Hydrothermal decomposition of glucose and fructose with inorganic and organic potassium salts

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HIGHLIGHTS

► The effect of inorganic and organic salts on hexose decomposition was studied.
► The decomposition rate constants and impact factors of hexoses were calculated.
► Anions influence the decomposition of hexose via different mechanisms.
► The relationship between impact factor and physical properties was demonstrated.

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ABSTRACT

The effects of 15 inorganic and organic acid potassium salts on hydrothermal decomposition of glucose, fructose and 5-hydroxymethylfurfural (5-HMF) were investigated at 180 °C. The rate constants for glucose, fructose and 5-HMF decomposition with anions were calculated by a pseudo first-order equation, and the impact factors of the rate constants were calculated, to demonstrate the catalytic effect of the different anions. Compared to the results without added salts, chloride, bromide, iodide and nitrate anions did not significantly accelerate the decomposition rate of glucose or improve the selectivity for 5-HMF, but increased the decomposition rate of fructose from 19% to 44%, and improved the selectivity for 5-HMF by 4–29%. Phosphate, fluoride, sulfate and all organic acid anions increased the decomposition rate of glucose and fructose by 23–2781%, but lowered the selectivity for 5-HMF from 36% to 100% as compared to the results without added salts. These findings provide insights on the reactivity and mechanism of the hydrothermal decomposition of glucose and fructose with inorganic and organic salts.

1. Introduction

The hydrothermal decomposition of cellulose or its constituent, glucose, to produce platform chemicals, such as 5-hydroxymethylfurfural (5-HMF) and levulinic acid is impacted by the presence of inorganic salts. For example, Fe^{3+}, La^{3+}, Zn^{2+} and Cu^{2+} are able to catalyze the decomposition of cellulose and glucose, and improve the selectivity for 5-HMF (Bicker et al., 2005; Lu and Lu, 2009; Rasrendra et al., 2010; Seri et al., 2002). A role of sulfate and chloride anions in the formation of humin from glucose has also been reported (Tyrlik et al., 1996). The current study was carried out to investigate the impact of a wider range of anions on the decomposition of glucose and fructose and to elucidate possible mechanisms by which these anions influence their decomposition.

Glucose and fructose were selected as model compounds, and the hydrothermal decomposition of these sugars in the presence of 15 types of potassium salts was conducted. The stability of 5-HMF in the presence of these salts was also investigated. The decomposition rate constant and impact factor of the rate constants were also calculated.

2. Experimental section

2.1. Materials

Glucose, fructose, and potassium fluoride, chloride, bromide, iodide, nitrate, sulfate, phosphate, formate, acetate, oxalate and citrate were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Potassium propionate, trifluoroacetate, benzoate and sorbate were obtained from Tokyo Chemical Industry Co. LTD, Japan. 5-Hydroxymethyl-2-furaldehyde (5-HMF) was purchased from Sigma, USA.

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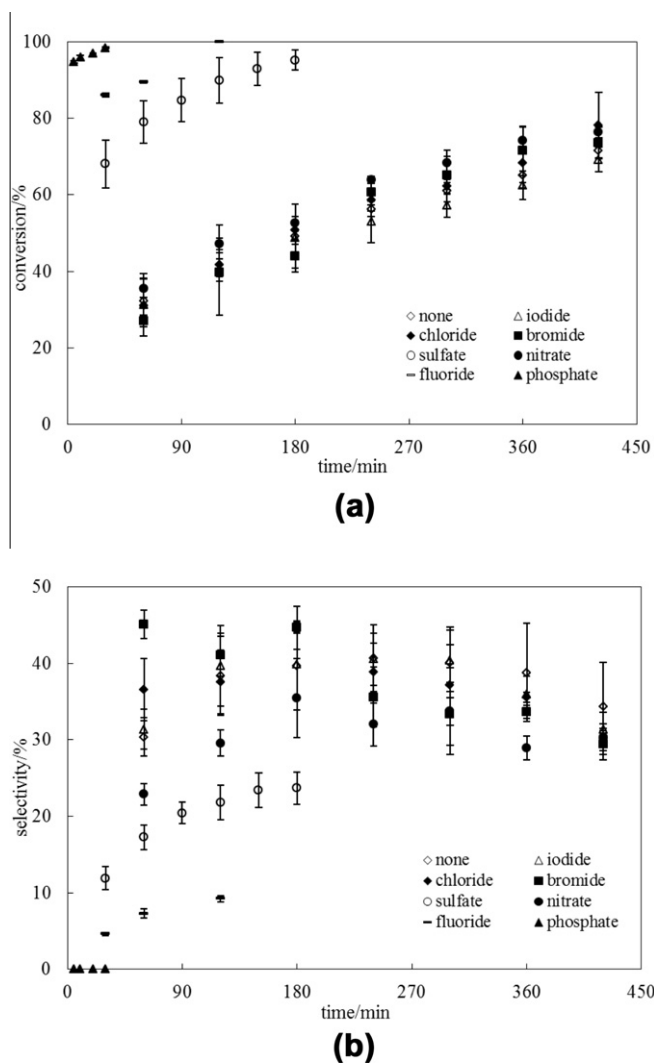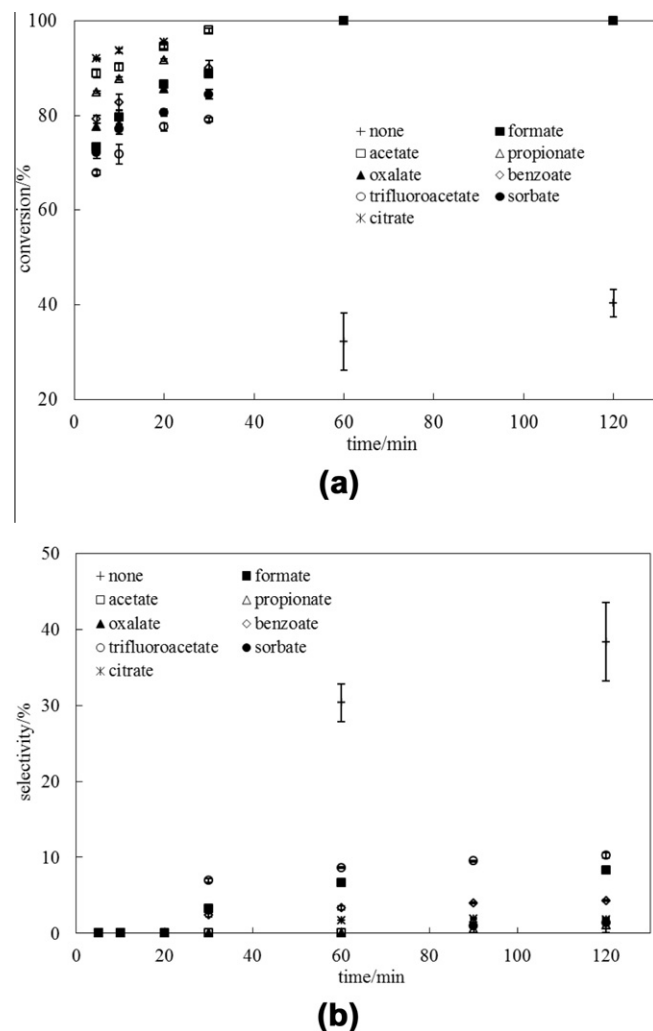E-mail addresses: jiefu@iastate.edu (J. Fu), luxiuyang@zju.edu.cn (X. Lu).

Fig. 1. Glucose conversions and selectivities for 5-HMF with inorganic acid anions based on 0.04 mol/L potassium concentration at 180 °C: (a) conversion of glucose; (b) selectivity for 5-HMF. The markers represent the average values as determined from four replicate experiments, and the error bars represent standard deviations from four replicate experiments.

Fig. 2. Glucose conversions and selectivities for 5-HMF with organic acid anions based on 0.04 mol/L potassium concentration at 180 °C: (a) conversion of glucose; (b) selectivity for 5-HMF. The markers represent the average values as determined from four replicate experiments, and the error bars represent standard deviations from four replicate experiments.

2.2. Reactor

The batch reactor was made of 316L stainless steel tubing and had a volume of about 13.5 mL. The internal diameter of the tube was 12 mm. It was sealed by a stopper, which had a seal diameter of 13.8 mm. A cap was employed to fix the tube and stopper. The reactor can withstand up 20 MPa of pressure and a temperature of up to 290 °C. It was heated by a steel box furnace that could heat up to 12 reactors at a time. The furnace could maintain the temperature within ±2%.

2.3. Experimental procedure

Glucose, fructose and 5-HMF were dissolved in deionized water at a concentration of 10 g/L. The desired amount (based on 0.04 mol/L potassium concentration) of a potassium salt was added to each solution and 10 mL was loaded into the tube. The tubes were heated to 180 °C over a 15-min period, and maintained at that temperature for 5–420 min. The reactors were quickly removed from the furnace and placed into water

to quench the reaction. The liquid samples were collected and stored in a 4 °C freezer to limit further decomposition. The standard deviations were determined from four replicate experiments.

2.4. Analysis

Analyses were done with an Agilent high-pressure liquid chromatograph 1100 (HPLC 1100) equipped with a Refractive Index Detector (RID) were established. For the analysis of 5-HMF, a 4 mm ID × 250 mm KNAUER C18 reverse-phase column was used. The temperature of the column and the RID was 35 °C, the mobile phase was 0.125 g/L of sulfuric acid and acetonitrile at a ratio of 92:8 with a flow rate of 0.6 mL/min. For the analysis of glucose and fructose, a 4.6 mm ID × 250 mm Kromasil NH$_2$ column was used. The temperature of the column and the RID was 30 °C, the mobile phase was 0.25 g/L of ammonia and acetonitrile at a ratio of 20:80 with a flow rate of 1.0 mL/min. Product identification was achieved by comparison of retention times with those of standard solutions of pure compounds, and identities were confirmed by GC–MS (Agilent 6890GC/5973 MSD).
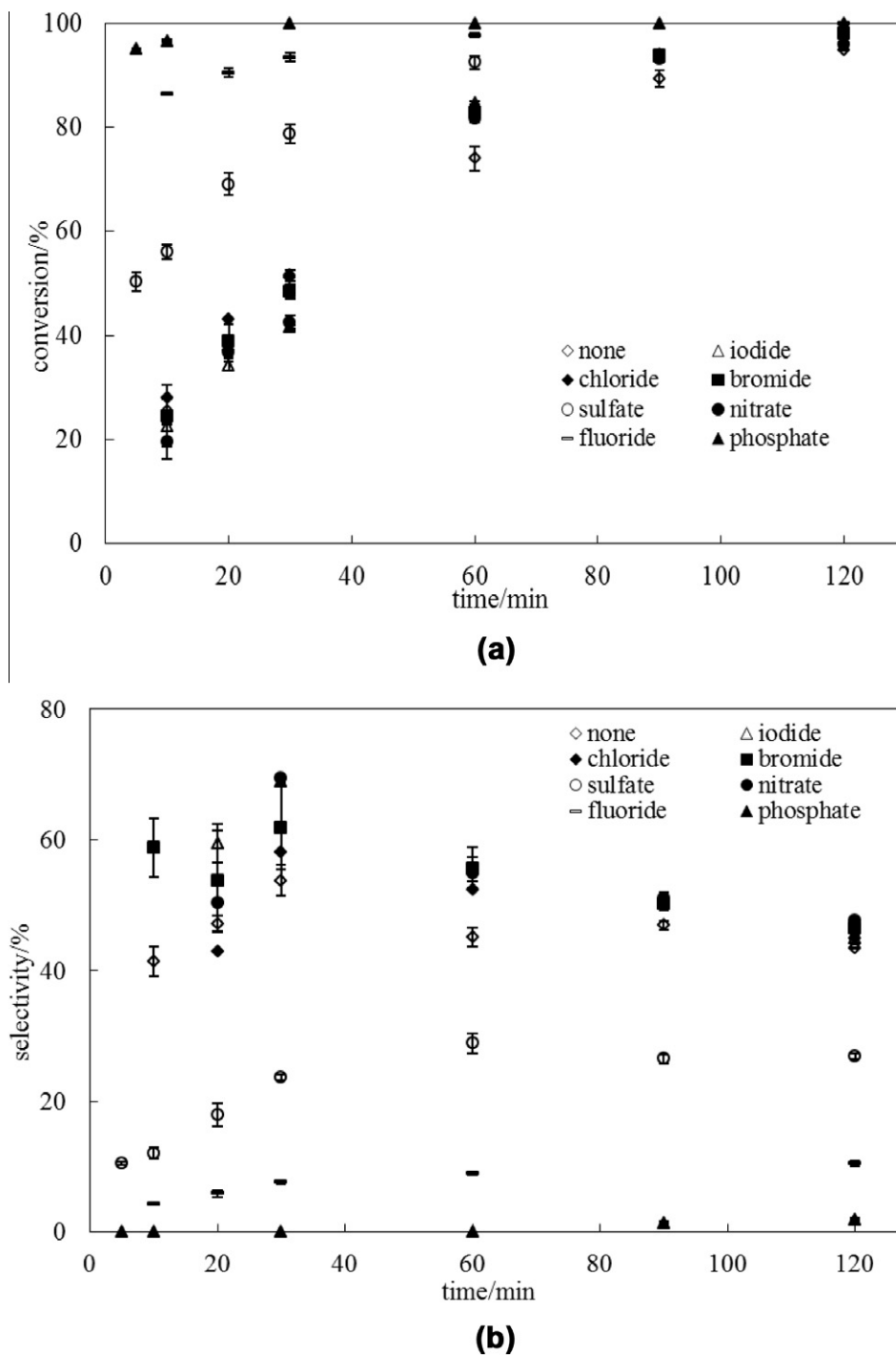
Fig. 3. Fructose conversions and selectivities for 5-HMF with inorganic acid anions based on 0.04 mol/L potassium concentration at 180 °C: (a) conversion of fructose; (b) selectivity for 5-HMF. The markers represent the average values as determined from four replicate experiments, and the error bars represent standard deviations from four replicate experiments.

3. Results and discussion

Potassium was selected as the cation because pervious work had proven that potassium did not affect the decomposition of glucose and the selectivity for 5-HMF (Lu and Lu, 2009). The loading of salts was conducted to achieve the same potassium molar concentration of 0.04 mol/L in the solution at room temperature.

3.1. Effect of anions on hydrothermal decomposition of glucose

Fig. 1 shows the effects of inorganic acid anion on the decomposition of glucose and selectivity for 5-HMF at 180 °C. Chloride,

bromide, iodide and nitrate anions did not significantly accelerate the decomposition rate of glucose or improve the selectivity for 5-HMF. The conversion rates and selectivities in the presence of these anions were close to those without salt addition throughout the reaction time. In contrast, conversions of 98.4% were achieved after 30 min with phosphate, 89.4% after 60 min with fluoride, and 74.5% after 60 min with sulfate. However, the selectivities to 5-HMF for these three anions were all lower than that without added salts and, in the presence of phosphate, no 5-HMF was detected.

Fig. 2 shows the effects of organic acid anions on the decomposition of glucose and selectivity for 5-HMF at 180 °C. Organic acid
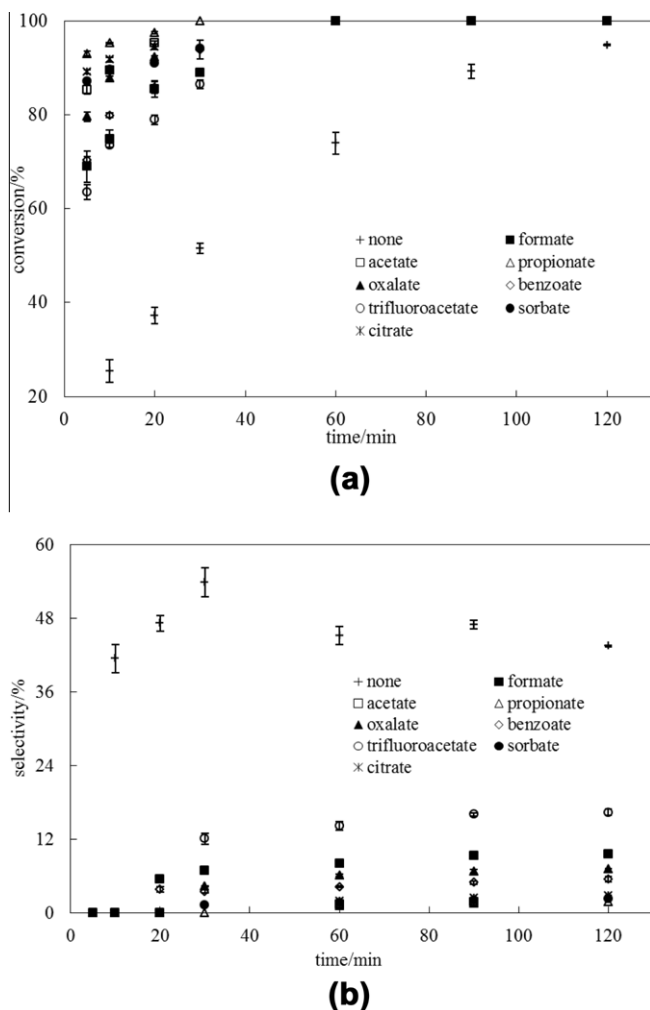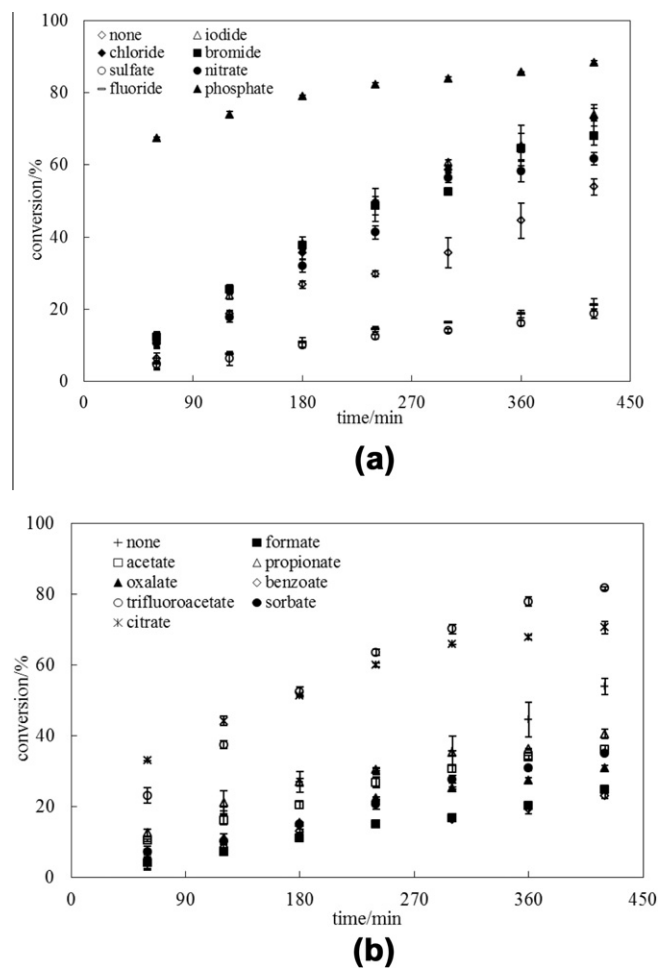
Fig. 4. Fructose conversions and selectivities for 5-HMF with organic acid anions based on 0.04 mol/L potassium concentration at 180 °C: (a) conversion of fructose; (b) selectivity for 5-HMF. The markers represent the average values as determined from four replicate experiments, and the error bars represent standard deviations from four replicate experiments.

Fig. 5. 5-HMF conversions with inorganic and organic acid anions based on 0.04 mol/L potassium concentration at 180 °C: (a) inorganic acid anion; (b) organic acid anion. The markers represent the average values as determined from four replicate experiments, and the error bars represent standard deviations from four replicate experiments.

anions were more effective than inorganic anions in catalyzing the decomposition of glucose. Trifluoroacetate had the worst catalytic ability among the organic anions, and the conversion was about 79% at 30 min, but this conversion was still higher than that with most inorganic acid anions. However, the selectivities for 5-HMF with organic acid anions were much lower than those without salt or with most inorganic salts. With oxalate, no 5-HMF was detected. These results indicate that the organic anions tend to significantly catalyze the decomposition of glucose to yield products other than 5-HMF.

3.2. Effect of anions on hydrothermal decomposition of fructose

Fig. 3 shows the effects of inorganic anions on the decomposition of fructose and selectivity for 5-HMF at 180 °C. Chloride, bromide, iodide and nitrate slightly accelerated the decomposition rate of fructose and improved the selectivity for 5-HMF, a result which is different from that seen with glucose. Phosphate, fluoride and sulfate had a strong catalytic effect on the decomposition of fructose, but the selectivity for 5-HMF was lower than that without added salts.

Fig. 4 shows the effects of organic anions on the decomposition of fructose and selectivity for 5-HMF at 180 °C. Similar to the effect on the decomposition of glucose, a much higher conversion of fructose and much lower selectivity for 5-HMF with organic anions than without the addition of salts or the addition of most inorganic anions were observed.

Glucose and fructose can isomerize. Under hydrothermal conditions, the glucose-to-fructose transformation is preferred, and 5-HMF is formed with higher selectivity from fructose than glucose due to its instable ring structure (Kabyemela et al., 1999). Although the reaction mechanisms for the decomposition of glucose and fructose are different, the effect of anions on the decomposition of glucose and fructose seems to be very similar.

3.3. Effect of anions on the stability of 5-HMF

5-HMF tends to decompose to small molecules such as levulinic acid and formic acid (Girisuta et al., 2006), or condense to soluble polymers and insoluble humins (Chheda et al., 2007). As shown in Fig. 5a, the conversion rates of 5-HMF with chloride, bromide, iodide, nitrate and phosphate were faster than that without added anions. In contrast, fluoride and sulfate were not effective in the decomposition of 5-HMF. However, the selectivities for 5-HMF with fluoride and sulfate from glucose or fructose were lower than that without added salts (Figs. 1b and 3b), which indicates that

Table 1
Rate constants of glucose, fructose and 5-HMF decomposition with inorganic and organic anions.

	Anion	Glucose/$\times 10^{-3}$ min^{-1}	Fructose/$\times 10^{-3}$ min^{-1}	5-HMF/$\times 10^{-3}$ min^{-1}
Inorganic acid anion	None	2.35 ± 0.08	24.2 ± 1	1.80 ± 0.1
	Fluoride	9.23 ± 0.01	35.1 ± 0.3	0.524 ± 0.02
	Chloride	2.94 ± 0.2	33.1 ± 1	3.26 ± 0.1
	Bromide	2.99 ± 0.2	33.8 ± 1	2.86 ± 0.1
	Iodide	2.09 ± 0.09	34.8 ± 2	3.39 ± 0.1
	Nitrate	2.88 ± 0.1	28.9 ± 2	2.59 ± 0.2
	Sulfate	12.5 ± 0.2	34.7 ± 0.5	0.444 ± 0.02
	Phosphate	44.9 ± 6	230 ± 90	2.72 ± 0.2
Organic acid anion	Formate	35.2 ± 5	42.9 ± 4	0.652 ± 0.03
	Acetate	67.7 ± 10	78.7 ± 4	0.973 ± 0.05
	Propionate	39.8 ± 1	69.8 ± 3	1.01 ± 0.08
	Oxalate	29.6 ± 4	62.9 ± 10	0.889 ± 0.06
	Trifluoroacetate	17.4 ± 3	37.5 ± 4	4.08 ± 0.09
	Benzoate	28.1 ± 1	60.3 ± 7	0.555 ± 0.04
	Citrate	38.0 ± 3	45.0 ± 4	2.34 ± 0.2
	Sorbate	22.3 ± 2	29.7 ± 4	1.04 ± 0.05

fluoride and sulfate anions might effectively catalyze reactions of glucose and fructose to yield other products.

As shown in Fig. 5b, except trifluoroacetate and citrate, organic anions such as formate, acetate, oxalate, sorbate and benzoate provided lower conversion rates of 5-HMF than that without additive, which reveals that these anions may play a role in stabilizing 5-HMF. However, the selectivities for 5-HMF from glucose or fructose with these organic anions were much lower than that without additive (Figs. 2b and 4b), indicating these organic acid anions tend to catalyze glucose and fructose to yield other products.

3.4. Impact factor of decomposition rate constant

The results of fitting the data from each experiment to a pseudo-first-order equation to obtain the conversion rate constants of glucose, fructose and 5-HMF are shown in Table 1. Division of these rate constants by the constant obtained with samples without added anions, provided an impact factor to compare the catalytic activity of different anions for the decomposition of glucose, fructose and 5-HMF (Fig. 6). The bigger the impact factor, the stronger the effect of anion. Except for chloride, bromide, iodide and nitrate, the anions catalyzed the decomposition of glucose (Fig. 6a) more efficiently than the decomposition of fructose (Fig. 6b) and 5-HMF (Fig. 6c). For example, the impact factor of glucose with formate was 14.9, much bigger than 1.8 from fructose and 0.4 from 5-HMF. In contrast, chloride, bromide, iodide and nitrate anions were the most conducive to the decomposition of 5-HMF, since the impact factor of 1.8 with chloride and 5-HMF was higher than 1.4 from fructose and 1.3 from glucose. The impact factors of glucose decomposition with inorganic acid anions (excluding phosphate) were in the range of 0.9–5.3. In contrast, the impact factors of glucose decomposition with organic anions were in the range of 7.4–28.8. Similar to the decomposition of glucose, the impact factors of fructose with inorganic anions (excluding phosphate: 1.2–1.5) were smaller than those with organic anions (excluding sorbate: 1.5–3.3). It suggests that organic acid anions have a greater impact on the decomposition of glucose and fructose than inorganic acid anions (excluding phosphate).

3.5. The relationship between impact factor of rate constant and physical properties

The evaluated anions showed huge differences in catalytic activity for the hydrothermal decomposition of glucose, fructose and 5-HMF, which may be caused by the physical properties such as dielectric constant, pK_b, and steric effect.

For a reaction with a transition state more polar than the reactants, an increase in solvent polarity increases the governing rate constant (Torry et al., 1992), which can be quantified through a Kirkwood analysis (Moore and Pearson, 1981), based on the dielectric constant as a measurement of polarity,

$$\ln K_H = \ln K_O + \text{const. } (\varepsilon - 1)/\varepsilon \tag{1}$$

where K_H and K_O are the rate constants with and without catalyst, respectively, ε is the dielectric constant. The rate constant increases as the dielectric constant grows (ε). Dielectric constant (ε) is estimated by Uematsu and Franck formalism (Uematsu and Franck, 1980),

$$\varepsilon = 1 + 0.00348\rho + 0.0000317\rho^2 - 1.41 \times 10^{-9}\rho^3 - 6.64 \times 10^{-12}\rho^4 \tag{2}$$

where ρ is the solution density. Under a critical salt concentration, the addition of salts is regarded as an increase in the polarity of the solution, and equivalent to that of pure water at the "effective density" (Huppert et al., 1989), which suggests that the addition of salts increases the effective density, and then increases the dielectric constant which leads to bigger rate constants. The decomposition of glucose or fructose is via a hydronium-ion-catalyzed mechanism (Asghari and Yoshida, 2006; Girisuta et al., 2006), regarded as a polar nucleophilic mechanism. Thus, most added salts, such as chloride and bromide can enhance the rate constant of glucose or fructose hydrothermal decomposition.

As shown in Fig. 6a, an impact factor of 19.1 from glucose was achieved when 2.83 g/L potassium phosphate (based on 0.04 mol/L potassium concentration) was added. However, the addition of potassium nitrate (4.04 g/L loading) led to an impact factor of 1.22 from glucose, which was much smaller than the impact factor with potassium phosphate. This finding is not consistent with the results derived from the Kirkwood and Uematsu and Franck formalisms. Therefore, other physical properties also might affect the catalytic activity of anion, such as pK_b of anion. The pK_b of anion at 180 °C can be calculated by the van't Hoff equation (Atkins and de Paula, 2006):

$$d\ln K/dT = \Delta H^\theta/RT^2 \tag{3}$$

where K is the ionization constant of the anion, T is the absolute temperature, $\triangle H^\Theta$ is the enthalpy change of ionization equilibrium of anion, R is the gas constant. The Eq. (3) can be solved to Eq. (4),

$$\ln K_2 = \Delta H^\theta/R(1/T_1 - 1/T_2) + \ln K_1 \tag{4}$$

K_1 and K_2 are the ionization constants of the anion at the temperatures of T_1 and T_2, respectively. To obtain the pK_b at 180 °C, the pK_b at room temperature and the $\triangle H^\Theta$ of anion ionization equilibrium
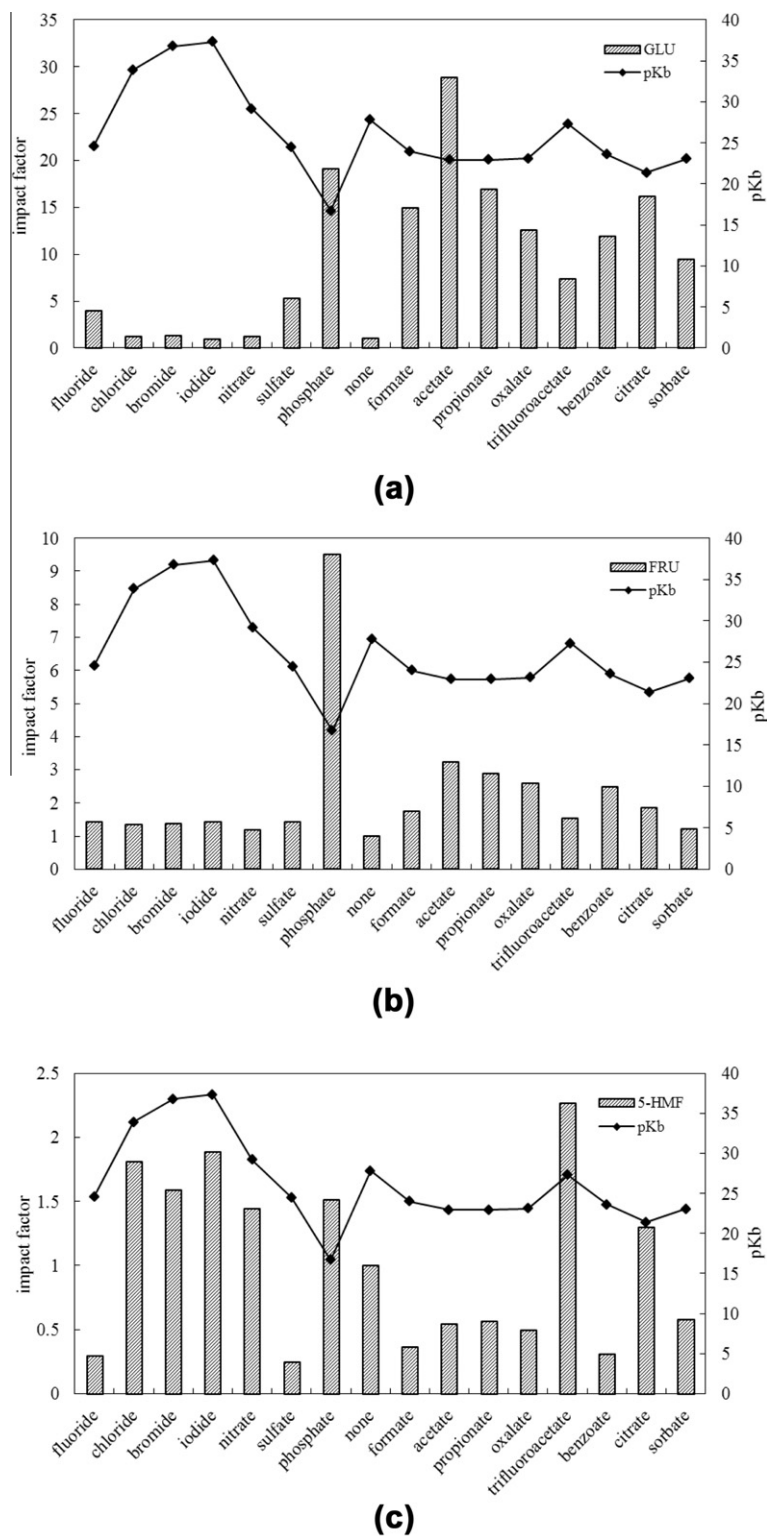
Fig. 6. Relationship between impact factor of the rate constant and pK_b with anions for the conversion of (a) glucose, (b) fructose, and (c) 5-HMF.

are needed. The pK_b values of anion at 25 °C were obtained in Lange's Handbook of Chemistry (Dean, 1998). The $\triangle H^{\Theta}$ was calculated by the standard enthalpies of products subtracted by the standard enthalpies of reactants (Dean, 1998) in the equilibrium equations of each anion. With these data, the pK_b value of the anion at 180 °C was calculated, and the relationship between the impact factor and the pK_b value of the anion are shown in Fig. 6. Anions,

whose pK_b values were below 28, such as organic acids, phosphate and sulfate, facilitated the decomposition of glucose and fructose (Fig. 6a and b). Moreover, anions with a smaller pK_b are more basic and have a much stronger catalytic effect on the decomposition. For example, in Fig. 6a, phosphate with a pK_b of 16.7 gave an impact factor of 19.1 from glucose, which was larger than those with formate (pK_b: 24, impact factor: 14.9) and sulfate (pK_b: 24.5, impact

factor: 5.3), but the selectivity for the dehydration product 5-HMF was lower than that with anions which had larger pK_b values (Fig. 1a and b). This finding suggests that more basic reaction media tend to catalyze the decomposition of carbohydrates to other products or condensation to polymer and humins. In contrast, anions with pK_b values larger than 28, such as chloride and bromide anions, tend to catalyze the decomposition of 5-HMF (Fig. 6c).

A huge difference in the impact factors among some anions with similar pK_b values was observed, indicating that other physical properties such as steric effect of the anions affected the catalytic activity. For instance, acetate (pK_b: 23), propionate (22.9) and sorbate (pK_b: 23) had similar pK_b values, but the impact factors with acetate (28.8) and propionate (16.9) from glucose were much larger than that with sorbate (9.5), which is probably caused by the weaker steric effect of acetate and propionate than sorbate. Tyrlik et al. (1996) reported that all –OH groups of hexose were hydrogen bonded to anions such as sulfate with oxygen as an electron donor, which is helpful to catalyze the decomposition of hexose, but lowers reaction selectivity. It also might affect the decomposition of glucose and fructose.

4. Conclusions

Chloride, bromide, iodide and nitrate anions do not significantly accelerate the hydrothermal decomposition rate of glucose or improve the selectivity for 5-HMF, but slightly accelerate the rate of fructose decomposition and improve the selectivity for 5-HMF. Phosphate, fluoride, sulfate and all organic acid anions drastically accelerate the decomposition rate of glucose, but lower the selectivity for 5-HMF. Organic acid anions have a greater impact on the decomposition of glucose and fructose than inorganic anions. The effect of anions on the decomposition rate of glucose is more significant than those on fructose and 5-HMF. Physical properties, such as effective density, pK_b, and steric effect, also impact the decomposition of glucose and fructose. These results provide insights on the reactivity and mechanism of the hydrothermal decomposition of glucose and fructose with inorganic and organic salts, and product distributions with these salts are needed, to further demonstrate the mechanism.

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