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ARTICLE

Direct Conversion of Cellulose into C₆ Alditols over Ru/C combined with H⁺-released Boron Phosphate in Aqueous Phase†

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Inedible cellulose has got considerable attention to be converted into valuable platform chemicals. Direct transformation of cellulose to C₆ alditols (mannitol and sorbitol) provides a sustainable route. A productive approach is presented in this work by using Ru/C catalyst combined with H⁺-released boron phosphate in aqueous phase. As high as 74.9% yield of C₆ alditols with 91% conversion of cellulose is achieved. By adding silica-alumina materials, the yield of C₆ alditols can be improved to 93.5% with complete conversion. The acid sites gradually released from boron phosphate under hydrothermal condition could promote the hydrolysis of cellulose without significant degradation of glucose. Furthermore, the interaction of boric acid with C₆ alditols may form the borate-polyol complexes which can enhance the stability of C₆ alditols to avoid the further hydrogenolysis and dehydration of C₆ alditols. Due to the adsorption ability for substrate, the addition of silica-alumina materials with higher content of silica presents the better performance.

Introduction

Lignocellulosic biomass is considered as the most abundant and cheapest carbon source.¹⁻⁴ Among its compositions, cellulose is the most considerable one which is existed as polymer consist 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 the commercial application.^{5, 6} However, its insolubility limits the possibility of cleavage of the cellulose chain, therefore hampers its usability.⁵ Hence, pretreatment has been proposed as an efficient access to improve its solubility in water. For instance, alkali-urea system which can dissolve cellulose in a low concentration through disruption of the hydrogen bond network in cellulose under the low temperature of 261 K,⁷ or ball-milled pretreatment which can lower its crystalline degree through mechanical interaction has been studied by researchers.^{8, 9} However, those approaches are questionable for the used high concentration of alkali solution to dissolve cellulose and the indispensable high energy cost for ball-milled pretreatment.

For cellulose-derived chemicals, C₆ alditols are one of the most important platform molecules to produce alkanes¹⁰ and high-value chemicals¹¹. Over metal-acid catalytic system, C₆ alditols can be achieved from the one-pot conversion of cellulose which is widely considered as the promising approach that avoids the two-step process. The operation of cellulose depolymerization is often taking place at the acid media or catalyzed by acid

catalyst. Metals are responsible for the hydrogenation reaction of 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 metal-supported catalysts have been proved as the catalysts to transform cellulose to C₆ alditols. And even hot water was used as the acid source for the hydrolytic hydrogenation process.¹⁷ However, these catalysts require long reaction time which is a barrier for commercial application. Moreover, even with the energy-cost ball milled cellulose or acid-impregnated cellulose, long reaction time is still a requirement for high yield of C₆ alditols. Besides, when acid function is too dominant in hydrolytic hydrogenation of cellulose, a build-up of free glucose and hexitols will cause selectivity loss 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 hydrolytic hydrogenation of cellulose. Among the studied metals, ruthenium possesses highest activity of hydrogenation which could shorten the reaction time and lower the reaction temperature. But it still cast the negative effect on this process by performing hydrogenolysis reaction of C₆ alditol products.³⁰ Hence, it is necessary for seeking an effective catalyst system with suitable balance between the acid and metal functions to avoid the C-C bond cleavage of C₆ alditols on ruthenium metal and the dehydration of C₆ alditols

and the glucose degradation on acid sites. Moreover, to achieve the high yield of C₆ alditols from cellulose, the better thermal stability of C₆ alditols is indispensable for a faster and more complete conversion of cellulose at the higher reaction temperature.

Boron phosphate is regarded as the acidic catalyst which contains both Brønsted acidic center and Lewis acidic center on the surface of boron phosphate.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 reported the boron phosphate-Ru/C catalytic system to directly convert cellulose into C₆ alditols. With the increase of released H⁺ concentration from the slow hydrolysis of boron phosphate in aqueous phase, the gradually enhanced acidic media could catalyze cellulose to cell-oligomers and could avoid the instant arrival of dominant acid function which causes glucose degradation and hexitol dehydration. Over the Ru/C catalyst, the cell-oligomers were transformed to C₆ alditols. More importantly, the boric acid and C₆ alditols can form the borate-polyol complexes which prevent the hydrogenolysis and dehydration due to the stronger steric hindrance. Hence, high yield of C₆ alditols can be obtained over the boron phosphate-Ru/C 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), Hβ (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 (CH₃(CH₂)₁₅N(Br)(CH₃)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 (ZnCl₂), Kaolin, and tartaric acid (C₄H₆O₆) 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.

Catalysts preparation and characterization

Boron phosphate catalyst (BP) was synthesized based on previous reports.^{38, 39} Stoichiometric mixture of boric acid and phosphoric acid was dried at 323 K. Boric acid was dissolved in phosphoric acid solution was observed at a stirring condition. The dried white powder was calcined at 1273 K for 5 h. Then the calcined powder was washed with hot deionized water of 333 K and dried in 373 K overnight. MCM-41, HZSM-5, Hβ,

HMOR, USY, and γ-Al₂O₃ were milled and were calcined at 823 K for 4 h. They were used after milled.

Zirconium phosphate (ZrP) was synthesized by precipitating the ZrOCl₂·8H₂O solution in the NH₄H₂PO₄ solution.⁴⁰ After 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 penta-ethoxide as the tantalum source was added into tartaric acid solution by using ethanol as the media. After the ethanol was evaporated, distilled water was added. Then the diammonium hydrogen phosphate solution was added under stirring condition to get a homogeneous solution. Certain amount of hexadecyl trimethyl 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 used, the resulted TaP was calcined at 823 K for 6 h.

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

Zn₃(PO₄)₂ (ZnP) was synthesized by using ZnCl₂ as zinc source. ZnCl₂ aqueous solution was dropwise added into H₃PO₄ solution at stirring condition. The mixed solution was neutralized with NH₃·H₂O. And the white precipitate 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 for verifying the borate-polyol complexes. The instrument was equipped with a MCT (mercury cadmium telluride). The Hitachi S-4800 instrument was used to analyze the morphological information (scanning electron microscope) of BP. The XRD information of BP was obtained by using XPert 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) was introduced into a 100 mL stainless reactor. The reactor was purified with pure hydrogen for six cycles and pressurized with 5 MPa H₂ (room temperature, RT). The autoclave was heated to 463 K under stirring condition and kept for 1 h. The autoclave was cooled to RT by placing it in the iced water after reaction and the liquid samples were collected. To improve the yield of C₆ 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. And the mobile phase was water and 0.005 M H₂SO₄, respectively. The gas samples were analyzed by an Agilent 7890A instrument.

Results and discussion

Effect of acids and reaction conditions on the hydrolytic hydrogenation of cellulose

Fig. 1 shows the performance of different acids and 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 converted ball-milled cellulose into C₆ alditols.⁴⁴ For SiW–Ru/C system, though it has been reported as an effective system to transform cellulose to hexitols,¹³ 1.0 h reaction time is too short to get a high yield and selectivity for C₆ alditols. For solid acids phosphates, the use of ZnP and AgP can cause the hydrogenolysis reaction to produce 16.6% yield of ethylene glycol and 8.5% yield of propylene glycol, respectively. Although the cellulose conversion is relatively high by using 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 high cellulose conversion (91%) with 82.1% selectivity of C₆ alditols for 1.0 h.

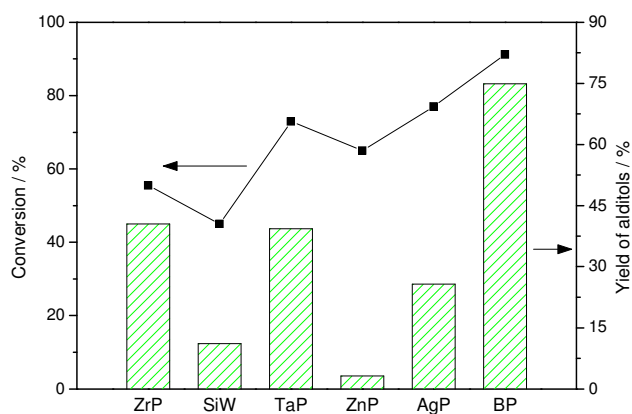


Fig. 1 Conversion of cellulose to alditols over different acids and Ru/C. Reaction conditions: 0.5 g acid, 0.8 g MCC, 0.1 g Ru/C, 40 mL H₂O, 5 MPa H₂ (RT), 463 K, 1 h.

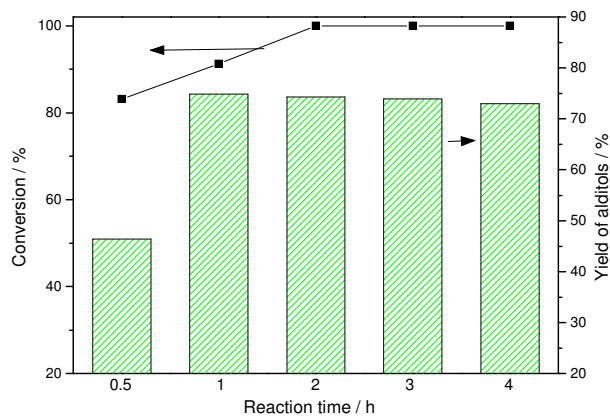


Fig. 2 The effect of reaction time of C₆ alditols yield over BP–Ru/C catalytic system. Reaction conditions: 0.5 g acid, 0.8 g MCC, 0.1 g Ru/C, 40 mL H₂O, 5 MPa H₂ (RT), 463 K.

The effect of reaction time was performed over BP–Ru/C catalytic system, and the results were given in the Fig.2. By increasing 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 C₆ alditols was achieved by 74.9% with 91% cellulose conversion. Surprisingly, the further prolongation of reaction time didn't cause the noticeable loss of C₆ alditols. After 4 h, the yield of C₆ alditols was only decreased from 74.9% to 72.9%, suggesting the stability of C₆ alditols is relative high at 463 K in current catalytic system. But we have already noticed that the conditions of long reaction time and high reaction temperature will lead to side reactions which were demonstrated in our previous study.⁴⁴ Specifically, C₆ alditols were underwent hydrogenolysis reaction to produce other polyols, such as ethylene glycol and propylene glycol, or dehydration reaction to yield sorbitan or isosorbide. In fact, sorbitol dehydration reactions can be processed at high temperature of 523–573 K without the addition of any acid catalysts,⁴⁵ indicating the hydrolytic hydrogenation of cellulose to produce C₆ alditols should be performed for a short reaction time at relative low temperature condition. Meanwhile, through the detection of liquid products, negligible cellobiose or glucose was observed in the reaction process which agrees with former study that Ru/C shows high hydrogenation activity outruns the hydrolysis rate of cellulose over the acid catalyst.⁴⁶ That also suggests the partial inhibition effect on the hydrogenolysis of C₆ alditols is ascribed to the Ru/C was enclosed by glucose or other intermediates.

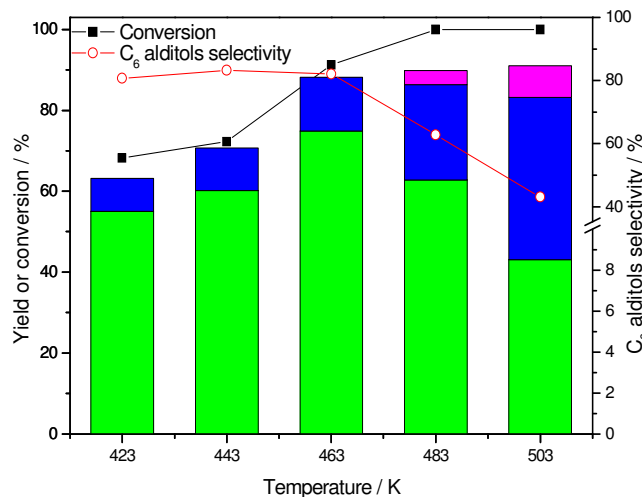


Fig. 3 The effect of reaction temperature of C₆ alditols yield over BP–Ru/C catalytic system. Reaction conditions: 0.5 g BP, 0.8 g MCC, 0.1 g Ru/C, 40 mL H₂O, 5 MPa H₂ (RT), 1 h. (Green: the yield of C₆ alditols; Blue: the yield of gas phase products; Magenta: the yield of small polyols and dehydration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

Furthermore, the effect of reaction temperature was carried out under the optimal conditions, and the result was shown in Fig.3. It is obvious that the cellulose conversion was increased as the reaction temperature increased. When the temperature increased to 483 K, the substrate was completely converted, but the yield of by-products was 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 cycle dehydration products (sorbitan and isosorbide) and small polyols (ethylene glycol and propylene glycol) was 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 the increase of by-products. This observation could be explained that the C-O and C-C cracking reactions of polyols can be easily performed in acid media at high temperature. It was found that the produced C₆ alditols can be dehydrated to sorbitan (monomolecular dehydration) and isosorbide (bimolecular dehydration) in the absence of catalyst at high temperature.⁴⁷ The yield of dehydration products could be promoted in acidic media.⁴⁸ The small polyols might be formed by retro-aldol condensation of carbohydrates, which has been studied by Zhang's group.⁴⁹ The increased yield of light alkanes was the consequence of the accelerated hydrocracking of C₆ alditols at high temperature.⁵⁰

To detect the leaching phenomenon of BP after the reaction, ion chromatography was used and the result showed the PO₄³⁻ and boric acid existed in the liquid phase (See Fig. S1). Further investigation on the pH of aqueous phase suggested the acidity in solution was improved after the reaction. This phenomenon disagrees with the former reports which illustrated the BP catalyst with 1273 K calcination process can't be dissolved in water.⁵¹

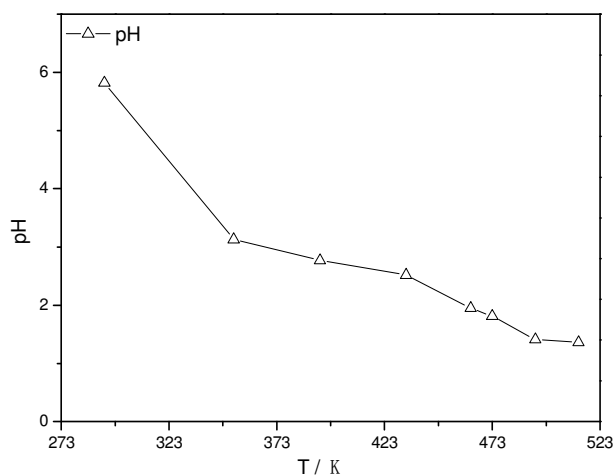


Fig. 4 The pH evolution of the liquid phase with the addition of 0.5 g BP in 40 mL distilled water under different temperature and atmosphere pressure.

Since the pH of the mixed solution after reaction was decreased, we measured the pH of water with the addition of BP at different temperature and atmosphere pressure which is shown in Fig. 4. By elevating the temperature from 293 K to 463 K, the pH of the mixture was decreased to 1.95. Further increasing the temperature, the acidity was continued to increase. It is clear that the hydrolysis process of cellulose accompanied with the hydrolysis of BP. In addition, BP was found fully transferred into aqueous phase in the cellulose conversion experiments which wasn't observed in the atmosphere pressure. Hence, this phenomenon would highly increase the reaction

system's acidity to improve the cellulose hydrolysis rate which is the rate-determinate step for hydrolytic hydrogenation of cellulose.^{46, 52} We should note that the BP hydrolysis process is gradual that the H⁺ was slowly released from BP. Since cellulose is probably adsorbed by BP in the surface area, the gradually released H⁺ can be direct used for the hydrolysis of cellulose which essentially avoided 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 low threshold of access to glycoside bonds, and therefore high yield of C₆ alditols can be achieved at 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 by H₃BO₄ (HB) and H₃PO₄ (HP), and this hydrolysis process may cast 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 the condition of the equivalent mol 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 was decreased, which is an consequence of the fact that the more dominant acid function derived from HP would cause glucose degradation or hexitol dehydration.¹² With the mixture of HB and HP, both the selectivity of C₆ alditols and the yield of C₆ alditols (Table 1, entry 3) were improved compared with the single HB or HP used as the acid function. This observation may be resulted from that the borate species and polyols form the borate-polyols complexes which suppress the dehydration reactions of C₆ alditols to form sorbitan or isosorbide.⁵⁴ As well as, the observed results showed the addition of HB can inhibit the C-C cleavage reaction of C₆ alditols to yield small polyols. Those results can be verified by entries 3, 5 and 6 in Table 1. When the different ratios of HB/HP was used for the tests, the higher the ratio of HB/HP, the lower yield of small polyols and gas phase products were observed with decrease of cellulose conversion. With decreasing ratio of HB/HP, the selectivity of C₆ alditols was decreased, while the yield of small polyols was increasing. It is indicated that the presence of dominant of HP could cause more side reactions such as dehydration and C-C bond hydrogenolysis of C₆ alditols, though it is effective for the cellulose hydrolysis. The addition of HB with a suitable content can effectively optimize the balance between hydrolysis and side reactions to improve the yield of C₆ alditols. This might be caused by the steric hindrance of borate-polyols which blocks the contact of Ru with C-C bond. Besides, HB is the weaker acid is less effective for dehydration of C₆ alditols. However, even with the increased selectivity of C₆ alditols by using the

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

^aReaction conditions: 463 K, 5 MPa H₂ (RT), 1 h, 0.1 g Ru/C, 0.8 g cellulose, H₂O 40 mL, equivalent mol of boron and phosphorus was added according to the used different acids. ND: not detected. ^bSmall polyols: ethylene glycol, propylene glycol. ^cOthers are the gas phase products which mainly include methane, ethane, and propane. ^dThe same amount of HB and HP (mole ratio = 1:1) to synthesize 0.5 g BP. ^eMole ratio of HB/HP is 3:1 (maintained the same amount of H⁺ mol of entry 3). ^fMole ratio of HB/HP is 1:3 (maintained the same amount of H⁺ mol of entries 3 and 5).

mixture of HB and HP, the yield of C₆ alditols was still inferior to 74.9% achieved by using the BP as 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 acid function released from BP and metal function. Most importantly, the gradually released H⁺ provide a favorable environment to catalyze the hydrolysis of cellulose, and simultaneously combined with Ru-catalyzed hydrogenation, the in-situ catalysis of released H⁺ and hydrogen can give the production of C₆ alditols. In this process, the hexitol dehydration and glucose degradation occurred on the dominant acid function could be significantly avoided to reduce the yield loss of C₆ alditols. Moreover, when the BP completely released the H⁺ in 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 formation of borate-polyols complexes, which it is another key factor for the improvement of yield and stability of C₆ alditols.

FT-IR characterization was performed to verify the presence of the borate-polyols complexes. As shown in Fig.5, the addition of HB into the sorbitol aqueous solution resulted in the appearance of CH₂ bend and enhanced intensity of CH₂ bend at 1460 cm⁻¹ band which was caused by electric withdrawing effect of borate complex. As increasing the concentration of HB, the peak at 1460 cm⁻¹ became stronger. Moreover, the peaks belong to the C-O groups region (1200 to 900 cm⁻¹), which were shifted toward lower frequencies by 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 that it can form complex 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 in the cellulose conversion. In current catalytic system, the formation of borate-polyol complexes would have an enhanced steric

hindrance to prevent the further hydrogenolysis and dehydration of C₆ alditols.

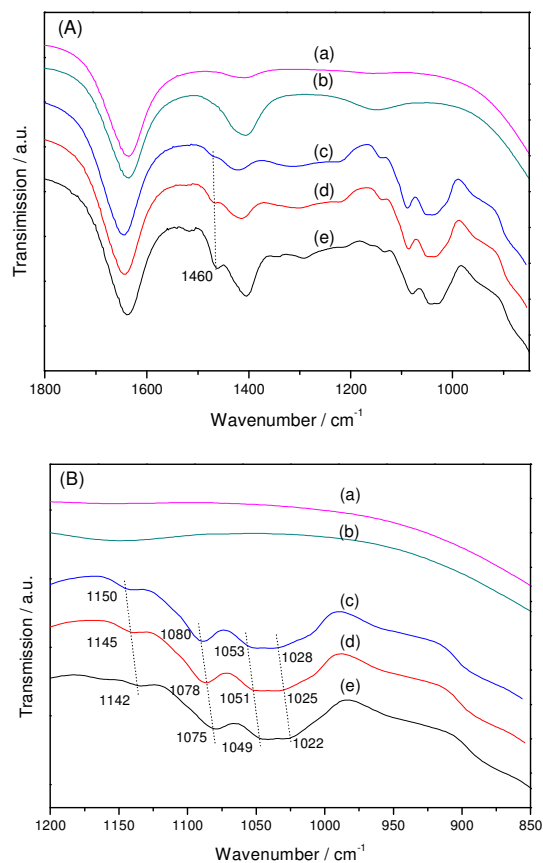


Fig. 5 FT-IR spectra of (a) 1 wt% H₃BO₃ aqueous solution, (b) 5 wt% H₃BO₃ aqueous solution, (c) 25 wt% sorbitol aqueous solution, (d) 1 wt% H₃BO₃ - 25wt% sorbitol aqueous solution, and (e) 5 wt% H₃BO₃ - 25wt% sorbitol aqueous solution.

It should be noted that the separation of C₆ alditols from the mixture is a necessity. Recent literatures suggest the recovery of H₃PO₄ from solution can be performed by using anion

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

Entry	Additive	Cellulose conversion/%	Product yield/%		Adsorption/mg·g ⁻¹			
			C ₆ alditols	Others in aqueous ^b	In gas ^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	H β	>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

^aReaction conditions: 0.8 g cellulose, 0.1 g Ru/C, 0.5 g BP, 0.2 g additive, 40 mL H₂O, 5 MPa H₂ (RT), 463 K, 1 h. The adsorption test was carried out under room temperature and atmosphere pressure overnight. ^bOthers in aqueous include isosorbide and small polyols. ^cIn gas: methane, ethane, and propane.

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 C₆ alditols solution.

Effect of silica-alumina materials

In current study, another interesting observation is that the yield of C₆ alditols from hydrolytic hydrogenation of cellulose can be further improved by using the silica-alumina materials or solid acids as the additives to be added into the catalytic system. As shown in Table 2, by using different additives, the glucose, cellobiose, isosorbide and small polyols were detected with the negligible amount or not, 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 result with 93.5% yield of C₆ alditols among the tested silica-alumina materials. As lowering the silica content of additives, the C₆ alditol yield was decreased. HZSM-5 and H β with a Si/Al ratio of 38 gave the C₆ alditol 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 82.7 % and 80.1% yield of C₆ alditols. With the pure alumina additive γ -Al₂O₃, the yield of C₆ alditols was almost the same with the results of previous experiment without the presence of additive. It is obvious that the silica-alumina materials can adsorb the oligomers in the aid of the affinity of the hydrophilic surface of silica-alumina materials for the intermediates of the C₆ alditols. This had been pioneered by Sels' group who studied the produced sugar alcohols 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 the affinity to cellulose-derived glucose and cellobiose which can be further hydrogenated to C₆ alditols. Among the tested silica-alumina materials, MCM-41 had the highest adsorption ability to the glucose and cellobiose molecules. On the contrary, the surface of γ -Al₂O₃ showed the reluctance of adsorption to the glucose and cellobiose. It might resulted from the silica is easier to adsorb the hydroxyl groups of the intermediates than the presence of alumina. On the other hand, the presence of these

silica-alumina materials exhibited much smaller amount of gas products (mainly methane, ethane, and propane) than without adding them. It is a fact that the Ru/C catalyst can be used as the hydrogenolysis catalyst which can catalyse the C₆ alditols to smaller alkanes.⁵⁸ With the yielded C₆ alditols were adsorbed by the additives, however, the contact of Ru/C with C₆ alditols was limited which lowered the possibility of the hydrogenolysis of C₆ alditols. Hence, the yield of C₆ alditols was improved.

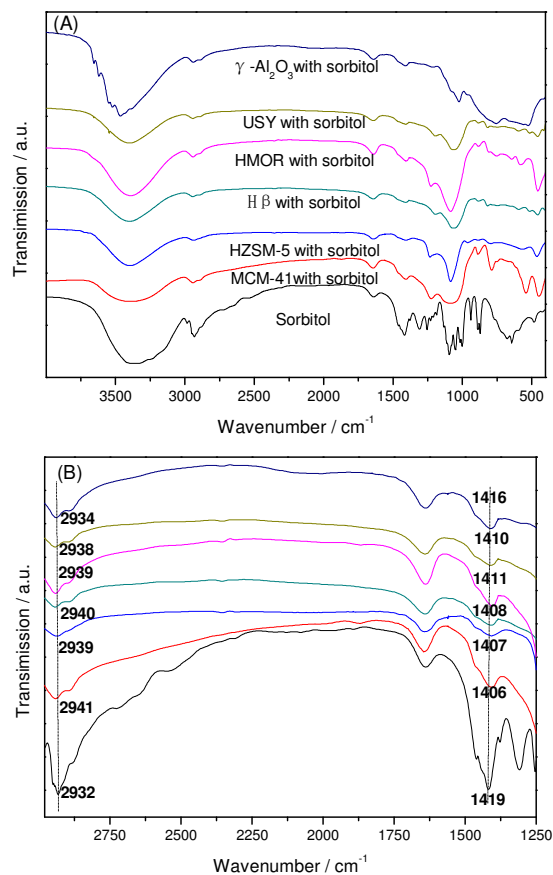
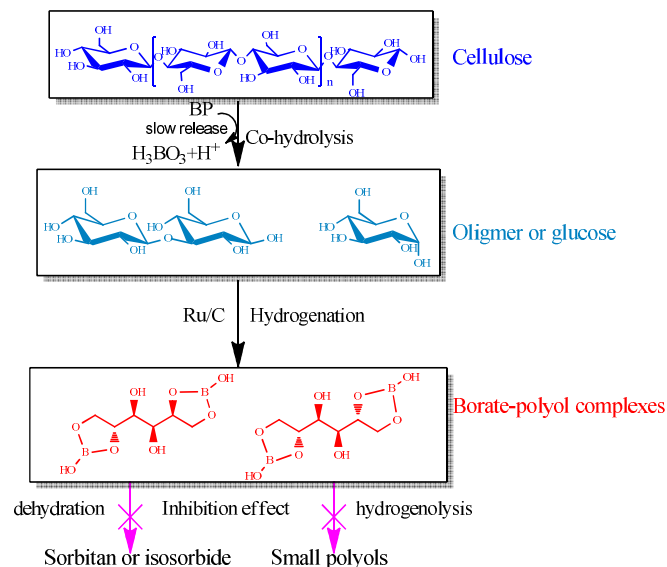


Fig. 6 FT-IR spectra of sorbitol with/without the additive. (A and B share the same color indicators of different samples)

FT-IR confirmed the adsorption of sorbitol on the surface of the additives (Fig. 6), and the peaks of 1224 cm^{-1} and 1091 cm^{-1} verified the Si-O-Si of silica-alumina materials while the $\gamma\text{-Al}_2\text{O}_3$ doesn't possess these frequencies (Fig. S6).⁵⁹ After immersion into the sorbitol solution overnight, these additives were dried in vacuum condition and analyzed by FT-IR. The sp^3 C-H stretching frequency of sorbitol appears at 2932 cm^{-1} , which wasn't found in these additives. It was found that the sp^3 C-H stretching frequency was shifted. Moreover, the 1419 cm^{-1} assigned to CH_2 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 existed hydrogen bonds of free sorbitol molecules in solution.⁶⁰ Since the carbon atoms of sorbitol are surrounded by oxygen and hydrogen atoms, the exposure of hydroxyl groups are the direct interaction media with the additives. Hence, the intermolecular and intramolecular hydrogen bonds of free sorbitol molecules in solution was destroyed, which resulted in the CH_2 bending frequency of sorbitol was shifted to lower region and the sp^3 C-H stretching frequency was shifted to higher region. As a result, the adsorption effect of additives stabilizes the C_6 alditols and prevents the C_6 alditols from degradation. Hence, the C_6 alditols yield from cellulose conversion can be enhanced by adsorption of the intermediates of C_6 alditols and the C_6 alditols themselves adsorption on the surface of additives.

Reaction pathway



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

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

create 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 released H^+ helps the solubility of cellulose which also accelerates the hydrolysis of cellulose. With the high hydrogenation reactivity of Ru/C, the sugar or cello-oligomers are rapidly converted into C_6 alditols. Thanks to the formed borate-polyol complexes, the side reactions, such as hydrogenolysis reaction of C_6 alditols over metal and dehydration reactions of C_6 alditols, are suppressed. Hence, high yield of C_6 alditols is achieved. In addition, 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 promotes the yield of C_6 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 reaction time, the untreated cellulose can be directly transformed to C_6 alditols with the yield of 74.9%. Compared with the tests over boric acid and/or phosphoric acid, the results suggested the better performance should be ascribed to the slow H^+ released effect and the negligible dehydration reactions of C_6 alditols or the negligible hydrogenolysis reaction over metal for the formed borate-polyol complexes. By introducing the silica-alumina materials, especially these with high silica content, into the catalytic system, the higher yield of C_6 alditols can be achieved, and the highest yield (93.5%) of C_6 alditols are given over pure silica MCM-41.

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Notes and references

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1. C. H. Zhou, X. Xia, C. X. Lin, D. S. Tong and J. Beltramini, *Chem Soc Rev*, 2011, **40**, 5588-5617.
2. D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Chem Soc Rev*, 2012, **41**, 8075-8098.
3. T. Deng, X. Cui, Y. Qi, Y. Wang, X. Hou and Y. Zhu, *Chem Commun*, 2012, **48**, 5494-5496.
4. B. Zhang, Y. Zhu, G. Ding, H. Zheng and Y. Li, *Green Chem*, 2012, **14**, 3402-3409.
5. M. Sankar, N. Dimitratos, P. J. Miedziak, P. P. Wells, C. J. Kiely and G. J. Hutchings, *Chem Soc Rev*, 2012, **41**, 8099-8139.
6. H. Wang, G. Gurau and R. D. Rogers, *Chem Soc Rev*, 2012, **41**, 1519-1537.
7. J. Cai, L. Zhang, J. Zhou, H. Qi, H. Chen, T. Kondo, X. Chen and B. Chu, *Advanced Materials*, 2007, **19**, 821-825.
8. H. Kim and J. Ralph, *Rsc Adv*, 2014, **4**, 7549-7560.
9. S. S. Paes, S. M. Sun, W. MacNaughtan, R. Ibbett, J. Ganster, T. J. Foster and J. R. Mitchell, *Cellulose*, 2010, **17**, 693-709.
10. Q. Zhang, T. Jiang, B. Li, T. J. Wang, X. H. Zhang, Q. Zhang and L. L. Ma, *ChemCatChem*, 2012, **4**, 1084-1087.
11. M. Rose and R. Palkovits, *ChemSusChem*, 2012, **5**, 167-176.
12. J. Geboers, S. Van de Vyver, K. Carpentier, P. Jacobs and B. Sels, *Chem Commun*, 2011, **47**, 5590-5592.
13. J. Geboers, S. Van de Vyver, K. Carpentier, K. de Blochouse, P. Jacobs and B. Sels, *Chem Commun*, 2010, **46**, 3577-3579.
14. R. Palkovits, K. Tajvidi, J. Procelewska, R. Rinaldi and A. Ruppert, *Green Chem*, 2010, **12**, 972-978.
15. Y. Ogasawara, S. Itagaki, K. Yamaguchi and N. Mizuno, *ChemSusChem*, 2011, **4**, 519-525.
16. R. Palkovits, K. Tajvidi, A. M. Ruppert and J. Procelewska, *Chem Commun*, 2011, **47**, 576-578.
17. C. Luo, S. Wang and H. Liu, *Angew Chem*, 2007, **119**, 7780-7783.
18. S. Van de Vyver, J. Geboers, W. Schutyser, M. Dusselier, P. Eloy, E. Dornez, J. W. Seo, C. M. Courtin, E. M. Gaigneaux, P. A. Jacobs and B. F. Sels, *ChemSusChem*, 2012, **5**, 1549-1558.
19. S. Van de Vyver, J. Geboers, M. Dusselier, H. Schepers, T. Vosch, L. A. Zhang, G. Van Tendeloo, P. A. Jacobs and B. F. Sels, *ChemSusChem*, 2010, **3**, 698-701.
20. D. S. Park, D. Yun, T. Y. Kim, J. Baek, Y. S. Yun and J. Yi, *ChemSusChem*, 2013.
21. A. Fukuoka and P. L. Dhepe, *Angew Chem Int Ed*, 2006, **45**, 5161-5163.
22. H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P. L. Dhepe, K. Kasai, K. Hara and A. Fukuoka, *Green Chem*, 2011, **13**, 326-333.
23. D. Wang, W. Niu, M. Tan, M. Wu, X. Zheng, Y. Li and N. Tsubaki, *ChemSusChem*, 2014, **7**, 1398-1406.
24. W. Deng, M. Liu, X. Tan, Q. Zhang and Y. Wang, *J Catal*, 2010, **271**, 22-32.
25. Y. Zhu, Z. N. Kong, L. P. Stubbs, H. Lin, S. Shen, E. V. Anslyn and J. A. Maguire, *ChemSusChem*, 2010, **3**, 67-70.
26. M. Liu, W. Deng, Q. Zhang, Y. Wang and Y. Wang, *Chem Commun*, 2011, **47**, 9717-9719.
27. J. Geboers, S. Van de Vyver, K. Carpentier, K. de Blochouse, P. Jacobs and B. Sels, *Chem Commun*, 2010, **46**, 3577-3579.
28. W. Deng, X. Tan, W. Fang, Q. Zhang and Y. Wang, *Catal Lett*, 2009, **133**, 167-174.
29. J. F. Pang, A. Q. Wang, M. Y. Zheng, Y. H. Zhang, Y. Q. Huang, X. W. Chen and T. Zhang, *Green Chem*, 2012, **14**, 614-617.
30. G. Liang, C. Wu, L. He, J. Ming, H. Cheng, L. Zhuo and F. Zhao, *Green Chem*, 2011, **13**, 839-842.
31. J. B. Moffat and H. L. Goltz, *Can J Chem*, 1965, **43**, 1680-&.
32. W. Gerrard and P. F. Griffey, *Chem Ind-London*, 1959, 55-55.
33. H. L. Goltz and J. B. Moffat, *J Catal*, 1971, **22**, 85-&.
34. Tartarel.R, M. Giorgini, A. Lucchesi, G. Stoppato and F. Morelli, *J Catal*, 1970, **17**, 41-&.
35. J. B. Moffat and J. F. Neeleman, *J Catal*, 1973, **31**, 274-277.
36. G. J. Hutchings, I. D. Hudson, D. Bethell and D. G. Timms, *J Catal*, 1999, **188**, 291-299.
37. S. Gao and J. B. Moffat, *J Catal*, 1998, **180**, 142-148.
38. M. Giorgini, Tartarel.R, R. Simula, P. F. Marconi and G. Monzani, *J Catal*, 1972, **24**, 521-&.
39. S. Gao and J. B. Moffat, *Catal Lett*, 1999, **61**, 61-64.
40. S. K. Shi, Q. Liu, X. Zhang and R. Hall, *Rsc Adv*, 2013, **3**, 8254-8260.
41. I. Jimenez-Morales, A. Teckchandani-Ortiz, J. Santamaria-Gonzalez, P. Maireles-Torres and A. Jimenez-Lopez, *Appl Catal B-Environ*, 2014, **144**, 22-28.
42. I. Jimenez-Morales, J. Santamaria-Gonzalez, P. Maireles-Torres and A. Jimenez-Lopez, *Appl Catal B-Environ*, 2012, **123**, 316-323.
43. X. Yang, H. Cui, Y. Li, J. Qin, R. Zhang and H. Tang, *ACS Catalysis*, 2013, **3**, 363-369.
44. Y. Liao, Q. Liu, T. Wang, J. Long, L. Ma and Q. Zhang, *Green Chem*, 2014, **16**, 3305-3312.
45. A. Yamaguchi, N. Hiyoshi, O. Sato and M. Shirai, *Green Chem*, 2011, **13**, 873.
46. C. Luo, S. A. Wang and H. C. Liu, *Angew Chem Int Edit*, 2007, **46**, 7636-7639.
47. A. Yamaguchi, N. Hiyoshi, O. Sato and M. Shirai, *Green Chem*, 2011, **13**, 873-881.
48. G. Fleche and M. Huchette, *Starch*, 1986, **38**, 26-30.
49. N. Ji, T. Zhang, M. Y. Zheng, A. Q. Wang, H. Wang, X. D. Wang and J. G. G. Chen, *Angew Chem Int Ed*, 2008, **47**, 8510-8513.

Journal Name

50. T. Jiang, T. J. Wang, L. L. Ma, Y. P. Li, Q. Zhang and X. H. Zhang, *Appl Energy*, 2012, **90**, 51-57.
51. P. Kmecl and P. Bukovec, *Acta Chim Slov*, 1999, **46**, 161-171.
52. W. P. Deng, M. Liu, X. S. Tan, Q. H. Zhang and Y. Wang, *J Catal*, 2010, **271**, 22-32.
53. A. Shrotri, L. K. Lambert, A. Tanksale and J. Beltramini, *Green Chem*, 2013, **15**, 2761.
54. W. R. Gunther, Q. Duong and Y. Román-Leshkov, *Journal of Molecular Catalysis A: Chemical*, 2013, **379**, 294-302.
55. J. E. Sponer, B. G. Sumpter, J. Leszczynski, J. Sponer and M. Fuentes-Cabrera, *Chem Eur J*, 2008, **14**, 9990-9998.
56. J.-Y. Kim, C.-H. Shin, H. Choi and W. Bae, *Sep Purif Technol*, 2012, **90**, 64-68.
57. T. Yanagida, S. Fujimoto, L. Bespyatko, S. Inoue, K. Tsukahara, S. Sawayama and T. Minowa, *J. Japan Soc. of Energy and Resources*, 2010, **31**, 15-20.
58. T. P. Vispute, H. Zhang, A. Sanna, R. Xiao and G. W. Huber, *Science*, 2010, **330**, 1222-1227.
59. J. S. Chou and S. C. Lee, *J Appl Phys*, 1995, **77**, 1805-1807.
60. D. Pavia, G. Lampman, G. Kriz and J. Vyvyan, *Introduction to spectroscopy*, Cengage Learning, 2008.