; ZrP+BMC: mixed ball-milled cellulose. Ball-milling time: 2 h

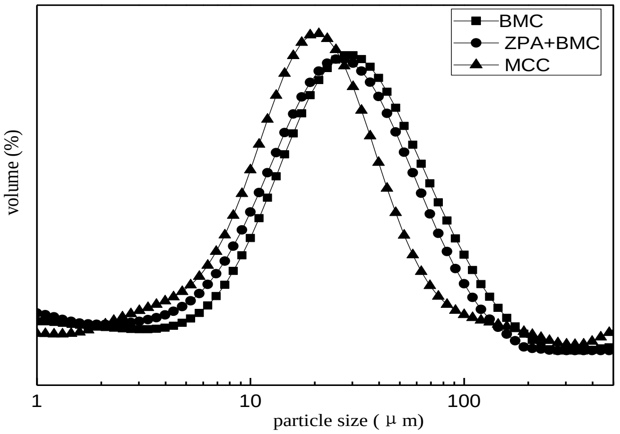

Fig. 4. Particle diameter distributions of cellulose. BMC: single ball-milled cellulose; MCC: microcrystalline cellulose; ZrP+BMC: mixed ball-milled cellulose

Considering the similar particle size of pristine, single and mixed ball-milling cellulose as indicated in Fig. 4, SEM measurements were further carried out to visualize the specific morphology of these cellulose specimens and the results are shown in Fig. 5. The surface of the pristine cellulose was quite smooth. However, after single ball-milling, the cellulose surface became rough and was composed of small particles and large blocks, indicating the cellulose particles was smaller than the pristine ones.

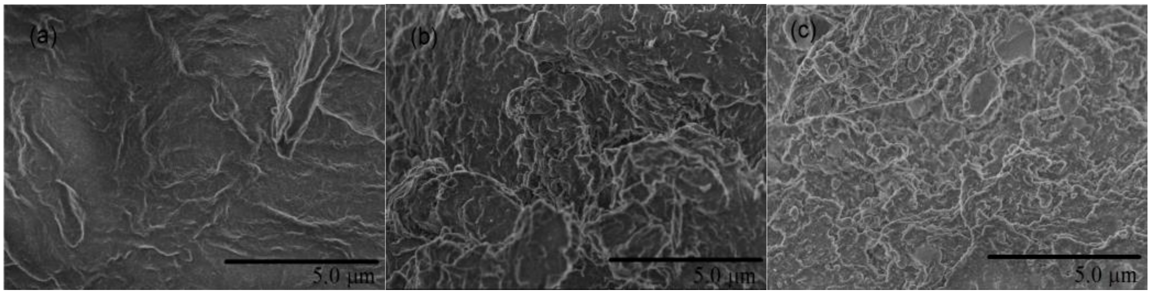

Fig. 5. SEM images of pristine (a), single ball-milling (b), and mixed ball-milling (c) cellulose

As the cellulose was pretreated by mixed ball-milling with ZrP, the surface roughness was more significant and the composed particles became smaller. These results showed that the mixed ball-milling could effectively reduce cellulose particle size and improve its rate-determined hydrolysis step for obtaining higher sugar alcohols yield. It is noted that the similar cellulose particles detected by Fig. 4 is perhaps responsible for the second aggregated ones from small particles.

These results illustrated that the single and mixed ball-milled cellulose had similar structural properties and the small particles were obtained by the latter pretreatment. Besides cellulose particle size, the excellent performance of the mixed ball-milling could be ascribed to the solid acid catalyst. The XRD and textural properties of ZrP are displayed in Fig. 6. The amorphous nature of ZrP was preserved after ball-milling (Fig. 6a). On the other hand, the surface area of ZrP was remarkably decreased to 12 m^2/g, as comparing to the fresh one (Fig. 6b).

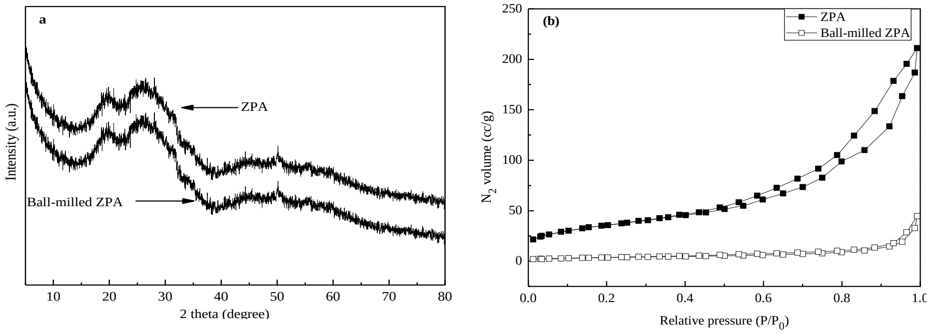

Fig. 6. The properties of ZrP before and after ball-milling (2 h): (a) XRD; (b) N_2 isothermal adsorption-desorption curves at 77 K

The single and mixed ball-milled cellulose presented similar crystallinity, but showed smaller particle size. The lower surface area of ZrP was predicted to reduce catalytic performance. However, the catalytic performance of the mixed ball-milling of cellulose and ZrP was better than the single ball-milling. Mixed ball-milling reduced the crystallinity of cellulose but also possibly promoted contact between cellulose and ZrP, enhancing the rate-determined cellulose hydrolysis for producing a higher sugar alcohols yield. The nature of contact between cellulose and ZrP for improving cellulose transformation is in progress.

CONCLUSIONS

1. Mixed ball-milling of cellulose and solid acid catalyst is a highly effective pretreatment technology for the hydrolytic-hydrogenation of cellulose to sugar alcohols.
2. Compared with traditional single ball-milling, the mixed ball-milling process showed a higher sugar alcohol yield at a shorter ball-milling time due to the significantly enhanced contact between substrate and catalyst.
3. Of the tested solid acid catalysts, ZrP produced the highest yield of sugar alcohols (90.3%) when combined with 5 wt% Ru/C.

ACKNOWLEDGMENTS

The authors are grateful for the support of the National Natural Science Foundation of China (51376185, 51576199 and 51536009) and the National Basic Research Program of China (2012CB215304).

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Article submitted: September 28, 2015; Peer review completed: December 2, 2015; Revised version received and accepted: December 15, 2015; Published: January 7, 2016.
DOI: 10.15376/biores.11.1.1843-1854