Electronic Supplementary Material (ESI) for RSC Advances

Microwave-assisted high efficient transformation of ketose/aldose to 5-hydroxymethylfurfural (5-HMF) in a simple phosphate buffer system**

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Experimental Section

Dehydration of saccharide to 5-HMF in the phosphate buffer system (PBS) and other acidic solution

All the PBSs with different component ratios or different concentrations as well as acidic solution were prepared according to their stoichiometric ratios in 50 mL flask. The dehydrations of various saccharides in the PBS and other acidic solution were performed in a Teflon reactor (60 mL) under microwave irradiation (Sineo MDS-6, Shanghai), and all the reactions were directly carried out in one pot. In detail, fructose (1.3-7.6 g) was dissolved in PBS or other acid solution (11.7-7.6 g), and the total volume of the reaction solution was kept at 12 mL. And then the mixture solution was treated under microwave irradiation at 150 ^{o}C for 10-30 min. For the system containing glucose, all the procedure was the same as fructose. However, the reaction time was prolonged to 30-90 min, and a certain amount of sodiumborate powder was added into the PBS containing glucose before microwave irradiation to increase the reaction rate. The additive amount of sodiumborate was different with the different concentrations of glucose solution according to our optimum conditions. For example, for glucose solution of 10 wt%, the molar ratio of B/glucose was 0.875. However, when the concentration of glucose solution was increased to 30 wt%, this ratio would decrease to 0.25.

Dehydration of saccharide to 5-HMF in the two phase system

For the two phase system, all the procedures were the same as the above PBS system, but the organic solvent with the same volume (12 mL) was added before microwave irradiation. Herein, the aqueous phase (12 mL) was PBS and the organic phase (12 mL) was methylisobutylketone/2-butanol (volume ratio: 7:3).

Product analysis

The products collected at different reaction time were analyzed using a high performance liquid chromatography (HPLC, Shimazu) equipped with a refractive index detector (RID) and a shodex SH1011 sugar column. A H_2SO_4 solution of 0.5 mM was employed as mobile phase at 40 ^{o}C with a flow rate of 1.0 mLmin^{-1}. Concentrations of substrates and products before and after reaction were determined from calibration curves obtained by their standard samples, while the yield (Y.) and selectivity (Selec.) of 5-HMF and conversion (Conv.) of saccharides were calculated by the following equations.

The PBS system:

$$\text{Conv.}_{PBS} = (1 - \frac{[\text{Saccharide}]_t \times V_t}{[\text{Saccharide}]_0 \times V_0}) \times 100\%$$

$$\text{Y.}_{PBS} = \frac{[\text{Product}]_t \times V_t}{[\text{Saccharide}]_0 \times V_0} \times 100\%$$

$$\text{Selec.}_{PBS} = \frac{\text{Y.}}{\text{Conv.}} \times 100\%$$

$[\text{Saccharide}]_0$, $[\text{Saccharide}]_t$ and $[\text{Pruduct}]_t$ represent the original molar concentration of saccharide, the molar concentration of saccharides and product (5-HMF, LA, FA etc.) at the reaction time of t, respectively. V_0 and V_t represent the volumes of reaction solution before and after reaction, respectively.

The two-phase system:

$$\text{Conv.} = (1 - \frac{[\text{Saccharide}]_{aq,t} \times V_{aq,t}}{[\text{Saccharide}]_0 \times V_0}) \times 100\%$$

$$\text{Y.} = \frac{[\text{Product}]_{aq,t} \times V_{aq,t} + [\text{Product}]_{org,t} \times V_{org,t}}{[\text{Saccharide}]_0 \times V_0} \times 100\%$$

$$\text{Selec.} = \frac{\text{Y.}}{\text{Conv.}} \times 100\%$$

The conversion of saccharide in the two phase system is consistent with that in PBS. However, because 5-HMF could be dispersed in both aqueous phase and organic phase, its concentration has to be determined by the two phases together. Therefore, $[\text{Product}]_{aq,t}$ and $[\text{Product}]_{org,t}$ separately represent the molar concentration of 5-HMF in the aqueous phase and in the organic phase at the reaction time of t. V_0, $V_{aq,t}$, $V_{org,,t}$ represent the original volume of reaction solution and the volume of the aqueous and organic phase after reaction, respectively.

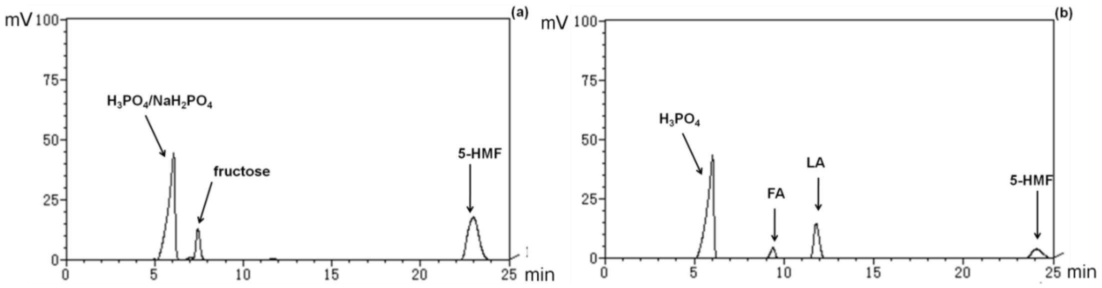

Fig. S1 High performance liquid chromatography (HPLC) results of dehydration products of fructose (10 wt%) in aqueous solution at 150 ^oC for 30 min: (a) $PBS_{2.1}$ system (0.5M H_3PO_4 /0.5M NaH_2PO_4) and (b) H_3PO_4 1M.

Table S1 The results of hydration of 5-HMF (1 wt%) in different acid solutions and $PBS_{2.1}$ system at 150 ^oC under microwave radiation.

Entry	Acid	T (min)	Conv. (%)	Y_{FA} (%)	Y_{LA} (%)
1	HCl/0.25M	10	93	65	42
2	H_3PO_4/1M	10	51	26	20
3	$PBS_{2.1}$	10	9	0	0
4	$PBS_{2.1}$	60	34	0	0

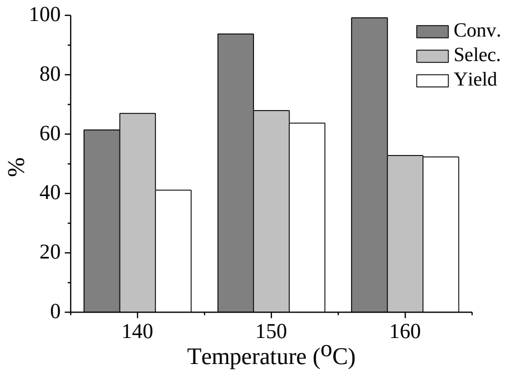

Fig. S2 The dehydrations of fructose (10 wt%) in $PBS_{2.1}$ system at different temperatures within 30 min under microwave radiation. Conversion of fructose increases with the increasing reaction temperature from 140 ^oC to 160 ^oC, but the insoluble/soluble polymeric compounds increase obviously at 160 ^oC, which results in the decrease of 5-HMF selectivity.

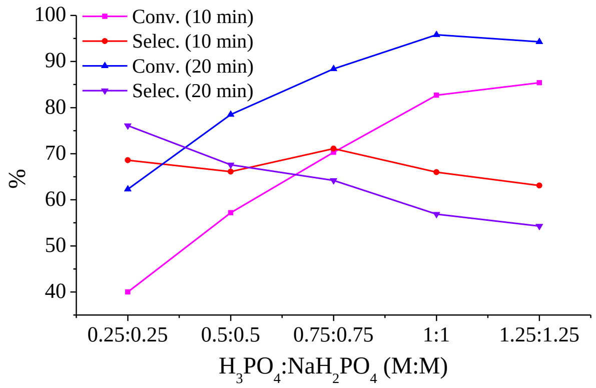

Fig. S3 Impact of $PBS_{2.1}$ concentration upon the conversion of fructose and the selectivity of 5-HMF (150 ^oC, 10 wt% fructose). The conversion of fructose increases with the increasing $PBS_{2.1}$ concentration, and gets up to an equilibrium at H_3PO_4:NaH_2PO_4 = 1M:1M. However, the selectivity of 5-HMF decreases with the increase of $PBS_{2.1}$ concentration and reaction time. Finally, taking both conversion and selectivity of reaction into consideration, a $PBS_{2.1}$ concentration of 0.5M H_3PO_4:0.5M NaH_2PO_4 is selected.

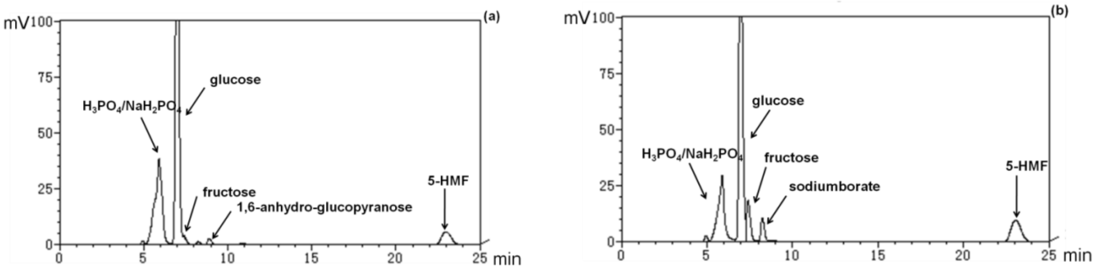

Fig. S4 HPLC results of dehydration of glucose (30 wt%) in the $PBS_{2.1}$ system containing sodiumborate as a promoter (b) or not (a) at 150 ^{o}C within 30 min under microwave radiation. Figure S4 indicates that glucose dehydrates into 5-HMF (retention time: 23.0 min) via an isomerization step from glucose (retention time: 6.97) to fructose (retention time: 7.40) in the $PBS_{2.1}$ system because of the appearance of fructose in the HPLC result. The increasing peak area of fructose in Figure S4b implies that borate can facilitate the isomerization from glucose to fructose indeed, and so accelerate the conversion of glucose into 5-HMF.