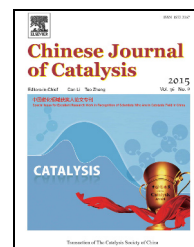


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Article (Special Issue for Excellent Research Work in Recognition of Scientists Who Are in Catalysis Field in China)

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-dimethyltetrahydrofuran (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 H₂-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.

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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/cm³), 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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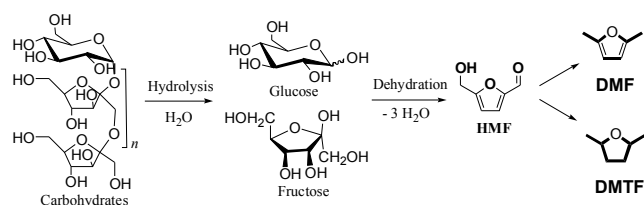
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er energy content than DMF and has better stability during storage because of its saturated furan ring structure [5]. DMTF can also serve as a substitute for tetrahydrofuran (THF) in the chemical industry [8].

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 hydrodeoxygena-



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

tion step, due to the influence of unfavorable impurities, the overall yields of DMF were only 15% and 9%, respectively, in the above two cases.

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-



Changzhi Li (Dalian Institute of Chemical Physics, Chinese Academy of Science) **received Min Enze Energy and Chemical Engineering Award in 2013**, which was jointly presented by Chinese Academy of Engineering and Sinopec Group, for his contribution in the area of "ionic liquids mediated biomass conversion". Dr Changzhi Li received his Ph.D. degree under the supervision of Prof. Zongbao (kent) Zhao, in Organic Chemistry from Dalian Institute of Chemical Physics, Chinese Academy of Sciences, in 2009; then he joined Prof. Tao Zhang's group where he was promoted to an associated professor in 2012. He has published more than 20 peer-reviewed papers with over 600 citations. In 2014, he won the First Prize for Dalian Science and Technology Innovation Award. His current research focuses on the catalytic depolymerization of lignin and the production of bulk and fine chemicals from renewable sources.



Tao Zhang (Dalian Institute of Chemical Physics, Chinese Academy of Science) **received the Catalysis Award for Young Scientists in 2008**, which was presented by The Catalysis Society of China. Professor Tao Zhang received his Ph.D. degree from Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences, in 1989, and he joined the same institute and was promoted to full professor in 1995. He did postdoctoral research with Prof. Frank Berry at Birmingham University in 1990. Prof. Zhang was an invited professor at University of Poitiers (France) in 2006-2007, and he has been a guest professor at University of Namur (Belgium) since 2011. He is currently the director of DICP (since 2007). Prof. Zhang has also received several research awards, including the Distinguished Award of Chinese Academy of Sciences (2010), Zhou Guangzhao Foundation Award for Applied Science (2009), National Award of Technology Invention (2008, 2006, 2005). He was selected as an academician of the Chinese Academy of Sciences. In the past decades, Prof. Zhang has successfully designed a great number of nano and subnano metallic catalysts for applications in energy conversion and environmental control. His research interests include (1) Design and synthesis of nano- and subnano catalytic materials; (2) utilization of biomass for production of chemicals.

ments, a homogeneous catalyst system composed of a soluble Rh salt was the catalyst, and HI and chlorobenzene as additives under a hydrogen atmosphere in water was applied. Hexose from a wide range of biomass-derived carbohydrates were converted into DMTF in good yields. Rauchfuss's group [13] also developed a formic acid participant process for the synthesis of DMF from fructose whereby three steps occurred in the one-pot, namely, dehydration of fructose to HMF, hydrogenation HMF to bis(hydroxymethyl)-furan (BHMF), and deoxygenation of BHMF to DMF. While promising, too much FA used (over 10 times molar amount than fructose) in the process is an issue that needs to be addressed.

Ionic liquids (ILs) are currently under intensive investigation as alternative solvents for biomass conversion because they possess tunable properties and readily dissolve biomass resources [15–18]. In our previous study, we developed the dehydration of carbohydrates for the production of HMF in ILs [19] and the one-pot conversion of carbohydrates to furan-based diols in a IL/water binary solvent mixture [20]. Here, the direct production of DMF and DMTF from fructose via one-pot tandem reaction in a biphasic IL/organic solvent system over Ru/C was rationally designed. This ensured the coupling of the relevant reactions and designed the selectivity to DMF and DMTF. The solvent effect and the role of IL in the transformation process were clearly explained.

2. Experimental

2.1. Materials

Fructose (99%) was purchased from Acros Organics. All the other chemicals were obtained from local supplier and were used as received without further purification. The Ru/C catalyst was prepared by incipient wet impregnation followed by reduction in H₂ at 300 °C for 1 h. 1-Butyl-3-methylimidazolium chloride ([BMIm]Cl) was prepared according to our previous study [20].

2.2. Conversion of fructose for the production of DMF and DHMTF

A typical process for the catalytic conversion of fructose is as follows. 0.36 g fructose and 1.0 g [BMIm]Cl were charged into an open autoclave and heated to 130 °C for 30 min to afford HMF. About 20 mg sample was withdrawn, weighed, quenched with cold water, and subjected to HPLC analysis to determine the fructose conversion and HMF yield. 25 mL organic solvent and 0.1 g metal catalyst were added to the residue reaction mixture. After the solution was mixed uniformly, the hydrodeoxygenation reaction was carried out with an initial H₂ pressure of 5 MPa (measured at room temperature) at 220 °C for a set time. After the one-pot transformation, the reaction solution was filtered and the clear filtrate was subject to GC-MS analysis using the external standard method.

The HPLC analysis of the products was conducted on a Agilent 1100 equipment with a Shodex SC-101 column using extra pure water as the mobile phase at a flow rate of 0.6 mL/min.

The pressure of the column was 2.8 MPa and the column temperature was 45 °C. The yield 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 DMF or DMTF was calculated by the equation: Selectivity (%) = (molar number of the product) ÷ (molar number of converted HMF) × 100. The total selectivity of furan-based fuels was calculated by the equation: Selectivity (%) = (Selectivity of DMF) + (Selectivity of DMTF). The total yield of furan-based diols was calculated by the equation: Total yield (%) = (Yield of HMF) × (Conversion of HMF) × (Total selectivity of furan-based fuels) × 100.

2.3. Characterization

Elemental analysis (C, H, N) of the catalyst was done on a Vario MICRO elemental analyzer. Raman spectra were measured with a Raman spectrometer (Renishaw in Via Raman Microscope) equipped with a He-Ne (514 nm) laser. A laser power of 0.1 mW was used to avoid overheating of the sample. H₂ temperature programmed reduction (TPR) was performed using a Micromeritics Autochem 2910 (USA) equipment with 5 vol% of H₂/N₂ (50 mL/min) at a heating rate of 10 °C/min from 50 to 800 °C. The sample (50 mg) was pretreated with He flow (30 mL/min) at 120 °C for 30 min. The outlet gas was analyzed by a TCD and mass spectroscopy (MS). X-ray photoelectron spectroscopy (XPS, JEOL JPC-9010MC) for the Ru 3p_{3/2} peak was obtained using Al K_α radiation (1486.6 eV) at 100 W and a pass energy of 30 eV. Samples were fixed on a double-stick carbon tape. The binding energies were calibrated using sputtered Au (4f_{7/2} peak at 83.8 eV).

3. Results and discussion

3.1. Fructose dehydration in ILs

A typical reaction profile in this work is a one-pot two-step procedure, i.e., dehydration of fructose to produce HMF, coupled with *in situ* hydrodeoxygenation of HMF to afford the target products DMF and DMTF. In the first step, the dehydration reaction in [BMIm]Cl without the addition of catalyst at 130 °C within 30 min afforded HMF in (78±3)% yield. Further prolonging the reaction time did not enhance the HMF yield, while the color of the mixture turned dark, suggesting the formation of black humins. As the fructose dehydration reaction in aqueous solution is inert when no catalyst is used [21], [BMIm]Cl plays the role not only of the appropriate solvent but also as an advantageous promoter for HMF production. In the following one-pot cascade conversion of carbohydrates experiments, the fructose dehydration reaction were all conducted at 130 °C for 30 min and then the next *in situ* hydrodeoxygenation step was performed.

3.2. *In situ* hydrodeoxygenation: solvent effect

In comparison to water and common organic solvents, most ILs including [BMIm]Cl have an undesirable high viscosity [22]. This property is especially unfavorable for mass transfer in the gas reactions. In the HMF hydrodeoxygenation step, to alleviate the negative effect of the high viscosity, after the dehydration reaction, another solvent with a lower viscosity was added into the reaction mixture for the hydrodeoxygenation reaction. As the IL/water mixture was proved to be not a choice for the hydrodeoxygenation of HMF [20], organic solvents with different properties were screened to find a proper system for the production of DMF and DMTF.

For the *in situ* hydrodeoxygenation step, it was found, as shown in Fig. 1, that HMF was completely consumed in all the solvent mixtures within 5 h over Ru/C, while the selectivities of the products were totally different. When dipolar organic solvents were applied in the hydrodeoxygenation step, they are miscible with [BMIm]Cl in all ratios. In this case, regardless whether they are protic (such as *i*-propanol and *n*-butanol) or aprotic (such as CH₃CN), rather poor yields between 11%–15% were obtained. The GC-MS analysis implied that severe side reactions occurred because many byproducts such as furan ring-opening products, carbonyl group and C=C bond hydrogenation products as well as demethylation products and some unknown products were detected.

It is interesting to note that THF, a weak dipolar aprotic solvent that is immiscible with [BMIm]Cl, afforded a much higher selectivity of furan-based fuels with a total yield of 68% (DMF: 49% and DMTF: 19%, based on HMF). In comparison to the above strong dipolar solvents, THF in IL greatly enhanced the selectivity of furan-based fuels. Although a clear explanation for the enhancement remains speculative, we would like to offer some discussion. First, in the biphasic solvent system of THF/IL, HMF was highly soluble in IL and Ru/C was also present in the IL phase. This “solvent cage effect” [23] increased the collision probability and thus made the catalyst more accessible to HMF. Furthermore, as soon as DMF and DMTF were

formed, the low solubility of these two products in the dipolar IL facilitated the shift of the products to the THF layer. Accordingly, ring-opening and other side reactions were avoided. In contrast, this “solvent cage effect” and the so called “reaction-extraction effect” did not exist in the binary solvent system comprising the IL and a dipolar organic solvent, such as CH₃CN, *i*-propanol and *n*-butanol, because these organic solvents are miscible with [BMIm]Cl. Besides, different solvents affect the equilibrium constant of a reaction by different stabilization of the reactant or product through H-bonding, dipole-dipole interactions, van der Waals interactions, etc. [23].

It should be pointed out that in THF/IL, the hydrodeoxygenation of neat HMF afforded a lower performance (DMF and DMTF yields of 40% and 16%, with the total yield of 56%) than that acquired directly from fructose (Fig. 1, the two comparative reactions in the THF/IL system). Noting that the dehydration reaction of fructose generated 23% byproducts, the comparative experiments with fructose and HMF indicated that the impurities formed in the dehydration reaction did not have an undesirable influence on the subsequent hydrodeoxygenation reaction. Therefore, the removal of the impurities was not a prerequisite in our experiment. This is an advantage over the stepwise technology because it avoided the isolation and purification of HMF without compromising the yield of furan-based fuels.

For the hydrotreating of biomass, the hydrogen pressure and the reaction temperature are two crucial factors affecting the conversion. In the THF/IL system, optimization of the reaction conditions showed that the catalytic performance was only slightly enhanced with the increasing of hydrogen pressure (Fig. 2(a)). In contrast, it was more sensitive to the reaction temperature (Fig. 2(b)), suggesting that hydrodeoxygenation is a thermodynamic controlling reaction in THF/IL over the Ru/C catalyst. These results were quite different from our previous study where in the hydrogenation of HMF to furan-based diols, the hydrogen pressure was the key factor that controlled the overall rate [20].

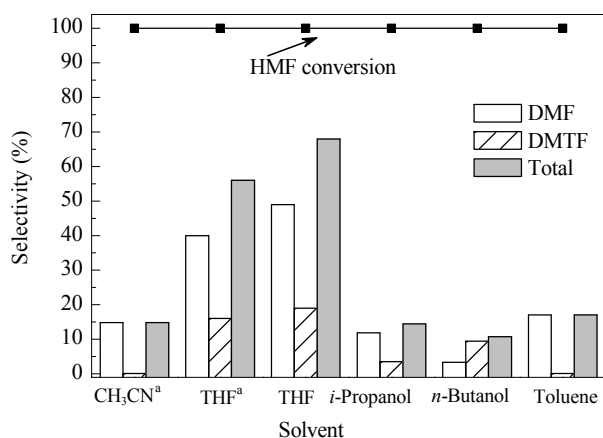


Fig. 1. Direct conversion of fructose into furan-based fuels in a binary mixture of [BMIm]Cl/organic solvent. Reaction conditions: 0.36 g fructose was dehydrated in 1.0 g [BMIm]Cl at 130 °C for 30 min, then 25 mL organic solvent and 0.1 g Ru/C (5 wt%) were added into the mixture for the hydrogenolysis reaction under 5 MPa H₂ at 220 °C for 5 h. ^a Neat HMF was used as the substrate for the hydrodeoxygenation reaction.

3.3. Effect of water on the *in situ* hydrodeoxygenation of HMF

It is known that in the fructose dehydration reaction, three water molecules are released for the formation of one HMF molecule. In the IL reaction system, once water is generated, it is hard to separate it from the IL due to the interactions between the IL and water [24,25]. To identify the influence of water in our system, we attempted the neat HMF hydrodeoxygenation reaction in THF/IL with different amounts of water. It is interesting to find in Table 1 that in a certain range, the yield of furan-based fuels increased with increasing water amount. For instance, on increasing the water amount from zero to 6 mmol (one molar equivalent of IL), the total yield of the target products increased from 56% (DMF 40%, DMTF 16%) to 67% (DMF 47%, DMTF 20%). These results oppose the common sense that water would induce side reactions which then decrease the product selectivity [26]. The following two reasons are believed to cause this exceptional positive effect: (1) improvement of the mass transfer, since low viscosity water is

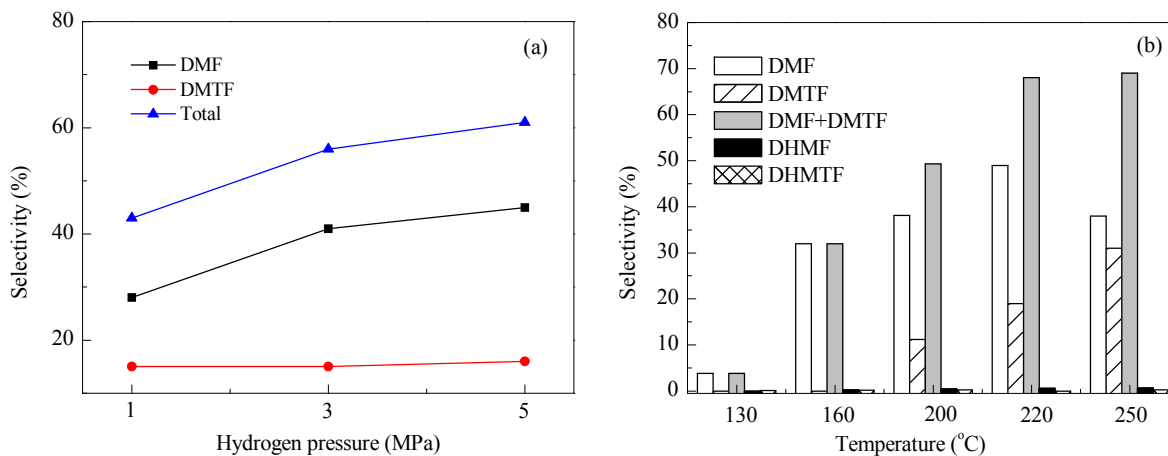


Fig. 2. Effects of hydrogen pressure (a) and reaction temperature (b) on the hydrodeoxygenation performance. Reaction conditions: (a) Dehydration reaction was first conducted in 1.0 g [BMIm]Cl at 130 °C with 0.36 g fructose for 30 min, then 25 mL THF and 0.1 g 5% Ru/C were added into the mixture for the hydrodeoxygenation reaction under H₂ atmosphere at 220 °C for 10 h; (b) The dehydration condition was the same; the hydrodeoxygenation reaction was carried out under 5 MPa H₂ at different temperatures for 5 h.

Table 1

Effect of water amount on the production of furan-based fuels ^a.

Entry	H ₂ O (g)	HMF conv. (%)	Yield (%)		
			DMF	DMTF	Total
1	0	>99	40	16	56
2	0.036	>99	48	18	66
3	0.108	>99	47	20	67
4	0.500	>99	33	18	51
5	1.000	>99	18	5	23

^a Reaction conditions: HMF 0.252 g, THF 25 mL, 5% Ru/C 0.1 g, [BMIm]Cl 1.0 g. The hydrogenation reaction was carried out under 5 MPa H₂ at 220 °C for 5 h.

miscible with IL in any ratio, and (2) strong interactions such as hydrogen bonds between water and IL suppressed water related side reactions, e.g. rehydration, hydrolysis of HMF and intermediates [24,25,27]. It should be noted that the effect of the IL-water interaction became weaker when much water is present in the reaction system. This is the reason why the yield of furan-based fuels reached a peak with the presence of 6 mmol water, and then decreased when the water amount was higher (entry 3 versus entries 4 and 5, Table 1). Actually, we also tested the reaction in a ternary solvent system ([BMIm]Cl/THF/H₂O, v/v/v = 1:15:10) over Ru/C at 220 °C. No DMF or DMTF was detected even on prolonging the reaction time to 10 h. Instead, 2,5-dihydroxymethylfuran (DHMF) and 2,5-dihydroxymethyltetrahydrofuran (DHMTF) were the dominant products with the total yield of 88%. This result is in accordance with our previous study [20] that HMF undergoes a hydrogenation reaction in a solvent system containing a large amount of water. Noting that the fructose concentration was far less than that of the IL, it can be concluded that the small amount of water formed in the fructose dehydration step did not cause a negative effect on the next hydrodeoxygenation reaction. In contrast, it is an advantage of the one-pot catalytic system over the stepwise technology since the water produced promoted the formation of DMF and DMTF.

3.4. The role of the IL on the *in situ* hydrodeoxygenation reaction

It is known that the IL plays an important role in the fructose dehydration reaction. To explore the function of the IL in the hydrodeoxygenation step, using HMF as the substrate, we compared the reaction with different amounts of IL under otherwise identical conditions.

As shown in Table 2 (entry 1), in the absence of the IL, although the fructose conversion was very high in the THF solvent, the products only comprised 2% DMTF and a trace amount of DMF. Instead, DHMTF, 5-methyl tetrahydrofurfuryl alcohol (MTFA), tetrahydrofurfuryl alcohol (TFA), 1,2-pentanediol, 2-hexanol and pentanol were detected as the main products in the liquid phase. In addition, gas products of CO₂, CH₄ and C₂H₆, and some insoluble humins were formed. According to the MS data and Ref. [11], we proposed the by-product formation pathways (Fig. 3): HMF was first saturated

Table 2

Effects of [BMIm]Cl amount on the production of furan-based fuels ^a.

Entry	[BMIm]Cl (mmol)	HMF conv. (%)	Yield (%)		
			DMF	DMTF	Total
1	0	>99	0	2	2
2	1.15	>99	32	1	33
3	2.87	>99	41	12	53
4	5.73	>99	47	20	67
5	11.46	>99	30	14	44
6 ^b	0	>99	66	1	67
7 ^c	5.73	>99	0	2	2
8 ^d	5.73	>99	40	19	59

^a HMF 0.252 g, THF 25 mL, 5% Ru/C 0.100 g and H₂O 0.108 g. The hydrodeoxygenation reaction was conducted at 220 °C under 5 MPa H₂ for 5 h.

^b Catalyst was Ru/C-IL, other conditions were the same as entry 4.

^c [BMIm]Cl was replaced by NaCl, other conditions were the same as entry 4.

^d [BMIm]Cl was replaced by 1-butyl-2,3-dimethyl-imidazolium chloride, other conditions were the same as entry 4.

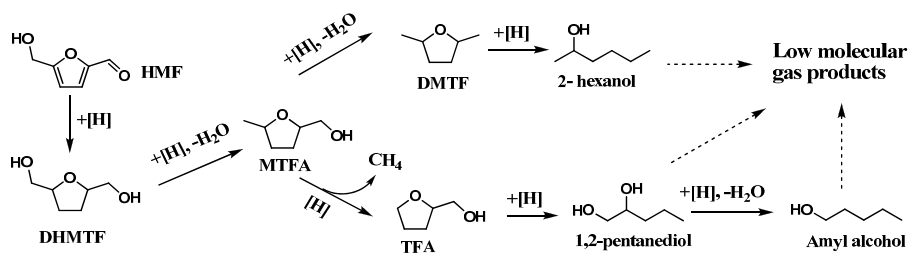


Fig. 3. Byproducts formation pathways for the hydrotreating of HMF with 5% Ru/C in THF without the addition of [BMIm]Cl.

in its furan ring and carbonyl group to generate DHMTF, which was converted to MTFA via hydrodeoxygenation reaction; subsequently, further hydrodeoxygenation and ring-opening reactions occurred on MTFA to afford DMTF and 2-hexanol; alternatively, MTFA was converted to TFA, 1,2-pentenediol and amyl alcohol via demethylation, ring-opening reaction and hydrodeoxygenation, respectively. Some of the above products were further cracked to gases, i.e. CO₂, CH₄ and C₂H₆, etc. As DMF was not detected in the reaction, it is suggested that the furan ring in HMF was very active in THF over Ru/C.

In a parallel trial with 0.2 g [BMIm]Cl, a DMF yield of 32% was attained (Table 2, entry 2). Clearly, the hydrogenation of the C=C bonds in the furan ring was significantly inhibited. Further increasing the IL amount to 0.5 and 1.0 g slightly increased the yield of DMF to 41% and 47%, and the yield of DMTF to 12% and 20%, respectively (Table 2, entries 3 and 4). The highest total yield of 67% was obtained with 1.0 g [BMIm]Cl. More IL did not further increase the yields of the target products (entry 5). We assume here that the presence of the IL should have modified the catalyst, and changed the reaction route to form DMF and DMTF. This hypothesis will be further discussed later with the element analysis, Raman spectroscopy, XPS and H₂-TPR characterization, together with a series of comparison experiments.

To confirm our hypothesis, the following experiment was designed. First, fresh Ru/C was treated in IL at 220 °C under 5 MPa H₂ for 2 h. This treated catalyst was then carefully washed with water to ensure the removal of all the physically adsorbed IL, and was dried under vacuum to obtain IL-treated Ru/C (denoted as Ru/C-IL) [28]. Using this catalyst, we performed HMF hydrodeoxygenation in pure THF under the same conditions as Table 2, entry 1. It was interesting to find that the yield of DMF and total yield reached 66% and 67%, respectively (Table 2, entry 6). Because there was no difference in the reaction conditions of the two experiments (Table 2, entries 1 and 6), this result suggested that there was a modification of Ru/C during the treatment of the catalyst in IL, which hence changed its catalytic activity.

The elemental analysis of Ru/C and Ru/C-IL supplied additional evidence of this. As the active carbon support was treated with HNO₃ before use, a N content of 0.92 wt% was detected in fresh Ru/C. However, Ru/C-IL comprised a much higher N content of 4.07 wt%. Since the IL contains 16 wt% of N and the physically adsorbed IL had been removed from Ru/C by water washing, the increased N content in Ru/C-IL should be attributed to a chemical interaction between Ru/C and the IL,

which anchored the IL on Ru/C.

As the IL is composed of 1-butyl-3-methylimidazolium cation ([BMIm]⁺) and Cl⁻ anion, to clarify the function of Cl⁻ on the catalyst activity, the IL was replaced by an equal molar amount of NaCl for the HMF hydrodeoxygenation reaction under the same condition as Table 2, entry 4. It was found that although the conversion was still very high, the reaction only afforded 2% total yield of DMF and DMTF (Table 2, entry 7). This result is similar to that obtained in THF without the IL (Table 2, entry 1), suggesting that NaCl has no influence on the yield of the target products. Taken together, entries 1, 4 and 7 in Table 2 indicated that the Cl⁻ did not help convert HMF to DMF and DMTF. Therefore, it was [BMIm]⁺ that played a role in the modification of Ru/C and its catalytic property.

Ru/C is a typical heterogeneous catalyst comprising Ru species and a carbon support. With the aim to identify which component interacted with [BMIm]⁺, Raman spectroscopy, a powerful tool for carbon characterization, was performed on fresh Ru/C and Ru/C-IL. As shown in Fig. 4, both catalysts have two strong bands at 1401 and 1519 cm⁻¹, which were assigned to the D and G bands of the active carbon, respectively. No shift was detected for the two bands of Ru/C-IL as compared to those of fresh Ru/C, and the value of I_D/I_G for both catalysts was 0.87. These facts indicated that the structure of the carbon support was not changed after the treatment of the catalyst in the IL. Thus, the high yield of the furan-based fuels can be ascribed to the interaction of [BMIm]⁺ with the metal species.

Kiefer and co-workers [29] have shown that H atom on the C₂ position of the positively charged ring in 1,3-dialkylimidazolium-based IL is very active. It is easy to eliminate, leaving a N-heterocyclic carbene structure on the imidazolium ring. The

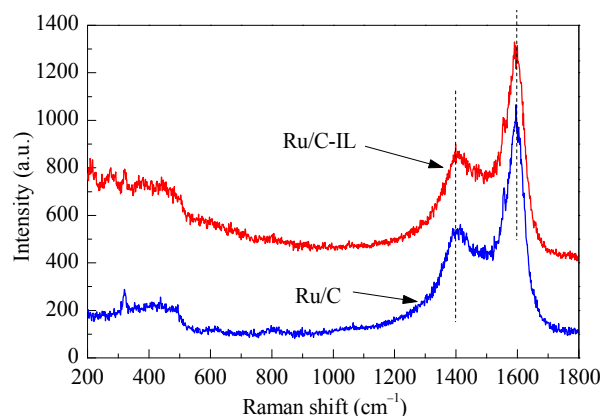


Fig. 4. Raman spectra of fresh Ru/C and Ru/C-IL.

presence of the carbene structure was suggested to have a remarkable effect on metal-catalyzed reactions through coordination [30,31]. To identify whether this “carbene effect” was present in our catalytic system, 1-butyl-2,3-dimethylimidazolium chloride ([BDMim]Cl) was prepared for the HMF hydrodeoxygenation reaction. Unlike [BMim]Cl, [BDMim]Cl cannot form a carbene structure since the C₂ site of the imidazolium ring is occupied by a methyl group. The result showed that under the same conditions, both the ILs gave similar performances (entry 4 versus entry 8, Table 2). This indicated that methylating the C₂ position did not affect the catalytic activity of the Ru species. Therefore, H atom on the C₂ position of the imidazolium ring is not the reason for the high yield of furan-based fuels.

The ligand effect is the use of a ligand to alter the electronic properties of the active metal by electron transfer from the ligand to the metal species [32]. This “ligand (or electronic) effect” significantly affects the catalytic activity and selectivity in various chemical reactions [33]. An obvious feature of the 1,3-dialkylimidazolium cation is that one of the N atoms in the imidazolium ring contains a lone pair electron [34]. This N atom can act as a ligand to coordinate with the Ru species and thus modify the electronic property of the active site. XPS characterization of the catalyst demonstrated the “ligand effect” of the IL on the Ru species. In the XPS measurement, since the Ru 3d_{5/2} peak overlapped with that of C 1s [35], the binding energy of the Ru 3p_{3/2} orbital was measured. As shown in Fig. 5(a), the binding energy of Ru/C-IL was 0.4 eV lower than that of fresh Ru/C (463.5 eV), indicating that the electron cloud density of the Ru species was increased after treating with the IL. Due to the conjugative effect of the imidazolium ring, the N 1s of [BMim]Cl in C-IL (IL treated carbon) [28] only exhibited one peak (401.6 eV, Fig. 5(b)). However, it was interesting to find that two N 1s peaks of 399.8 and 401.2 eV appeared in the Ru/C-IL sample (Fig. 5(b)), suggesting that one N atom was coordinated with the Ru species, resulting in the different binding energy for the two N atoms in the imidazolium ring of [BMIM]Cl.

H₂-TPR measurement further confirmed the modification of

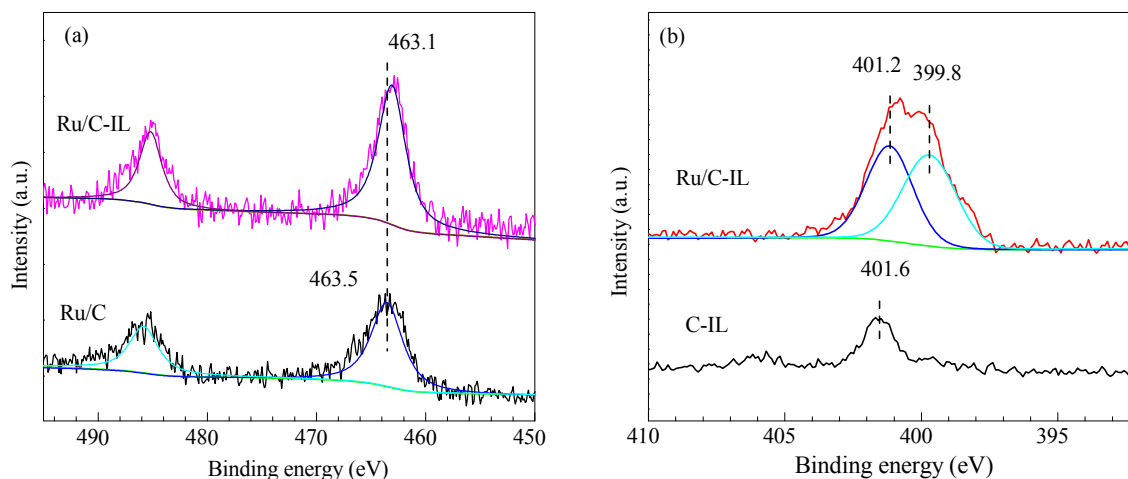


Fig. 5. XPS spectra of Ru/C, Ru/C-IL and C-IL. (a) Ru 3p_{3/2}; (b) N 1s.

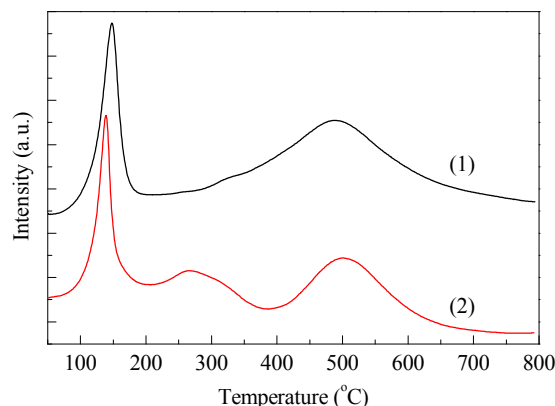


Fig. 6. H₂-TPR profiles of Ru/C (1) and Ru/C-IL (2).

the Ru electron properties. Fig. 6 summarizes the TPR profiles of fresh Ru/C and Ru/C-IL. In the low temperature region of 140 °C, only one peak was detected for both catalysts, which was ascribed to the reduction of RuO₂. The hydrogen consumption signals at 270 °C and 510 °C were accompanied by the formation of methane (confirmed by MS analysis), suggesting that some carbon species were reduced to methane. In the TPR profile of Ru/C-IL, it is interesting that the peak at 270 °C was much larger than that of Ru/C. Obviously, after treating with the IL, the Ru species was greatly changed in property, which probably led to some methanation of the support. These changes to the Ru species are believed to be responsible for the much improved hydrodeoxygenation performance.

4. Conclusions

We achieved the direct production of furan-based fuels, DMF and DMTF, from fructose via one-pot tandem reactions. The nature of the organic solvent in the IL containing binary solvent mixture and the water amount strongly affected the reaction. Characterization of the catalysts and the parallel experiments indicated that the interaction between the cations of the IL and Ru species changed the charge density of the metal

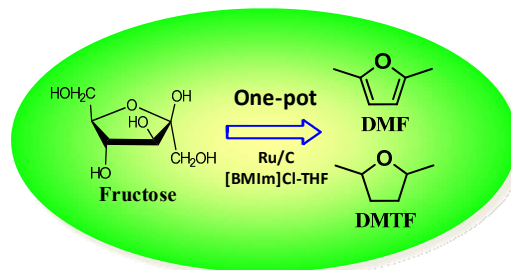
Graphical Abstract

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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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One-pot production of 2, 5-dimethylfuran and 2, 5-dihmethyltetrahydrofuran from fructose by optimizing the synergic effect of ionic liquid promoted Ru/C catalyst and solvent effect was reported.



species, which is the reason for the high selectivity of the furan-based fuels. The advantages of the IL in the fructose dehydration reaction, its role in the modification of the Ru species, as well as the biphasic [BMIm]Cl/THF solvent system together gave the high yield of furan-based fuels. This catalytic system featured a simple process with no need for intermediate separation processes and it gave a high performance, which brings this technology nearer to the cost-efficient production of biofuels from biomass.

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