One-pot chemo-enzymatic conversion of *D*-xylose to furfuralcohol by sequential dehydration with oxalic acid plus tin-based solid acid and bioreduction with whole-cells
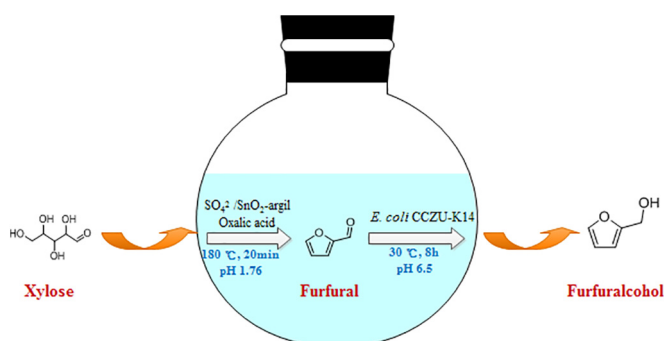
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In this study, organic acid could be used as co-catalyst for assisting solid acid SO_4^{2-}/SnO_2-argil to convert hemicellulose-derived *D*-xylose into furfural. The relationship between pKa of organic acid and turnover frequency (TOF) of co-catalysis with organic acid plus SO_4^{2-}/SnO_2-argil was explored on the conversion of *D*-xylose to furfural. Oxalic acid (pKa = 1.25) (0.35 wt%) was found to be the optimum co-catalyst for assisting SO_4^{2-}/SnO_2-argil (3.6 wt%) to synthesize furfural from *D*-xylose (20 g/L) at 180 °C for 20 min, and the furfural yield and TOF could be obtained at 57.07% and 6.26 h^{-1}, respectively. Finally, the obtained furfural (107.6 mM) could be completely biotransformed to furfuralcohol by recombinant *Escherichia coli* CCZU-K14 whole-cells at 30 °C and pH 6.5 in the presence of 1.5 mol glucose/mol furfural and 400 mM *D*-xylose. Clearly, this strategy shows high potential application for the effective synthesis of furfuralcohol from biomass-derived *D*-xylose.

1. Introduction

Furfuralcohol (FOL) is known as an important industrial chemical, which has been widely used for the production of such as vitamin C, lysine, plasticizer, adhesives, cements, fiber glass, furan resins, lubricant, polymer concrete, etc. (Halilu et al., 2016; He et al., 2017a). Currently, FOL is mainly produced via the catalytic hydrogenation of furfural (FAL) in the gas phase or in the liquid phase (Audemar et al.,

2015; He et al., 2017c). Different types of catalysts have been used for the reduction of FAL to FOL. Co/SBA-15 at 150 °C and 20 bar of H_2 for 1.5 h and Cu/Fe at 160 °C and 90 bar of H_2 for 5 h gave the FOL yield at over 80% (Audemar et al., 2015). 100% FAL conversion and 86.4% FOL yield were achieved from 20 g/L FAL with 18% Cu-2% Pd/Al_2O_3 at 190 °C for 3 h in near-critical isopropanol (Ruan et al., 2017). Using 0.2 g Pt (2%)-Re (1%)/TiO_2-ZrO_2 (1:1) catalyst, 1.5 mL FAL could be completely transformed to FOL with the selectivity of 95.7% at 130 °C under 5 MPa for 8 h (Xu et al., 2013). The characteristics of their high pressure and/or noble metals associated with high-energy consumption have limited their use to some extent.

In recent years, biocatalytic synthesis of FOL from FAL is gaining great attention due to its highly selective reactions, energy-saving operation and environmentally friendly process (Di et al., 2018; Li et al., 2017a; Xue et al., 2018). Some bacteria can convert or degrade FAL (Abdulrashid and Clark, 1987; Dong et al., 2018; Koenig and Andreesen, 1989). *Saccharomyces* spp., *Escherichia coli, Pseudomonas putida S12* and *Meyerozyma guilliermondii* have been successfully applied to the reduction of FAL into FOL (Almeida et al., 2008; He et al., 2017a; Koopman et al., 2010; Li et al., 2017a). FOL was obtained from the bioreduction of 50 mM FAL at 83% yield by *Meyerozyma guilliermondii* SC1103 at 35 °C and pH 7.2 (Li et al., 2017a). He et al. (2017b) reported 100% FOL yield for bioreduction of FAL was achieved in the toluene-water (1:3, v:v) media with *E. coli* CCZU-T15 cells at 30 °C and pH 6.5. 200 mM FAL was completely transformed by *E. coli* CCZU-K14 whole cells at 30 °C and pH 6.5 after 24 h (He et al., 2017a). Clearly, it is feasible to employ whole-cells for the catalytic reduction of FAL to FOL.

D-Xylose is the main pentose generated by the hydrolysis of hemicellulose in lignocellulosic biomass, which is one of inexpensive starting materials for FAL production through the thermo-chemical process (Campos Molina et al., 2012; Chheda et al., 2007; García-Sancho et al., 2014; Guo et al., 2018; Serrano-Ruiz et al., 2012; Wang et al., 2014). Solid acid catalysts with the good thermal and chemical stabilities have been implemented in the FAL production process (Li et al., 2014, 2015; Zhang et al., 2013; Zhang et al., 2017, 2018). Using mesoporous Nb_2O_5 as solid acid catalyst, *D*-xylose conversion and a FAL yield were higher than 90% and 50% at 170 °C for 1.5 h, respectively (García-Sancho et al., 2014). With the carbon solid acid catalyst, the conversion of *D*-xylose and corn stalk into FAL were accomplished in γ-valerolactone, which resulted in the yield of 79% at 170 °C for 30 min and a 61% FAL yield from corn stalk in 100 min at 200 °C (Zhang et al., 2016). Using SO_4^{2-}/SnO_2-montmorillonite (3.0 wt% loading) as catalyst, a highest FAL yield of 41.9% was achieved from *D*-xylose at 170 °C for 20 min. Similarly, the highest FAL yield of 44% was achieved from corncob-derived *D*-xylose with 3.6 wt% SO_4^{2-}/SnO_2-attapulgite at 170 °C for 20 min. In addition, corncob-derived *D*-xylose (19.8 g/L) could be converted to FAL at 60.1% yield with solid acid catalyst SO_4^{2-}/SnO_2-attapulgite (3.6 wt% catalyst loading) in the water-toluene (3:1, v/v) media at 170 °C for 20 min (He et al., 2017a,c; Xue et al., 2018).

Recently, various homogeneous Brönsted acids including formic acid, oxalic acid, acetic acid, HCl, and H_2SO_4, have been used as a catalyst for converting *D*-xylose to FAL (Lamminpää et al., 2015; Rong et al., 2012; Yang et al., 2012, 2013; Zhang et al., 2014). Formic acid (HCOOH, 10 g/L) could convert 40 g/L *D*-xylose to FAL in the yield of 74% at 180 °C (Yang et al., 2012). Under the microwave-assisted condition at 180 °C for 20 min, HCl, H_2SO_4, and HCOOH could give the FAL yields at 37.5%, 31.9%, and 23.8%, respectively (Yemis and Mazza, 2011). However, high loading of Brönsted acids were used in these cases. Compared with inorganic acids, organic acids have relatively low corrositivity. It deserves the challenge to employ dilute organic acids for the converting *D*-xylose into FAL.

In this study, a newly prepared solid acid SO_4^{2-}/SnO_2-argil was attempted to synthesize FAL in the presence of dilute organic acid. Furthermore, chemo-enzymatic synthesis of FOL from *D*-xylose via the tandem catalysis with dilute organic acid-assisted solid acid SO_4^{2-}/

SnO_2-argil catalyst and recombinant *E. coli* CCZU-K14 whole-cells were conducted in one-pot system. Moreover, effects of various parameters (e.g., organic acid types, organic acid dosage, SO_4^{2-}/SnO_2-argil loading, reaction temperature, reaction time, and substrate *D*-xylose concentration) on the FAL production were investigated. In addition, various bioreduction reaction parameters (e.g., reaction pH, reaction temperature, and substrate FAL loading, etc.) were optimized for converting FAL to FOL using the whole cell of recombinant *E. coli* CCZU-K14. Finally, an effective strategy for FOL production was successfully demonstrated in this study.

2. Materials and methods

2.1. Materials

Argil was purchased from Zhanteng mineral processing factory (Hebei, P.R. China). $SnCl_4$·$5H_2O$, oxalic acid, maleic acid, fumaric acid, citric acid, glyoxylic acid, *DL*-malic acid, formic acid, succinic acid, acetic acid, propionic acid, *D*-xylose, *L*-aspartic acid, *D*-aspartic acid, *L*-glutamine, *D*-glutamine, *L*-ribose, *D*-ribose, NAD^+, glycine, glucose, FAL and other chemicals were purchased from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, P.R. China).

2.2. Preparation of solid acid SO_4^{2-}/SnO_2-argil catalyst

After the mixture containing 1.4 g $SnCl_4$ and 4.2 g argil in 100 mL ethanol solution was stirred at 30 °C under atmospheric pressure to form the homogeneous liquid phase. The SO_4^{2-}/SnO_2-argil solid catalyst was prepared as the previous operation procedure (He et al., 2017a).

2.3. Chemical conversion of D-xylose to FAL with SO_4^{2-}/SnO_2-argil in the presence of various organic acids

To test the effects of organic acid on the catalytic activity of SO_4^{2-}/SnO_2-argil, various organic acids (e.g., acetic acid, citric acid, formic acid, fumaric acid, glyoxylic acid, maleic acid, *D,L*-malic acid, oxalic acid, propionic acid, succinic acid) (0.35 wt%) and SO_4^{2-}/SnO_2-argil (3.6 wt%) were added to 40 mL single aqueous phase system containing *D*-xylose (20 g/L) in a sealed stainless steel reactor (Zhenjiang Dantu Universal Electrical Equipment Co., P.R. China) (500 rpm), respectively. The dehydration reactions of *D*-xylose to FAL were carried out at 180 °C for 20 min. To investigate the effects of oxalic acid concentration on the dehydration of *D*-xylose to FAL, *D*-xylose (20 g/L) was mixed with SO_4^{2-}/SnO_2-argil (3.6 wt%) and oxalic acid (0.1–0.7 wt%) in the sealed stainless steel reactor (500 rpm) in 40 mL deionized water at 180 °C for 20 min. To investigate the effects of SO_4^{2-}/SnO_2-argil loading, reaction temperatures and time on the dehydration of *D*-xylose to FAL, *D*-xylose (20 g/L) was mixed with SO_4^{2-}/SnO_2-argil (0.6–6.0 wt%) and oxalic acid (0.35 wt%) in the sealed stainless steel reactor (500 rpm) in 40 mL deionized water, and this dehydration of *D*-xylose was conducted at 150–190 °C for 10–40 min in a 100-mL sealed stainless steel reactor. To investigate the effects of substrate *D*-xylose concentration on the dehydration of *D*-xylose to FAL, *D*-xylose (10–300 g/L) was mixed with SO_4^{2-}/SnO_2-argil (3.6 wt%) and oxalic acid (0.35 wt%) in the sealed stainless steel reactor (500 rpm) in 40 mL deionized water at 180 °C for 20 min. The FAL yield, FAL selectivity, and *D*-xylose conversion were calculated as follows:

$$FAL\ yield\ (\%) = \frac{FAL\ produced\ (g)}{Initial\ D{-}xylose\ in\ hydrolysate\ (g)} \times \frac{150}{96} \times 100$$

$$FAL\ selectivity\ (\%) = \frac{FAL\ produced\ (g)}{D{-}Xylose\ consumed\ (g)} \times \frac{150}{96} \times 100$$