

Zirconium phosphate combined with Ru/C as a highly efficient catalyst for the direct transformation of cellulose to C₆ alditols†

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Yuhe Liao,^{a,b} Qiying Liu,^a Tiejun Wang,^{*a} Jinxing Long,^a Longlong Ma^{*a} and Qi Zhang^a

The selective transformation of cellulose to C₆ 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 C₆ alditols (sorbitol and mannitol) under hydrothermal conditions. The yield of C₆ alditols reached 63.5% and 85.5% with microcrystalline cellulose and ball-milled cellulose as the feedstock, respectively. This hybrid catalyst was developed to convert concentrated cellulose to obtain C₆ alditols with a high concentration of 68.8 mg mL⁻¹ in the final products. The high yield of C₆ alditols from cellulose was ascribed to the fact that ZPA favoured the adsorption of cellulose and promoted its depolymerization to cellobiose and glucose, which was hydrogenated immediately to C₆ alditols over Ru/C. The weak adsorption of C₆ alditols over ZPA inhibited the dehydration of C₆ alditols to sorbitan. Furthermore, ZPA exhibited excellent hydrothermal stability and could be reused for several runs.

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Introduction

The production of chemicals and fuels from renewable biomass has attracted worldwide attention due to the 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 vast number of hydrogen bonds make it insoluble in water and other conventional solvents,⁷ causing its efficient utilization to remain a significant challenge. The general valorisation of cellulose depends on its hydrolysis to mono-/oligosaccharides 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 a low concentration of saccharides in the hydrolysate and significant side reactions of the saccharides. It renders the production of biomass derived chemicals by such energy-

intensive and two-step transformation an open drawback. C₆ alditols derived from cellulosic biomass are key platform molecules, which have been shown to have wide applications in the organic and fine chemical industries.^{6,8–10} The production of C₆ alditols from the one-pot conversion of cellulose could circumvent the drawback of using the general two-stepped hydrolysis and hydrogenation approach and is thus regarded as the promising route in biomass transformation.^{11,12} As the saccharides produced *in situ* can be hydrogenated to stable alditols, the side reactions of the saccharides intermediates are significantly suppressed.

Acidic and metal catalysts have been used for hydrolysis and hydrogenation steps, respectively, in the one-pot conversion of cellulose to C₆ alditols. Liquid acids like HCl,¹³ H₂SO₄,^{13,14} H₃PO₄,^{13,14} and heteropoly acids (HPAs)^{15,16} combined with supported ruthenium catalysts were proven to be efficient catalysts, but acid catalyst recovery and waste water emissions are obstacles. Moreover, the strongly acidic liquid acids^{13,15} and high reaction temperature¹⁷ promotes the dehydration of C₆ alditols to byproducts (mainly 1,4-sorbitan and 3,6-sorbitan), which decreases the yield of C₆ alditols. Solid catalysts such as Pt/γ-Al₂O₃,¹¹ Ru/C,¹⁷ Ni/CNF,^{18,19} Ir–Ni/MC,²⁰ Ru/Cs₃PW₁₂O₄₀²¹ were also used for this process. However, the yield of C₆ alditols and/or cellulose conversion were rather low when microcrystalline cellulose was used as the feedstock. When ball-milled cellulose was used, an enhanced conversion and C₆ alditols yield could be obtained under mild conditions,

^aCAS Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, 510640, P.R. China.
E-mail: mall@ms.giec.ac.cn, wangtj@ms.giec.ac.cn; Fax: +86-20-8705-7673;
Tel: +86-20-8705-7673

^bUniversity of Chinese Academy of Sciences, Beijing, 100049, P.R. China

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but the reaction time was very long (usually 24 h). Compared with liquid acids, it is difficult to achieve the transformation of concentrated cellulose with these solid catalysts.

As a solid catalyst, ZPA has been used in the dehydration of glucose or fructose to 5-hydroxymethylfurfural or levulinic acid,^{22–27} in the transformation of sorbitol or xylitol to gasoline or isosorbide,^{28–30} and in the production of high-quality diesel from furfural and 2-methylfuran.³¹ However, studies on cellulose depolymerization by ZPA are rare.^{32,33} Hence, we designed a hybrid catalyst that combined amorphous zirconium phosphate (ZPA) with commercial 5 wt% Ru/C for the direct conversion of cellulose to C₆ alditols. In this approach, cellulose was depolymerized to saccharides over acidic ZPA, followed by hydrogenation of saccharides to C₆ alditols over 5 wt% Ru/C. The weak adsorption of C₆ alditols over ZPA prohibited their further dehydration to by-products, which allowed high target product yields to be obtained.

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 octahydrate (ZrOCl₂·8H₂O) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, P. R. China). Ammonium dihydrogen phosphate (NH₄H₂PO₄) was purchased from Tianjin Fu Chen Chemical Reagents Factory (Tianjin, P. R. China). Sodium silicate (Na₂SiO₃·9H₂O), hydrochloric acid (37% HCl), sulfuric acid (98% H₂SO₄), ammonium hydroxide (NH₃·H₂O), ammonium nitrate (NH₄NO₃) and aluminium hydroxide (Pural Boehmite) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, P. R. China). Tungstic acid (H₂WO₄) 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 (ZrO₂) were purchased from Aladdin Industrial Inc. (Shanghai, P. R. China) and were used as received. HZSM-5, HMOR and γ-Al₂O₃ 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 ZrO₂ container and the ball-milling was carried out at a speed of 500 rpm with ZrO₂ balls for 24 h. To avoid thermal degradation of the microcrystalline cellulose, the temperature of the cellulose was kept below 333 K during the ball-milling. Ball-milled cellulose was obtained as a powder and was dried at 343 K 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 ZrOCl₂·8H₂O (1.0 mol dm⁻³, 100 mL) with NH₄H₂PO₄ (1.0 mol 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 SiO₂-ZrO₂ catalyst was in line with the previously reported literature.³⁵ The Si(OH)₄ precipitate was obtained by adding NH₄NO₃ saturated solution into the Na₂SiO₃ 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, addition of the NH₃·H₂O solution into the ZrOCl₂·8H₂O 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 for the complete removal of chloride ions. 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 literature.³⁶ Zr(OH)₄ was prepared by adding the NH₃·H₂O solution into the ZrOCl₂·8H₂O solution with constantly stirring until the pH of solution was 9. The precipitate was filtered and washed with deionized water to completely remove any chloride ions, and then the precipitate was dried at 383 K overnight. Subsequently, tungstic acid (H₂WO₄) was exchanged with Zr(OH)₄ in hydrogen peroxide solution (30%), and the process was performed in an ice-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 using the same method as for ZrW.³⁶ The tungstic acid (H₂WO₄) 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 H₂SO₄ 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

The X-ray powder diffraction (XRD) diffractogram of the 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 N₂ isothermal adsorption-desorption profiles at 77 K using a QUADRASORB SI-MP-10/PoreMaster 33

analyzer equipped with QuadraWin software. The ZPA was crushed to obtain a particle size of ≤ 250 mesh and was degassed under vacuum at 523 K for 20 h prior to measurement. Multi-point BET analysis was performed with a relative pressure range 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 ground with KBr and pressed into a wafer.

Ammonia-temperature programmed desorption (NH_3 -TPD) measurements were conducted in a U-tube quartz reactor using an ASIQUACIV200-2 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 any undesirable physically adsorbed species. After cooling to 373 K, NH_3 was introduced to adsorb for 30 min to reach a saturation state. Afterwards, the NH_3 -adsorbed 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. A thermal conductivity detector (TCD) was used to monitor the desorbed NH_3 . The quantitative analysis of the acidic sites of ZPA was achieved using a calibration loop of 250 μL .

SEM images were recorded using a S-4800 instrument operated at 10 kV. The sample was placed on conductive carbon tape adhered to an aluminium holder. The 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-coated copper grid and then dried in air.

The PO_4^{3-} in the filtrate was detected by an ion chromatograph (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^{-1}).

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 several times to remove any residue air and pressurized to 6 MPa of hydrogen pressure at room temperature. Then, the reactor was heated to a given temperature under rigorous agitation and kept at the given temperature for a certain period of time. 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 three times, and then calcined at 673 K for 4 h in air before reuse. The filtrate of the 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 achieved by the 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 chromatograph (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^{-1} . 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 the reaction. The yield of product was determined by the carbon moles in the products and carbon moles in the cellulose before reaction; the relevant formulae are listed in the ESI.†

Results and discussion

Hydrolytic hydrogenation of microcrystalline cellulose to C_6 alditols

Fig. 1 shows the yield of C_6 alditols and microcrystalline cellulose conversion over different solid acid catalysts combined with 5 wt% Ru/C. The $\gamma\text{-Al}_2\text{O}_3$, ZrO_2 and $\text{SiO}_2\text{-ZrO}_2$ catalysts gave very low C_6 alditols yields and microcrystalline cellulose conversions. For H-MOR and HZSM-5, the cellulose conversion was above 50%, but the C_6 alditols yield was less than 30%. Although Amberlyst 15 and ZrS gave high cellulose conversions of above 85%, their high acid strength resulted in significant by-products *via* the dehydration reaction, which resulted in the low C_6 alditols yield. For the ZrW and AlW catalysts, cellulose was mainly converted to the hydrogenolysis by-products (ethy-

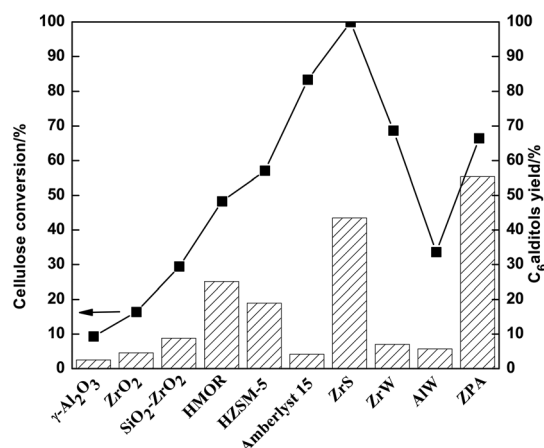


Fig. 1 Transformation of microcrystalline cellulose with different solid acid catalysts and 5 wt% Ru/C. Reaction conditions: 488 K, 6 MPa of initial H_2 pressure (room temperature), 1.5 h, microcrystalline cellulose 0.5 g, H_2O 50 mL, solid acid 0.9 g, Ru/C 0.0375 g.

lene glycol and propylene glycol yield of 28.9% and 7.8%, respectively), which led to the low C₆ alditols yield of less than 10%. The poor performance observed over ZrW and AlW can be possibly attributed to the strong tungsten promoted cleavage of C–C bonds.^{37,38} It is clear that ZPA combined with Ru/C exhibited the highest C₆ alditols yield (55.4%) with 66.5% microcrystalline cellulose conversion. The XRD pattern of ZPA (Fig. S1†) demonstrates that ZPA has an amorphous structure, and the SEM image shows that the particle size of ZPA was below 100 nm (Fig. S2†). The average Ru particle size was about 3 nm as measured by TEM and statistical analysis (Fig. S3†).

The direct transformation of cellulose to C₆ alditols is a coupling process (cellulose depolymerization to saccharides and the *in situ* hydrogenation of saccharides to C₆ alditols), therefore the ZPA–Ru/C hybrid catalyst possessed a metal–acid balance between ZPA and Ru/C. We adjusted the metal–acid balance by changing the dosage 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 C₆ 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 C₆ alditols yield remained almost unchanged until the amount of Ru/C reached 0.05 g. However, further increasing the Ru/C dosage caused the C₆ alditols selectivity to decrease, which is owed to the C₆ alditols being hydrogenolyzed into small molecular alcohols by the excess Ru/C. Considering that 0.0375 g Ru/C showed the maximal C₆ alditol yield, we optimized the amount of ZPA with the fixed Ru/C dosage of 0.0375 g. The cellulose conversion increased with the increasing amount of ZPA (Fig. 2(b)), which implies that cellulose depolymerization was determined by the ZPA catalyzed hydrolysis. The C₆ alditols selectivity initially increased as the dosage of ZPA was increased from 0.5 g to 0.9 g and then decreased with ZPA amounts above 0.9 g. The decreased selectivity over the excessive ZPA indicates that some of the produced C₆ alditols are dehydrated to sorbitan. Here, we chose 0.9 g ZPA and 0.0375 g 5 wt% Ru/C as the balanced dosage for the transformation of microcrystalline cellulose to C₆ alditols.

The effect of reaction time was further investigated using the indicated hybrid catalyst, with the results being listed in Table 1. The cellulose conversion increased sharply from 44.7% to 100% with increasing reaction time from 0.5 h to 4 h. A 99% cellulose conversion and 63.5% C₆ alditols yield was achieved at 488 K for 3 h (Table 1, entry 3). The selectivity of C₆ alditols decreased consistently from 90.9% to 57.4% with prolonging of the reaction time. The decreased selectivity can be attributed to the dehydration of C₆ alditols to sorbitan and hydrogenolysis to other small molecules like glycerol, ethylene glycol, propylene glycol and so on (Fig. S7 and S8†). However, the C₆ alditols yield and selectivity decreased slowly from 63.5% to 57.4% when cellulose was completely converted, indi-

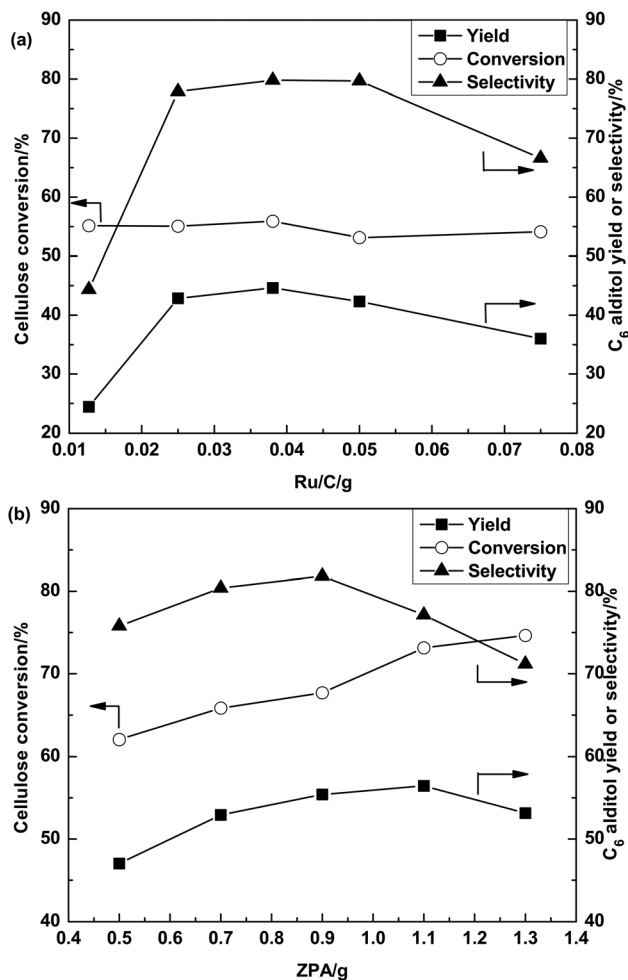


Fig. 2 Optimizing the amounts of ZPA and 5 wt% Ru/C in microcrystalline cellulose conversion. Reaction conditions: 488 K, 6 MPa of initial H₂ pressure (room temperature), 1.5 h, microcrystalline cellulose 0.5 g, H₂O 50 mL, (a) ZPA 0.3 g, (b) Ru/C 0.0375 g.

Table 1 The effect of reaction time over ZPA and Ru/C and replaced HCl with different pH and Ru/C in microcrystalline cellulose 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 H₂ pressure (room temperature), microcrystalline cellulose 0.5 g, H₂O (entries 1–6) or acidic solution (entries 7–10) 50 mL, Ru/C 0.0375 g. ^b Productivity of C₆ alditols = 1268.3 g L⁻¹ h⁻¹ g_{Ru}⁻¹. ^c Filtrate: treatment ZPA with water under the reaction conditions for 3 h.

cating that C₆ alditols are quite stable under the present reaction conditions. Further analysis of the product distribution showed that only cellobiose and glucose (no oligosaccharides) were detected, which is different from the previous reports where significant amounts of oligosaccharides were detected when using liquid and some solid acids in the depolymerization of cellulose.^{13,15,18,19} As the hydrogenation of glucose and hydrogenolysis of C₆ alditols simultaneously take place at the surface of Ru, the hydrogenation is dominant as the glucose is supplied sufficiently and fast.¹⁵ This effect is in favour of improving the yield of C₆ alcohols with partial suppression of the hydrogenolysis reaction.

Because ZPA possibly releases phosphoric acid into the solution as a result of leaching, the depolymerization of cellulose possibly proceeds *via* a homogenous pathway. To investigate the possible homogeneous catalysis, we combined the filtrate of the hydrothermally treated ZPA with fresh Ru/C (Table 1, entry 6). The result indicated that 36.5% of cellulose was converted with 42.5% C₆ alditols selectivity. The ion chromatography test demonstrated that PO₄³⁻ existed in the filtrate.

In order to compare the present ZPA with inorganic liquid acid, we replaced ZPA by HCl solution with different pH values (Table 1, entries 7–10) since HCl has been proven to be an efficient inorganic liquid acid in cellulose depolymerization.^{13,39} The conversion of cellulose sharply decreased from 100% to 27.4% when the pH of the HCl solution increased from 2 to 5 (Table 1, entries 7–10). However, the C₆ alditols yield of 18.7% in the pH = 2 HCl solution was much lower than the 51.8% in the pH = 3 HCl solution, which is caused by the fact that more dissociated H⁺ could promote the dehydration of the C₆ alditols to sorbitan. Of particular note, the C₆ alditols yield of 51.8% in pH = 3 HCl solution (Table 1, entry 8) is also lower than the 63.5% achieved by ZPA (Table 1, entry 3). Even with a similar cellulose conversion, the C₆ alditols selectivity of 73.1% in the pH = 3 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 superiority of ZPA is possibly due to its large surface of 164 m² g⁻¹, mesoporous size of 9.67 nm (Fig. S4†), its large total acidic amount of 1.8 mmol g⁻¹ and the simultaneous presence of weak and strong acid sites from NH₃-TPD (Fig. S6†), which is favourable for increased contact between cellulose and the catalyst, accelerated cellulose hydrolysis and fast diffusion rate of the hydrolytic cellobiose and glucose intermediates.

Hydrolytic hydrogenation of ball-milled cellulose to C₆ alditols

The decreases in the crystalline and polymerization degree of cellulose can improve the degradability of cellulose,⁴⁰ which is beneficial for the reduction of the reaction temperature and the suppression of side reactions, and eventually the enhancement of the yield of C₆ alditols. Here, we used ball-milling pre-

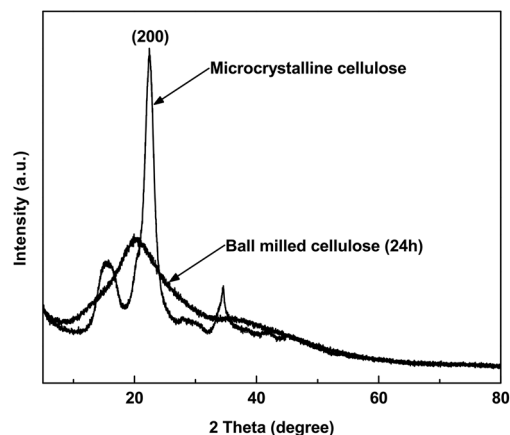


Fig. 3 XRD patterns of microcrystalline cellulose and ball-milled cellulose.

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°, which indicates the typical I crystalline form. The ball-milling pre-treatment did not change the type of cellulose, but the intensity of the characteristic peak ((200) plane) became wider, demonstrating that the crystallinity decreased and more amorphous regions were 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 the reaction temperature on the transformation of ball-milled cellulose is shown in Fig. S10.† The optimal temperature was 463 K.

The performance of ZPA and Ru/C in the conversion of ball-milled cellulose is listed in Table 2. By increasing the reaction time, the amount of cellobiose and glucose decreased gradually due to further hydrogenation. Compared with microcrystalline cellulose, the yield of C₆ alditols was improved significantly for the conversion of ball-milled cellulose. The maximum yield and selectivity for C₆ alditols reached 85.5% and 90.3% respectively, which are similar to the results of combining the mechanocatalytic depolymerization of cellulose with hydrogenolysis of the intermediates to C₆ alditols by H₂SO₄ and Ru/C at 433 K.⁴¹ It is also comparable to the results of the hydrogenation of cellobiose to C₆ 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 HCl solution combined with Ru/H-USY, the complete conversion for ball-milled cellulose was achieved in 24 h,¹³ which implies that the rapid cellulose depolymerization for obtaining the high C₆ alditols yield is not entirely attributed to the acidity of the catalyst. The potential reasons for this needs to be further studied.

The composition of liquid products showed that the yield of C₂–C₃ polyols was 6.5% and only a trace amount of sorbitan can be detected (Table 2, entry 3). However, the yield of

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 H₂ pressure (room temperature), ball-milled cellulose 0.5 g, H₂O 50 mL, ZPA 0.9 g, Ru/C 0.0625 g. ND: not detected. ^b Productivity of C₆ alditols = 1229.5 g L⁻¹ h⁻¹ g_{Ru}⁻¹.

Table 3 Conversion of concentrated cellulose to C₆ 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/g L ⁻¹ h ⁻¹ g _{Ru} ⁻¹
1	2.5 g BMC	0.075	2.5	463	82.2	68.4	83.2	4098.4
2	2.5 g MCC	0.075	3.0	488	79.4	55.7	70.2	2781.2
3 ^c	5.0 g BMC	0.100	2.5	463	72.5	61.2	84.4	5500.4
4	5.0 g MCC	0.100	3.0	488	75.1	51.9	69.1	3887.2

^a Reaction conditions: 6 MPa of initial H₂ pressure (room temperature), H₂O 50 mL, ZPA 0.9 g. ^b MCC: microcrystalline cellulose, BMC: ball-milled cellulose. ^c Concentration = $m_{\text{cellulose},0}/162 \times 182 \times \text{Yield}(\%)/V_{\text{liquid}} = 5000/162 \times 182 \times 61.2\%/50 = 68.8 \text{ mg mL}^{-1}$.

sorbitan reached around 15%–25% in the literature.^{13,15,17} Based on these results, we speculate that the suppression of the C₆ alditols dehydration reaction is the main reason for the high C₆ alditols yield and selectivity.

Hydrolytic hydrogenation of concentrated cellulose to C₆ alditols

A wide variety of studies have reported the conversion of cellulose by solid acid catalysts with low mass ratios of substrate/catalyst.^{44,45} In this work, the transformation of concentrated cellulose was performed with a fixed amount of ZPA and a slightly varied dose of Ru/C. The corresponding results are presented in Table 3. Under the high substrate/catalyst mass ratios, both the microcrystalline and the ball-milled cellulose can be effectively degraded to obtain more than 50% yields of C₆ alditols. As compared with the low concentrated cellulose, the high ones gave significantly increased C₆ alditols productivity under comparable reaction conditions (Table 1, entry 3; Table 2, entry 3; Table 3, entry 1–4). The highest concentration of C₆ alditols reached up to 68.8 mg mL⁻¹ (Table 3, entry 3), which was close to the monosaccharide concentration of the liquid acid (HCl) hydrolysis of corn stover,⁴⁶ illustrating the potential application of ZPA and Ru/C in this process. Most importantly, the mass ratio of cellulose to Ru/C reached 50 (Table 3, entries 3–4), which was the highest mass ratio not only for the conversion of cellulose but also for the hydrogenation of cellobiose and glucose over solid catalysts,^{42,43} showing the obvious advantage of this economical production of C₆ alditols from cellulose.

Hydrothermal stability of ZPA and the reaction pathway

Considering that the hydrothermal stability of a solid catalyst is a crucial aspect of the aqueous phase conditions for biomass transformations, we further investigated the hydrothermal stability of this hybrid catalyst. Ru/C has already been proven to be a highly stable catalyst in the aqueous phase hydrogenation reaction, so we merely studied the stability of ZPA. We performed the 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 C₆ alditols yield declined to 55% after the first treatment, and the ZPA catalyst maintained its activity in the subsequent runs. The decreased C₆ alditols yield is responsible for the P leaching of fresh ZPA under the hydrothermal reaction conditions, which was demonstrated by the comparison experiment using the ZPA filtrate for further cellulose conversion (Table 1, entry 6). The maintained performance of the sequentially hydrothermally treated ZPA indicates that no P leaching had taken place after the first hydrothermal treatment. This feature of ZPA was further confirmed by Fig. 5 using the filtrate of the hydrothermally treated ZPA for cellulose conversion. After the second run, the C₆ alditols yields were maintained at about 7%, which is very similar to that when using Ru/C alone for this process. This indicates that the structure of the ZPA is stable and no P leaching occurs after the first hydrothermal treatment under these reaction conditions.

The exceptional performance of ZPA cannot be adequately attributed to the acid strength of ZPA, as the pH = 3 HCl solution did not rapidly convert the microcrystalline cellulose or even the ball-milled cellulose. The catalysis mechanism of ZPA

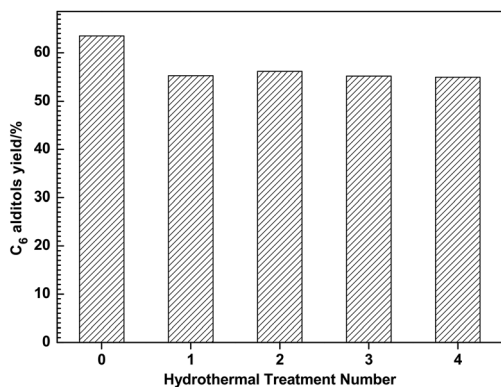
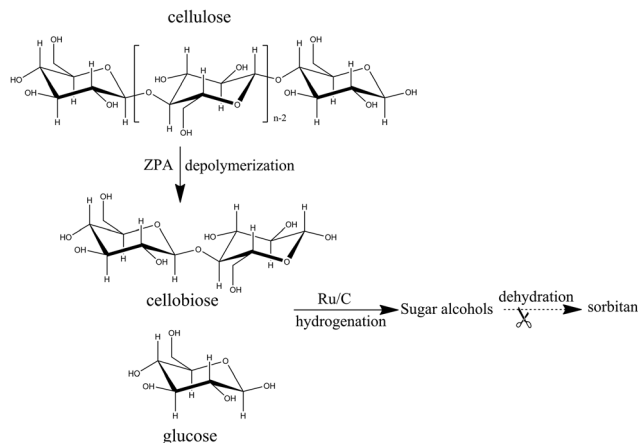


Fig. 4 Transformation of microcrystalline cellulose by hydrothermally treated ZPA and Ru/C. Reaction conditions: 488 K, 6 MPa of initial H₂ pressure (room temperature), 3 h, microcrystalline cellulose 0.5 g, H₂O 50 mL, ZPA 0.9 g, Ru/C 0.0375 g. Hydrothermal treatment conditions: 488 K, 6 MPa of initial H₂ pressure (room temperature), 3 h, H₂O 50 mL, ZPA 0.9 g.



Scheme 1 Reaction pathway for the one-pot conversion of cellulose to C₆ alditols by ZPA and Ru/C.

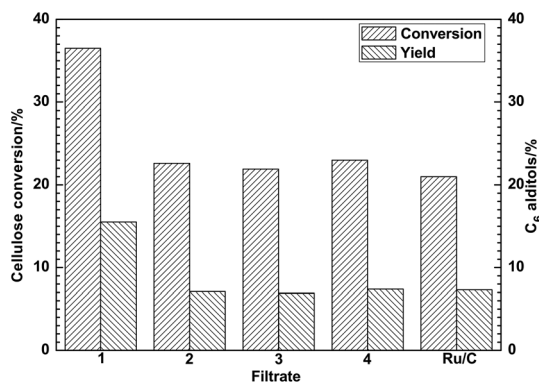


Fig. 5 Transformation of microcrystalline cellulose by the filtrate of the hydrothermally treated ZPA and Ru/C. Reaction conditions: 488 K, 6 MPa of initial H₂ pressure (room temperature), 3 h, microcrystalline cellulose 0.5 g, H₂O 50 mL, Ru/C 0.0375 g. 1, 2, 3 and 4 represent the hydrothermal treatment number. For Ru/C, the catalyst is solely Ru/C without use of ZPA.

was thus investigated by performing adsorption experiments with cellobiose, glucose and sorbitol as the probe molecules, respectively. It was found that the uptakes of cellobiose and glucose on the ZPA were 2.74 mg g⁻¹ and 1.13 mg g⁻¹, respectively. The adsorption amount of cellobiose on ZPA was two times more than glucose, by which we speculate that ZPA has a favourable affinity for cellulose. The carbon of the 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 oligomers are hydrolyzed to cellobiose and glucose at the surface of ZPA. Subsequently, the obtained cellobiose and glucose are absorbed and hydrogenated to C₆ alditols by the Ru/C catalyst, and the dehydration reaction of obtained C₆ alditols is suppressed due to the very weak adsorption of C₆ alditols on ZPA (the undetectable adsorption of sorbitol on ZPA surface).

Conclusion

In summary, ZPA was proven to be an effective solid acid catalyst, which was combined with Ru/C for the direct production of C₆ alditols from cellulose. 85.5% and 63.5% C₆ alditols yields were obtained with ball-milled cellulose and microcrystalline cellulose as feedstock, respectively. The results of the 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 values provided results that the performance of heterogeneous ZPA is better than homogeneous liquid acid.

The ZPA and Ru/C catalyst were adapted to the high cellulose/catalyst mass ratios (especially for the higher cellulose/(Ru/C)) and a high C₆ alditols concentration of 68.8 mg mL⁻¹ was obtained. Moreover, ZPA maintained excellent hydrothermal stability with hydrothermal treatment. The high yield of C₆ alditols from cellulose was ascribed to the fact that ZPA favoured the cellulose adsorption and the promotion of its depolymerization to cellobiose and glucose, which were further hydrogenated immediately over Ru/C to C₆ alditols. The weak adsorption of C₆ alditols over ZPA prohibited the dehydration of C₆ alditols to by-products.

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