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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:

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

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

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,