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“One-pot” conversions of carbohydrates to 5-hydroxymethylfurfural using Sn-ceramic powder and hydrochloric acid

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ABSTRACT

5-Hydroxymethylfurfural (HMF), converted from sustainable biomass resources, is a versatile intermediate in chemical industry. A kind of ceramic powder containing Sn^{4+} ions (Sn-CP) with good hardness was synthesized by a rapid method for the isomerization of glucose. HCl was introduced for catalysing the fructose-to-HMF reaction and promoting the isomerization reaction. Production of HMF from glucose catalysed by Sn-CP/HCl demonstrated high HMF yield (63.9%) and effective catalyst recyclability (HMF yield > 53.7%). Moreover, when fructose and poly-saccharides (sucrose, inulin, starch and maltose) as feedstocks, HMF yields of more than 55% were obtained. Hence integration of catalytic reaction and conversion of carbohydrates to HMF provided a green process over inexpensive catalyst.

1. Introduction

The production of substitutes for petroleum-derived chemicals from biomass is currently regarded as the most interesting processes due to its environmental and strategic advantages. Among current processes, 5-hydroxymethylfurfural (HMF) converted from renewable carbohydrates is considered to be a green one and has attracted much scientific interests. Many high value chemicals, such as alternative fuels, diesel fuel additives, industrial solvents and bio-derived polymers, could be produced via the conversion of HMF and its derivatives [1,2].

Many carbohydrates (such as cellulose, inulin, glucose, fructose, agarose and red-algae gracilaria verrucosa) were widely investigated [3–7]. Among these carbohydrates, fructose is the most suitable substrate in the direct conversion of carbohydrate into HMF. The HMF yield of 77% was achieved in acid-free and metal-free heterogeneous catalytic system using ethanol as the low boiling solvent [8]. When using sulfonated carbon sphere solid acid catalysts, high HMF yield of 90% was achieved in DMSO solvent at 160 °C after 1.5 h reaction time [9]. A HMF yield of 52% from inulin (composed of fructose) was obtained in ChCl/betaine hydrochloride/H_2O system [10]. Because glucose is produced by the photosynthesis of carbon dioxide and water, the glucose and glucose-based carbohydrate (cellulose) are the most widespread carbohydrates [11,12]. In order to break the cellulosic rigid structure, chemical methods, physicochemical methods and biological methods have been extensively researched [13,14]. Many research were focused on the conversion of glucose-to-fructose. Lee et al. studied the immobilized enzyme for the conversion of cellulose-to-glucose-to-fructose [15].

Currently, the research on the production of HMF from glucose is mainly focused on the ionic liquids (ILs) [16,17], Sn-BEA zeolite [18,19], catalyst containing Lewis and Brønsted acid sites [4,20], and chemo-enzymatic catalytic reaction [21–23]. Although ILs have low vapor pressure and could achieve high yields [24,25], the possible problems of deactivation by small amounts of water and high cost are need to be overcome [26,27]. High catalytic efficiency has been achieved by Sn-Beta/HCl catalyzed reaction in biphasic system [18,19], which showed the promising industrial application prospect. But the difficulty in synthesizing Sn-Beta, especially the long crystallization time of around 40 days, limits its application [28].

Besides the raw feedstock and catalyst, the reaction system was also investigated. As the catalyst and reaction solvent, ILs was investigated widely and could catalyze most of the sugars (such as cellulose, glucose and fructose) to HMF [29]. Dumesic and coworkers have developed a biphasic system (aqueous/organic phase) to enable the conversion of fructose to high-yield HMF, and achieved 80% HMF selectivity at 90% fructose conversion [30]. Because the organic solvent could extract the

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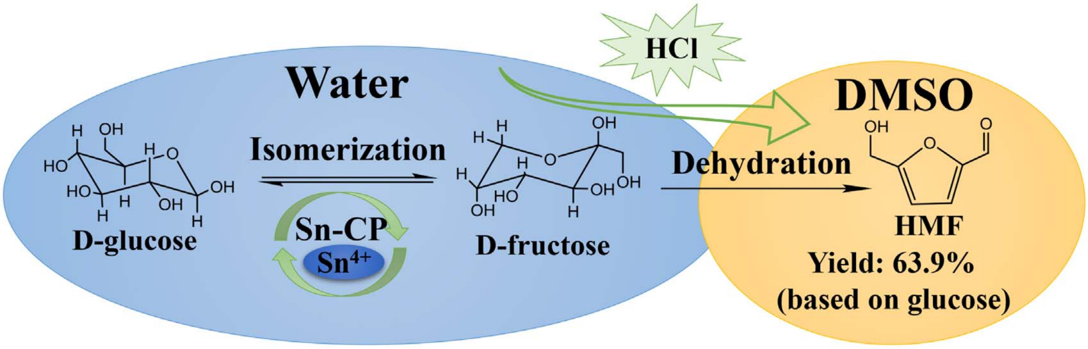

Scheme 1. Reaction system for HMF production from glucose.

HMF from the aqueous phase continuously, the side reactions in this reaction process were lessened. The production of HMF in single organic solvent was also investigated widely. Formic acid-catalysed dehydration of fructose in DMSO could suppress the side reaction and achieve a HMF yield of 99% [31]. Furthermore, via the extraction process (ethyl acetate), as high as 91% of DMSO could recover, and the HMF purity of 95% was achieved [32]. Therefore, as reaction solvent, the addition of DMSO provides a promising approach for the production of HMF.

In our previous work, a novel metal ceramic powder (MCP) with excellent hardness and abrasive resistance was synthesized as the carrier of amylase [33]. On this basis, a kind of ceramic powder containing Sn^{4+} ions (Sn-CP) was made for the glucose-to-fructose reaction. When acid catalyst (such as HCl) was added, the reaction was further toward to the generation of HMF. Herein, an efficient approach for the production of HMF from glucose catalysed by Sn-CP and HCl was obtained in H_2O/DMSO solvent system (Scheme 1). In this work, there are many advantages to be listed: (1) one-pot reaction system and shorter synthesis time of Sn-CP (less than 2 days), was benefit for the industrial application; (2) Sn-CP with good hardness and abrasive resistance, was convenient for the use and recycling; (3) isomerization reaction from glucose to fructose catalyzed by Sn-CP was stable and effective; (4) DMSO, a good co-solvent for the production of HMF; (5) poly-saccharides could catalyzed with high HMF yield.

2. Experimental

2.1. Materials

5-Hydroxymethylfurfural (HMF), glucose, fructose, sucrose, maltose, starch and levulinic acid (LA) were of reagent-grade (> 99%) and purchased from Sigma. Inulin (> 97%) was purchased from WEDA Company (China). All other chemicals were of analytical grade and used without purification, unless otherwise noted.

2.2. Catalyst preparation

$SnCl_4$ was dissolved in deionized water until saturation. Sufficient amount of NaOH was added into $SnCl_4$ solution slowly with vigorous stirring. Then, the obtained metal hydroxide precipitation was filtered and washed for 3 times with deionized water, and dried at 70 °C for 24 h. The Sn-CP was prepared by mixing 22 g of matrix (containing 10 g SiO_2, 5 g Al_2O_3, 5 g Na_2SiO_3, 1 g MgO, 1 g CaO), 10 g deionized water and metal hydroxide precipitation at a certain precipitation/matrix ratio (P/M ratio, w/w). The Sn-CP was obtained by drying at 150 °C in muffle for 2 h. Then Sn-CP was calcined at 850 °C for 4 h. Before use, the Sn-CP was washed with 5% H_2SO_4 solution for one time and washed with distilled water until pH near 7.0.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded on a D/max 2500 XRD spectrometer. The scan rate was 12°/min from 5° to 50° and Cu Kα X-ray source. The XPS spectra were collected using a PHI-5000 Versaprobe II equipped with a multichannel hemispherical analyser and aluminium anode X-ray source. The BET-N_2 adsorption experiment was measured at F-sorp 2400 (liquid nitrogen temperature).

2.4. Catalytic conversion of carbohydrates to HMF

The dehydration reactions were carried out in 25 mL steel sealed reactor with PTFE lining. The typical procedure was as follows: 1 g glucose was dissolved in mixture solution (4 mL aqueous solutions and 12 mL of 100% DMSO), and then 0.5 g Tin-ceramic powder and 60 uL of 37 wt% HCl (12 mol/L) were added, so the final concentration of HCl was 0.05 mol/L. This mixture solution was poured into the reactor. Then, the reactor was put into an oil bath with a magnetic stirrer at 170 °C for 4 h. After the reaction, the reactor was cooled to room temperature. The HMF product, glucose and fructose were analyzed and quantified by high performance liquid chromatography (HPLC). The quantities of other carbohydrates used in this study were also 1 g. The other reaction conditions were in accord with the typical procedure above, unless otherwise noted.

2.5. Analytical method

The compositions of mixture solution were analyzed by HPLC (refractive index detector) equipped with Bio-Rad Aminex HPX-87H column. The parameters of HPLC analysis were as follows: 0.6 mL/min of 0.005 mol/L (v/v) H_2SO_4 as the flow rate of eluent, column temperature of 65 °C, and injection volume of 20 μL.

The carbohydrates conversion, the HMF selectivity and yield were evaluated by Eqs. (1)–(3), respectively:

$$Conversion = \frac{[\text{Carbohydrates}] \times V - [\text{Carbohydrates}]' \times V}{[\text{Carbohydrates}] \times V} \quad (1)$$

$$Yield = \frac{[C] \times V}{[\text{Carbohydrates}] \times V} \times \frac{\mathrm{M_a}}{\mathrm{M_b}} \quad (2)$$

$$Selectivity = \frac{Yield}{Conversion} \quad (3)$$

where [Carbohydrates] was initial concentration of carbohydrates in solution; [Carbohydrates]' was the finial concentration of carbohydrates in solution; [*C*] was the finial concentration of HMF, fructose or LA, respectively. V was the volume of mixture solution; M_a was the molecular weight of glucose ; M_b was the molecular weight of HMF, fructose or LA, respectively. If the carbohydrates were poly-saccharides, the molecular weight would substract the corresponding molecular weight of H_2O.