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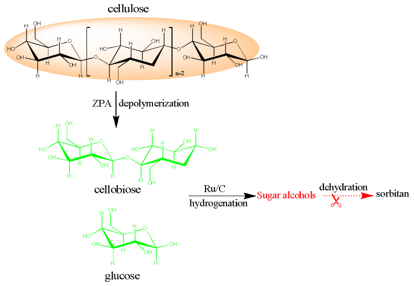

85.5% yield of C_6 alditols was achieved from ball milled cellulose by amorphous zirconium phosphate (ZPA) combined with Ru/C.

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ARTICLE TYPE

Zirconium phosphate combined with Ru/C as a highly efficient catalyst for direct transformation of cellulose to C_6 alditols

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Abstract

Selectively transformation of cellulose to C_6 alditols provides a feasible route towards the sustainable synthesis of chemicals and fuels. Herein, the catalytic performance of amorphous zirconium phosphate (ZPA) combined with 5 wt% Ru/C was evaluated in the direct conversion of cellulose to C_6 alditols (sorbitol and mannitol) under hydrothermal conditions. The yield of C_6 alditols reached 63.5% and 85.5% with microcrystalline cellulose and ball milled cellulose as the feedstock, respectively. This hybrid catalyst was performed to convert concentrated cellulose to obtain C_6 alditols with the high concentration of 68.8 mg mL^{-1} in the final products. The high yield of C_6 alditols from cellulose was ascribed to the fact that ZPA favoured the adsorption of cellulose to promote its depolymerization to cellobiose and glucose, which was hydrogenated immediately to C_6 alditols over Ru/C. The weak adsorption of C_6 alditols over ZPA inhibited the dehydration of C_6 alditols to sorbitan. Furthermore, ZPA exhibited excellent hydrothermal stability and could be reused for several runs.

Introduction

Production of chemicals and fuels from renewable biomass has attracted worldwide attention, due to depletion of fossil resources and environmental problems induced by overuse of fossil resources. Among the primary components of lignocellulosic biomass, cellulose is the most abundant one, which can be converted into fuels and chemicals.[1-6] However, the crystalline structure and plenty of hydrogen bonds make it insoluble in water and other conventional solvents,[7] remaining its efficient utilization a significant challenge. A general valorisation of cellulose depends on its hydrolysis to mono-/oligo-saccharides under mineral acids and harsh reaction conditions, followed by further conversion to diversified chemicals. Nonetheless, the widely used percolation process for biomass hydrolysis results in the low concentration of saccharides in hydrolysate and significant side reactions of saccharides. It renders the production of biomass derived chemicals by such energy-intensive and two-step transformation an open drawback. C_6 alditols derived from cellulosic biomass present as the key platform molecules, which shows wide applications in organic and fine chemical industries.[6, 8-10] Production of C_6 alditols from one-pot conversion of cellulose could circumvent the drawback with using the general two-stepped hydrolysis and hydrogenation approach and is thus regarded as the promising route in biomass transformations.[11, 12] As the saccharides produced in-situ can be hydrogenated to the stable alditols, the side reactions of the saccharides intermediates are significantly suppressed.

Acidic and metal catalysts were used for hydrolysis and hydrogenation respectively in one-pot conversion of cellulose to C_6 alditols. Liquid acids like HCl,[13] H_2SO_4,[13, 14] H_3PO_4[13, 14] and heteropoly acids (HPAs)[15, 16] combined with supported ruthenium catalysts were proven to be the efficient catalysts, but acid catalyst recovery and waste water emission are the obstacles. Moreover, the strongly acidic liquid acids[13, 15] and high reaction temperature[17] promote dehydration of C_6 alditols to byproducts (mainly 1,4-sorbitan and 3,6-sorbitan), which decrease the yield of C_6 alditols. Solid catalysts such as Pt/γ-Al_2O_3,[11] Ru/C,[17] Ni/CNF,[18, 19] Ir-Ni/MC,[20] Ru/$Cs_3PW_{12}O_{40}$[21] were also used for this process. However, the C_6 alditols yield and/or cellulose conversion were rather low when microcrystalline cellulose was used as the feedstock. When ball milled cellulose was used, then enhanced conversion and C_6 alditols could be obtained at mild conditions, but the reaction time was very long (usually 24 h). Compared with liquid acids, these solid catalysts were difficult to achieve transformation of concentrated cellulose.

As a solid catalyst, ZPA has been used in dehydration of glucose or fructose to 5-hydroxymethylfurfural or levulinic acid,[22-27] transformation of sorbitol or xylitol to gasoline or isosoribide,[28-30] and production of high-quality diesel by furfural and 2-methylfuran[31]. But there are rare studies on cellulose depolymerization by ZPA.[32, 33] Hence, we designed a hybrid catalyst that combined amorphous zirconium phosohate (ZPA) with commercial 5 wt% Ru/C for direct conversion of cellulose to C_6 alditols. In this approach, cellulose was depolymerized to saccharides over acidic ZPA, followed by hydrogenation of saccharides to C_6 alditols over 5 wt% Ru/C. The weak adsorption of C_6 alditols over ZPA prohibited their further dehydration to by-products and obtained the high target product yields.

Experimental section

Materials

Microcrystalline cellulose (MCC, Avicel® PH101, Fluka) was purchased from Sigma-Aldrich, and was dried overnight at 343 K prior to use. Zirconium Oxychloride Octahydrat ($ZrOCl_2.8H_2O$) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, P. R. China). Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) was purchased from Tianjin Fu Chen Chemical Reagents Factory (Tianjin, P. R. China). Sodium silicate ($Na_2SiO_3.9H_2O$), hydrochloric acid (37% HCl), sulfuric acid (98% H_2SO_4), ammonium hydroxide ($NH_3.H_2O$), ammonium nitrate (NH_4NO_3) and aluminium hydroxide (Pural Boehmite) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, P. R. China). Tungstic acid (H_2WO_4) was purchased from Aladdin Industrial Inc. (Shanghai, P. R. China). Unless otherwise indicated, all chemicals were used as received.

5 wt% Ru/C, Amberlyst 15 and zirconium oxide (ZrO_2) were purchased from Aladdin Industrial Inc. (Shanghai, P. R. China) and were used as received. HZSM-5, HMOR and γ-Al_2O_3 were purchased from The Catalyst Plant of Nankai University (Tianjin, P. R. China), and were calcined in air at 773 K for 4 h prior to use.

Ball milled cellulose (BMC)

Ball milled cellulose was prepared using a ball miller (QM-3SP04, Nanjing NanDa Instrument Plant) at room temperature. Microcrystalline cellulose was charged in a 100 mL ZrO_2 container and the balling was carried out at a speed of 500 rpm with ZrO_2 balls for 24 h. To avoid thermal degradation of the microcrystalline cellulose, the temperature of cellulose was controlled below 333 K during the ball milling. Ball milled cellulose was obtained as a powder and was dried at 343 K for overnight prior to use.

Catalyst preparation

The zirconium phosphate catalyst (ZPA) was obtained by the previously reported method.[33, 34] Namely, it was prepared by precipitation of $ZrOCl_2.8H_2O$ (1.0mol dm^{-3}, 100 mL) with $NH_4H_2PO_4$ (1.0mol dm^{-3}, 200 mL) at the P/Zr mole ratio of 2. The solution was stirred for 1 h and then filtered. The white precipitate was washed with deionized water until the pH of the filtrate was 4, and then was dried at 373 K overnight. Before reaction, ZPA was calcined at 673 K for 4 h in air.

The preparation procedure for the SiO_2-ZrO_2 catalyst was referred by the previously reported literature.[35] The $Si(OH)_4$ precipitate was obtained by adding NH_4NO_3 saturated solution into the Na_2SiO_3 solution with continuous agitation until the pH of solution was 8. The $Zr(OH)_4$ precipitate was prepared by the same method but with ammonia (28%) as the precipitator. Namely, adding the $NH_3\cdot H_2O$ solution into the $ZrOCl_2\cdot 8H_2O$ solution with continuous agitation until the pH of solution was 8. Subsequently, the $Si(OH)_4$ and $Zr(OH)_4$ was mixed at a mole ratio of Si/Zr=3 and stirred. The mixed precipitate was aged at 348 K overnight. The precipitate was filtered and washed with deionized water to remove chloride ions completely. The filter cake was dried at 393 K for 12 h and then calcined at 773 K for 5 h prior to reaction.

Tungstated zirconia (ZrW) was prepared by the method described in the previously reported literature.[36] $Zr(OH)_4$ was prepared by adding the $NH_3\cdot H_2O$ solution into the $ZrOCl_2\cdot 8H_2O$ solution with constantly stirring until the pH of solution was 9. The precipitate was filtered and washed with deionized water to remove chloride ions completely, and then the precipitate was dried at 383 K for overnight. Subsequently, tungstic acid (H_2WO_4) was exchanged with $Zr(OH)_4$ in hydrogen peroxide solution (30%), and the process was performed in an iced water bath. The solid was filtered and dried at 353 K overnight. Finally, the solid was calcined in air at 973 K for 3 h prior to reaction.

Tungstated alumina (AlW) was obtained with using the same method as ZrW preparation.[36] The tungstic acid (H_2WO_4) was exchanged with aluminium hydroxide (Pural Boehmite) in hydrogen peroxide solution (30%). The solid was filtered and dried overnight at 353 K. Finally, the solid was calcined in air at 973 K for 3 h prior to reaction.

Sulfated zirconia (ZrS) was prepared by the method reported in the literature.[36] Firstly, $Zr(OH)_4$ was prepared using the above mentioned procedure. Then, the $Zr(OH)_4$ was added to H_2SO_4 solution under agitation. The sulfated solid was filtered and dried at 353 K overnight. Finally, the solid was calcined at 823 K for 2 h before reaction.

Catalyst characterization

X-ray powder diffraction (XRD) diffractogram of sample was measured by a X-ray diffractometer (XPert Pro MPD, Philip) with Cu Kα radiation (λ=0.154 nm) operated at 40 kV and 100 mA. The 2θ angles were scanned from 5° to 80°.

The BET specific surface area and average pore diameter were measured by the N_2 isothermal adsorption-desorption profiles at 77 K with using a QUADRASORB SI-MP-10/PoreMaster 33 analyzer equipped with QuadraWin software. The ZPA was crushed to obtain a particle size of $\leq$ 250 mesh and was degassed under vacuum at 523 K for 20 h prior to measurement. Multi-point BET analysis was performed ranging the relative pressure of P/P_0 from 0.05 to 0.3.

FT-IR spectrum of ZPA was recorded on a TENSOR27 FT-IR spectrometer. Prior to analysis, ZPA was dried at 378 K overnight, fully grinded with KBr and pressured to a wafer.

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, US). A sample of 300 mg was firstly degassed at 673 K in pure helium for 2 h to remove undesirable physically adsorbed species. After cooling to 373 K, NH_3 was introduced to absorb for 30 min to reach a saturation state. Afterwards, the NH_3-absorbed sample was purged at the same temperature for 1.5 h by helium gas to remove any physically adsorbed NH_3. NH_3-TPD was performed at a heating rate of 10 K min^{-1} from 373 K to 973 K in helium gas. Thermal Conductivity Detector (TCD) was used to monitor the desorbed NH_3. The quantitative analysis of acidic sites of ZPA was performed by using a calibration loop of 250 µl.

SEM images were recorded using S-4800 instrument operated at 10 kV. The sample was placed on a conductive carbon tape adhered to an aluminium holder. TEM image was collected on a Gatan Ultra scan camera on a JEOL JEM-2100F instrument (operated at 200 kV with a LaB6 source). The samples were ultrasonically dispersed into ethanol, and drops of the suspension were placed on a carbon-coating copper grid and then dried in air.

The PO_4^{3-} in filtrate was detected by an ion chromatography (883 Basic IC plus 1) equipped with a Metrosep A Supp4-250/4.0 column. A mixed aqueous solution of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ was used as the mobile phase (the flow rate of 1. 0 ml/min).

Transformation of cellulose

The given amount of ZPA, 5 wt% Ru/C, cellulose and H_2O were added into a 100 mL stainless steel autoclave. Before reaction, the reactor was flushed with hydrogen for several times to remove the residue air and pressurized to 6 MPa of hydrogen pressure at room temperature. Then, the reactor was heated to a given temperature under rigor agitation and kept at the given temperature for a certain period. After reaction, the reactor was quickly cooled to room temperature with iced water. The product mixture was separated by filtration, and the water soluble products were detected by a HPLC instrument.

Hydrothermal treatment of ZPA was performed by treating the ZPA under the reaction conditions of cellulose. The treated ZPA was washed with water for three times, and then calcined at 673 K for 4 h in air before reuse. The filtrate of hydrothermal treatment was used as the solvent combined with Ru/C to convert cellulose.

Adsorption of cellobiose, glucose and C_6 alditols on the ZPA was conducted by addition of 1 g of ZPA into a solution of 0.05 g cellobiose, 0.05 g glucose or C_6 alditols in 10 mL water. The mixture was stirred for 5 h at room temperature. The amount of adsorbed cellobiose, glucose or C_6 alditols was determined by measuring the remaining counterpart in water.

Product analysis

The aqueous products were analyzed by a high performance liquid chromatography (HPLC; Waters e2695) equipped with an autosampler and a refractive index detector (RID 2414). An Inertsustain C18 column was applied to detect the polyols, and the mobile phase was water with a flow of 0.5 mL/min. A Shodex SUAGER SH1011 column was applied to detect the sugars with the mobile phase of 0.005 M H_2SO_4 solution. External standard method was used for quantification of polyols and sugars. The cellulose conversion was determined by the weight difference of cellulose before and after reaction. The yield of product was determined by the carbon moles in the products and carbon moles in the cellulose before reaction, and the relevant formulae were listed in supporting information.

Results and discussion

Hydrolytic hydrogenation of microcrystalline cellulose to C_6 alditols

Fig. 1 shows the C_6 alditols yield and microcrystalline cellulose conversion over different solid acid catalysts combined with 5wt% Ru/C. The γ-Al_2O_3, ZrO_2 and SiO_2-ZrO_2 catalysts have very low C_6 alditols yield and microcrystalline cellulose conversion. For the H-MOR and HZSM-5, cellulose conversion was above 50%, but the C_6 alditols yield was less than 30%. Although Amberlyst 15 and ZrS have high cellulose conversion of above 85%, their high acid strength resulted in significant by-products via dehydration reaction, which resulted in the low C_6 alditols yield. For ZrW and AlW catalysts, cellulose was mainly converted to the hydrogenolysis by-products (ethylene glycol and propylene glycol yield of 28.9% and 7.8%, respectively), which led to the low C_6 alditols yield of less than 10%. The poor performance observed over ZrW and AlW are possibly attributed to their strong cleavage of C-C bonds promoted by tungsten.[37, 38] It is clear that ZPA combined with Ru/C exhibited the highest C_6 alditols yield (55.4%) with 66.5% of microcrystalline cellulose conversion. The XRD pattern of ZPA (Fig. S1) demonstrates that ZPA was amorphous structure, and the SEM image shows that particle size of ZPA was below than 100 nm (Fig. S2). The average Ru particle size was about 3 nm as measured by TEM

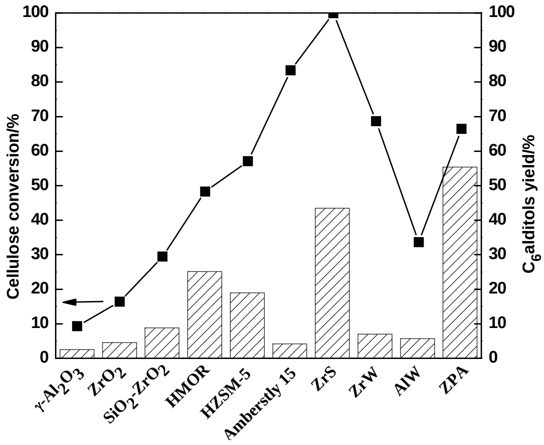


Fig. 1 Transformation of microcrystalline cellulose with kinds of solid acids and 5 wt% Ru/C. Reaction conditions: 488 K, 6 MPa of initial H_2 pressure (room temperature), 1.5 h, microcrystalline cellulose 0.5 g, H_2O 50 mL, solid acid 0.9 g, Ru/C 0.0375 g.

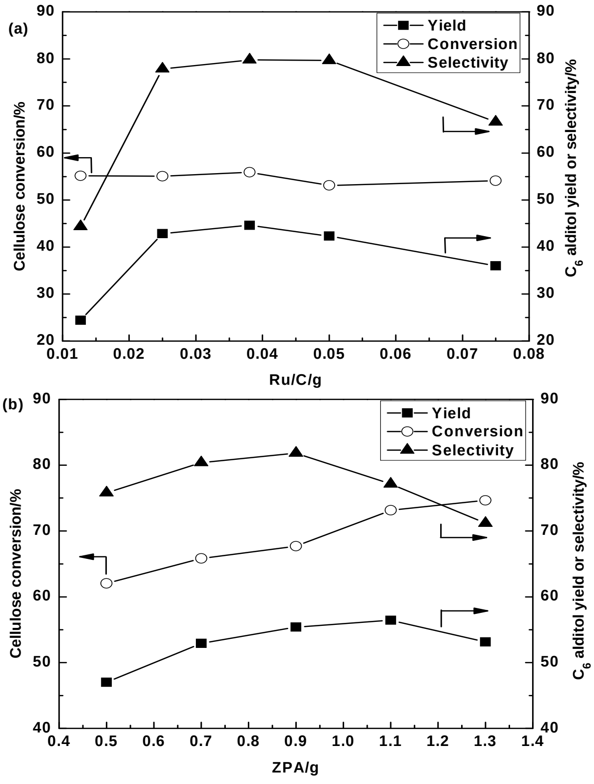


Fig. 2 Optimizing the amounts of ZPA and 5 wt% Ru/C in microcrystalline cellulose conversion. Reaction conditions: 488 K, 6 MPa of initial H_2 pressure (room temperature), 1.5 h, microcrystalline cellulose 0.5 g, H_2O 50 mL, (a) ZPA 0.3 g, (b) Ru/C 0.0375 g.

Table 1 The effect of reaction time over ZPA and Ru/C and replaced HCl with different pH and Ru/C in microcrystalline conversion [a]

Entry	Acid catalyst	Reaction time/h	Cellulose conversion/%	C_6 alditols yield/%	C_6 alditols selectivity/%
1	0.9 g ZPA	0.5	40.7	37.0	90.9
2	0.9 g ZPA	1.5	66.5	55.4	83.3
3[b]	0.9 g ZPA	3.0	99.0	63.5	64.1
4	0.9 g ZPA	4.0	100.0	60.3	60.3
5	0.9 g ZPA	5.0	100.0	57.4	57.4
6[c]	filtrate	3.0	36.5	15.5	42.5
7	pH=2 HCl solution	3.0	100.0	18.7	18.7
8	pH=3 HCl solution	3.0	70.9	51.8	73.1
9	pH=4 HCl solution	3.0	33.5	13.4	40.0
10	pH=5 HCl solution	3.0	27.4	8.8	32.1

[a] Reaction conditions: 488 K, 6 MPa of initial H_2 pressure (room temperature), microcrystalline cellulose 0.5 g, H_2O (entry 1-6) or acidic solution (entry 7-10) 50 mL, Ru/C 0.0375 g. [b] Productivity of C_6 alditols=1268.3 $gL^{-1}h^{-1}g^{-1}{}_{Ru}$. [c] Filtrate: treatment ZPA with water under the reaction conditions for 3 h.

and statistical analysis (Fig. S3).

Direct transformation of cellulose to C_6 alditols is a coupling process (cellulose depolymerization to saccharides and in-situ hydrogenation of saccharides to C_6 alditols), therefore ZPA-Ru/C hybrid catalyst existed a metal-acid balance between ZPA and Ru/C. We adjusted the metal-acid balance by changing the dosages of ZPA and 5 wt% Ru/C (Fig. 2). Considering that Ru/C is a noble metal catalyst, the dosage of Ru/C was first investigated at a fixed ZPA amount of 0.3 g. Results indicate that cellulose conversion kept at 55% with increasing Ru/C dosage (Fig. 2. (a)), but the selectivity of C_6 alditols increased sharply from 44.4% to 77.9% as the Ru/C was increased from 0.0125 g to 0.025 g, and this high C_6 alditols yield kept almost unchangeable until the Ru/C of 0.05 g. Further increasing the Ru/C dosage, however, the C_6 alditols selectivity decreased owing to the C_6 alditols were hydrogenolyzed to small molecular alcohols by the excessive Ru/C. Considering the 0.0375 g Ru/C showed the maximal C_6 alditol yield, we optimized the amount of ZPA with fixing the Ru/C dosage of 0.0375 g. Cellulose conversion increased with increasing the amount of ZPA (Fig. 2(b)), which implies that cellulose depolymerization was determined by ZPA catalyzed hydrolysis. The C_6 alditols selectivity initially increased as the dosage of ZPA was increased from 0.5 g to 0.9 g and then decreased with the ZPA amount of above 0.9 g. The decreased selectivity over the excessive ZPA indicates that a part of produced C_6 alditols was dehydrated to sorbitan. Here, we choose the 0.9 g ZPA and 0.0375 g 5 wt% Ru/C as the balanced dosage for transformation of microcrystalline cellulose to C_6 alditols.

The effect of reaction time was further investigated by using the indicated hybrid catalyst and the results are listed in Table 1. The cellulose conversion increased sharply from 44.7% to 100% with increasing the reaction time from 0.5 h to 4 h. 99% of cellulose conversion and 63.5% of C_6 alditols yield were achieved at 488 K for 3 h (Table 1, entry 3). The selectivity of C_6 alditols decreased consistently from 90.9% to 57.4% with prolonging the reaction time. The decreased selectivity can be attributed to C_6 alditols dehydration to sorbitan and hydrogenolysis to other small molecules like glycerol, ethylene glycol, propylene glycol and so on (Fig. S7 & S8). However, the C_6 alditols yield and selectivity decreased slowly from 63.5% to 57.4% when cellulose was converted completely, indicating that C_6 alditols are quite stable under the present reaction conditions. Further analysis for products distribution showed that only cellobiose and glucose (no oligosaccharides) were detected, which is different from the previous reports that significant amounts of oligosaccharides were detected with using liquid and some solid acids in depolymerization of cellulose.[13, 15, 18, 19] Regarding hydrogenation of glucose and hydrogenolysis of C_6 alditols takes place at the surface of Ru simultaneously, the hydrogenation is dominated as the glucose is supplied sufficiently and fast.[15] This effect is in favour of improving the yield of C_6 alcohols with partially suppressing the hydrogenolysis reaction.

Because ZPA possibly releases phosphoric acid to solution by leaching, the depolymerization of cellulose possibly proceeds via a homogenous way. To investigate the possible homogeneous catalysis, we conducted this process by combining the filtrate of hydrothermally treated ZPA with fresh Ru/C (Table 1, entry 6). The result indicated that 36.5% of cellulose was converted with obtaining 42.5% of C_6 alditols selectivity. And the test result of ion chromatography demonstrated that there existed PO_4^{3-} in the filtrate.

In order to compare the present ZPA with inorganic liquid acid, we replaced ZPA by HCl solution with different pH (Table 1, entry 7-10) since HCl has been proven to be the efficient inorganic liquid acid in cellulose depolymerization.[13, 39] The conversion of cellulose sharply decreased from 100% to 27.4% with the pH of HCl solution increased from 2 to 5 (Table 1, entry 7-10). However, the C_6 alditols yield of 18.7% in pH=2 of HCl solution was much lower than that 51.8% in pH=3 of HCl solution, which is caused by the fact that more dissociated H^+ could promote C_6 alditols dehydration to sorbitan. Especially, the C_6 alditols yield of 51.8% in pH=3 of HCl solution (Table 1, entry 8) is also lower than that 63.5% by ZPA (Table 1, entry 3). Even with the similar cellulose conversion, the C_6 alditols selectivity of 73.1% in pH=3 of HCl solution (Table 1, entry 8) was also inferior to the 83.3% obtained with ZPA (Table 1, entry 2). These results illustrated that the heterogeneous ZPA was better than the homogeneous HCl as the acid catalyst in this process.

The reasons for the superiority of the ZPA are possibly dependent on its large surface of 164 m^2/g with mesoporous size of 9.67 nm (Fig. S4) and large total acidic amount of 1.8 mmol/g with simultaneous presence of weak and strong acid sites by NH_3-TPD (Fig. S6), which is favourable for the contact of cellulose and catalyst, the accelerated cellulose hydrolysis and the fast diffusion of the hydrolytic cellubiose and glucose intermediates.

Hydrolytic hydrogenation of ball-milling cellulose to C_6 alditols

Table 2 Conversion of ball milled cellulose over ZPA and Ru/C[a]

Entry	Reaction time/h	Cellulose conversion/%	C_6 alditols selectivity/%	Yield/%		
				C_6 alditols yield/%	Cellobiose yield/%	Glucose yield/%
1	0.5	67.6	83.7	56.6	1.1	1.6
2	1.5	90.4	89.5	80.9	ND	0.47
3[b]	2.5	94.7	90.3	85.5	ND	ND
4	3.0	96.7	87.3	84.4	ND	ND

[a] Reaction conditions: 463 K, 6 MPa of initial H_2 pressure (room temperature), ball milled cellulose 0.5 g, H_2O 50 mL, ZPA 0.9 g，Ru/C 0.0625 g. ND: not detected. [b] Productivity of C_6 alditols=1229.5 $gL^{-1}h^{-1}g^{-1}_{Ru}$.

The decreases of the crystalline and polymerization degree of cellulose can improve the degradability of cellulose,[40] which is beneficial to reduce the reaction temperature and then suppress the side reactions, and eventually enhance the yield of C_6 alditols. Here, we used ball-milling pre-treatment (24 h) to improve the degradability of cellulose. The XRD patterns of the microcrystalline cellulose and ball milled cellulose are shown in Fig. 3. Microcrystalline cellulose presented a broadened diffraction at 15.4°, two peaks at 22.4° and 34.4°, indicating the typical I crystalline form. The ball milling pre-treatment did not change the type of cellulose, but the intensity of characteristic peak ((200) plane) became wider, demonstrating the crystallinity decreased and more amorphous regions formed. The depolymerization rate of ball milled cellulose is different from microcrystalline cellulose, therefore we optimized the dosage of Ru/C at a fixed ZPA dosage of 0.9 g, and the optimal dosage of Ru/C was 0.0625 g (Fig. S9).The effect of reaction temperature in transformation of ball milled cellulose is shown in Fig. S10. The optimal temperature was 463 K.

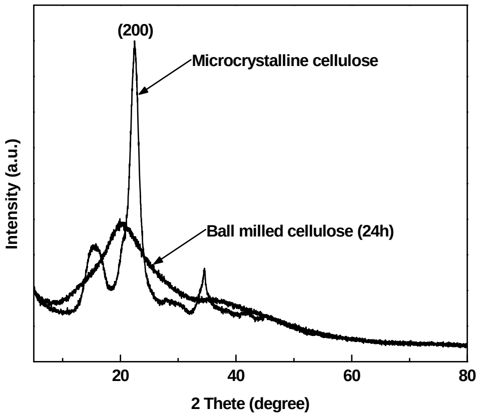


Fig. 3 XRD patterns of microcrystalline cellulose and ball milled cellulose.

The performance of ZPA and Ru/C in conversion of ball milled cellulose is listed in Table 2. Increasing the reaction time, the amount of cellobiose and glucose decreased gradually by further hydrogenation. Compared with microcrystalline cellulose, the yield of C_6 alditols improved significantly in conversion of ball milled cellulose. The maximum yield and selectivity for C_6 alditols reached 85.5% and 90.3% respectively, which are similar to the results of combining mechanocatalytic depolymerization of cellulose with hydrogenolysis of the intermediates to C_6 alditols by H_2SO_4 and Ru/C at 433 K.[41] It's also comparable to the results in hydrogenation of cellobiose to C_6 alditols by different catalysts.[42, 43] The ZPA and Ru/C catalyst almost completely converted the ball milled cellulose within 3 h, but by using the pH=3 of HCl solution combined with Ru/H-USY, the complete conversion for ball milled cellulose was 24 h,[13] which implies that the rapid cellulose depolymerization for obtaining the high C_6 alditols yield are not entirely attributed to the acidity of catalyst. The potential reason needs to be further studied.

The composition of liquid products showed that the yield of C_2-C_3 polyols was 6.5% and only trace amount of sorbitan can be detected (Table 2, entry 3). However, the yield of sorbitan reached around 15%-25% in the literature.[13, 15, 17] Based on these results, we speculate that suppressing the C_6 alditols dehydration reaction is the main reason for the high C_6 alditols yield and selectivity.

Hydrolytic hydrogenation of concentrated cellulose to C_6 alditols

A wide variety of works were reported to convert cellulose by solid acid catalysts with low mass ratio of substrate/catalyst.[44, 45] In this work, transformation of concentrated cellulose was performed while fixing the amount of ZPA and changing the dosage of Ru/C slightly. The corresponding results are presented in Table 3. Under the high substrate/catalyst mass ratios, both of the microcrystalline and the ball milled cellulose can be effectively degraded to obtain the yields of C_6 alditols of more than 50%. As compared with the low concentrated cellulose, the high ones gave the significantly increased C_6 alditols productivity at the comparable reaction conditions (Table 1, entry 3; Table 2, entry 3; Table 3, entry 1-4). The highest concentration of C_6 alditols reached up to 68.8 mg mL^{-1} (Table 3, entry 3), which was close to the monosaccharide concentration of liquid acid (HCl) hydrolysis of corn stover,[46] illustrating the potential application of ZPA and Ru/C in this process. And most importantly, the mass

Table 3 Conversion of concentrated cellulose to C_6 alditols over ZPA and Ru/C[a]

Entry	Substrate/g[b]	Ru/C/g	Reaction time /h	Reaction temperature /K	Cellulose conversion /%	C_6 alditols yield /%	C_6 alditols selectivity/%	C_6 alditols productivity/$gL^{-1}h^{-1}g^{-1}_{Ru}$
1	2.5g BMC	0.075	2.5	463	82.2	68.4	83.2	4098.4
2	2.5g MCC	0.075	3.0	488	79.4	55.7	70.2	2781.2
3[c]	5.0g BMC	0.100	2.5	463	72.5	61.2	84.4	5500.4
4	5.0g MCC	0.100	3.0	488	75.1	51.9	69.1	3887.2

[a] Reaction conditions: 6 MPa of initial H_2 pressure (room temperature), H_2O 50 mL, ZPA 0.9 g. [b] MCC: microcrystalline cellulose, BMC: ball milled cellulose. [c] Concentration=$m_{Cellulose,0}/162\times182\times Yield(\%)/V_{liquid}=5000/162\times182\times61.2\%/50=68.8$ mg mL^{-1}

ratio of cellulose to Ru/C reached 50 (Table 3,entry 3-4), which was the highest mass ratio not only in conversion of cellulose but also in hydrogenation of cellobiose and glucose over solid catalyst,[42,43] showing the obvious advantage for more economical production of C_6 alditols from cellulose.

Hydrothermal stability of ZPA and reaction pathway

Considering hydrothermal stability of solid catalyst is a crucial aspect in the aqueous phase conditions for biomass transformation, we further investigated the hydrothermal stability of this hybrid catalyst. Ru/C has been proven to be high stability catalyst in aqueous phase hydrogenation reaction, and we merely studied the stability of the ZPA. We applied hydrothermal treatment of ZPA under the reaction conditions, and subsequently the treated ZPA was calcined at 673 K in air for 4 h prior to reuse. As shown in Fig. 4, the C_6 alidtols yield declined to 55% after the first treatment, and the ZPA catalyst maintained its activity in the subsequent runs. The decreased C_6 alditols yield is responsible for the P leaching of fresh ZPA during the hydrothermal reaction condition, which was demonstrated by the comparison experiment with using the ZPA filtrate for further cellulose conversion (Table 1, entry 6). The maintained performance for the sequential hydrothermally treated ZPA indicates that no P leaching taken place after first hydrothermal treatment. This feature of ZPA was further confirmed by Fig. 5 with using the filtrate of hydrothermally treated ZPA for cellulose conversion. After the second run, the C_6 alditols yields were maintained at about 7%, which is very similar to that with using the sole Ru/C for this process. This indicates that the structure of the ZPA is stable and no P leaching occurs after the first hydrothermal treatment in this reaction condition.

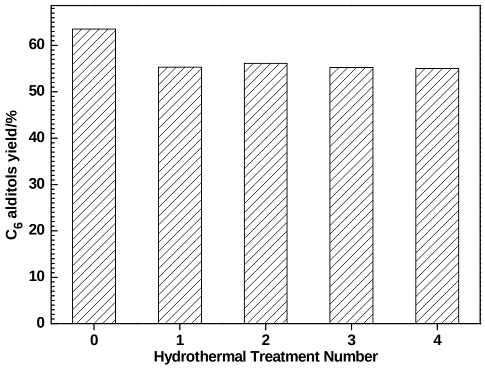


Fig. 4 Transformation of microcrystalline cellulose by hydrothermally treated ZPA and Ru/C. Reaction conditions: 488 K, 6 MPa of initial H_2 pressure (room temperature), 3 h, microcrystalline cellulose 0.5 g, H_2O 50 mL, ZPA 0.9 g, Ru/C 0.0375 g. Hydrothermal treatment conditions: 488 K, 6 MPa of initial H_2 pressure (room temperature), 3 h, H_2O 50 mL, ZPA 0.9 g.

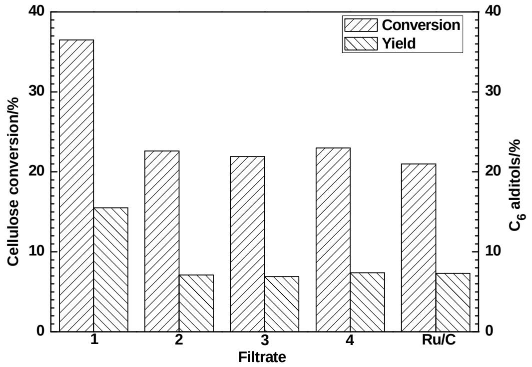
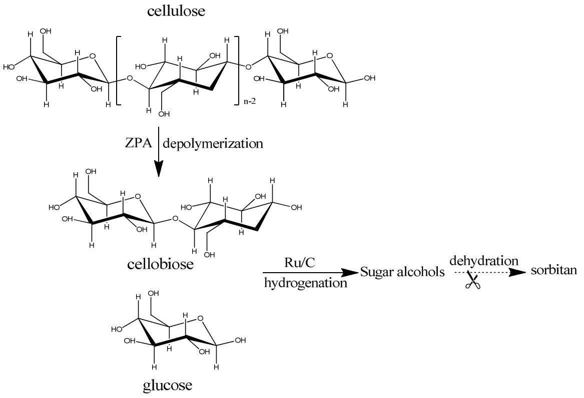


Fig. 5 Transformation of microcrystalline cellulose by filtrate of hydrothermally treated ZPA and Ru/C. Reaction conditions: 488 K, 6 MPa of initial H_2 pressure (room temperature), 3 h, microcrystalline cellulose 0.5 g, H_2O 50 mL, Ru/C 0.0375 g. 1, 2, 3 and 4 represent the hydrothermal treatment number. For Ru/C, the catalyst is sole Ru/C without use of ZPA.

The exceptional performance of ZPA cannot be adequately attributed to the acid strength of ZPA, as the pH=3 of HCl solution did not convert the microcrystalline cellulose and even the ball milled cellulose rapidly. The catalysis mechanism of ZPA was thus investigated by performing adsorption experiments with cellobiose, glucose and sorbitol as the probe molecules, respectively. It was found that the uptake of cellobiose and glucose on the ZPA were 2.74 mg g^{-1} and 1.13 mg g^{-1}, respectively. Adsorption amount of cellobiose on ZPA was two times more than glucose, by which we speculate that ZPA has a favourable affinity for cellulose. Carbon of Ru/C catalyst also has a strong affinity for cellobiose and glucose.[20] Therefore, we propose the following reaction pathway (Scheme 1): cellulose is hydrolyzed to oligomers by hot water and ZPA, and then the oligmers are hydrolyzed to cellobiose and glucose at the surface of ZPA. Subsequently, the obtained cellobiose and glucose are absorbed and hydrogenated to C_6 alditols by Ru/C catalyst, and the dehydration reaction of obtained C_6 alditols is suppressed due to the very weak adsorption of C_6 alditols on ZPA (the undetectable adsorption of sorbitol on ZPA surface).



Scheme 1 Reaction pathway for the one-pot conversion of cellulose to C_6 alditols by ZPA and Ru/C

Conclusion

In summary, ZPA was proven to be an effective solid acid catalyst, which was combined with Ru/C for direct production of C_6 alditols from cellulose. 85.5% and 63.5% C_6 alditols yield were obtained with ball milled cellulose and microcrystalline cellulose as feedstock, respectively. The results of Ru/C combined with the filtrate of ZPA illustrated that the exceptional performance of ZPA was not ascribed to the phosphoric acid released from ZPA during the reaction. Replacing the ZPA by HCl solutions with different pH, the results indicated that the performance of heterogeneous ZPA is better than homogeneous liquid acid.

ZPA and Ru/C catalyst adapted to high cellulose/catalyst mass ratios (especially for the higher cellulose/(Ru/C)) and obtained the high C_6 alditols concentration of 68.8 mg mL^{-1}. Moreover, ZPA maintained excellent hydrothermal stability with hydrothermal treatment. The high yield of C_6 alditols from cellulose was ascribed to the fact that ZPA favoured the cellulose adsorption to promote its depolymerization to cellobiose and glucose, which was further hydrogenated immediately over Ru/C to C_6 alditols. The weak adsorption of C_6 alditols over ZPA prohibited the dehydration of C_6 alditols to by-products.

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Notes and references

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