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Direct conversion of cellulose into C_6 alditols over Ru/C combined with H⁺-released boron phosphate in an aqueous phase[†]

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Non-edible cellulose has attracted considerable attention to be converted into valuable platform chemicals. Direct transformation of cellulose to C_6 alditols (mannitol and sorbitol) provides a sustainable route. A productive approach is presented in this work using a Ru/C catalyst combined with H⁺-released boron phosphate in an aqueous phase. A yield of C_6 alditols as high as 74.9% with a 91% conversion of cellulose is achieved. By adding silica–alumina materials, the yield of C_6 alditols can be improved to 93.5% with complete conversion. The acid sites gradually released from boron phosphate under hydrothermal conditions could promote the hydrolysis of cellulose without significant degradation of glucose. Furthermore, the interaction of boric acid with C_6 alditols may form borate–polyol complexes, which can enhance the stability of the C_6 alditols to avoid further hydrogenolysis and dehydration of the C_6 alditols formed. Due to the adsorption ability of the substrate, the addition of silica–alumina materials with a high content of silica leads to improved performance.

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Introduction

Lignocellulosic biomass is considered the most abundant and cheapest carbon source.1-4 Among its compositions, cellulose is the most abundant, which exists as a polymer consisting of repeating units of glucose linked by β -(1,4)-glycoside bonds. Through deoxygenation of cellulose or cellulose-derived carbohydrates or sugar alcohols, biofuel and chemicals can be achieved for commercial application.5,6 However, its insolubility limits the possibility of cleavage of the cellulose chain, and therefore hampers its usability.5 Hence, pretreatment has been proposed as an efficient method to improve its solubility in water. For instance, an alkali-urea system can dissolve cellulose in a low concentration through disruption of the hydrogen bond networks in cellulose at a low temperature of 261 K.7 In addition, ball-milled pretreatment can lower the degree of crystallinity of cellulose through mechanical interactions has been studied by researchers.^{8,9} However, those approaches are questionable because they use high concentrations of alkali solution to dissolve cellulose and the indispensible high energy cost for ball-milled pretreatment.

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For cellulose-derived chemicals, C₆ additols are the most important platform molecules to produce alkanes¹⁰ and highvalue chemicals.¹¹ Over a metal-acid catalytic system, C₆ alditols can be achieved from the one-pot conversion of cellulose, which is widely considered as a promising approach that avoids the two-step process involving a pre-treatment step. The operation of cellulose depolymerization is often takes place in acidic media or catalyzed by an acid catalyst. Metals are responsible for the hydrogenation reaction of the carbonyl groups in the cellulose-derived carbohydrates. Inorganic acids like H2SO4,12,13 HCl,^{12,14} and H₃PO₄,^{12,14} or heteropoly acids like H₅BW₁₂O₄₀,¹⁵ H₄SiW₁₂O₄₀,^{13,15,16} and H₃PW₁₂O₄₀,^{13,16} combined with metalsupported catalysts have been proved as catalyst systems used to transform cellulose to C6 alditols. In addition, even hot water could be used as the acid source for the hydrolytic hydrogenation process.¹⁷ However, these catalysts require long reaction times, which is a barrier for their commercial application. Moreover, even with the energy-cost of ball milled cellulose or acid-impregnated cellulose, a long reaction time is still a requirement for high yields of C₆ alditols. Besides, when the acid functionality is too dominant in the hydrolytic hydrogenation of cellulose, a build-up of free glucose and hexitols causes a loss of selectivity through glucose degradation and hexitol dehydration. For metal catalysts, Ni,18,19 Pt,20-23 Ru,16,24-27 and Ir^{28,29} were studied for the hydrolytic hydrogenation of cellulose. Among the studied metals, ruthenium possesses the highest activity during hydrogenation, which could shorten the reaction time and lower the reaction temperature. But it still casts the negative effect on the process by performing the

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hydrogenolysis reaction on the C_6 alditol products formed.³⁰ Hence, it is necessary to seek for an effective catalyst system with a suitable balance between the acid and metal functions to avoid the C–C bond cleavage of the desired C_6 alditol products on the ruthenium metal, and also avoid the dehydration of the desired C_6 alditols as well as glucose degradation on the acidic sites. Moreover, to achieve a high yield of C_6 alditols from cellulose, the improved thermal stability of C_6 alditols is indispensable for a faster and more complete conversion of cellulose at higher reaction temperatures.

Boron phosphate is regarded as an acidic catalyst, which contains both a Brønsted acidic center and Lewis acidic center its surface.³¹⁻³⁵ It has been used for the dehydration reaction of alcohols36 and isomerization reactions.37 But it has never been used in the hydrolytic hydrogenation of cellulose. Herein, we report a boron phosphate-Ru/C catalytic system to directly convert cellulose into C₆ alditols. With a gradual increase in the concentration of H⁺ arising from the slow hydrolysis of boron phosphate in the aqueous phase, the gradually enhanced acidic media can catalyze the transformation of cellulose to cellulose oligomers. This can avoid the instant arrival of a dominant acidic functionality, which causes glucose degradation and hexitol dehydration. Over the Ru/C catalyst, the cellulose oligomers were transformed to C₆ additols. More importantly, the boric acid and C₆ alditols produced can form borate-polyol complexes, which prevent further hydrogenolysis and dehydration due to their larger steric hindrance. Hence, a high yield of C₆ alditols can be obtained over the boron phosphate-Ru/C catalytic system.

Experimental section

Materials

Microcrystalline cellulose (MCC) and tantalum(v) ethoxide (C10H25O5Ta) were bought from Alfa Aesar. Ru/C (5 wt%) and Tungstosilicic acid (H₄SiW₁₂O₄₀, SiW) were purchased from Aladdin. Phosphoric acid (H₃PO₄), boric acid (H₃BO₃), and ethanol were supplied by Tianjin Fuyu Fine Chemical Co., Ltd. MCM-41(pure silica), HZSM-5 (Si/Al = 38), H β (Si/Al = 38), HMOR (Si/Al = 25), USY (Si/Al = 9), and γ -Al₂O₃ were purchased from Catalyst Plant of NanKai University. Na2HPO4, ammonium dihydrate phosphate (NH₄H₂PO₄), and hexadecyl trimethyl ammonium bromide $(CH_3(CH_2)_{15}N(Br)(CH_3)_3)$ were bought from Tianjin FuChen Chemical Reagents Factory. Ammonium hydroxide (NH₃·H₂O) was purchased from Guangzhou Chemical Reagent Factory. Silver nitrate (AgNO₃), zinc chloride $(ZnCl_2)$, kaolin, and tartaric acid $(C_4H_6O_6)$ were purchased from Tianjin Damao Chemical Reagent Factory. RuCl3 was purchased from Shaanxi Kaida Chemical Engineering Co., Ltd. Zirconium oxychloride octahydrate (ZrOCl₂·8H₂O) was supplied by Sinopharm Chemical Reagent Co., Ltd.

Catalyst preparation and characterization

The boron phosphate catalyst (BP) was synthesized based on previous reports.^{38,39} A stoichiometric mixture of boric acid and phosphoric acid was dried at 323 K. Boric acid was dissolved in

the phosphoric acid solution with stirring. The dried white powder was calcined at 1273 K for 5 h. Then, the calcined powder was washed with hot deionized water at 333 K and dried at 373 K overnight. MCM-41, HZSM-5, H β , HMOR, USY, and γ -Al₂O₃ were milled and then calcined at 823 K for 4 h. They were used after the milling process.

Zirconium phosphate (ZrP) was synthesized by precipitation of a $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution in $\text{NH}_4\text{H}_2\text{PO}_4$ solution.⁴⁰ After being washed with deionized water, the white precipitate was dried at 373 K for 12 h and calcined at 673 K in air for 4 h.

Tantalum phosphate (TaP) was prepared based on previous reports.^{41,42} Tantalum pentaethoxide as the tantalum source was added to a tartaric acid solution using ethanol as the media. After the ethanol was evaporated, distilled water was added. Then, a diammonium hydrogen phosphate solution was added with stirring to get a homogeneous solution. A certain amount of hexadecyltrimethyl ammonium bromide was added with vigorous stirring for 0.5 h. The white precipitate was sealed in a Teflon autoclave for 24 h at 403 K. The precipitate was washed with distilled water and ethanol, and dried at 343 K. Before being used, the resulting TaP was calcined at 823 K for 6 h.

Ag₃PO₄ (AgP) was synthesized by dropwise addition of an Na₂HPO₄ aqueous solution into a AgNO₃ aqueous solution.⁴³ After filtration and washing with distilled water, the golden yellow precipitate of AgP was dried in air at 343 K overnight.

 $Zn_3(PO_4)_2$ (ZnP) was synthesized using $ZnCl_2$ as the zinc source. A $ZnCl_2$ aqueous solution was added dropwise into a H_3PO_4 solution with stirring. The mixed solution was neutralized with $NH_3 \cdot H_2O$ and a white precipitate of ZnP was formed. The white precipitate was washed with distilled water and dried at 343 K overnight.

A Nicolet iS50 FT-IR (Fourier transform infrared spectrometer) spectrophotometer (Thermo Scientific, USA) was used to verify the borate–polyol complexes. The instrument was equipped with a MCT (mercury cadmium telluride) detector. The Hitachi S-4800 instrument was used to analyze the morphological information (scanning electron microscopy) of BP. The XRD information of BP was obtained using X' Pert Pro MPD equipment. The surface area and pore properties were analyzed by a Quantachrome instrument.

Cellulose conversion experiment

In a typical procedure, Ru/C (0.1 g), cellulose (0.8 g), co-catalyst (0.5 g), and water (40 mL) were introduced into a 100 mL stainless steel reactor. The reactor was purified with pure hydrogen for six cycles and pressurized with 5 MPa of H_2 (room temperature, RT). The autoclave was heated to 463 K with stirring and kept at this temperature for 1 h. The autoclave was cooled to RT by placing it into an ice–water bath after the reaction and liquid samples were collected. To improve the yield of C_6 alditols, 0.2 g zeolite or solid acid as an additive was added.

A Waters e2695 high performance liquid chromatography (HPLC) apparatus was used to qualitatively analyze the aqueous samples. The HPLC was equipped with an Inertsustain C18 column to quantify the polyols and a Shodex Sugar SH1011

column to detect the sugars. The mobile phase was water and 0.005 M H₂SO₄, respectively. The gas phase samples were analyzed using an Agilent 7890A instrument.

Results and discussion

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The effect of various acids and the reaction conditions on the hydrolytic hydrogenation of cellulose

Fig. 1 shows the performance of different acids and the Ru/C catalyst for the transformation of cellulose to alditols at 463 K for 1.0 h. ZrP shows a low cellulose conversion and the yield of alditols is about 46%, though our previous studies suggested ZrP can efficiently convert ball-milled cellulose into C₆ alditols.44 For the SiW-Ru/C system, though it has been reported as an effective system to transform cellulose to hexitols,13 the 1.0 h reaction time is too short to get a high yield and selectivity for C₆ alditols. For solid acid phosphates, the use of ZnP and AgP could cause the hydrogenolysis reaction to produce a 16.6% yield of ethylene glycol and 8.5% yield of propylene glycol. Although the cellulose conversion is relatively high using the TaP-Ru/C catalytic system, the selectivity of C₆ alditols is 54%, which lead to a low yield. However, the BP-Ru/C catalytic system exhibits a high cellulose conversion (91%) with 82.1% selectivity for C₆ alditols after 1.0 h.

The effect of reaction time was performed using the BP–Ru/C catalytic system, and the results given in the Fig. 2. By increasing the reaction time from 0.5 h to 2 h, the substrate cellulose was completely converted. After 1 h reaction time at 463 K, the yield of C_6 alditols achieved was 74.9% with a 91% cellulose conversion. Surprisingly, further prolongation of reaction time didn't cause any noticeable loss of C_6 alditols. After 4 h, the yield of C_6 alditols only decreased from 74.9% to 72.9%, suggesting the stability of the C_6 alditols formed is relatively high at 463 K using the current catalytic system. But we have already noted that reaction conditions requiring a long reaction time and high reaction temperatures will lead to side reactions, which were demonstrated in our previous study.⁴⁴ Specifically, C_6 alditols underwent a further hydrogenolysis



Fig. 1 Conversion of cellulose to alditols over different acids and Ru/C. Reaction conditions: 0.5 g acid, 0.8 g MCC, 0.1 g Ru/C, 40 mL H₂O, 5 MPa of H₂ (RT), 463 K, 1 h.



Fig. 2 The effect of reaction time on the yield of C_6 alditols over the BP–Ru/C catalytic system. Reaction conditions: 0.5 g acid, 0.8 g MCC, 0.1 g Ru/C, 40 mL H₂O, 5 MPa of H₂ (RT), 463 K.

reaction to produce other polyols, such as ethylene glycol and propylene glycol, or a dehydration reaction to yield sorbitan or isosorbide. In fact, sorbitol dehydration reactions can be occur at high temperatures of 523–573 K without the addition of any acid catalysts,⁴⁵ indicating the hydrolytic hydrogenation of cellulose to produce C_6 alditols should be performed for a short reaction time at relatively low temperatures. Meanwhile, through characterization of the liquid products, negligible cellobiose or glucose was observed in the reaction process, which agrees with the former study that Ru/C shows high hydrogenation activity that outruns the hydrolysis rate of cellulose over an acid catalyst.⁴⁶ This also suggests a partial inhibition effect on the hydrogenolysis of C_6 alditols is ascribed to the Ru/C when enclosed by glucose or other intermediates.

Furthermore, the effect of reaction temperature was carried out under the optimized conditions, and the results shown in



Fig. 3 The effect of reaction temperature on the yield of C₆ alditols over the BP–Ru/C catalytic system. Reaction conditions: 0.5 g BP, 0.8 g MCC, 0.1 g Ru/C, 40 mL H₂O, 5 MPa of H₂ (RT), 1 h. (Green: the yield of C₆ alditols; blue: the yield of gas phase products; magenta: the yield of small polyols and dehydration products).

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Fig. 3. It is obvious that the cellulose conversion increased as the reaction temperature was increased. When the temperature increased to 483 K, the substrate was completely converted, but the yield of by-products also increased. Specifically, the yield of gas phase products, which are mainly methane, ethane, and pentane sharply increased from 8.2% to 40.3%, and in the liquid phase, the yield of dehydration products (sorbitan and isosorbide) and small polyols (ethylene glycol and propylene glycol) were increased to 7.8%. It's clear that the selectivity of C₆ alditols dramatically decreased from 83.3% to 43.1% since the higher reaction temperature led to an increase in by-products. This observation could be explained by the fact that the C-O and C-C cracking reactions of polyols can be easily performed in an acidic media at high temperatures. It was found that the C₆ alditols produced can be dehydrated to sorbitan (monomolecular dehydration) and isosorbide (bimolecular dehydration) in the absence of a catalyst at high temperatures.⁴⁷ The yield of dehydration products could be promoted in an acidic media.48 The small polyols might be formed by a retro-aldol condensation of carbohydrates, which has been studied by Zhang's group.49 The increased yield of light alkanes was a consequence of the accelerated hydrocracking of C₆ alditols at high temperatures.50

To detect the leaching phenomenon of BP after the reaction, ion chromatography was used and the result showed that PO_4^{3-} and boric acid existed in the liquid phase (See Fig. S1[†]). Further investigation on the pH of the aqueous phase suggested the acidity of the solution was increased after the reaction. This phenomenon disagrees with the former reports, which illustrated the BP catalyst prepared using 1273 K calcination process could not be dissolved in water.⁵¹

Since the pH of the mixed solution after reaction was decreased, we measured the pH of water upon the addition of BP at different temperatures and atmosphere pressure as shown in Fig. 4. By elevating the temperature from 293 K to 463 K, the pH of the mixture decreased to pH = 1.95. By further increasing



Fig. 4 The pH evolution of the liquid phase upon the addition of 0.5 g BP in 40 mL distilled water at different temperatures and atmosphere pressure.

the temperature, the acidity continued to increase. It is clear that the hydrolysis process of cellulose was accompanied with the hydrolysis of BP. In addition, BP was found fully transferred into the aqueous phase in the cellulose conversion experiments, which wasn't observed at atmosphere pressure. Hence, this phenomenon would significantly increase the acidity of the reaction system to improve the cellulose hydrolysis rate, which is the rate-determinate step for the hydrolytic hydrogenation of cellulose.^{46,52} We should note that the BP hydrolysis process is gradual and that H⁺ was slowly released from BP. Since cellulose is probably adsorbed by BP on its surface, the gradually released H⁺ can be directly used for the hydrolysis of cellulose, which essentially avoids the diffusion process. Moreover, with the increasing acidity of the mixed solution, cellulose can be partially dissolved. This dissolution of cellulose in water can further enhance the rate of cellulose hydrolysis via transformation to smaller oligomer fractions. Through breaking the glycoside bonds of soluble oligosaccharides, which possess a low threshold of access to glycoside bonds, a high yield of C₆ alditols can therefore be achieved in a short reaction time. In fact, previous research has confirmed this acid effect on the hydrolytic hydrogenation of cellulose to produce polyols.53

We have noticed that the BP catalyst was synthesized using H₃BO₄ (HB) and H₃PO₄ (HP), and this hydrolysis process may cast a negative impact on the hydrolytic hydrogenation of cellulose. To rule out this hypothesis, comparative experiments were performed by substituting BP with boric acid and/or phosphoric acid under reaction conditions with an equivalent molar ratio of boron and phosphorus. The cellulose conversion decreased to 68.5% by replacing the BP catalyst with HB, and the yield of C₆ alditols was sharply lowered from 74.9% to 42.8% (Table 1, entry 1). Compared with the inorganic acid HB, the cellulose conversion was increased from 68.5% to 91.9% over HP and Ru/C (Table 1, entry 2). However, the selectivity for C₆ alditols decreased, which is a consequence of the fact that the more dominant acid functionality derived from HP would cause glucose degradation or hexitol dehydration.12 With a mixture of HB and HP, both the selectivity of C₆ alditols and the yield of C₆ alditols (Table 1, entry 3) were improved when compared with the use of HB or HP as the acid functionality. This observation may be a result that the borate species and polyols form boratepolyol complexes, which suppress the dehydration reaction of C₆ alditols to form sorbitan or isosorbide.⁵⁴ In addition, the observed results show that the addition of HB can inhibit the C-C cleavage reaction of C6 alditols to yield small polyols. These results can be verified by entries 3, 5 and 6 in Table 1. When different ratios of HB/HP were used for the tests, the higher the ratio of HB/HP, the lower the yield of small polyols and gas phase products were observed along with a decrease in cellulose conversion. With a decreasing ratio of HB/HP, the selectivity for C₆ alditols decreased, while the yield of small polyols was increased. It is indicated that the presence of a dominant amount of HP could cause more side reactions such as dehydration and C-C bond hydrogenolysis of C₆ alditols, though it is effective for cellulose hydrolysis. The addition of HB at a suitable content can effectively optimize the balance between hydrolysis and side reactions to improve the yield of C₆ alditols.

Table 1 Conversion of cellulose over different acids and Ru/C^a

Entry	Acid	Cellulose conversion/%	C ₆ alditols selectivity/%	Yield/%					
				C ₆ alditols	Glucose	Cellobiose	Isosorbide	Small polyols ^b	Others ^c
1	HB	68.5	62.5	42.8	2.9	1.5	ND	ND	12.9
2	HP	91.9	42.9	39.4	1.2	0.5	7.5	6.9	24.5
3^d	HB + HP	83.9	75.6	61.5	1.1	0.6	1.5	1.1	15.1
4	BP	91.3	82.1	74.9	ND	ND	ND	ND	13.3
5^e	HB + HP	77.8	59.1	46.0	1.9	1.1	3.9	3.3	19.4
6 ^f	HB + HP	87.9	58.2	51.1	1.6	0.8	5.1	4.8	22.7

^{*a*} Reaction conditions: 463 K, 5 MPa of H₂ (RT), 1 h, 0.1 g Ru/C, 0.8 g cellulose, H₂O 40 mL, an equivalent molar ratio of boron and phosphorus was added according to the different acids used. ND: not detected. ^{*b*} Small polyols: ethylene glycol, propylene glycol. ^{*c*} Others are the gas phase products, which mainly include methane, ethane, and propane. ^{*d*} The same amount of HB and HP (molar ratio = 1 : 1) was used to synthesize 0.5 g BP. ^{*e*} The molar ratio of HB–HP is 3 : 1 (maintained the same amount of H⁺ mol as entry 3). ^{*f*} The molar ratio of HB–HP is 1 : 3 (which maintained the same amount of H⁺ mol as entry 3).

This might be caused by the steric hindrance of the boratepolyol complexes formed, which blocks the contact of Ru with the C–C bonds. Besides, HB is the weaker acid and is less effective towards the dehydration of C_6 alditols. However, even with an increased selectivity of C_6 alditols by using a mixture of HB and HP, the yield of C_6 alditols was still inferior to the 74.9% achieved using the BP acid catalyst. These results indicated that the BP catalyst is better than the relative inorganic acids.

As noted above, the superiority of the BP catalyst is ascribed to the balance between the acidic functionality released from BP and the metal functionality. Most importantly, the gradual release of H⁺ provides a favorable environment to catalyze the hydrolysis of cellulose, and when simultaneously combined with the Ru-catalyzed hydrogenation, the in situ catalysis of released H⁺ and hydrogen can give rise to the production of C₆ alditols. In this process, the hexitol dehydration and glucose degradation occurring with a dominant acidic functionality could be significantly avoided and reduced the yield loss of C₆ alditols. Moreover, when the BP completely released the H⁺ in the aqueous phase, the formed HB from BP may play an important role to suppress the dehydration and C-C bond cleavage reactions of C₆ alditols by forming borate-polyol complexes, which is another key factor for the improvement in yield and stability of the C₆ alditols.

FT-IR characterization was performed to verify the presence of the borate-polyol complexes. As shown in Fig. 5, the addition of HB into a sorbitol aqueous solution resulted in the appearance of a CH₂ bend and the enhanced intensity of the CH₂ bend at 1460 cm⁻¹, which was caused by the electron withdrawing effect of the borate complex. By increasing the concentration of HB, the peak at 1460 cm^{-1} became stronger. Moreover, the peaks belonging to the C-O groups (1200 to 900 cm⁻¹) were shifted towards lower frequencies upon increasing the concentration of boric acid in the solution of sorbitol. It's clear that the boric acid can coordinate with sorbitol. In contrast, HP doesn't give this shift effect in the sorbitol solution (See Fig. S5[†]). In fact, borate minerals were found to form complexes with cis-diols of organic molecules, such as ribose, arabinose, and xylose.55 Hence, the complexation with borate minerals actually stabilizes the products of C6 alditols formed during the

cellulose conversion process. In the current catalytic system, the formation of borate–polyol complexes would have an enhanced steric hindrance to prevent any further hydrogenolysis and dehydration of the C₆ alditols formed.

It should be noted that the separation of C_6 alditols from the mixture is a necessity. Recent literature suggests the recovery of H_3PO_4 from the solution can be performed using anion



Fig. 5 FT-IR spectra of: (a) 1 wt% H_3BO_3 aqueous solution, (b) 5 wt% H_3BO_3 aqueous solution, (c) 25 wt% sorbitol aqueous solution, (d) 1 wt% $H_3BO_3 - 25$ wt% sorbitol aqueous solution, and (e) 5 wt% $H_3BO_3 - 25$ wt% sorbitol aqueous solution.

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exchange membranes.^{56,57} Since the solubility of boric acid in water at room temperature is very low, it can be separated from the mixture by simply lowering the temperature. After filtration, we can obtain the C_6 additols solution.

The effect of silica-alumina materials

In the current study, another interesting observation was that the yield of C₆ alditols from the hydrolytic hydrogenation of cellulose can be further improved using silica-alumina materials or solid acids as additives to be added into the catalytic system. As shown in Table 2, using different additives, the glucose, cellobiose, isosorbide and small polyols were detected in negligible amounts or not at all, and the yield of C₆ alditols was different with the change of C1-C4 alkane yield. MCM-41 composed of pure silica gave the best results among the tested silica-alumina materials with a 93.5% yield of C₆ alditols. By lowering the silica content of the additive, the C₆ alditol yield decreased. HZSM-5 and H β with a Si/Al ratio of 38 gave a C₆ alditols yield of 87.6% and 86.1%, respectively. The additives with lower Si/Al ratios such as HMOR (Si/Al = 25) and USY (Si/Al = 9) showed a 82.7% and 80.1% yield of C_6 additols, respectively. With the pure alumina additive γ -Al₂O₃, the yield of C₆ additols was almost the same as the results of the previous experiments without the presence of an additive. It is obvious that the silicaalumina materials can adsorb the oligomer intermediates during the formation of the C₆ additols due to their affinity to the hydrophilic surface of the silica-alumina material. This had been pioneered by Sels' group who studied the sugar alcohols produced from cellulose over Ru/HUSY.12 The adsorption test was run by adding additives into the cellobiose, sorbitol, and glucose solution, which verified the additives possess an affinity to the cellulose-derived glucose and cellobiose, which can be further hydrogenated to C₆ alditols. Among the silica-alumina materials tested, MCM-41 had the highest adsorption ability towards glucose and the cellobiose molecules. On the contrary, the surface of γ -Al₂O₃ showed a reluctance towards the adsorption of glucose and cellobiose. It might be a result from the fact silica can adsorb the hydroxyl groups of the intermediates easier by itself than it does in the presence of alumina. On the other hand, the presence of these silica-alumina

materials exhibit much smaller amounts of gas phase products (mainly methane, ethane, and propane) than that observed without adding them. It is a fact that the Ru/C catalyst used as the hydrogenolysis catalyst can also catalyse the conversion of the C_6 alditols to smaller alkanes.⁵⁸ The C_6 alditols produced were adsorbed by the additives, therefore, the contact of Ru/C with the C_6 alditols was limited, which lowered the possibility of the hydrogenolysis of the C_6 alditols formed. Hence, the yield of C_6 alditols was improved.



Fig. 6 FT-IR spectra of sorbitol with/without an additive (A and B share the same color indicators for the different samples).

Entry	Additive	Cellulose conversion/%	Product yiel	d/%	Adsorption/mg g ⁻¹			
			C ₆ alditols	Others in aqueous phase ^b	In gas phase ^c	Glucose	Cellobiose	Sorbitol
1	_	91.3	74.9	ND	13.3	_	_	_
2	MCM-41	98.7	93.5	0.5	3.6	1.75	2.43	1.88
3	HZSM-5	99.4	87.6	1.3	8.1	1.68	2.18	1.73
4	Нβ	>99.9	86.1	3.1	8.3	1.66	1.95	1.55
5	HMOR	>99.9	82.7	3.9	7.9	1.67	2.04	1.38
6	USY	96.5	80.1	2.5	8.6	1.58	1.77	1.43
7	γ -Al ₂ O ₃	90.7	75.1	4.7	9.3	1.13	1.42	1.01

Table 2 The effect of additives combined with Ru/C and BP on the cellulose conversion and adsorption tests^a

^{*a*} Reaction conditions: 0.8 g cellulose, 0.1 g Ru/C, 0.5 g BP, 0.2 g additive, 40 mL H₂O, 5 MPa of H₂ (RT), 463 K, 1 h. The adsorption test was carried out at room temperature and atmosphere pressure overnight. ^{*b*} Others in the aqueous phase include isosorbide and small polyols. ^{*c*} In gas phase: methane, ethane, and propane.

FT-IR spectroscopy confirmed the adsorption of sorbitol on the surface of the additives (Fig. 6), and the peaks at 1224 cm^{-1} and 1091 cm⁻¹ verified the Si-O-Si bonds of the silica-alumina materials while the γ -Al₂O₃ doesn't possess these frequencies (Fig. S6[†]).⁵⁹ After immersion into the sorbitol solution overnight, these additives were dried in vacuo and analyzed by FT-IR spectroscopy. The sp³ C-H stretching frequency of sorbitol appears at 2932 cm⁻¹, which wasn't found in these additives. It was found that the sp³ C-H stretching frequency was shifted. Moreover, the peak at 1419 cm⁻¹ assigned to the CH₂ bending region of sorbitol was shifted to a lower frequency, which suggests these additives can effectively adsorb the sorbitol molecules. These shifts confirmed that the addition of these additives actually played an important role in damaging the hydrogen bonds between the free sorbitol molecules in solution.⁶⁰ Since the carbon atoms of sorbitol are surrounded by oxygen and hydrogen atoms, the hydroxyl groups are in direct interaction with the additives. Hence, the intermolecular and intramolecular hydrogen bonds of free sorbitol molecules in solution were destroyed, which resulted in the CH₂ bending frequency of sorbitol to be shifted to the lower region and the sp³ C-H stretching frequency was shifted to a higher region. As a result, the adsorption effect of the additives stabilizes the C₆ alditols and prevents the C6 alditols from degradation. Hence, the C₆ alditols yielded from the cellulose conversion can be enhanced by the adsorption of the C₆ alditols intermediates and the C₆ additols themselves onto the surface of additives.

Reaction pathway

Our catalytic system of Ru/C–BP shows exceptional performance to yield C_6 additols from cellulose in a short time. We propose the following pathway to rationalize the system (Scheme 1). The use of hot water and the slow release of H^+ from BP are responsible for the breakdown of the cellulose chains to create



Scheme 1 Proposed reaction pathway for the hydrolytic hydrogenation of cellulose to C_6 additols.

soluble oligomers and glucose. Also, the interaction of BP with cellulose can directly use the released H⁺, which eliminates the considerable diffusion path. Meanwhile, the enhanced acidity from the H⁺ released helps to improve the solubility of cellulose, which also accelerates the hydrolysis of cellulose. With the high hydrogenation reactivity of Ru/C, the sugar or cellulose oligomers are rapidly converted into C₆ alditols. Thanks to the borate-polyol complexes formed, the side reactions, such as the hydrogenolysis reaction and the dehydration reaction of the C₆ alditols formed are suppressed. Hence, a high yield of C6 alditols is achieved. Also, the addition of silica-alumina materials can adsorb the cellobiose and glucose, which prevents the intermediates from degradation. Plus, the product sorbitol can be adsorbed by these additives, which stabilized the desired products. Therefore, the addition of silica-alumina materials can further promote the yield of C₆ alditols.

Conclusions

In summary, our novel reaction system provides a highly productive approach to produce C_6 alditols from the hydrolytic hydrogenation of cellulose. Within 1 h of reaction time, the untreated cellulose can be directly transformed to C_6 alditols with a yield of 74.9%. Compared with tests using boric acid and/ or phosphoric acid, the results suggested the better performance should be ascribed to the slow release of H^+ and the negligible dehydration reaction and hydrogenolysis reaction of the borate–polyol complexes formed. By introducing silica– alumina materials as additives, especially those with high silica content, into the catalytic system, a higher yield of C_6 alditols can be achieved with the highest yield (93.5%) of C_6 alditols produced using pure silica MCM-41.

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