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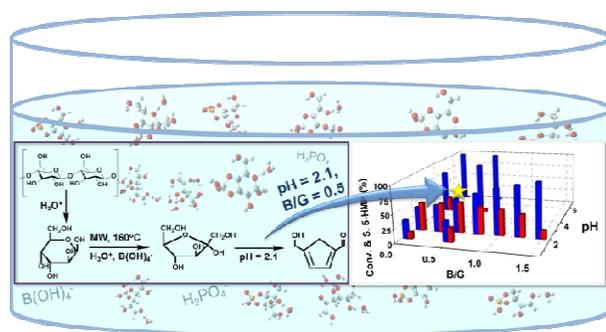
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# Condition Screening and Process Investigation of Aldose Transformation in Borate-containing Acidic Phosphate Buffer System under Microwave Irradiation

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Aldose transformation process in borate-containing acidic phosphate buffer system is systematically studied under microwave irradiation.

## ARTICLE

# Condition Screening and Process Investigation of Aldose Transformation in Borate-containing Acidic Phosphate Buffer System under Microwave Irradiation

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The high-selective isomerization and dehydration of various carbohydrates (glucose, xylose, cellobiose and cellulose) are one-pot conducted in a simple borate-containing phosphate buffer solution (PBS) under microwave irradiation. It is demonstrated that the key of glucose converting into 5-hydroxymethylfurfural (5-HMF) with high selectivity is the matching between the isomerization and dehydration processes of glucose at the appropriate boron/glucose mole ratio (B/G) and pH of PBS with the aid of microwave irradiation. Also, the interaction between borate and glucose in the isomerization process is demonstrated by both Raman spectra and theoretical calculation. Moreover, the reusability of such PBS system with borate has been accomplished by successive addition of glucose and continual removal of 5-HMF in a biphasic system. These results not only deepen the understanding of the isomerization and dehydration behavior of glucose, but also provide the possibility of practical application owing to the green, inexpensive and sustainable characteristics of such catalytic system.

## Introduction

The interest on searching of the green, renewable and sustainable resources of energy and chemicals is increasing during recent years, due to the limited fossil resources, exhausted gas emissions and growing energy demands.<sup>[1]</sup> Biomass resource containing rich carbohydrates is one of the most promising alternative carbon sources for the construction of chemicals and materials for human survival in the future. More importantly, it is well-sourced, environmental friendly and low cost.<sup>[2]</sup> Therefore, the study on the comprehensive utilization of biomass resource attracts more and more concerns. Among them, 5-hydroxymethylfurfural (5-HMF), firstly reported at the end of 19th century by heating inulin with oxalic acid solution,<sup>[3]</sup> is one of the most significant biomass-derived platform compounds. As an important intermediate, 5-HMF could be converted into various useful compounds such as dimethylfuran, furandicarboxylic acid, levulinic acid (LA) and  $\gamma$ -valerolactone.<sup>[4-6]</sup> Consequently, 5-HMF provides the possibility to synthesize chemicals and biofuels from carbohydrates, and so alleviates the demand pressure of fossil resources.

Generally, 5-HMF is mainly obtained from the dehydration of hexoses such as fructose, and glucose or disaccharides like sucrose and cellobiose.<sup>[6,7]</sup> So far, most preparations of 5-HMF are derived from fructose as the raw material for its higher selectivity and yield of 5-HMF compared to other hexoses. However, the relatively high cost of fructose greatly restricts its

prospect in industrial application. Unlike the fructose, glucose has more source in the natural world since it can be obtained from the hydrolysis of cellulose.<sup>[8]</sup> But unfortunately, glucose suffers a poor dehydration performance on the preparation of 5-HMF due to its much more stable aldose structure than fructose.<sup>[9]</sup> Nevertheless, the much lower cost still enables the direct conversion of glucose into 5-HMF to be the focus of the scientific attention. Besides glucose, cellobiose and cellulose are the two most desired raw materials to be converted directly into 5-HMF for their much lower cost and higher availability compared with the other carbohydrates in nature.<sup>[10]</sup> But in fact, the conversion of cellulose is much more difficult than glucose and disaccharides, because its special  $\beta$ -1,4-glycosidic bonds lead to the poor solubility and difficult conversion in aqueous solution.<sup>[6]</sup> Thus, some extreme strategies, such as high acid concentration and reaction temperature or expensive ionic liquid, have to be used to swell and convert cellulose.<sup>[11]</sup> Therefore, the one-pot conversion of cellulose into 5-HMF is an encouraging route but is still far from being practical.

In addition, it is worth mentioning that the main reason for the unsatisfied results of aldose conversion into 5-HMF, based on a plenty of research results, is believed that a pretreatment process is needed before the dehydration. Taking glucose as an example, it has to isomerize into fructose at first, and then fructose dehydrates into 5-HMF.<sup>[7]</sup> During the whole reaction, the converting rate of glucose mainly depends on its isomerizing rate.<sup>[8,12,13]</sup> Moreover, the formation of 5-HMF in aqueous solution is largely affected by some undesirable by-

products obtained from the rehydration of 5-HMF like LA and formic acid (FA), as well as the insoluble/soluble polymeric compounds like humins. So far, the conversion of glucose into 5-HMF has not achieved in large-scale industrial production yet for its low converting rate and 5-HMF selectivity which is believed as the greatest challenge by now.

Recently, an acidic phosphate buffer solution (PBS) using sodium borate as a promoter is developed to high-selectively catalyze glucose dehydrating into 5-HMF under microwave irradiation by our group.<sup>[14]</sup> Herein, the evolution process of the glucose conversion is highlighted in the borate-assistant PBS medium and the key factors such as the effect of pH, buffer system, the boron/glucose mole ratio (B/G) on the conversion of glucose and selectivity of 5-HMF as well as the effect of microwave irradiation are studied systematically. And highly selective conversion of various carbohydrates (glucose, xylose, cellobiose and  $\alpha$ -cellulose) into 5-HMF/furfural is thereby accomplished in such system. Moreover, the interaction between borate and glucose as well as its effect on the glucose isomerization are proved by Raman spectra and theoretical calculation. Finally, a biphasic system is employed to further improve the selectivity of 5-HMF and to achieve the sustainability of the homogenous catalytic system.

## Experimental

### Chemicals

D-(+)-glucose ( $\geq 99.5\%$ ) was purchased from Sigma-Aldrich. D-(+)-xylose ( $\geq 99\%$ ), D-(+)-cellobiose (98.0%) and  $\alpha$ -cellulose (25  $\mu\text{m}$ ) were purchased from Aladdin.  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  ( $\geq 99.5\%$ ), methyl-isobutylketone (MIBK) ( $\geq 99.0\%$ ) and 2-butanol ( $\geq 98.0\%$ ) were purchased from Sinopharm Chemical Reagent Co., Ltd.  $\text{H}_3\text{PO}_4$  (85.0%) was purchased from Shanghai Feida chemical Co., Ltd.  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  ( $\geq 99.0\%$ ) and HCl (36.0%-38.0%) were purchased from Jiangsu Chemical Co., Ltd. NaOH (96.0%) was purchased from Shanghai Fourth Reactant Factory. All the chemicals were used without further purification. Deionized water produced from laboratory water purification system (RO DI Digital plus) was used to prepare all the aqueous solutions.

### Dehydration of Carbohydrates

All the PBSs with different components as well as acidic solution were prepared according to their stoichiometric ratios in 50 mL flask. The catalytic reactions in the PBS containing borate were performed in a 30 mL reactor under the microwave irradiation provided by Nova-2S from Preekem Scientific Instruments Co., Ltd. In a typical procedure, glucose (1.2 g) and borax (0.3 g) were dissolved by the ultrasonic bath in the above PBS system, and the total volume of the reaction solution was kept at 12 mL. Then the mixture was put in the microwave-assisted reactor at 160 °C. For xylose and cellobiose conversion, only the glucose was replaced by xylose and cellobiose of 1.2 g in the above process. For cellulose conversion,  $\alpha$ -cellulose (2.4 g) and NaCl (3.0 g) were dissolved by the ultrasonic bath in 1.5 M  $\text{H}_3\text{PO}_4$  (10.0 g) and the mixture was put in the microwave-assisted reactor for 15 min at 160 °C. After the reaction, filtered the solution,  $\text{NaH}_2\text{PO}_4$  and borax were added to keep the  $\text{H}_3\text{PO}_4$ :  $\text{NaH}_2\text{PO}_4 = 1:1$  and B/G = 0.5. Finally, the mixture solution was put in the microwave-assisted reactor for 30 min at 160 °C. For the conventional heating experiments, the above glucose reaction system was heated in the oven at the same temperature. For the biphasic system, all the procedures were the same as the above PBS system, but the organic solvent consists of MIBK and 2-butanol (volume ratio = 7:3) was added before microwave irradiation.

### Computational Details

First principle density functional theory (DFT) calculations were performed with the M06-2x/6-31+G(d) method.<sup>[15,16]</sup> M06-2X is by far one of the most accurate DFT functionals in predicting energy barriers.<sup>[15]</sup> To account for solvation effect, the calculations were performed with the IEFPCM solvation model<sup>[17]</sup> with radii and non-electrostatic terms for Truhlar and coworkers' SMD solvation model.<sup>[18]</sup> All the geometry optimizations and vibrational frequency analyses were performed with solvation effect considered. Default geometry convergence criterion of Gaussian 09<sup>[19]</sup> was used. The integral grid used for all the DFT calculation is a pruned (99,590) grid (the "ultrafine" grid as defined by Gaussian 09). To consider the effect of pH while reducing computational efforts to a manageable degree, a solvated proton was simplified as a  $\text{H}_3\text{O}^+$  during the calculations. Since the computed harmonic vibrational frequencies were systematically higher than experimental vibrational frequencies,<sup>[20]</sup> the calculated vibrational frequencies were scaled by a factor of 0.97 in order to directly compare to experimental spectra. All these calculations were performed by using the Gaussian 09 quantum software package.<sup>[19]</sup>

### Products Analysis

Samples were taken at setting time and analyzed via external standard method by high performance liquid chromatography (HPLC) equipped with a refractive index detector and a shodex SH1011 sugar column purchased from Shimadzu Corporation.

The HPLC was detected at 40 °C with 5 mM  $\text{H}_2\text{SO}_4$  mobile phase in a flow rate of 1.0 mL/min. Before being injected into HPLC, samples needed to be filtered through a micro syringe filter (VWR, 0.22  $\mu\text{m}$  PTFE for the organic samples and PES for the aqueous samples). The retention times (HPLC) of each reactants and products were determined with the standard samples, and are shown as follows: glucose (7.0 min), fructose (7.4 min), xylose (7.5 min), erythrose (8.4 min), glycolal (8.8 min), FA (9.4 min), AA (10.6 min), LA (11.7 min), 5-HMF (23.3 min) and furfural (35.7 min), respectively. Raman spectra data were obtained by taking 400  $\mu\text{L}$  of each sample interrogated in 8 mm glass vials and detected by the Inspector785 (200-2000  $\text{cm}^{-1}$ ) purchased from SciAps Inc.

To avoid the operating error, concentrations of products would be corrected by an internal standard. The yields (%) and selectivities (%) of products were based on the initial concentration of carbohydrates and calculated as:

$$\text{Yield (\%)} = \frac{\text{Product Concentration}}{\text{Theoretical Product Concentration}} \times 100\%$$

$$\text{Conversion (\%)} = \left(1 - \frac{\text{Carbohydrate Concentration}}{\text{Initial Carbohydrate Concentration}}\right) \times 100\%$$

$$\text{Selectivity (\%)} = \frac{\text{Yield}}{\text{Conversion}} \times 100\%$$

## Results and discussion

### Dehydration of glucose, xylose, cellobiose and $\alpha$ -cellulose

The dehydration condition of various carbohydrates in aqueous solution is optimized by a series of experiments, including pH of the PBS system and the borate content, which will be explained in detail later. Table 1 shows the results of glucose, xylose, cellobiose and  $\alpha$ -cellulose converting into 5-HMF/furfural in the optimum borate-assistant PBS system under microwave irradiation. With the assistance of microwave irradiation and borate, 62.0% of glucose is converted into 34.6% of 5-HMF with a selectivity of 55.8% in 90 min at 160 °C (Entry 1). However, the selectivity of 5-HMF displays

a decrease with the prolonged reaction time due to the formation of by-products such as LA, FA and humins. For example, with the prolonging of the reaction time from 90 to 150 min, the conversion of glucose increases from 62.0% to 79.4% while the selectivity of 5-HMF decreases from 55.8% to 45.1%. Moreover, xylose displays the same trend as the glucose in conversion and selectivity. (Entry 2) Therefore, the timely removal of product has to be taken into consideration.

**Table 1.** The dehydration results of glucose, cellobiose and  $\alpha$ -cellulose in the PBS system under microwave irradiation.<sup>[a]</sup>

Entry	Aldose	Time (min)	Conv. (%)	Y. <sup>[b]</sup> (%)	S. <sup>[b]</sup> (%)
1	Glucose	90	62.0	34.6	55.8
		120	71.3	37.1	52.0
		150	79.4	35.8	45.1
2	Xylose <sup>[c]</sup>	30	56.8	27.6	48.6
		60	86.1	37.1	43.1
3	Cellobiose	90	51.7	30.5	59.0
		120	60.5	33.2	54.9
4	$\alpha$ -Cellulose <sup>[d]</sup>	15	--	25.9	--
5	As-prepared Glucose (5.2 wt.%) <sup>[e]</sup>	30	43.0	21.0	48.8

<sup>[a]</sup> Reaction conditions: 10 wt.% glucose, cellobiose in 0.5M H<sub>3</sub>PO<sub>4</sub> / 0.5M NaH<sub>2</sub>PO<sub>4</sub> PBS system, Borax = 0.3 g, and reaction temperature = 160 °C. <sup>[b]</sup> Yield and selectivity of 5-HMF for Entry 1, 3 and 5; Yield and selectivity of furfural for Entry 2; Yield of glucose for Entry 4; <sup>[c]</sup> 10 wt.% xylose in 0.5M H<sub>3</sub>PO<sub>4</sub> / 0.5M NaH<sub>2</sub>PO<sub>4</sub> PBS system with B/X = 0.25. <sup>[d]</sup> Reaction condition: 20 wt.%  $\alpha$ -cellulose in 1.5 M H<sub>3</sub>PO<sub>4</sub> solution with 3 g NaCl in 15.4 g reaction solution; <sup>[e]</sup> Filtered solution from Entry 3 reacted in 1.5M H<sub>3</sub>PO<sub>4</sub> / 1.5M NaH<sub>2</sub>PO<sub>4</sub> PBS system with B/G = 0.5. Conv.: Conversion, Y.: Yield, S.: Selectivity.

Cellobiose and cellulose, which are composed of multi-glucose molecules, are considerably promising to be applied in the preparation of 5-HMF for their low cost and adequate source. Herein, under the same condition as glucose, the conversion of cellobiose reaches 60.5% and produces as much as 5-HMF of 33.2% in 120 min, which is quite good performance for cellobiose in aqueous solution (Entry 3). For cellulose, it is inspiring that a fast hydrolysis of  $\alpha$ -cellulose is observed in a NaCl-assisted H<sub>3</sub>PO<sub>4</sub> system and a 25.9% yield of glucose (5.2 wt.%) is obtained from 20 wt.%  $\alpha$ -cellulose solution without any pretreatment in 15 min under microwave irradiation (Entry 4). Furthermore, a 48.8% selectivity of 5-HMF based on the as-prepared glucose can be achieved from the above hydrolytic solution of  $\alpha$ -cellulose in such PBS system (Entry 5). These impressed results are believed to be attributed to the

**Table 2.** The conversion of glucose (10 wt.%) and the corresponding product distributions in PBS at different pH values under microwave irradiation.<sup>[a]</sup>

Solution	pH	Conv. (%)	Y. <sub>5-HMF</sub> (%)	Y. <sub>Fru.</sub> (%)	Y. <sub>LA</sub> (%)	Y. <sub>FA</sub> (%)	Y. <sub>AA</sub> (%)	Y. <sub>Ery.</sub> (%)
1.0M H <sub>3</sub> PO <sub>4</sub>	1.1	37.0	9.7	0.0	3.1	16.0	0.0	0.0
0.5M H <sub>3</sub> PO <sub>4</sub> /0.5M NaH <sub>2</sub> PO <sub>4</sub>	2.1	62.0	34.6	3.8	0.7	11.1	0.0	0.0
1.0M NaH <sub>2</sub> PO <sub>4</sub>	4.7	93.1	6.6	0.0	0.0	11.3	3.9	8.3
0.5M NaH <sub>2</sub> PO <sub>4</sub> /0.5M Na <sub>2</sub> HPO <sub>4</sub>	6.8	94.8	0.0	0.0	0.0	14.1	4.2	36.9

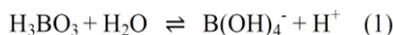
<sup>[a]</sup> Reaction conditions: reaction time = 90 min, B/G = 0.5, and reaction temperature = 160 °C. 5-HMF: 5-hydroxymethylfurfural; Fru.: Fructose; LA: levulinic acid; FA: formic acid; AA: acetic acid; Ery.: Erythrose; Conv.: Conversion; Y.: Yield.

Since the pH value of the reaction system has dramatic effect on the conversion of glucose, the use of buffer system is critical for its ability of maintaining pH value during the reaction. A series of

solution acidity, the buffer system and the effect of borate, which lead to the perfect matching of the isomerization and dehydration speed during the glucose/xylose conversion.

## 2.2 Effect of PBS system

Different mineral acidic solutions at different pH values containing a fixed amount of borate have been employed to study the isomerization and dehydration of glucose. As shown in Table 2, glucose in the PBS system at different pH values can be transformed to various products. At the stronger acid system (pH = 1.1), 5-HMF, LA and FA are formed, indicating the instability of 5-HMF at such pH value. When pH reaches 4.7, glucose seems to prefer other converting route rather than the dehydration way, such as retro-aldol condensation, and so erythrose is detected in the reaction system. Furthermore, the formation of erythrose becomes predominant at pH of 6.8, and no 5-HMF could be observed. Only at pH of 2.1, the reaction displayed the best result. Besides, it is found that the conversion of glucose decreases with the increasing acidity of the system, i.e., the lowest conversion is obtained at pH of 1.1. This is contrary to the results of fructose conversion in the solution at different pH values.<sup>[14]</sup> Moreover, it is surprising that other reaction systems, such as diluted strong acid system at different pH values (Table 3) and PBS systems without borate addition (Figure S1, supporting information), also display the same trend not only for the selectivity of 5-HMF but also for the conversion of glucose, i.e. the best performance of the reaction at pH of 2.1 and the lowest conversion of glucose at pH of 1.1. These results clearly show the importance of acidity in the glucose dehydration. On one hand, when the pH value is lower than 2.1, the ring-structure of glucose is more stable and not easy to isomerize into fructose even with the existence of borate. It is believed that B(OH)<sub>4</sub><sup>-</sup> can form stable chelate complexes with carbohydrates and catalyze the isomerization of aldoses to ketoses.<sup>[21-24]</sup> However, in the strong acidic system, the concentration of B(OH)<sub>4</sub><sup>-</sup> is quite low due to the limitation of borate hydrolysis equilibrium as shown by Equation 1.



The higher H<sup>+</sup> concentration will suppress the shift of equilibrium from left to right at lower pH value, and thereby influence the glucose isomerization rate. Furthermore, in the strong acid solution, the formed 5-HMF is inclined to rehydrate into LA and FA, which leads to a poor selectivity of 5-HMF. On the other hand, when the pH value is higher than 2.1, such as 4.7 and 6.8, the increase of glucose isomerization rate and other side-reaction rate causes a higher conversion of glucose and a lower selectivity of 5-HMF. These also can be demonstrated by the conversion of xylose into furfural. As shown in Figure 1A, the highest selectivity of furfural is achieved at pH of 2.1, and the high acidity (pH 1.1) leads to a low conversion of xylose in the borate-containing PBS system.

experiments have been conducted to study the effect of buffer system during the glucose dehydration in the H<sub>2</sub>SO<sub>4</sub> solution with different pH values, similar to those in the PBS systems. As shown

in Table 3, after being irradiated for 90 min, glucose converts only 16.0% and the yield of 5-HMF is merely 8.2% which is far less than the results obtained in the buffer system at the same pH value (2.1). It is obvious that the solution only with an appropriate pH value at the beginning is not enough for a good catalytic performance during the whole reaction. The generation of FA during the reaction at all the pH values range from 1.1 to 6.8 will have the impact on the acidity of the reaction system. Therefore, it is difficult for the diluted acid solution consisted of  $\text{H}_2\text{SO}_4$  to maintain its pH value during the reaction and so its acidity becomes stronger along with the generation of the organic acid. This can be demonstrated by its product distributions at different pH values which are regularly moved to more acidic ones compared to those of PBS systems (Table 2). Moreover, the shift of pH value towards the stronger acidic system will also suppress the conversion of glucose, as indicated above. On the contrary, PBS system is able to provide a self-regulation reaction environment, and so the acidity of the solution would not be infected notably by the generated organic acids. In consequence, the use of PBS system is one of the indispensable keys for the high selectivity of 5-HMF and the fast conversion of glucose.

**Table 3.** The conversion of glucose (10 wt.%) and the corresponding product distributions in  $\text{H}_2\text{SO}_4$  solution at different pH values under microwave irradiation.<sup>[a]</sup>

pH	Conv. (%)	Y. <sub>5-HMF</sub> (%)	Y. <sub>FA</sub> (%)	Y. <sub>Ery.</sub> (%)	Y. <sub>Gly.</sub> (%)
1.1	13.9	3.6	10.0	0.0	0.0
2.1	16.0	8.2	3.2	0.0	0.0
4.7	26.3	10.6	1.1	4.8	0.0
6.8	71.8	0.0	6.2	14.1	16.1

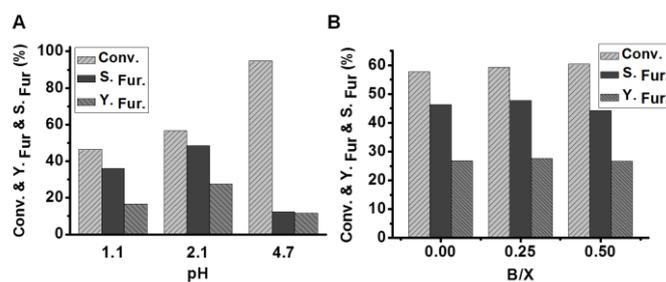
<sup>[a]</sup> Reaction conditions: reaction time = 90 min, B/G = 0.5, and reaction temperature = 160 °C. 5-HMF: 5-hydroxymethylfurfural; FA: formic acid; Ery.: Erythrose; Gly.: Glycolal; Conv.: Conversion; Y.: Yield.

**Table 4.** Influence of B/G ratio on the conversion of glucose into 5-HMF under microwave irradiation.<sup>[a]</sup>

B/G	Time (min)	Conv. (%)	Y. <sub>5-HMF</sub> (%)	S. <sub>5-HMF</sub> (%)	Y. <sub>Fru.</sub> (%)	Y. <sub>LA</sub> (%)	Y. <sub>FA</sub> (%)
0	90	43.0	22.0	51.1	0.0	1.1	7.0
0.25	90	48.2	24.8	51.5	0.3	0.7	5.6
0.5	90	62.0	34.6	55.8	3.8	0.7	11.1
	120	71.3	37.1	52.0	4.0	1.8	17.7
0.75	90	71.9	36.6	50.9	5.5	1.3	17.5
1	60	69.3	33.7	48.6	7.4	0.3	0.0
	90	83.2	39.5	47.5	3.9	0.7	0.0
1.25	60	82.7	34.9	42.2	5.1	0.0	0.6
	90	91.7	37.1	40.5	3.9	0.5	1.8
1.5	30	86.0	21.6	25.1	4.0	0.0	0.0
	60	93.9	23.0	24.5	2.1	0.0	0.8
	90	98.6	16.3	16.5	0.0	0.0	1.8

<sup>[a]</sup> Reaction conditions: 10 wt.% glucose in 0.5M  $\text{H}_3\text{PO}_4$  / 0.5M  $\text{NaH}_2\text{PO}_4$  PBS system, B/G = 0-1.5, and reaction temperature = 160 °C. 5-HMF: 5-hydroxymethylfurfural; Fru.: Fructose; LA: levulinic acid; FA: formic acid; Conv.: Conversion; Y.: Yield; S.: Selectivity.

However, the selectivity of 5-HMF displays a quite different trend with the increasing B/G ratio, that is, the highest selectivity of 5-HMF is obtained at B/G = 0.5 with a relatively high conversion of glucose. When B/G ratio is lower, the accelerating effect of borate for the isomerization of glucose is not enough although there is an acceptable selectivity of 5-HMF. When B/G ratio becomes higher, such as B/G = 1.5, the reaction shows the fastest conversion of glucose and the lowest selectivity of 5-HMF. Moreover, the yields of by-products LA and FA derived from the rehydration of 5-HMF also



**Figure 1.** Effects of pH value (A) and B/X ratio (B) on the conversion of xylose (10 wt.%) into furfural under microwave irradiation. All the reaction time is 30 min and reaction temperature is 160 °C. Fur.: Furfural; Conv.: Conversion; Y.: Yield; S.: Selectivity.

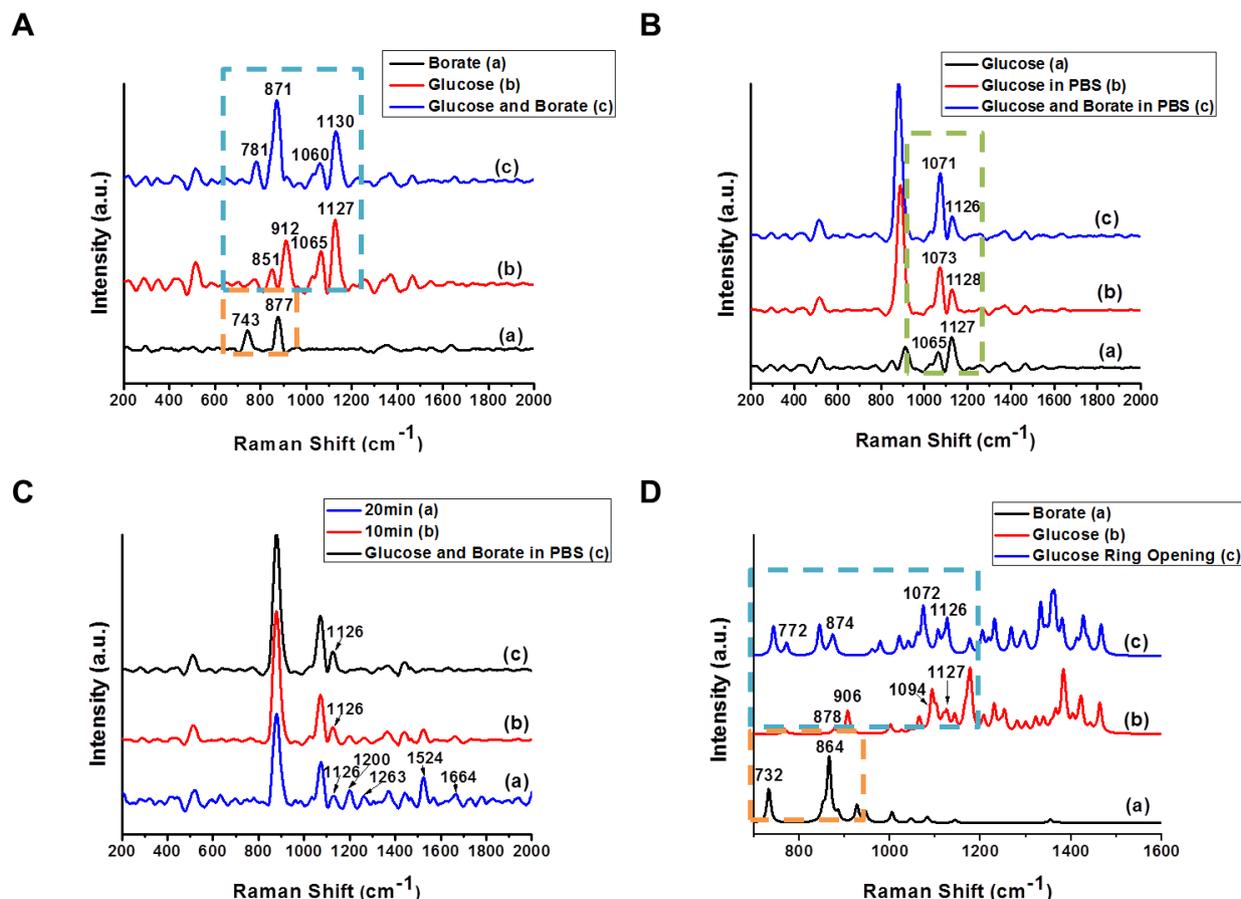
### 2.3 Effect of borate

Table 4 displays the effect of B/G ratios on the conversion of glucose into 5-HMF. Obviously, an increasing B/G ratio leads to an accelerative converting rate of glucose but a different yield and selectivity of 5-HMF within the same reaction time when pH value of the reaction system is fixed at 2.1. According to Table 4, without the addition of borate, the conversion of glucose is only 43.0% in 90 min. On the contrary, the glucose converts faster with the addition of borate, and the conversion of glucose can reach 86.0% at the 1.5 of B/G ratio in 30 min. This result is consistent with those of Table 2 and Figure S1 (supporting information). It is clear that borate can accelerate the converting rate of glucose. Moreover, in the borate-containing reaction system, fructose is detected during the reaction, which indicates that borate has a positive effect on the isomerization of glucose into fructose. Moreover, it can be further supported by theoretical calculations (see below). During the reaction, glucose isomerizes into fructose firstly and then fructose dehydrates into 5-HMF continuously with the assistance of mineral acid and borate in the PBS system.

show the same trend as that of 5-HMF, indicating that the decrease of 5-HMF selectivity at the high B/G ratio could be assigned to the occurrence of other side-reaction before dehydration of fructose. Although  $\text{B}(\text{OH})_4^-$ , which is formed by hydrolysis of boric acid, can facilitate the isomerization of aldoses into ketoses by forming stable chelate complexes with aldoses/ketoses, the strong complexation between  $\text{B}(\text{OH})_4^-$  and glucose/fructose will also block the elimination of water in the first step of fructose conversion into 5-HMF and induce other side-reaction.<sup>[24]</sup> Therefore, an excessive

amount of borate will upset the dehydration of fructose although it can accelerate the conversion of glucose into fructose, which can be proved by the results of fructose dehydration with borate-containing PBS system (Table S1, supporting information). As shown in Table S1, a high boron/fructose mole ratio (B/F) also results in a low selectivity of 5-HMF. Moreover, the content of glucose is stable with the increasing B/F ratios during the reaction, which implies that the high B/F ratio shows a great influence on the conversion of fructose rather than its isomerization towards glucose. Furthermore, the similar conversion of fructose and the low yield of 5-HMF further

indicate the occurrence of other side reaction during the dehydration of fructose with the increase of B/F ratio. In addition, the same trend is also observed in the dehydration of xylose into furfural in the Figure 1B. With the increasing of B/X ratio, the conversion of xylose into furfural is accelerated, but the best result can be obtained at B/X = 0.25. Consequently, it can be concluded that a suitable B/G ratio is the key to the isomerization of glucose and dehydration of fructose, and the good yield of 5-HMF is only achieved at the good matching between them.



**Figure 2.** Raman spectra of the reaction system. (A) Raman spectra of borate solution (a), 10 wt.% glucose solution (b) and 10 wt.% glucose solution containing borate (c); (B) Raman spectra of 10 wt.% glucose solution (a), 10 wt.% glucose in PBS (b) and 10 wt.% glucose in PBS containing borate (c); (C) Raman spectra of the system reacted for 20 min (a) and 10 min (b), and the original reaction system (c); (D) Theoretical Raman spectra of borate solution (a), glucose solution (b), and the ring-opening form of the  $B(OH)_4^-$ -glucose chelate complex (c).

To further study the effect of borate, a series of Raman spectra are measured, as shown in Figure 2A-C. Also, theoretical spectra are given in Figure 2D to verify these Raman analyses. For the pure borate solution (Figure 2Aa), only the characteristic peaks of  $B(OH)_4^-$  and  $H_3BO_3$  appear at  $743\text{ cm}^{-1}$  and  $877\text{ cm}^{-1}$ , respectively.<sup>[25]</sup> In the pure glucose solution (Figure 2Ab), the peaks emerging at the  $912\text{ cm}^{-1}$  and  $851\text{ cm}^{-1}$  are assigned to the in-plane stretching vibration of C-C=O, and the signals at  $1127\text{ cm}^{-1}$ ,  $1065\text{ cm}^{-1}$  are the peaks of out-of-plane stretching vibration of C-C=O.<sup>[26]</sup> However, in the solution of borate and glucose mixture (Figure 2Ac), the in-plane stretching vibration of C-C=O in glucose molecule displays a greatly change compared to that of pure glucose solution, and moves to lower wave number ( $781\text{ cm}^{-1}$  and  $871\text{ cm}^{-1}$ ), which indicates the formation of  $B(OH)_4^-$ -glucose chelate complexes. Moreover, this interaction could also be proved by the theoretical calculations as

well, that is, borate does have the effect on the ring opening process of glucose during the reaction, as shown in Figure 2Dc. In addition, the out-of-plane stretching vibration of its C-C=O also shows a clear change although the change is slight. However, when glucose is dissolved in PBS medium consisted of  $0.5\text{ M } H_3PO_4$  and  $0.5\text{ M } NaH_2PO_4$ , the in-plane stretching vibration of C-C=O in glucose is totally covered by the strong peaks caused by the mineral acid and salt (Figure 2Bb). Only the small change on the out-of-plane stretching vibration of C-C=O could still be observed (Figure 2Bc).

To get a better understanding of the conversion process of glucose, the reaction was determined by Raman spectra every 10 min under the microwave irradiation. It is clear that, during the reaction, some new peaks arise at  $1664\text{ cm}^{-1}$ ,  $1524\text{ cm}^{-1}$ ,  $1263\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$  respectively in the Figure 2C, which can be assigned to the

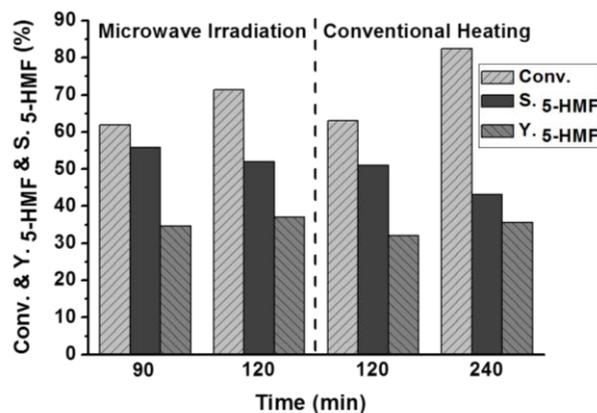
generation of 5-HMF.<sup>[27]</sup> In addition, the increasing intensity of 5-HMF characteristic peaks and the decreasing glucose peak at 1126  $\text{cm}^{-1}$  also imply the conversion of glucose into 5-HMF (Figure 2C).

Besides, these experimental Raman spectra agree well with the calculation results, especially in the spectra of borate and glucose ring-opening process. The experimental results of  $\text{B}(\text{OH})_4^-$  and  $\text{H}_3\text{BO}_3$  at 743  $\text{cm}^{-1}$  and 877  $\text{cm}^{-1}$  in Figure 2Aa are consistent with the theoretical ones at 732  $\text{cm}^{-1}$  and 864  $\text{cm}^{-1}$  in Figure 2Da. As shown in Figure 2Ac, the characteristic peaks at 781  $\text{cm}^{-1}$ , 871  $\text{cm}^{-1}$ , 1060  $\text{cm}^{-1}$  and 1130  $\text{cm}^{-1}$  of glucose solution containing borate are corresponding with the calculated ones of the ring-opening form of the  $\text{B}(\text{OH})_4^-$ -glucose chelate complex (Figure 2Dc). Accordingly, it is believed that tetrahydroxyborate [ $\text{B}(\text{OH})_4^-$ ] plays an important role in the isomerization of glucose.

## 2.4 Effect of microwave irradiation

The effect of microwave heating on the conversion of glucose also was studied, and the results were shown in Figure 3. Obviously, microwave irradiation leads to a faster conversion of glucose and a higher selectivity of 5-HMF compared with the results under oven heating. For example, the reaction system under microwave heating can achieve a glucose conversion of 62.0% with a 5-HMF selectivity of 55.8% within 90 min at 160 °C, but that under oven heating just reaches a glucose conversion of 63.1% with a 5-HMF selectivity of 50.9% within 120 min at the same temperature. The observed rate enhancement can be contributed to the nature of microwave direct, volumetric heating model and the reaction system with a high ion concentration.<sup>[28]</sup> This acidic PBS solution containing borate contains abundant of ions such as  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{B}(\text{OH})_4^-$ ,  $\text{H}_3\text{O}^+$ ,  $\text{Na}^+$ , and so leads to a rapid temperature rise under microwave irradiation because ionic conduction is one of two main microwave heating models.<sup>[29]</sup> Such instantaneous heating process results in not only a fast conversion of glucose but also a high selectivity of 5-HMF, because an extended reaction time could cause the formation of by-products and the decrease of selectivity.<sup>[29]</sup> These results also can explain the reason of the similar results of glucose conversion in the pure water heated by conventional ways and microwave irradiation (Figure S2, supporting information). The ion concentration in the water is very low, and so instantaneous heating effect of microwave field becomes insignificant. Therefore, the

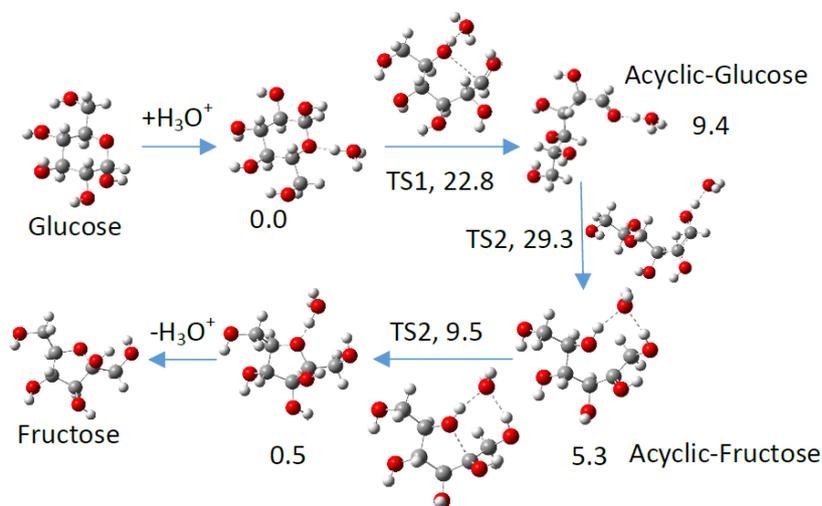
difference of glucose conversion in the pure water between the conventional heating and microwave cannot be observed clearly. Therefore, microwave irradiation is also another influence factor of high-selective conversion of glucose into 5-HMF in such PBS system.



**Figure 3.** The conversions of 10 wt.% glucose in the borate-containing PBS system under microwave irradiation and conventional heating at 160 °C. 5-HMF: 5-hydroxymethylfurfural; Conv.: Conversion; Y.: Yield; S.: Selectivity.

## 2.5 Computational study

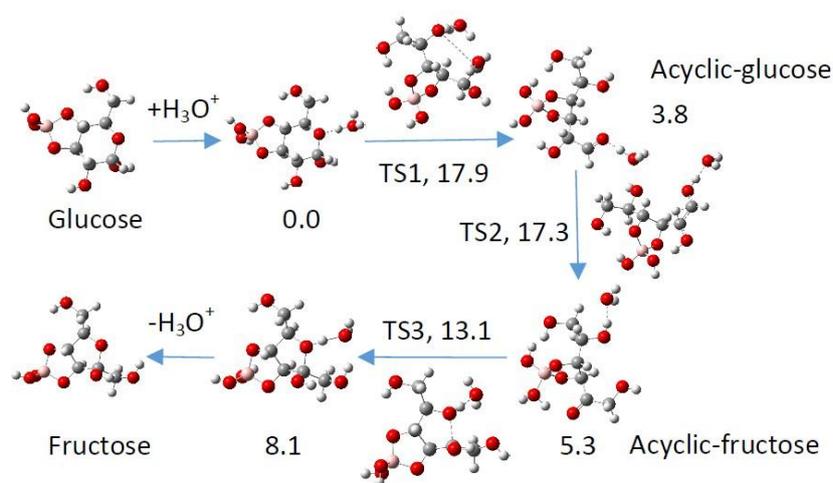
Theoretical calculations were performed to understand the isomerization mechanism of glucose to fructose in acidic solution with or without borate. The calculations indicate that the isomerization begins with the opening of the 6-member ring-close form of glucose (glucopyranose) by breaking its C-O bond in the ring with the help of a proton. The resulting opening form of glucose (acyclic-glucose) undergoes an intramolecular hydrogen transfer to the opening form of fructose (acyclic-fructose). Acyclic-fructose then undergoes a ring closing process to form the ring-close form of fructose. The Gibbs free-energy profiles and the structures of the intermediates and transition states of the isomerization process without borate are presented in Figure 4. The result in Figure 4 shows that the overall free-energy barrier for the isomerization of glucose into fructose is 29.3 kcal/mol when borate is absent.



**Figure 4.** Gibbs free-energy profiles at 298.15 K and structures of the intermediates and transition states of the isomerization of glucose to fructose with the help of proton. The numbers are relative free energies (in kcal/mol) to the complex between glucose and  $\text{H}_3\text{O}^+$ .

In the reaction system containing borate,  $B(OH)_4^-$  can form stable chelate complex, boroglucofuranose, with glucose by anchoring with two hydroxyl groups of glucose through removal of two water molecules. Similar to the results of Anders Riisager et al.,<sup>[24]</sup> we find that 4,6-boroglucofuranose and 3,4-boroglucofuranose are the two most stable complexes between  $B(OH)_4^-$  and glucose, and the former is slightly more stable than the latter by 3.2 kcal/mol at 298.15 K in Gibbs free energy. Under the reaction conditions, these two complexes can be viewed as in equilibrium with each other. Starting from either 4,6-boroglucofuranose or 3,4-boroglucofuranose, a similar isomerization pathway as that one without borate as presented in Figure 4 can be determined in Figure 5 and Figure S3 (supporting information). However, it is found that the pathway starting with 4,6-boroglucofuranose has higher energy barrier (with

an overall free-energy barrier of 25.5 kcal/mol, Figure S3, supporting information) than that starting with 3,4-boroglucofuranose (Figure 5). The latter one has an overall free-energy barrier of just 17.9 kcal/mol. As can be seen from Figures 4 and 5, the addition of borate can greatly lower the energy barrier of the isomerization. Binding with  $B(OH)_4^-$  increases the tension of the 6-membered ring of glucose, which lowers its Gibbs free-energy barrier for the opening from close form to open form through the transition state TS1 from 22.8 kcal/mol to just 17.9 kcal/mol. The second step, the hydrogen migration from  $-C^{(2)}HOH-$  to the terminal  $-C^{(1)}H=O$  of acyclic-glucose to form acyclic-fructose, is also greatly enhanced with a free-energy-barrier lowering from 19.9 kcal/mol to 13.5 kcal/mol.



**Figure 5.** Gibbs free-energy profiles at 298.15 K and structures of the intermediates and transition states of the isomerization of glucose to fructose via 3,4-boroglucofuranose with the help of proton. The numbers are relative free energies (in kcal/mol) to the complex between D-glucose and  $H_3O^+$ .

In the calculation,  $B(OH)_4^-$  is also replaced by  $H_3PO_4$  to study if  $H_3PO_4$  can accelerate the isomerization of glucose as well. Similar pathway as presented in Figure 5 is computed (Figure S4, supporting information). The overall Gibbs free-energy barrier in the reaction system containing  $H_3PO_4$  is 25.1 kcal/mol, which is higher than that with the help of  $B(OH)_4^-$  (17.9 kcal/mol, Figure 5) but is lower than that with only protons but without other additives (29.3 kcal/mol, Figure 4). This means that  $H_3PO_4$  can also facilitate the isomerization of glucose but its effect is weaker than that of borate. The results are consistent with experimental data and prove the key role of borate in accelerating the isomerization of glucose. In addition, it is worthy to mention that the pathway by anchoring two glucose molecules with one  $B(OH)_4^-$  is considered to mimic the effect of borate concentration changed from B/G ratio of 1 to 0.5. When the borate content is decreased, the overall Gibbs free-energy barrier of glucose isomerization process is increased to 20.9 kcal/mol. This implies that the isomerization is faster with a B/G ratio of 1 than that of 0.5, which is also consistent with experimental results (Table 4). Besides, our calculations also indicate that the ring opening form of 3,4-boroglucofuranose is a stable intermediate during the isomerization process: Its relative free energy to 3,4-boroglucofuranose is just 3.8 kcal/mol (Figure 5). Its conversion back to 3,4-boroglucofuranose has a free-energy barrier of 14.1 kcal/mol (transition state TS1) while its isomerization to acyclic-fructose through hydrogen-migration is 13.5 kcal/mol (transition state TS2). Therefore, it is probable to observe this intermediate

during the isomerization process. In fact, the Raman spectrum of this intermediate agree well with experimental Raman spectrum of glucose in the PBS solution containing borate (Figure 2). This agreement is also a strong evidence for the reliability of our theoretical calculations and the proposed isomerization mechanism.

## 2.6 Sustainability of PBS system with borate

Compared with the solid acid catalyst, one of the biggest disadvantages of liquid acids is the poor reusability. The solid acid catalysts could be easily recycled and reused after a series of processes while liquid acids catalyst normally could not be recycled and used again after the reaction. Moreover, the general mineral acids (HCl and  $H_2SO_4$ ) are highly corrosive for the reaction vessel. Compared to them, this PBS system consisted with phosphoric acid/acid phosphate and borate is safer and less corrosive. Furthermore, as indicated by Dumesic,<sup>[30]</sup> such PBS system can also achieve a possibility of the recycling by a biphasic system, that is, the continuous removing of 5-HMF by organic solvents and the continual feed of glucose. Herein, three stepwise additions of glucose and organic phase are used to investigate the possibility of the reusability of this system. As shown in Table 5, the selectivity of 5-HMF could be maintained after three additions of glucose, and reaches 60% even if the total glucose concentration is up to 20 wt.%. Moreover, the result of separately addition one is higher than not only that of 10 wt.% glucose in pure PBS phase (Entry 1, Table 1)

but also the result directly obtained from 20 wt.% glucose in biphasic system (Table 5), although the conversion of glucose is almost at the same level. In addition, the PBS catalysts can also be recovered by neutralizing them into their salts such as  $\text{Na}_3\text{PO}_4$ . Generally, the solubility of  $\text{Na}_3\text{PO}_4$  in water is poorer and more sensitive to the temperature compared to its acidic form, and easy to be re-crystallized. For example, if the PBS solution is neutralized to  $\text{Na}_3\text{PO}_4$  by the addition of NaOH, 31 wt.%, 53 wt.% and 74 wt.% of  $\text{Na}_3\text{PO}_4$  should be recovered in theory at 20 °C, 10 °C and 0 °C, respectively.<sup>[31]</sup> According to our experiments, more than 90% of the theoretical amount of  $\text{Na}_3\text{PO}_4$  could be obtained. These results provide a possible reusability of PBS system for the future practical application.

**Table 5.** The sustainability of the PBS system with borate.<sup>[a]</sup>

	Glucose (wt.%)	Time (min)	Conv. (%)	Y. <sub>5-HMF</sub> (%)	S. <sub>5-HMF</sub> (%)
Run 1	10	90	57.8	34.6	60.0
Run 2	5	90	51.3	30.5	59.5
Run 3	5	90	43.9	26.0	59.2
Total	20	270	74.0	44.7	60.4
Original	20	90	74.9	39.6	52.9

<sup>[a]</sup> Reaction conditions: reaction temperature = 160 °C and B/G = 0.5 in a biphasic system. An organic phase (MIBK: 2-butanol = 7:3) with the same volume as the aqueous phase is added into above PBS system before reaction. 5-HMF: 5-hydromethylfurfural; Conv.: Conversion; Y.: Yield; S.: Selectivity.

## Conclusions

In sum, the PBS system containing borate with an appropriate pH could convert glucose, cellobiose and  $\alpha$ -cellulose into 5-HMF/furfural directly with a high selectivity. It is found that the key factor of the high selective conversion of glucose to 5-HMF is the matching of isomerization and dehydration processes of glucose, i.e. the matching among appropriate pH (2.1), B/G ratio (0.5) and PBS system under microwave irradiation. Only under that unique condition, glucose can isomerize into fructose and then dehydrate into 5-HMF continuously at the matched speed. Both Raman spectra and theoretical calculations prove the interaction between borate and glucose as well as the borate-assistant isomerization process of glucose. Additionally, the PBS system with borate is expected to achieve its reusability and stable catalytic performance by the biphasic system. These results not only deepen the understanding of the one-pot conversion process of glucose to 5-HMF involving in the matching of isomerization and dehydration processes, but also present the possibility of achieving a sustainable green process of carbohydrates conversion.

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## Notes and references

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Electronic Supplementary Information (ESI) available: the data of the conversion of glucose into 5-HMF in the PBS system without borate addition, the conversions of glucose in the pure water under microwave irradiation and conventional heating, the influence of B/F ratio on the conversion of fructose into 5-HMF, and two kinds of Gibbs free-energy profiles and structures of the intermediates and transition states of the isomerization of glucose to fructose. See DOI: 10.1039/b000000x/.

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