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Hydrothermal conversion of xylose, glucose, and cellulose under the catalysis of transition metal sulfates

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ABSTRACT

Hydrothermal conversion (HTC) is an important thermochemical process to upgrade low-cost biomass into valuable chemicals or fuels. As compared with non-catalytic HTC, catalytic HTC shows high energy efficiency on biomass upgradation. In this work, the catalytic performances of various transition metal sulfates (Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) in the HTCs of xylose, glucose, and cellulose under different conditions were explored. Among these catalysts, Zn^{2+} and Ni^{2+} showed obvious effects on the conversions of xylose, glucose, and cellulose into lactic acid, while Cu^{2+} and Fe^{3+}, which could significantly accelerate the hydrolysis of cellulose into glucose at 200 °C, displayed high efficiency on converting glucose and cellulose into levulinic acid and formic acid at high temperature. Additionally, significant positive correlative relationships among xylose, glucose, and cellulose degradations were observed. This study is helpful for screening appropriate catalysts for biomass upgradation through catalytic HTC of monosaccharide.

1. Introduction

For decades, excessive consumption of fossil fuels has caused serious energy and environment issues. As the most abundant, green, and renewable resource in the world, biomass is considered as an important alternative to fossil fuels for providing fuels and various chemicals. Several technologies, such as direct combustion, pyrolysis, hydrolysis, and hydrothermal conversion (HTC), have been developed to upgrade biomass into valuable fuels or chemicals. Among these methods, HTC is a promising approach because of its applicability for wet biomass, lower temperature than pyrolysis, and high energy efficiency (Möller, Nilges, Harnisch, & Schröder, 2011; Tekin, Karagöz, & Bektaş, 2012).

To better understand the conversion of biomass under hydrothermal conditions, HTCs of monosaccharides, cellulose, and hemicelluloses have been extensively explored (Kabyemela, Adschiri, Malaluan, & Arai, 1999; Knežević, van Swaaij, & Kersten, 2009; Tekin & Karagoez, 2013). It was proposed that the key reactions involved in the HTCs of cellulose and hemicelluloses might include hydrolysis, dehydration, isomerization, retro-aldol condensation, and so on (Chheda, Huber, & Dumesic, 2007; Sasaki et al., 1998; Srokol et al., 2004). During the HTC process, cellulose and hemicelluloses are initially hydrolyzed into oligosaccharides and monosaccharides (Sasaki, Hayakawa, Arai, & Adschiri, 2003). These oligosaccharides and monosaccharides can be further degraded into small molecule compounds, such as 5-hydroxymethyl furfural (HMF), lactic acid (LaA), levulinic acid (LeA), furfural (FF), formic acid (FA), and acetic acid (AA) (Pińkowska, Wolak, & Złocińska, 2011; Sasaki et al., 1998). Some degradation products can form humic materials at elevated temperature via condensation and resinification reactions, resulting in low yields of desired products (Patil, Heltzel, & Lund, 2012). Generally, there are mainly two degradation directions during the HTC of monosaccharides, especially glucose and xylose. One is dehydration to form FF or HMF. The other is retro-aldol condensation to release glycolaldehyde, glyceraldehyde, dihydroxyacetone, and their further degradation products. Under non-catalytic hydrothermal conditions, because the two reactions have similar activation barrier (about 101–141 kJ/mol) (Choudhary, Pinar, Sandler, Vlachos, & Lobo, 2011; Jing & Lü, 2007; Sasaki et al., 2003), various kinds of hydrothermal products with relatively low yields are generally observed in the non-catalytic hydrothermal liquid of biomass (Kabyemela et al., 1999; Kruse & Gawlik, 2002). The high

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dispersion and low yields of these non-catalytic hydrothermal products could cause many problems in following separation and utilization of these products.

Catalysts can increase the rate of chemical reactions and change the reaction selectivity by reducing the activation barrier of specific pathway. Catalytic HTC processes have been applied to convert biomass into desired chemicals with high efficiency. It was reported that acid could catalyze the dehydrations of cellulose, hemicelluloses, and their monosaccharides to produce HMF or FF, while alkali could catalyze the retro-aldol condensations of cellulose, hemicelluloses, and their monosaccharides to produce glycolaldehyde, glyceraldehyde, dihydroxyacetone, and their further degradation products (Esposito & Antonietti, 2013; Srokol et al., 2004; Yin & Tan, 2012). Additionally, many literatures reported that glucose and/or cellulose could be converted into important chemicals, such as furans, acids, and polyols, with high yield under the catalysis of metal salts (Ding et al., 2012; Peng et al., 2010; Wang et al., 2013; Zhao, Holladay, Brown, & Zhang, 2007). Zhao et al. (2007) investigated the effects of various metal chlorides on converting glucose into HMF in ionic liquids. Among these metal chlorides, $CrCl_2$ was found to be significantly effective, and about 70% of glucose could be converted into HMF at 80 °C for 3 h by using 6 mol% of $CrCl_2$ as a catalyst. Peng et al. (2010) studied the effects of various metal chlorides on the conversion of cellulose into LeA under hydrothermal conditions, and found that $CrCl_3$ showed the highest efficiency on converting cellulose into LeA and 67 mol% of cellulose could be converted into LeA at 200 °C for 3 h. Wang et al. (2013) investigated the effects of various metal ions on converting cellulose into LaA in hydrothermal conditions. Among these metal ions, Pb^{2+} displayed high efficiency on converting cellulose into LaA, and an outstanding yield (about 68%) was achieved in the presence of Pb^{2+} (7 mmol/mL) at 190 °C for 4 h. Therefore, different metal salts display different catalytic performances in the HTC of biomass. Screening suitable catalysts are very important for upgrading biomass into high value-added products with high energy efficiency and atom economy. However, the screening of catalysts directly using compact biomass macromolecules is ineffective and time-consuming because of their low HTC rates. Exploring the degradation correlations between monosaccharide and polysaccharide during HTC process is helpful to screen appropriate catalysts for biomass upgradation.

The objective of this study is to examine the catalytic performances of various transition metal sulfates (Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) in the HTCs of xylose, glucose, and cellulose under different temperatures. Furthermore, the hydrothermal degradation products of xylose, glucose, and cellulose were compared for investigating their degradation correlative relationships. This work will be helpful for further studies on screening appropriate catalysts for the HTC of biomass.

2. Material and methods

2.1. Materials

D-Xylose (>99%), D-glucose (>99.5%), and cellulose powder (particle size 90 μm) used were purchased from Aladdin-Reagent. Transition metal sulfates, $MnSO_4{\cdot}H_2O$, $FeSO_4{\cdot}7H_2O$, $Fe_2(SO_4)_3$, $CoSO_4{\cdot}7H_2O$, $NiSO_4{\cdot}6H_2O$, $CuSO_4{\cdot}5H_2O$, and $ZnSO_4{\cdot}7H_2O$, were all of analytical grade and purchased from Aladdin-Reagent.

2.2. Methods

The hydrothermal process was conducted in a batch reactor made of 316L stainless steel (50 mL capacity, 35 mm i.d.). After xylose or glucose (1.0 g) was dispersed in distilled water (50 mL) containing transition metal sulfate (10 mmol/L), the mixture was magnetically stirred at 500 rpm. The reactor was purged with nitrogen for five times to remove the inside air. The reactor was first heated up to 160 °C and hold at this temperature for 10 min. Then, hydrothermal liquid (about 1 mL) was collected online. Next, the reactor was successively heated up to 180, 200, 220, and finally 240 °C (holding at each temperature for 10 min), and the hydrothermal liquid (about 1 mL) was collected at each temperature. Since cellulose powder was insoluble in water, the HTC of cellulose was performed in batch mode. Cellulose powder (1.0 g) was dispersed in distilled water (50 mL) containing transition metal sulfate (10 mmol/L) with magnetically stirred at 500 rpm. The reactor was purged with nitrogen for five times to remove the inside air. Then, the mixture was heated up to 200 °C or 240 °C and maintained at this temperature for 30 min. Upon completion of the reaction, the reactor was cooled down first by fan and then immersed into cold water to room temperature. The hydrothermal liquid was filtrated with a 0.22 μm filter and further analyzed with High Performance Liquid Chromatography (HPLC).

Glucose (Glu), xylose (Xyl), lactic acid (LaA), formic acid (FA), acetic acid (AA), levulinic acid (LeA), 5-hydroxymethyl furfural (HMF) and furfural (FF) concentrations in the filtrates were quantified by HPLC (Aminex HPX-87H column) with refractive index detection. 0.005 M sulfuric acid was used as mobile phase at a flow rate of 0.6 mL/min. The column temperature and detector temperature were maintained at 60 °C and 50 °C, respectively.

The conversion rates of xylose and glucose and the formation selectivity of hydrothermal products were calculated according to the following equations:

$$\text{Conversion rate } (\%) = \frac{C_{\text{initial}} - C_{\text{residual}}}{C_{\text{initial}}} \times 100\% \quad (1)$$

$$\text{Selectivity } (\%) = \frac{C_{\text{product}}}{C_{\text{initial}} - C_{\text{residual}}} \times 100\% \quad (2)$$

where C_{initial} is the initial concentration of xylose or glucose (20 mg/mL), C_{residual} is the residual concentration of xylose or glucose, C_{product} is the concentration of hydrothermal product, such as LaA, FF, FA, LeA, AA, and HMF.

2.3. Statistical analysis

All statistical analysis was performed using the SPSS 20.0 statistical software program. Pearson correlation coefficients (R) were calculated to determine the correlative relationships between xylose, glucose, and cellulose degradation under both catalytic and non-catalytic hydrothermal conditions. A probability value of $P < 0.05$ was considered statistically significant (two-tailed).

3. Results and discussion

3.1. Hydrothermal conversion of xylose under various transition metal sulfates catalysis

The concentrations of xylose and hydrothermal products under the catalysis of various transition metal sulfates as a function of hydrothermal temperature are plotted in Fig. 1. The initial concentration of xylose was 20 mg/mL for both catalytic and non-catalytic HTC processes. As can be seen in Fig. 1a, the concentration of xylose gradually decreased with the increase of hydrothermal temperature. However, in the presences of catalysts, the concentrations of xylose were lower than those of non-catalyst (NC), suggesting that these transition metal sulfates could accelerate the conversion of xylose to varying degrees. The conversion rates of xylose and the formation selectivity of hydrothermal products are shown in Supplementary Table S1. Comparing with the low conversion rate of xylose in non-catalytic HTC (8.23% at 160 °C, 15.68% at 180 °C,

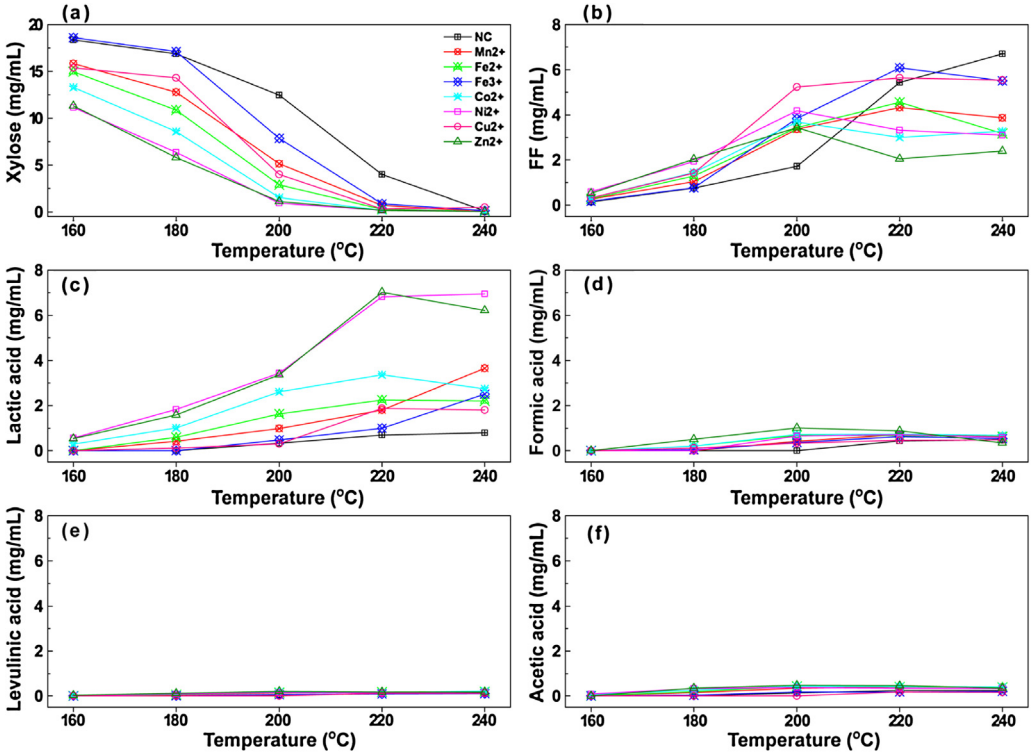

Fig. 1. The concentrations of (a) xylose, (b) FF, (c) LaA, (d) FA, (e) LeA, and (f) AA under the catalysis of various transition metal sulfates as a function of hydrothermal temperature.

and 37.73% at 200 °C), the conversion rates of xylose in catalytic HTC reached 6.94–52.48% at 160 °C, 14.4–71.11% at 180 °C, and 60.87–95.44% at 200 °C, respectively. Among these catalysts, Zn^{2+} and Ni^{2+} had significant promoting effect on xylose conversion, and about 43–52% of xylose was converted into other compounds at 160 °C. As the temperature further increased from 200 °C to 220 °C, above 95% of xylose was degraded in the presences of transition metal sulfates. Meanwhile, the conversion rate of xylose in non-catalytic HTC increased dramatically from less than 40% to above 80%, indicating that a rapid degradation of xylose occurred at 220 °C.

The concentrations of the hydrothermal degradation products of xylose, such as FF, LaA, FA, LeA, and AA, in the presences of catalysts as a function of hydrothermal temperature are shown in Fig. 1b–f. The concentrations of these degradation products are all plotted on the same coordinate scale to facilitate comparison. As can be seen, FF was the major degradation product of xylose in non-catalytic HTCs, while besides FF, high concentrations of LaA were also observed in the hydrothermal liquids of xylose in catalytic HTCs. Most transition metal sulfates could result in high concentration of FF at relatively low hydrothermal temperatures (160–200 °C). As the hydrothermal temperature increased from 200 °C to 220 °C, the concentration of FF increased dramatically under the catalysis of Cu^{2+} and Fe^{3+}. Except Cu^{2+} and Fe^{3+}, the concentrations of FF under the catalysis of other transition metal sulfates were lower than that in non-catalytic HTC at 220 °C. The highest concentration of FF obtained under non-catalytic HTC was observed at 240 °C, while the highest concentrations of FF obtained in the presences of catalysts were observed at 200 °C or 220 °C. It implied that a high concentration of FF could be achieved at relatively low hydrothermal temperature in the presences of transition metal sulfates.

Very low concentration (0.0–0.8 mg/mL) of LaA was found in the non-catalytic hydrothermal products of xylose. The addition of transition metal sulfates during the HTC process could significantly increase LaA concentration in the hydrothermal liquid of xylose. As can be seen in Fig. 1c, Zn^{2+} and Ni^{2+} displayed obvious promoting effect on converting xylose into LaA. The highest concentration of LaA obtained under the catalysis of Zn^{2+} and Ni^{2+} were 7.0 and 6.9 mg/mL, respectively, which were comparative to the highest concentration of FF (6.7 mg/mL). Other degradation compounds, like FA, LeA, and AA, were observed in the hydrothermal liquid with very low concentrations. The highest concentration of FA, LeA, and AA was 0.93, 0.22, and 0.40 mg/mL, respectively. Overall, these transition metal sulfates, especially Zn^{2+} and Ni^{2+}, showed obvious promoting effect on converting xylose into LaA.

The main degradation pathway of xylose in the HTC process is shown in Fig. 2. Xylose can be decomposed into many compounds, such as FF, LaA, FA, and AA. Many literatures reported that the direct dehydration of xylose into furfural was likely the most preferred pathway under non-catalytic hydrothermal conditions, which had a low activation barrier (about 101–119 kJ/mol) (Aida, Shiraishi, Kubo, Watanabe, & Smith, 2010; Choudhary et al., 2011; Jing & Lü, 2007). Meanwhile, xylose dissociation into glycolaldehyde, dihydroxyacetone, and glyceraldehyde through retro-aldol reaction was also probably the dominant reaction in non-catalytic HTC process, which also showed a low activation barrier (about 102–141 kJ/mol) (Aida et al., 2010; Sasaki et al., 2003). Both glyceraldehyde and dihydroxyacetone can further dehydrate into pyruvaldehyde, which is a crucial intermediate for producing LaA, FA, and AA. Pyruvaldehyde can convert into LaA by means of benzilic rearrangement (Srokol et al., 2004). FA and AA are likely formed through the α-dicarbonyl cleavage of pyruvaldehyde (Srokol et al., 2004). A possible pathway for producing LeA from xylose and FF has also been proposed (Bui, Luo, Gunther, & Román-Leshkov, 2013; Chamnankid, Ratanatawanate, & Faungnawakij, 2014). FF can be converted into furfuryl alcohol through a transfer-hydrogenation by using alcohols as hydrogen donors, and subsequently transformed into LeA via hydrolytic ring opening reaction. As shown in Supplementary Table S1, the addition of transition metal sulfates

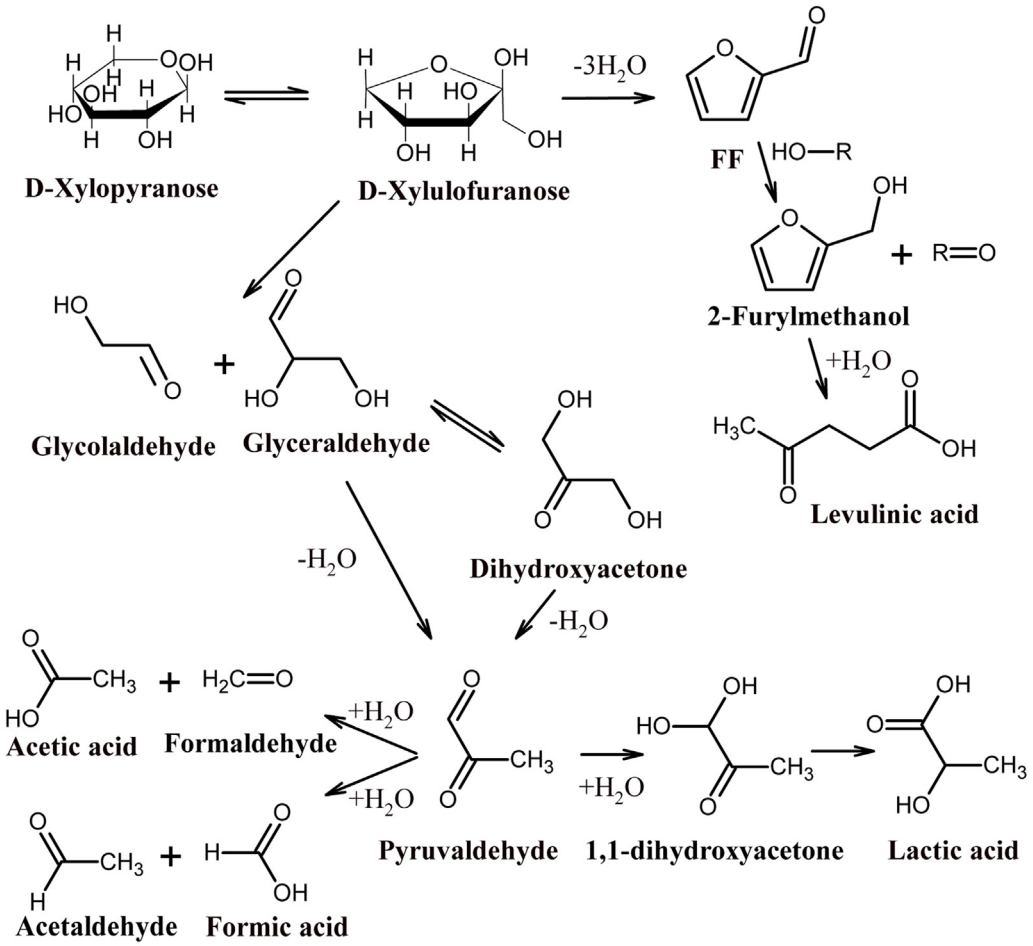

Fig. 2. The main degradation pathway of xylose in the HTC process.

could effectively increase the formation selectivity of LaA (especially Zn^{2+} and Ni^{2+}) as compared with the non-catalytic HTC. It suggested that these transition metal sulfates could reduce the activation barrier of xylose to LaA to varying degrees and further change the selectivity of xylose conversion.

3.2. Hydrothermal conversion of glucose under various transition metal sulfates catalysis

The concentrations of glucose and hydrothermal products under various transition metal sulfates catalysis as a function of hydrothermal temperature are plotted in Fig. 3. Because of the similar polyol structure of glucose and xylose, the degradation of glucose was similar to that of xylose. As can be seen in Fig. 3a, the concentration of glucose gradually decreased with the increase of hydrothermal temperature. In most cases, the concentrations of glucose under the catalysis of transition metal sulfates were lower than those of NC, suggesting that these transition metal sulfates could also accelerate the conversion of glucose to varying degrees. The conversion rates of glucose and the formation selectivity of hydrothermal products were calculated and shown in Supplementary Table S2. Comparing with the low conversion rate of glucose under non-catalytic conditions (9.85% at 160 °C, 12.20% at 180 °C, 30.90% at 200 °C, and 52.79% at 220 °C), the conversion rates of glucose under the catalysis of transition metal sulfates could reach 7.40–31.47% at 160 °C, 16.68–50.08% at 180 °C, 36.89–88.32% at 200 °C, and 85.68–99.41% at 220 °C, respectively. Among these metal sulfates, Zn^{2+} and Ni^{2+} showed significant promoting effect on accelerating glucose conversion at a relatively low hydrothermal temperature, while Fe^{3+} and Cu^{2+} showed less effect on accelerating glucose conversion, which was in line with the results from the HTC of xylose. However, for both catalytic and non-catalytic HTC processes, the concentration of glucose was higher than that of xylose at the same hydrothermal condition, indicating that the hydrothermal stability of glucose was higher than that of xylose to some degree. As the temperature further increased from 220 to 240 °C, above 97% of glucose was converted into other components in the presences of catalysts, while the conversion rate of non-catalytic HTC of glucose increased dramatically from about 53% to above 92%, indicating that rapid degradation of glucose occurred at 240 °C.

The concentrations of the degradation products of glucose (HMF, LaA, FA, LeA, and AA) under the catalysis of different transition metal sulfates as a function of hydrothermal temperature are shown in Fig. 3b–f. The concentrations of these degradation products are all plotted on the same coordinate scale to facilitate comparison. As can be seen, HMF was the major degradation product of non-catalytic HTC, while HMF and LaA were the major degradation products of catalytic HTC. For HMF, a relatively high concentration of HMF was observed in the hydrothermal liquid of catalytic HTC at 160–200 °C as compared with that in non-catalytic HTC, while the concentration of HMF dramatically decreased as the hydrothermal temperature further increased from 220 °C to 240 °C in the presences of catalysts. Additionally, the concentration of HMF started to decrease at 220 °C in the presence of Cu^{2+}. The decreased concentration of HMF at high temperatures under the catalysis of transition metal ions was likely related to the further degradation or condensation of HMF.

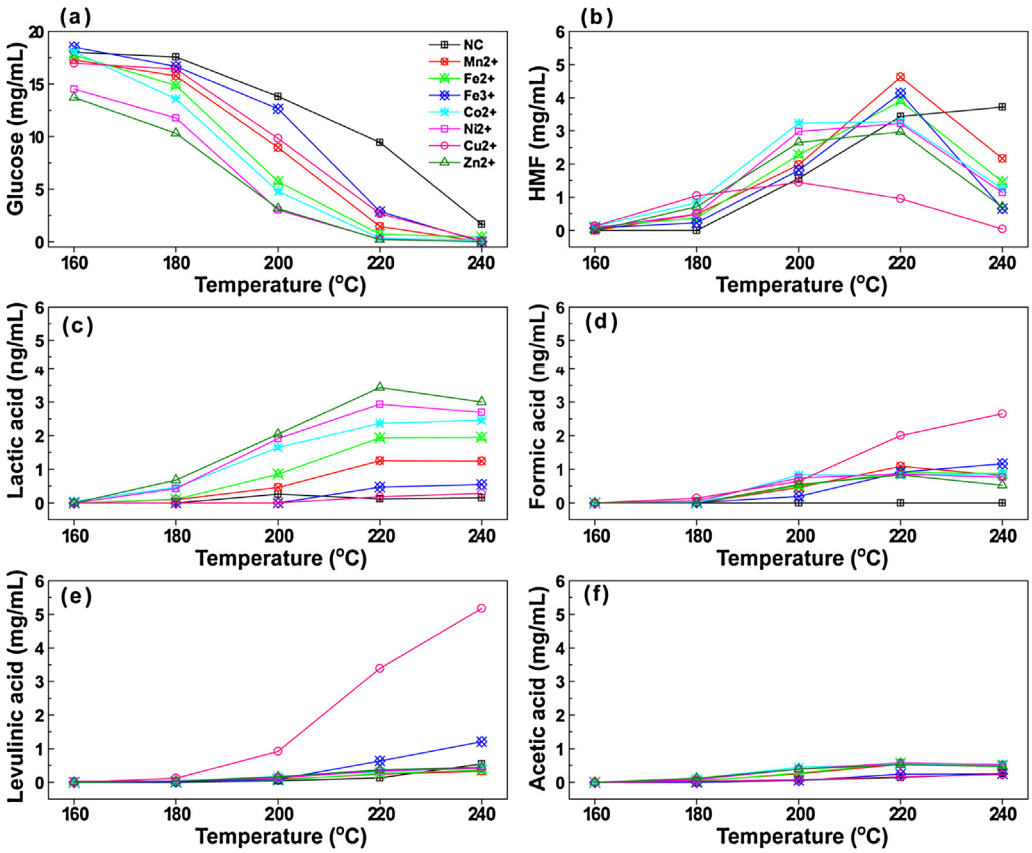

Fig. 3. The concentrations of (a) glucose, (b) HMF, (c) LaA, (d) FA, (e) LeA, and (f) AA under the catalysis of various transition metal sulfates as a function of hydrothermal temperature.

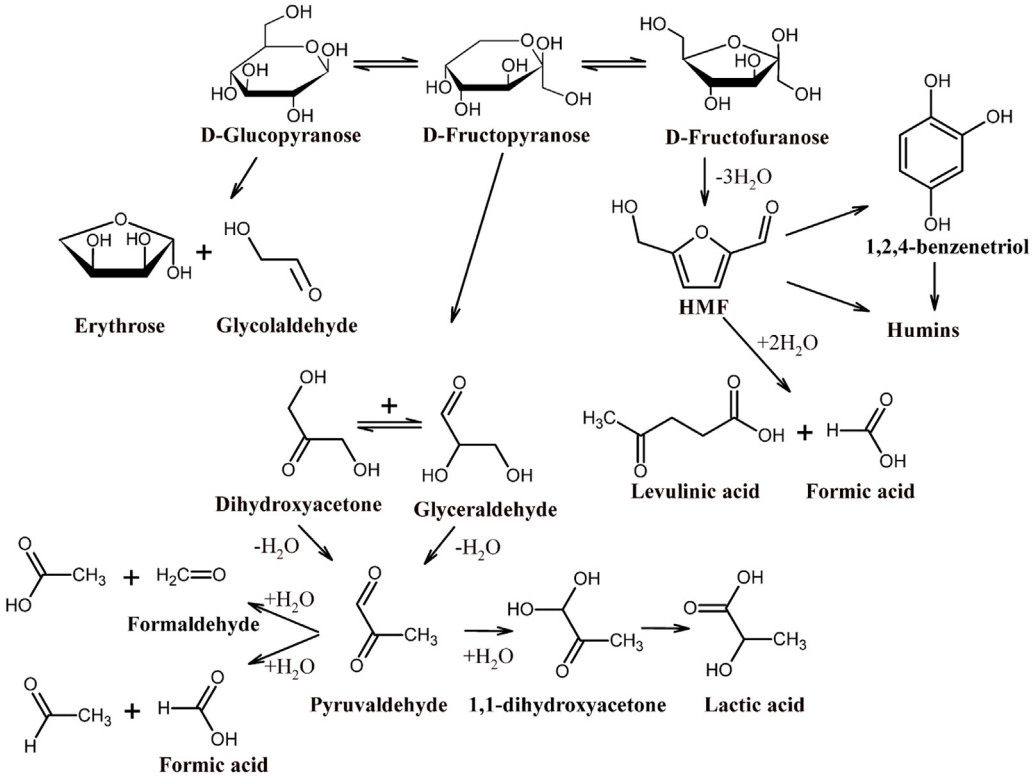

Fig. 4. The main degradation pathway of glucose in the HTC process.

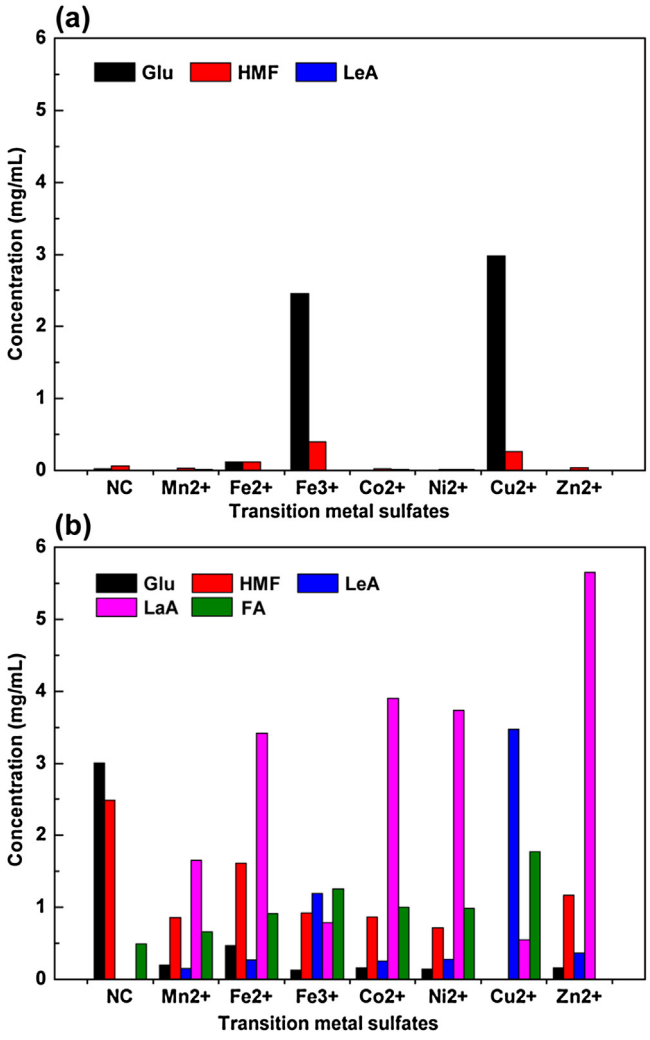

Fig. 5. The concentrations of the hydrothermal degradation products of cellulose under the catalysis of various transition metal sulfates: (a) at 200 °C for 30 min and (b) at 240 °C for 30 min.

Most transition metal sulfates led to higher LaA concentration as compared with the non-catalytic HTC process. Among these catalysts, Zn^{2+} and Ni^{2+}, which displayed higher catalytic activities on converting xylose into LaA, also showed obvious effect on converting glucose into LaA. As can be seen in Fig. 3d–e, high concentrations of LeA and FA were found in the hydrothermal liquids of Cu^{2+} and Fe^{3+} catalyzed HTCs at high temperatures, indicating that Cu^{2+} and Fe^{3+} had high catalytic activities on converting glucose into LeA and FA, instead of catalyzing glucose into LaA or HMF. Low concentrations of FA and LeA were observed in the hydrothermal liquids of other metal sulfates catalyzed and non-catalyzed HTCs. Additionally, low concentration of AA was found in all HTCs of glucose. Overall, most transition metal sulfates displayed similar catalytic performances in the HTC of glucose as compared with catalytic HTC of xylose, except that Cu^{2+} and Fe^{3+} showed high efficiency on converting glucose into LeA and FA at high temperature.

The main degradation pathway of glucose in the HTC process is shown in Fig. 4. As can be seen in Fig. 4, glucose can isomerize into fructose and then dehydrates into HMF, which can be further decomposed into LeA and FA by hydration and benzilic rearrangement (Horvat, Klaić, Metelko, & Šunjić, 1985), or 1,2,4-benzenetriol via hydrolysis, rearrangement and dehydration (Luijkx, van Rantwijk, & van Bekkum, 1993; Sasaki et al., 1998). Furthermore, HMF and 1,2,4-benzenetriol can condense or polymerize into humins, resulting in the formation of hydrochar (Sevilla & Fuertes, 2009). The direct dehydration of glucose into HMF is likely the most preferred pathway in non-catalytic process because of the high concentration of HMF detected in the hydrothermal liquid. Meanwhile, glucose can be dissociated into dihydroxyacetone and glyceraldehyde through retro-aldol reaction, which can further dehydrate into pyruvaldehyde as a crucial intermediate for LaA, FA, and AA (Wang et al., 2013). Overall, these transition metal sulfates could change the HTC selectivity of glucose and showed obvious promoting effect on converting glucose into LaA or LeA and FA (Supplementary Table S2). Among these catalysts, Zn^{2+} and Ni^{2+} showed obvious effect on converting glucose into LaA. Cu^{2+} and Fe^{3+} showed high efficiency on converting glucose into LeA and FA at high temperature.

3.3. Hydrothermal conversion of cellulose under various transition metal sulfates catalysis

Unlike glucose, the degradation of cellulose is based on the hydrolysis of cellulose into glucose (Sasaki et al., 1998). Because of the polymeric and semicrystalline structure of cellulose, it is resistant to hydrolysis. Therefore, the degradation of cellulose is likely to lag behind that of glucose. The concentrations of the hydrothermal degradation products of cellulose under the catalysis of various transition metal sulfates at 200 °C and 240 °C for 30 min are plotted in Fig. 5. As can be seen in Fig. 5a, very low concentrations of hydrothermal products were found in most hydrothermal liquids. However, high concentrations of glucose (2.5–3.0 mg/mL) were observed in the hydrothermal liquids under the catalysis of Cu^{2+} and Fe^{3+}, suggesting that Cu^{2+} and Fe^{3+} had high activities on promoting the hydrolysis of cellulose into glucose. Furthermore, the concentration of HMF from the HTC of cellulose under the catalysis of Cu^{2+} and Fe^{3+} was in the order of $Fe^{3+} > Cu^{2+}$, which was in line with the results obtained from the HTC of glucose at 200 °C. Since very low concentration of glucose was observed in other transition metal sulfates catalyzed and non-catalyzed HTC processes, further degradation of cellulose was impeded at 200 °C.

As the hydrothermal temperature increased to 240 °C, lots of degradation products were detected as shown in Fig. 5b. High concentrations of glucose and HMF were found in the non-catalytic hydrothermal liquids of cellulose. It implied that large amounts of cellulose could be hydrolyzed into glucose and further dehydrated into HMF even without the assistance of catalyst. However, relatively low concentrations of glucose and HMF were observed in the catalytic hydrothermal liquids. It was agreed with the high conversion rates of glucose in the presences of catalysts (Fig. 3a) and low HMF concentrations observed in these catalytic hydrothermal liquids of glucose at 240 °C (Fig. 3b). In the presences of catalysts, except Cu^{2+} and Fe^{3+}, high concentrations of LaA were observed in most hydrothermal liquids of cellulose. The concentration of LaA observed in the hydrothermal liquid of cellulose was in the order of $Zn^{2+} > Co^{2+} > Ni^{2+} > Fe^{2+} > Mn^{2+} > Fe^{3+} > Cu^{2+} >$ NC, which was agree with the results obtained from the HTC of glucose at 240 °C ($Zn^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Fe^{3+} > Cu^{2+} >$ NC). Furthermore, Zn^{2+} and Ni^{2+} also showed the highest efficiency on converting xylose into LaA as compared with the low concentration of LaA observed under the catalysis of Cu^{2+} and Fe^{3+}. Additionally, at 240 °C, high concentrations of LeA and FA were observed in the hydrothermal liquids of cellulose under Cu^{2+} and Fe^{3+} catalysis, which was in line with the high concentrations of LeA and FA observed in the hydrothermal liquids of glucose under the catalysis of Cu^{2+} and Fe^{3+}.

Overall, these transition metal sulfates showed similar catalytic performance in catalyzing the HTCs of xylose, glucose, and cellulose. Zn^{2+} and Ni^{2+} showed obvious effect on converting biomass into LaA. Cu^{2+} and Fe^{3+} displayed relatively

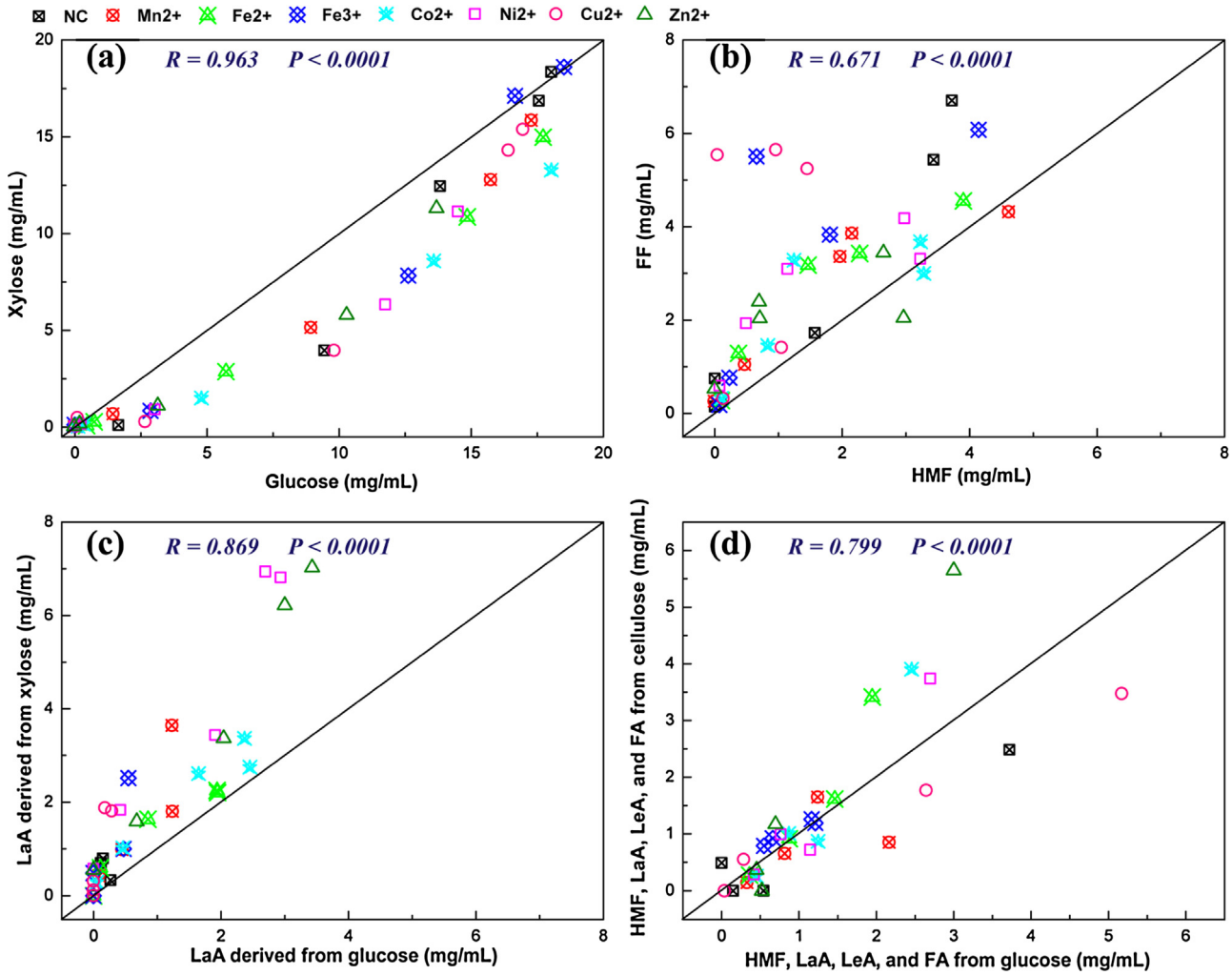

Fig. 6. Correlative relationships among xylose, glucose, and cellulose degradations: (a) the residual concentration of xylose versus that of glucose; (b) the concentration of FF versus that of HMF; (c) the concentration of LaA derived from xylose versus that derived from glucose at different hydrothermal temperatures under both catalytic and non-catalytic HTC processes; and (d) the concentrations of cellulose degradation products (HMF, LeA, LaA, and FA) versus those of glucose degradation products at 240 °C under both catalytic and non-catalytic hydrothermal conditions.

high efficiency on converting glucose and cellulose into LeA and FA at high temperature. Furthermore, Cu^{2+} and Fe^{3+} showed high activities on accelerating the hydrolysis of cellulose into glucose at 200 °C.

3.4. Correlations among xylose, glucose, and cellulose degradation

Because of the similar polyol structure of xylose and glucose, the correlation between xylose and glucose degradations under catalytic and non-catalytic HTC conditions was investigated. The residual concentration of xylose versus that of glucose, the concentration of FF versus that of HMF, and the concentration of LaA derived from xylose versus that derived from glucose at different hydrothermal temperatures under both catalytic and non-catalytic HTC processes are plotted and illustrated in Fig. 6. If these points are all located on the diagonal line, it means that the conversion of xylose and formations of FF and LaA are totally uniform with the conversion of glucose and formations of HMF and LaA. As shown in Fig. 6a, most points were arrayed close to but slightly below the diagonal, indicating that the degradation of glucose was slower than that of xylose. Pearson correlation coefficient (R) of Fig. 6a was calculated to determine the correlative relationships between xylose and glucose degradations under both catalytic and non-catalytic HTC conditions. A significant positive correlative relationship between xylose and glucose degradations was observed ($R = 0.963$, $P < 0.0001$). Pearson correlation coefficients of Fig. 6b–c were also calculated to determine the correlative relationships between FF and HMF formations and between LaA from xylose and LaA from glucose under both catalytic and non-catalytic hydrothermal conditions. Significant positive correlations between FF and HMF formations ($R = 0.671$, $P < 0.0001$) and between LaA from xylose and LaA from glucose ($R = 0.869$, $P < 0.0001$) were also observed. Results suggested that a strong correlation was existed between xylose and glucose HTCs.

Since the HTC of cellulose is based on the hydrolysis of cellulose into glucose, the hydrothermal products of cellulose are likely to show some correlation to the hydrothermal products of glucose. The concentrations of cellulose degradation products (HMF, LeA, LaA, and FA) versus those of glucose degradation products at 240 °C under both catalytic and non-catalytic conditions are plotted and illustrated in Fig. 6d. Result showed that a significant positive correlation between cellulose and glucose degradations was observed ($R = 0.799$, $P < 0.0001$), indicating that the formations of HMF, LeA, LaA, and FA during the HTC of cellulose were significantly correlative to the formations of HMF, LeA, LaA, and FA during the HTC of glucose.

4. Conclusions

In this work, the catalytic performances of various transition metal sulfates (Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) in the HTCs of xylose, glucose, and cellulose under different hydrothermal conditions were explored. Most transition metal sulfates could accelerate the degradations of xylose and glucose into LaA to varying degrees and promote the formation of FF or HMF at low temperatures. Among these catalysts, Zn^{2+} and Ni^{2+} showed high efficiency on converting xylose, glucose, and cellulose into LaA, while Cu^{2+} and Fe^{3+} displayed high efficiency on converting glucose and cellulose into LeA and FA at high temperatures. Furthermore, Cu^{2+} and Fe^{3+} also showed high activities on accelerating the hydrolysis of cellulose into glucose at 200 °C. Additionally, significant positive correlative relationships between xylose, glucose, and cellulose degradations were observed in both catalytic and non-catalytic conditions. This work is beneficial to the catalysts screening for biomass upgradation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.10.069.

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