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Biomass into chemicals: One-pot production of furan-based diols from carbohydrates via tandem reactions

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ABSTRACT

In this work, the direct production of furan-based diols from carbohydrates and their upstream raw materials via one-pot tandem reactions in ionic liquid/water system is presented. In this novel reaction system, ionic liquid serves as an advantageous solvent for polysaccharide (cellulose, inulin, sucrose) hydrolysis and hexose dehydration reactions, and heterogeneous Pd, Pt, Ir, Ni, Ru-based catalysts catalyze HMF hydrogenation reaction under relatively mild condition (50 °C, 6 MPa H_2) to afford moderate to high yield (34.0–89.3%) of furan-based diols, namely, 2,5-dihydroxymethylfuran (DHMF) and 2,5-dihydroxymethyltetrahydrofuran (DHMTF). Our results show that the metal species strongly affects the selectivity of the products, while the nature of the support influences the activity of the catalysts significantly. By selecting the proper metal species and the support, controllable production of DHMF or DHMTF was realized. Based on the intermediates identified and the conversion results, the proposed reaction pathway, including possible side reactions were presented. Taken together, our catalytic system featured with simple process, mild condition, high yield of diols and adjustable product selectivity. The direct conversion of the carbohydrates and the upstream materials drives our technology nearer to real application for cost-efficient production of chemicals from biomass.

1. Introduction

Biomass is renewable candidate that assumes the potential to serve as a sustainable feedstock *in lieu of* diminishing fossil resources, for future biofuels and chemicals [1]. With the increasing cost of fossil fuels and the concerns related to their environmental impact and greenhouse gas effect, extensive research and development programs have been initiated worldwide to convert biomass, such as forestry wastes, agricultural residues and energy crops, into valuable products [2–5].

Furan-based diols 2,5-dihydroxymethylfuran (DHMF) and 2,5-dihydroxymethyl-tetrahydrofuran (DHMTF) are bulk chemicals in the manufacture of polyesters and heat insulating material, which are currently produced predominantly from petroleum resource [6–8]. Theoretically, this kind of diols could be generated from hexoses and their upstream materials, such as oligosaccharides, inulin and cellulose, as well as the raw biomass via hydrolysis, dehydration and subsequently selective hydrogenation reactions (Scheme 1). However, each step in the whole process is typically complex and includes severe side reactions [1,7,9]. In addition, the low selectivity makes the separation and purification of the intermediate products a big problem. To improve the conversion efficiency, a great number of studies focus individually on polysaccharide (including cellulose) hydrolysis, hexoses dehydration and 5-hydroxymethylfurfural (HMF) hydrogenation reactions.

For instance, to make β-1,4-glycosidic bonds in cellulose more accessible to chemical transformation, ionic liquids (ILs) [10–12] that capable of dissolving cellulose, and robust solid acids [13–18] are applied in cellulose hydrolysis reaction and some good results are obtained. In the dehydration step, improved performances have also been made for both ketohexose (e.g. fructose) and aldohexose (e.g. glucose) conversion to afford 5-hydroxymethylfurfural (HMF) in homogeneous or heterogeneous systems including water, organic solvents, ILs [19,20], and two-phase solvents [21] with liquid acids, solid acids and metal chloride ($CrCl_2$, $CrCl_3$, $GeCl_4$, etc.)

Abbreviations: DHMF, 2,5-dihydroxymethylfuran; DHMTF, 2,5-dihydroxymethyltetrahydrofuran; ILs, ionic liquids; HMF, hydroxymethylfurfural; [BMIm]Cl, 1-butyl-3-methylimdazolium chloride; [EMIm]Cl, 1-ethyl-3-methylimdazolium chloride; HT, hydrotalcite.

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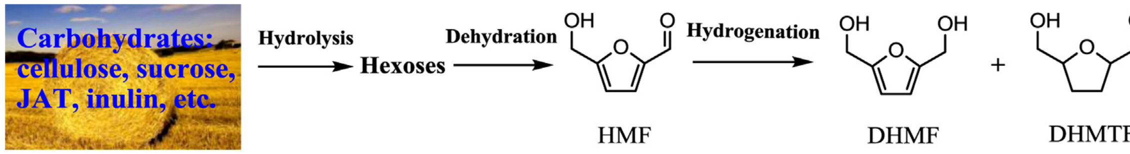

Scheme 1. Schematic illustration of the steps from biomass-derived carbohydrates to furan-based diols DHMF and DHMTF.

and other catalysts [22]. In addition, hydrogenation of HMF and furfural to valuable furan-based alcohols, such as DHMF [23], DHMTF [24,25] furfuryl alcohol, and tetrahydrofurfuryl alcohol [26] have been reported with various metallic catalysts. In despite of these progresses, mainly because of the low selectivity and incompatible reaction conditions of each step, few literature succeed in the direct conversion of carbohydrates and their upstream raw materials to produce furan-based diols. As a similar example, Bell's group [27] realized the two-step approach for the catalytic conversion of glucose to 2,5-dimethylfuran in ionic liquid/CH_3CN mixture. In their study, heteropoly acid 12-molybdophoric acid exhibited exceptionally activity for the dehydration of glucose to HMF, the extracted HMF then underwent hydrogenation reaction in 1-ethyl-3-methylimdazolium chloride [EMIm]Cl/CH_3CN mixture to obtain 2,5-dimethylfuran (DMF) with the yield of 15% [27].

In this work, direct production of furan-based diols DHMF and DHMTF from carbohydrates and their upstream materials via one-pot tandem reactions in IL/water system is presented. In this novel reaction system, IL serves as efficient medium for polysaccharide (cellulose, inulin) hydrolysis and hexose dehydration reactions, and heterogeneous Pd, Pt, Ir, Ni, Ru-based catalysts catalyze HMF hydrogenation reaction under relatively mild condition (50 °C, 6 MPa H_2) to afford moderate to high yield (34.0–89.3%) of furan-based diols. More importantly, after exploring the effects of the metal species and the supports on the products distribution, selectively production of DHMF or DHMTF from fructose is realized.

2. Experimental

2.1. Materials

Fructose (99%), inulin and microcrystalline cellulose (extra pure, average particle size 90 μm) were purchased from Acros Organics. Glucose (AR) was bought from Tianjin Kemiou Chemical Reagent Co., Ltd. All the other chemicals were obtained from local supplier and were used as received without further purification.

Supported transition-metal catalysts including Pd/C, Ir/C, Pt/C, Ru/C, Ni/C, Pd/Al_2O_3, Pd/SiO_2, Pd/TiO_2, and Pd/HT were prepared by means of incipient wet impregnation followed by reduction in H_2 at 300 °C. The nominal transition-meta loadings were 5 wt%.

1-butyl-3-methylimdazolium chloride ([BMIm]Cl) and [EMIm]Cl were prepared according to our previous study [11], the water content was determined as (0.0975 ± 0.0005)% and (0.1275 ± 0.0005)%, respectively, through Karl–Fischer titration.

2.2. Typical conversion process of fructose for the production of DHMF and DHMTF

A typical process for the catalytic production of furan-based diols is as follows: 0.18 g fructose and 0.5 g [BMIm]Cl was charged in an open autoclave and was heated to 130 °C for 20 min to afford HMF. About 20 mg samples were withdrawn, weighed, quenched with cold water, and subjected to HPLC analysis. 35 ml cool water and 50 mg metal catalyst were added to the residue reaction mixture. After the solution was mixed uniformly, the hydrogenation reaction was carried out with an initial H_2 pressure of 6 MPa (measured at room temperature) at 50 °C for set time. After the one-pot transformation, the reaction solution was filtered and the clear filtrate was analyzed by HPLC.

The HPLC analysis of the products was conducted on Agilent 1100 with a Shodex SC-101 column, using extra-pure water as mobile phase at a flow rate of 0.6 ml/min, the pressure of column was 28 bar, the column temperature was 45 °C. The yields of HMF was calculated by the equation: Yield (%) = (molar number of HMF)/(molar number of fructose) × 100. The conversion of HMF was calculated by the equation: Conversion (%) = (1 − (molar number of the left HMF)/(molar number of HMF from substrates)) × 100. The selectivity of DHMF or DHMTF were calculated by the equation: Selectivity (%) = (molar number of the product)/(molar number of converted HMF) × 100. Total selectivity of furan-based diols was calculated by the equation: Selectivity (%) = (Selectivity of DHMF) + (Selectivity of DHMTF). Total yields of furan-based diols were calculated by the equation: Total yield (%) = (Yield of HMF) × (Conversion of HMF) × (Total selectivity of furan-based diols) × 100.

3. Results and discussion

3.1. Optimization reaction conditons

3.1.1. Fructose dehydration in ionic liquids

As introduced above, the direct conversion of carbohydrate to DHMF and DHMTF includes several reaction steps. In order to couple the individual reactions, taking fructose as the substrate, we first explored the dehydration reaction to obtain HMF. In our previous study [20], we presented an efficient strategy for selective production of HMF from concentrated fructose in ILs under microwave irradiation without addition of catalysts. Considering that conventional oil-bath heating is simple and more available, in this study, we tried the catalyst-free dehydration reaction in IL [BMIm]Cl with oil-bath heating. The results are shown in Fig. 1. It was found that although fructose conversion was laggardly at low temperature of

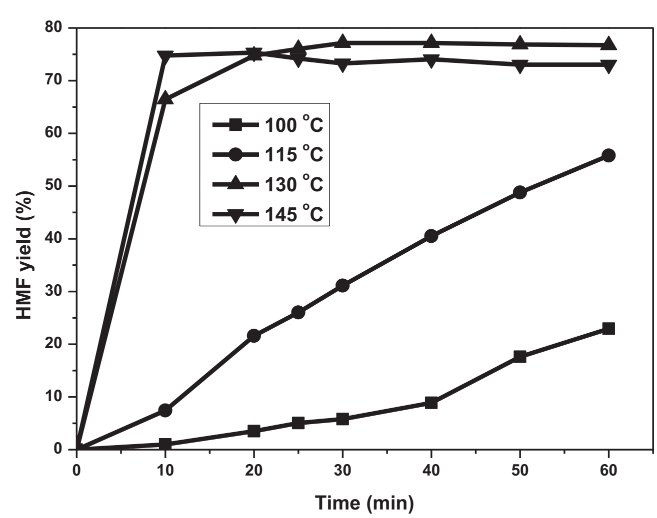

Fig. 1. Fructose dehydration results in [BMIm]Cl. Reaction condition: 0.7 g fructose, 2.0 g [BMIm]Cl, 130 °C.