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Tailored one-pot production of furan-based fuels from fructose in an ionic liquid biphasic solvent system

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ABSTRACT

The one-pot catalytic transformation of biomass to useful products is desirable for saving cost and time. The integration of the various reaction steps need to address the presence of incompatible reaction conditions and numerous side reactions. We report a novel process for the one-pot production of furan-based fuels, 2,5-dimethylfuran (DMF) and 2,5-dihmethyltetrahydrofuran (DMTF), from fructose by optimizing the synergic effect of an ionic liquid promoted Ru/C catalyst and the solvent effect. The dehydration of fructose and subsequent *in situ* hydrodeoxygenation of HMF to DMF and DMTF on Ru/C were enhanced by the use of an ionic liquid and a biphasic [BMIm]Cl/THF solvent. Elemental analysis, X-ray Photoelectron Spectroscopy, Raman spectroscopy and H_2-temperature programmed reduction–mass spectroscopy characterization showed that the ionic liquid modified the electronic density of the Ru species to favor HMF *in situ* hydrodeoxygenation. Moreover, THF served as a reaction-extraction solvent that extracted DMF and DMTF from the reaction layer to avoid further side reactions. A rational design that gave enhancement of the catalytic performance and product protection provides a promising strategy for the one-pot conversion of biomass to desired fuels.

1. Introduction

With the increasing depletion of fossil fuels and the concerns over their environmental impact and greenhouse gas effect, the development of renewable energy resources becomes more urgent. Biomass is the only renewable organic carbon source in nature, which endows it with unique advantages in producing fuels and industrially important chemicals [1–4]. Among the various valuable compounds derived from biomass, 2,5-dimethylfuran (DMF) and 2,5-dimethyltetrahydrofuran (DMTF) have received particularly attention because they are good biofuel candidates and important intermediates in the chemical industry. As a fuel replacement, DMF has an ideal boiling point (92–94 °C), high energy density (30 kJ/cm^{-3}), and high research octane number (RON = 119) [5]. It is also an intermediate for making *p*-xylene, one of the highest volume bulk chemical presently derived from petroleum [6,7]. DMTF is the extensively reduced product of DMF. It has a high-

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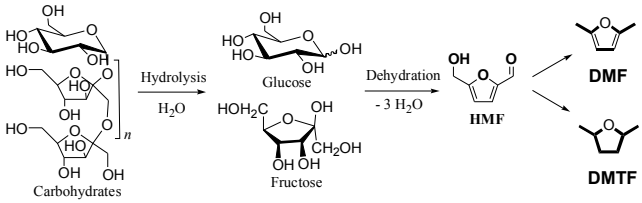
er energy content than DMF and has better stability during storage because of its saturated furan ring structure [5]. DMTF can also serve as a substitute for tetrahydrofuran (THF) in the chemical industry [8].

In principle, DMF and DMTF can be generated from carbohydrates via hydrolysis, dehydration and subsequently selective hydrogenation reactions (Scheme 1). Currently, most studies are focused on the hydrodeoxygenation of 5-hydroxymethylfurfural (HMF) to produce DMF and DMTF [9, 10]. However, HMF is a versatile compound with many important applications, thus using cheap and abundant biomass derived carbohydrate instead of the more expensive HMF as the substrate for the production of these two products is more cost effective and preferable.

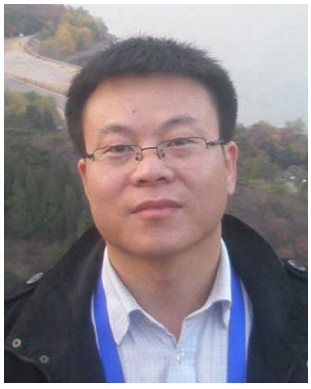
As an example of starting from carbohydrates, Dumesic's group [5] pioneered a biphasic two-step process for the conversion of fructose into DMF. In this study, fructose was first dehydrated to HMF in an aqueous/organic system over an acid catalyst. The purified HMF was subsequently converted to DMF via liquid- or vapour phase hydrodeoxygenation reaction over CuRu/C. The highest overall yield of 50% was obtained directly from carbohydrates in a relatively complicated reaction system with the use of a number of additives. Subsequently, Chidambaram et al. [11] and Binder et al. [12] used glucose and corn stover as substrates for the production of DMF via two- or multi-step approaches. Both studies obtained fairly good yields of the intermediate HMF. Unfortunately, in the hydrodeoxygenation step, due to the influence of unfavorable impurities, the overall yields of DMF were only 15% and 9%, respectively, in the above two cases.



Scheme 1. Reaction route for the conversion of biomass to furan-based fuels DMF and DMTF.

One-pot catalysis is a powerful strategy in green chemistry. Combining multi-step transformations in one-pot cascade catalysis would provide advantages over conventional processes with stepwise reactions, mainly by reducing the time used and yield losses during the isolation and purification of the reaction products. In the catalytic transformation of carbohydrates to DMF and DMTF, due to the incompatible reaction conditions of each step and the numerous side reactions, it is a challenge to perform a one-pot conversion process [13]. Therefore, in the above three examples, the isolation of the intermediate HMF was a prerequisite for the subsequent hydrodeoxygenation reaction.

Sen et al. [14] recently provided an elegant example of the one-pot conversion of carbohydrates to DMTF. In their experi-



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