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Selective Transformation of 5-Hydroxymethylfurfural into the Liquid Fuel 2,5-Dimethylfuran over Carbon-Supported Ruthenium

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Supporting Information

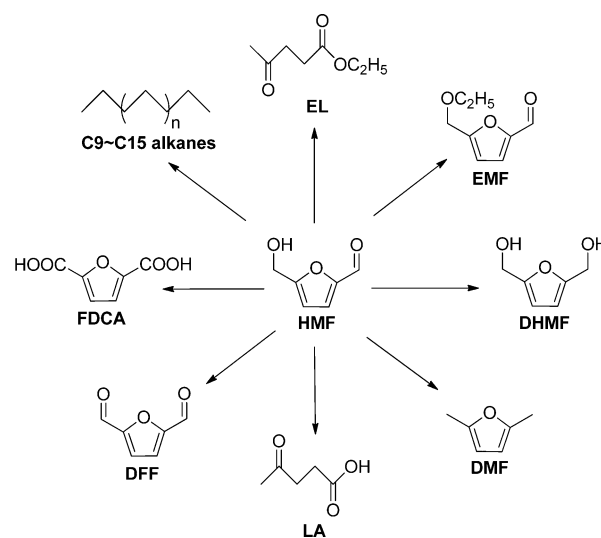
ABSTRACT: A simple and efficient process was presented for the selective hydrogenation of 5-hydroxymethylfurfural (HMF) into the high-quality liquid fuel 2,5-dimethylfuran (DMF) in the presence of tetrahydrofuran (THF). Among the employed metal catalysts, the relatively inexpensive carbon-supported ruthenium (Ru/C) displayed the highest catalytic performance, which led to 94.7% DMF yield with 100% HMF conversion at a relatively mild reaction temperature of 200 °C for only 2 h. Although Ru/C had a little loss in the catalytic activity when it was used for five successive reaction runs, the partially deactivated Ru/C could be easily regenerated by heating at a mixed flow of H₂ and N₂. Moreover, the plausible mechanism involving an aldehyde group, a hydroxyl group, and a furan ring for the selective hydrogenation of HMF into DMF was also proposed. Subsequently, DMF was separated from the crude hydrogenation mixture according to their various boiling points by the combination of atmospheric distillation and vacuum distillation, and then, the chemical structures and physical properties of the separated DMF were confirmed to be consistent with the authentic DMF. More gratifyingly, Ru/C and THF were also found to be a good combination for the direct hydrogenation of carbohydrate-derived HMF into DMF, which is very important for the practical production of DMF from a variety of biomass-derived carbohydrates such as fructose, glucose, sucrose, maltose, cellobiose, starch, and cellulose.

1. INTRODUCTION

With the diminishing petroleum reserves and the increasing energy demand along with the growing concerns about environmental pollution and greenhouse gas emission, the transformation of renewable biomass into chemicals has attracted much more attention in both scientific and industrial communities.^{1–3} Among the many possible chemicals, 5-hydroxymethylfurfural (HMF), which can be produced from a variety of biomass-derived carbohydrates,^{4–8} is recognized as a versatile intermediate (Scheme 1), and it can be further converted into a series of high-quality fuels such as ethyl levulinate (EL),⁹ 5-ethoxymethylfurfural (EMF),¹⁰ 2,5-dimethylfuran (DMF),¹¹ C9–C15 alkanes,¹² and high-value chemicals such as levulinic acid (LA),¹³ 2,5-dihydroxymethylfurfural (DHMF),¹⁴ 2,5-diformylfuran (DFF),¹⁵ and 2,5-furandicarboxylic acid (FDCA).¹⁶ Among the above compounds, DMF, a product of HMF hydrogenation,^{11,17–23} is particularly attractive.

As is well-known, ethanol that can be produced by the fermentation of various biomass-derived sugars is by far the dominating renewable liquid fuel in the market;^{24,25} however, it is not a good candidate for the petroleum-derived liquid fuels in the transportation sector, because it suffers from several limitations including low energy density (23 MJ/L), high volatility (bp 78.4 °C), and high water solubility (completely miscible).^{26,27} Conversely, compared to ethanol, DMF possesses a higher energy density (31.5 MJ/L) and a lower

Scheme 1. Synthesis of Various Derivatives from HMF



Received: December 31, 2013

Revised: January 19, 2014

Accepted: February 1, 2014

Published: February 2, 2014

volatility (bp 92–94 °C) and is not soluble in water;^{28–30} these excellent performances make DMF a more appropriate and promising renewable liquid transportation fuel.²¹

In the past few years, much effort has been devoted to studying the production of DMF. In 2007, Román-Leshkov et al. proposed a catalytic strategy for the hydrogenation of HMF using 6.8 bar of H₂ as a hydrogen source over CuRu/C catalyst in 1-butanol. 71% DMF yield was achieved at 220 °C for 10 h.¹ In 2010, the hydrogenation of HMF was investigated in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl). The yield of DMF with 15% was observed under 62 bar of H₂ pressure using Pd/C as a catalyst at 120 °C for 1 h.¹⁸ In the same year, Thananathanachon and Rauchfuss presented a new catalytic process for the hydrogenation of HMF in tetrahydrofuran (THF) using formic acid (FA) as a hydrogen source over Pd/C catalyst. DMF yield up to 95% was reached at 70 °C for 15 h.¹⁷ In 2012, the hydrogenation of HMF was carried out over Cu-PMO catalyst and the yield of DMF with 34% was obtained in supercritical methanol at 300 °C for 0.75 h.¹⁹ More recently, Zu et al. also reported the hydrogenation of HMF in THF over Ru/Co₃O₄ catalyst using 7 bar of H₂ as a hydrogen source, resulting in 93.4% DMF yield at 130 °C for 24 h.²⁰ Although excellent DMF yields (as high as 95%) were gained, these catalytic systems required a higher reaction temperature (300 °C), a longer reaction time (10–24 h), or a higher hydrogen pressure (62 bar), which is unfavorable for the practical production of DMF.

On the basis of the above-mentioned research situations and existing problems, a more efficient process for the selective hydrogenation of HMF into DMF over the relatively inexpensive Ru/C catalyst in the presence of THF (it can be directly synthesized from carbohydrate-derived furfural) under relatively mild reaction conditions was reported in the present work. In addition, various reaction parameters such as temperature, time, catalyst loading, H₂ pressure, HMF concentration, and agitation speed were optimized and the reusability of the catalyst was evaluated. Moreover, a plausible mechanism for the selective hydrogenation of HMF into DMF and a simple procedure for the separation of DMF from the crude hydrogenation mixture were also investigated.

2. EXPERIMENTAL SECTION

2.1. Materials. HMF (99%) was supplied by Shanghai Energy Chemical Co. Ltd. (Shanghai, China). DMF (99%), Pd/C (5 wt % Pd), Pt/C (5 wt % Pt), Rh/C (5 wt % Rh), Ru/C (5 wt % Ru), activated carbon (200 mesh), and Raney-Ni (50 μm) were purchased from Shanghai Aladdin Reagent Co. Ltd. (Shanghai, China). THF and other chemicals were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used without further purification.

2.2. Typical Procedure for the Hydrogenation of HMF into DMF. All the hydrogenation reactions were carried out in a stainless steel Parr reactor (50 mL) with the external temperature and stirring controllers, and each preset reaction was repeated three times. For a typical reaction, the reactor was charged with 2.5 wt % HMF, 5 mol % catalyst, and 20 mL of THF, and the reactor was sealed and purged five times with H₂. Then, the reactor was pressurized with 20 bar of H₂, heated at 180 °C, and stirred at a speed of 500 rpm for 2 h. After reaction, the reactor was immediately quenched to room temperature in an ice–water bath, the hydrogenation reaction mixture was sampled and centrifuged at 10 000 rpm for 5 min,

and the supernatant was also filtered with a 0.22 μm syringe membrane filter.

2.3. Product Analysis. HMF, DMF, and various intermediates were analyzed by GC (Agilent 7890) and GC-MS (Shimadzu QP2010 SE) equipped with a FID detector and an HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). For GC and GC-MS analysis, the initial column temperature of 40 °C was held for 2 min, and then, the temperature was ramped at 5 °C/min until 100 °C was reached and held for 2 min; after that, the temperature was ramped at 10 °C/min until 250 °C was reached and held for 2 min. Moreover, the injection volume was 1 μL, the injector temperature was 250 °C, the detector temperature was 270 °C, the ion source temperature was 200 °C, and the carrier gas was N₂ with a flow rate of 1 mL/min. It should be pointed out that HMF conversion and DMF yield were based on the external standard method and calculated using the following equations:

$$\begin{aligned} \text{HMF conversion (\%)} \\ = \left(1 - \frac{\text{moles of HMF in products}}{\text{starting moles of HMF}} \right) \times 100 \end{aligned} \quad (1)$$

$$\text{DMF yield (\%)} = \frac{\text{moles of DMF in products}}{\text{starting moles of HMF}} \times 100 \quad (2)$$

2.4. Catalyst Characterization. X-ray diffraction (XRD) patterns were recorded with an X'Pert PRO powder XRD spectrometer (Panalytical, Netherlands) using a Cu Kα radiation source (λ = 0.154 nm). The microstructures were observed with an S-4800 scanning electron microscope (Hitachi, Japan) at 30 kV. Elemental analysis was performed with an Optima-2000DV inductively coupled plasma atomic emission spectrometer (ICP-AES) (PerkinElmer, USA).

2.5. DMF Characterization. The chemical structures of the separated DMF were determined with a Nicolet330 Fourier transform infrared (FT-IR) spectrometer (Thermo, USA) using the standard KBr disc method over the range from 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹ and an Advance II 400 M nuclear magnetic resonance (NMR) spectrometer (Bruker, Germany) using CDCl₃ as the solvent, respectively. The physical properties of the separated DMF such as boiling point, liquid density, and refractive index were measured by the atmospheric distillation method, pycnometer method, and automatic Abbe refractometer, respectively.

3. RESULTS AND DISCUSSION

3.1. The Hydrogenation of HMF into DMF over Different Metal Catalysts. As is known to all, HMF, possessing an aldehyde group, a hydroxyl group, and a furan ring, is very reactive, and its hydrogenation products are very complicated; therefore, how to ensure the hydrogenation priorities of the aldehyde group and the hydroxyl group and avoid further hydrogenation of the furan ring are the principal issues in the hydrogenation of HMF into DMF. To solve these issues, it is very important to choose the appropriate catalyst; thus, a series of metal catalysts including Raney-Ni, Pd/C, Pt/C, Rh/C, and Ru/C were first screened in the presence of THF, and the results are shown in Table 1. As can be seen from Table 1, although 100% HMF conversion was obtained when Raney-Ni was used at 180 °C for 2 h, the yield of DMF was only 9.6%. Similarly, when Pd/C, Pt/C, and Rh/C were tested, the poor catalytic activities were also observed, which led to 9.5,

Table 1. Hydrogenation of HMF into DMF over Different Metal Catalysts^a

entry	catalyst	HMF conversion (%)	DMF yield (%)
1	Raney-Ni	100.0	9.6
2	Pd/C	69.8	9.5
3	Pt/C	50.9	16.2
4	Rh/C	47.3	9.4
5	Ru/C	90.7	80.6
6	none	1.1	0
7 ^b	none	1.3	0
8 ^c	none	0.8	0
9 ^d	C	5.2	0

^aReaction conditions: HMF, 2.5 wt %; catalyst, 5 mol %; THF, 20 mL; H₂, 20 bar; agitation speed, 500 rpm; temperature, 180 °C; time, 2 h. Note: HMF concentration is relative to THF, and catalyst loading is relative to HMF. ^bWater was used as solvent. ^cHexane was used as solvent. ^d0.4 g of activated carbon.

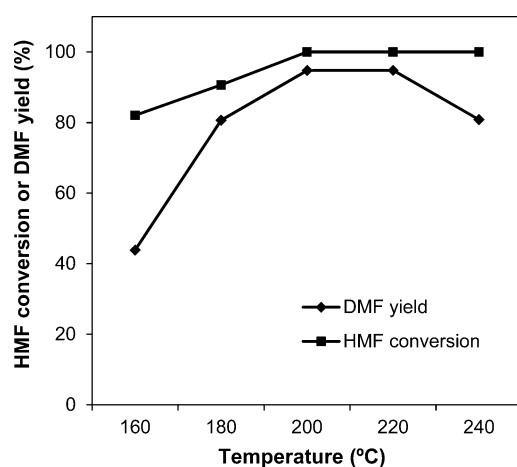


Figure 1. Effect of reaction temperature on HMF conversion and DMF yield. Reaction conditions: HMF, 2.5 wt %; Ru/C, 5 mol %; THF, 20 mL; H₂, 20 bar; agitation speed, 500 rpm; time, 2 h. Note: HMF concentration is relative to THF, and catalyst loading is relative to HMF.

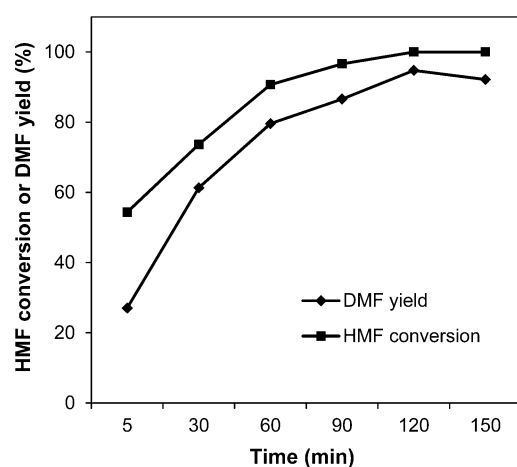


Figure 2. Effect of reaction time on HMF conversion and DMF yield. Reaction conditions: HMF, 2.5 wt %; Ru/C, 5 mol %; THF, 20 mL; H₂, 20 bar; agitation speed, 500 rpm; temperature, 200 °C. Note: HMF concentration is relative to THF, and catalyst loading is relative to HMF.

Table 2. Effect of Catalyst Loading on HMF Conversion and DMF Yield^a

entry	Ru/C (mol %)	HMF conversion (%)	DMF yield (%)
1	1	39.0	6.3
2	2	55.9	37.8
3	3	78.4	65.2
4	4	95.8	82.2
5	5	100.0	94.8
6	6	100.0	94.1
7	7	100.0	90.6

^aReaction conditions: HMF, 2.5 wt %; THF, 20 mL; H₂, 20 bar; agitation speed, 500 rpm; temperature, 200 °C; time, 2 h. Note: HMF concentration is relative to THF, and catalyst loading is relative to HMF.

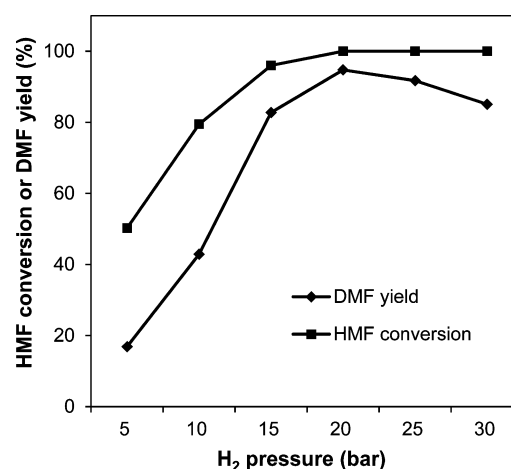


Figure 3. Effect of H₂ pressure on HMF conversion and DMF yield. Reaction conditions: HMF, 2.5 wt %; Ru/C, 5 mol %; THF, 20 mL; agitation speed, 500 rpm; temperature, 200 °C; time, 2 h. Note: HMF concentration is relative to THF, and catalyst loading is relative to HMF.

Table 3. Effect of HMF Concentration on HMF Conversion and DMF Yield^a

entry	HMF concentration (wt %)	HMF conversion (%)	DMF yield (%)
1	1.25	100.0	95.5
2	2.50	100.0	94.8
3	3.75	97.7	77.9
4 ^b	3.75	100.0	93.9
5	5.00	86.9	37.9
6 ^c	5.00	100.0	93.2

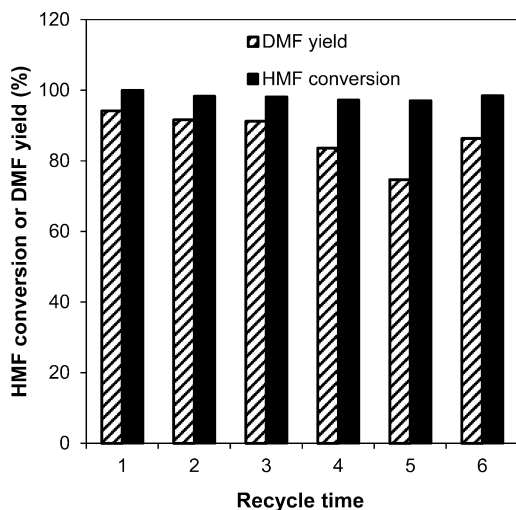
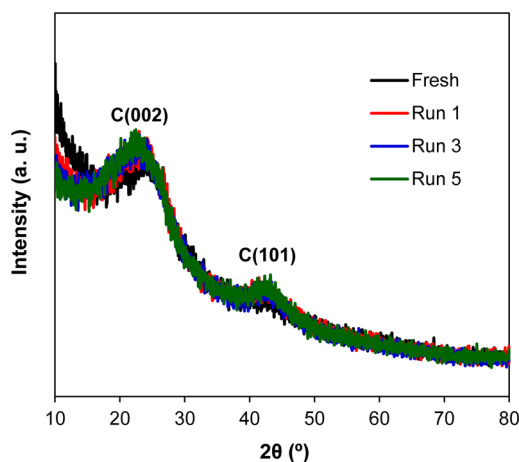
^aReaction conditions: Ru/C, 5 mol %; THF, 20 mL; H₂, 20 bar; agitation speed, 500 rpm; temperature, 200 °C; time, 2 h. Note: HMF concentration is relative to THF, and catalyst loading is relative to HMF. ^b25 bar of H₂. ^c35 bar of H₂.

16.2, and 9.4% DMF yields with 69.8, 50.9, and 47.3% HMF conversion, respectively. Gratifyingly, an excellent DMF yield of 80.6% with 90.7% HMF conversion was achieved when Ru/C was used under the same reaction conditions, indicating that Ru/C exhibited wonderful catalytic activity in the preliminary study on the hydrogenation of HMF into DMF. Moreover, to determine whether THF or acid sites on the carbon support can promote the hydrogenation of HMF into DMF, the reactions without Ru/C and over activated carbon were also studied. In the absence of Ru/C, the conversion of HMF was almost negligible, which implied that THF, just like water and

Table 4. Effect of Agitation Speed on HMF Conversion and DMF Yield^a

entry	agitation speed (rpm)	HMF conversion (%)	DMF yield (%)
1	100	93.5	78.3
2	200	97.2	84.4
3	300	100.0	88.2
4	400	100.0	94.7
5	500	100.0	94.8
6	600	100.0	94.9

^aReaction conditions: HMF, 2.5 wt %; Ru/C, 5 mol %; THF, 20 mL; H₂, 20 bar; temperature, 200 °C; time, 2 h. Note: HMF concentration is relative to THF, and catalyst loading is relative to HMF.

**Figure 4.** Successive use of Ru/C. Reaction conditions: HMF, 2.5 wt %; Ru/C, 5 mol %; THF, 20 mL; H₂, 20 bar; agitation speed, 400 rpm; temperature, 200 °C; time, 2 h. Note: HMF concentration is relative to THF, and catalyst loading is relative to HMF.**Figure 5.** XRD patterns of the fresh and used Ru/C.

hexane, did not play an active role and it acted only as a solvent in the hydrogenation of HMF into DMF. Conversely, the reaction over activated carbon showed 5.2% HMF conversion. The result suggested that acid sites on the carbon support were to some extent responsible for the side reactions such as the etherification reaction.¹¹ However, it is worth noting that the complete hydrogenation of HMF into DMF was not feasible without Ru, which demonstrated that the hydrogenation of

HMF into DMF was mainly catalyzed by Ru. According to the above-mentioned description, Ru/C was confirmed to be a suitable catalyst for the hydrogenation of HMF into DMF in the present work.

3.2. The Hydrogenation of HMF into DMF under Various Reaction Conditions. In addition to the type of catalyst, the catalytic activity of the catalyst for the hydrogenation of HMF into DMF strongly depends on various reaction conditions; therefore, temperature, time, catalyst loading, H₂ pressure, HMF concentration, and agitation speed were subsequently optimized to gain the maximum DMF yield in the presence of Ru/C and THF.

3.2.1. Effect of Reaction Temperature. As described in Figure 1, when the reaction temperature was 160 °C, only 43.8% DMF yield with 82.1% HMF conversion was observed. With the increase of the reaction temperature from 180 to 200 °C, HMF conversion and DMF yield were correspondingly increased from 90.7 to 100% and from 80.6 to 94.8%, respectively. However, when the reaction temperature was further increased to 220 °C, the yield of DMF was not further increased, which indicated that the hydrogenation of HMF into DMF has reached a balance when the reaction temperature was increased to 200 °C; thus, there is no need to continue to increase the reaction temperature. The appropriate reaction temperature was 200 °C.

3.2.2. Effect of Reaction Time. As shown in Figure 2, only 54.4% HMF conversion and 27.0% DMF yield were obtained in 5 min at 200 °C. When the reaction time was prolonged from 30 min to 2 h, HMF conversion was increased from 73.7 to 100% and DMF yield was increased from 61.3 to 94.8%, respectively. When the reaction time was further prolonged to 150 min, HMF conversion remained constant at 100%; however, the yield of DMF was decreased to 92.2%, which demonstrated that more and more undesired byproducts were possibly formed when the reaction time exceeded a certain point. On the basis of it, 2 h was chosen as the suitable reaction time.

3.2.3. Effect of Ru/C Loading. As listed in Table 2, when the loading of Ru/C was below 5 mol %, HMF conversion and DMF yield were continuously increased with the increase of Ru/C loading, respectively. When the loading of Ru/C was further increased to 7 mol %, although all HMF was converted, the yield of DMF was decreased to 90.6%. It is suggested that the increase of Ru/C loading in a certain scope not only promoted the hydrogenation of HMF but also facilitated the formation of DMF. However, once the loading of Ru/C exceeded a critical value, the excessive Ru/C would accelerate the occurrence of side reactions and increase the production costs of DMF; thus, 5 mol % Ru/C loading was selected in the present work.

3.2.4. Effect of H₂ Pressure. As presented in Figure 3, HMF conversion and DMF yield were only 50.2 and 16.9% when 5 bar of H₂ was used, respectively, meaning that the hydrogenation of HMF into DMF was incomplete at a lower H₂ pressure. When H₂ pressure was increased to 20 bar, 94.8% DMF yield with 100% HMF conversion was achieved, which might be ascribed to the fact that the increase of H₂ pressure raised the solubility of H₂ in THF and then facilitated the hydrogenation of HMF into DMF. When H₂ pressure was further increased to 30 bar, the superabundant H₂ might promote the further opening and hydrogenation of the furan ring and then lead to a sharp decrease in DMF yield. Furthermore, the increase of H₂ pressure not only improved

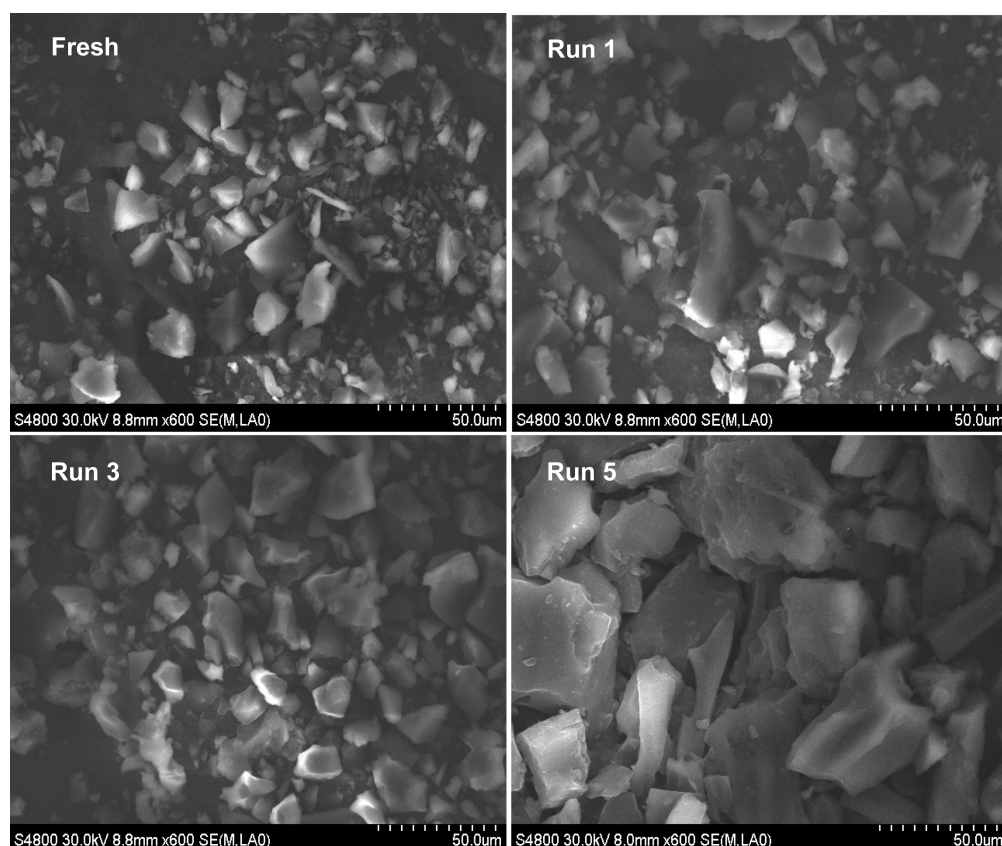


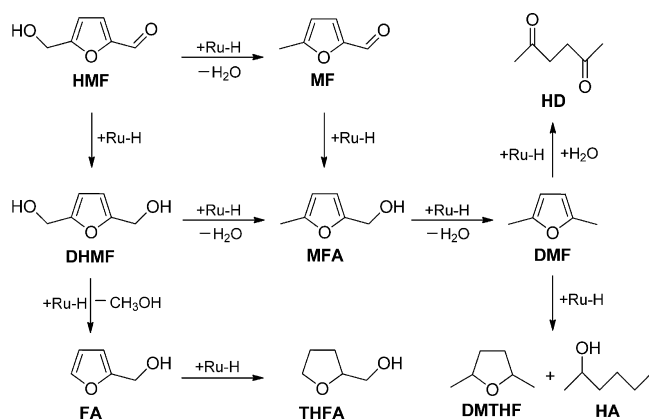
Figure 6. SEM images of the fresh and used Ru/C.

Table 5. Ru Content of the Fresh and Used Ru/C^a

recycle time	Ru content (wt %)
fresh	4.87
1	4.70
3	4.56
5	3.85

^aRu content was detected by ICP-AES.

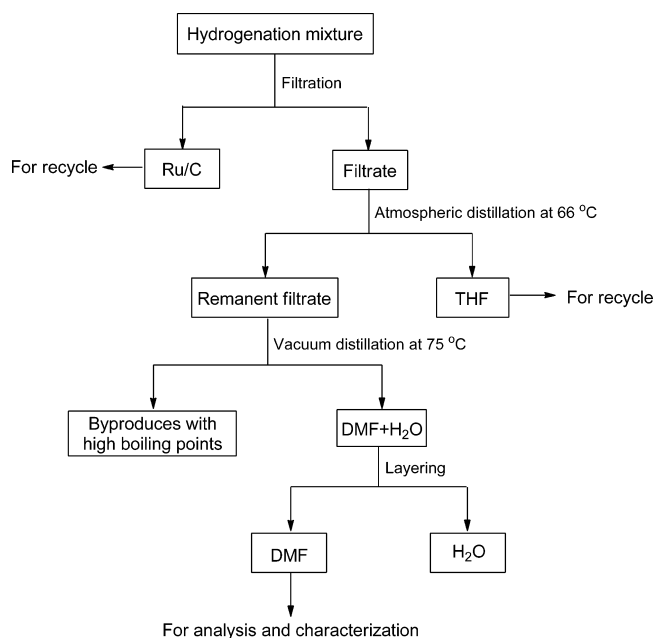
Scheme 2. Plausible Mechanism for the Hydrogenation of HMF into DMF over Ru/C



the apparatus and production costs but also increased the operational risks; therefore, the preferred H₂ pressure was 20 bar in the present work.

3.2.5. Effect of HMF Concentration. As given in Table 3, when the concentration was 1.25 and 2.50 wt %, all HMF was

Scheme 3. Separation of DMF from the Hydrogenation Mixture



converted and the yields of DMF were more than 94.5%. However, when the concentration of HMF was increased to 3.75 and 5.00 wt %, the hydrogenation of HMF was incomplete and the yields of DMF were decreased to 77.9 and 37.9%, respectively. To better understand the decrease of DMF yields at high HMF concentration, two additional experiments were

Table 6. Synthesis of DMF from Biomass-Derived Carbohydrates

entry	carbohydrate	HMF yield ^a (%)	DMF yield ^b (%)
1	fructose	82.5	92.7
2	glucose	47.4	88.1
3	sucrose	63.2	90.4
4	maltose	46.8	87.3
5	cellobiose	45.1	86.2
6	starch	43.9	84.6
7	cellulose	41.6	82.3

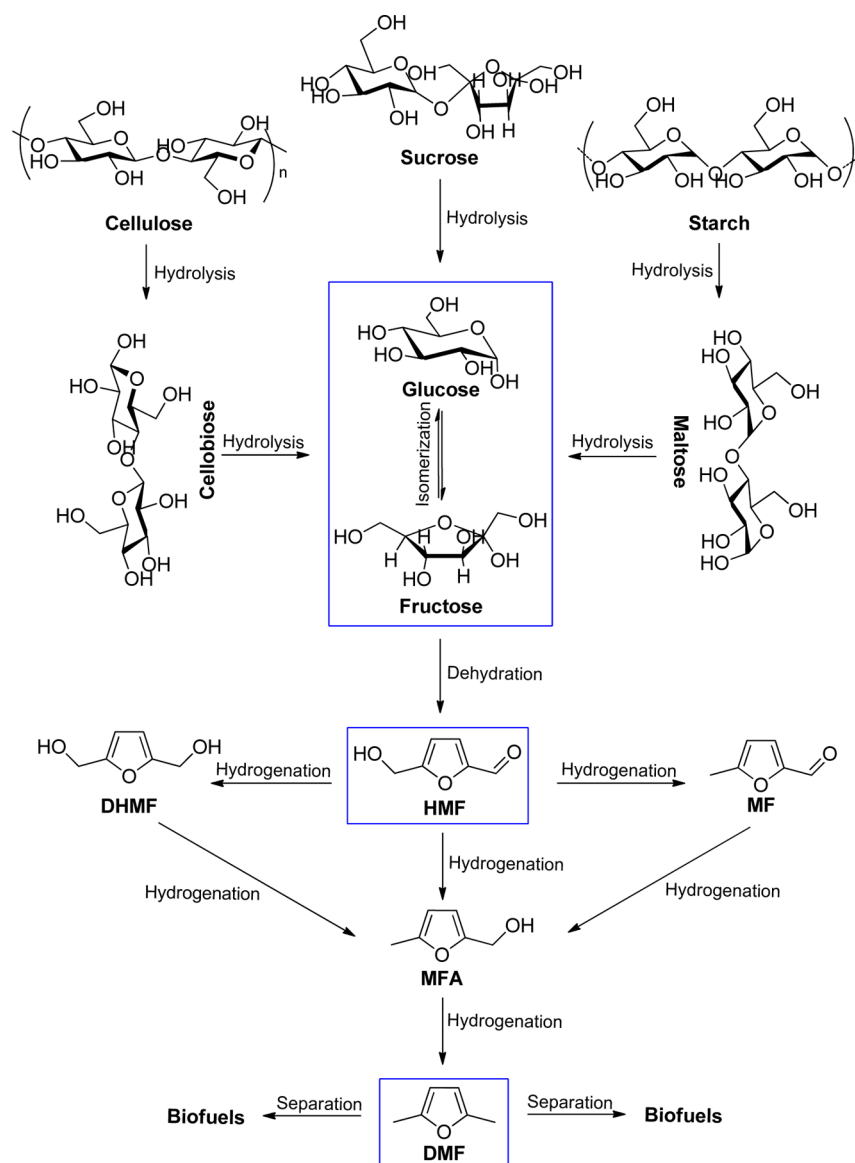
^aReaction conditions for HMF synthesis: carbohydrate, 100 mg; CCC, 40 mg; [BMIM]Cl, 1 g; temperature, 160 °C; time, 15 min. Note: HMF yield is based on carbohydrate. ^bReaction conditions for DMF synthesis: extracted HMF, 2.5 wt %; Ru/C, 5 mol %; THF, 20 mL; H₂, 20 bar; agitation speed, 400 rpm; temperature, 200 °C; time, 2 h. Note: HMF concentration is relative to THF, catalyst loading is relative to HMF, and DMF yield is based on the extracted HMF.

carried out under the higher H₂ pressure. In this case, HMF was also completely converted and DMF yields were increased to

93.9 and 93.2%, respectively, which implied that the decrease of DMF yields at high HMF concentration was mainly due to the lack of H₂. Moreover, the above results also indicated that Ru/C catalyst had excellent catalytic activity for the hydrogenation of HMF into DMF.

3.2.6. Effect of Agitation Speed. As indicated in Table 4, HMF conversion was increased from 93.5 to 100% and DMF yield was increased from 78.3 to 94.7% when the agitation speed was increased from 100 to 400 rpm, respectively. However, when the agitation speed was further increased to 500 and 600 rpm, no obvious increase in the yields of DMF was observed, respectively, demonstrating that the interfacial mass transfer resistance between the catalyst surface (Ru/C) and the liquid phase (THF) was negligible when the agitation speed was above 400 rpm; thus, the appropriate agitation speed was set to 400 rpm in the present work.

3.3. Recycling Potential of Catalyst. The recyclability of catalyst is of great importance for the hydrogenation of HMF into DMF in the practical production. In the present work, after the first reaction run, Ru/C catalyst was separated from the

Scheme 4. Technology Roadmap for the Transformation of Carbohydrates into DMF

reaction mixture by filtration, washed 10 times with 5 mL of THF, and dried at 65 °C for 24 h in a vacuum oven. Subsequently, the recovered Ru/C was added into fresh THF and used for the next reaction run under the same reaction conditions. As depicted in Figure 4, 91.2% DMF yield with 98.1% HMF conversion was still achieved after three successive reaction runs, which clearly indicated that Ru/C had good stability and catalytic activity for the hydrogenation of HMF into DMF. When Ru/C was continuously used an extra two times, HMF conversion was not noticeably influenced and kept more than 97%; however, DMF yield was decreased to 74.7%. To get more insight into the deactivation of Ru/C after five successive reaction runs, the fresh and used Ru/C were well characterized by XRD, scanning electron microscopy (SEM), and inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the results are shown in Figure 5, Figure 6, and Table 5, respectively.

It can be seen from Figure 5 that the fresh and used Ru/C exhibited two broad and weak diffraction peaks at 2θ angles of 15–30 and 35–50° that can be assigned to C(002) and C(101). No diffraction peaks corresponding to Ru were observed, demonstrating that Ru was highly dispersed on the carbon support. As depicted in Figure 6, compared to the fresh Ru/C, the carbon particle size of Ru/C after three successive reaction runs had little change; however, when Ru/C was used five times, the size of carbon particles was largely increased. In addition, ICP-AES analysis of Ru/C (Table 5) showed no obvious loss of Ru after three successive reaction runs; however, 20.9% Ru was leached when Ru/C was used five times. From the above results, it can be concluded that the agglomeration of carbon particle and the loss of Ru, leading to an apparent decrease in the specific surface area of carbon support and catalytic sites on carbon support and then reducing the catalytic activity, were the main reasons for the deactivation of Ru/C. Furthermore, it should be pointed out that the partially deactivated Ru/C could be regenerated by heating at 300 °C under the mixture of 10% H₂ and 90% N₂ flow for 2 h, and when the regenerated Ru/C was used in the sixth reaction run (Figure 4), more than 86% DMF yield with almost 100% HMF conversion could be regained under the same reaction conditions.

3.4. Plausible Mechanism for the Hydrogenation of HMF into DMF. To better understand the reaction process for the hydrogenation of HMF into DMF, a special reaction was carried out at 180 °C for 1 h, and then, the reaction mixture was analyzed by GC and GC-MS. As can be seen from GC chromatograms (Figure S1, Supporting Information) and GC-MS chromatograms (Figure S2, Supporting Information), in addition to the unreacted HMF and generated DMF, many other products such as 2,5-dihydroxymethylfurfural (DHMF), 5-methylfurfural (MF), 5-methylfurfuryl alcohol (MFA), furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), 2,5-hexanedione (HD), 2,5-dimethyltetrahydrofuran (DMTHF), and 2-hexanol (HA) were also detected.

It is generally known that the presence of the conjugate field consisting of an aldehyde group, a hydroxyl group, and a furan ring and the electron-withdrawing effect of oxygen on the aldehyde group make the C5-hydroxyl group and C2-aldehyde group in HMF unstable, and they can be readily hydrogenated in the presence of catalyst and hydrogen. According to the above-mentioned properties of HMF combined with the analysis results of GC-MS and the previous reported literature,^{1,11,17,18,20} the plausible mechanism for the hydro-

genation of HMF into DMF over Ru/C in the presence of THF was proposed. As shown in Scheme 2, the hydrogen was first absorbed on the surface of Ru to form the activated Ru–H, and then, the activated Ru–H would attack the C5-hydroxyl group and C2-aldehyde group in HMF to form DHMF and MF, respectively. Subsequently, DHMF and MF were further hydrogenated into DMF via the intermediate of MFA. Moreover, a molecule of methanol could be removed from DHMF under the attack of the activated Ru–H to form FA, which could be further hydrogenated into THFA. DMF could also be further hydrogenated and hydrated into DMTHF, HA, and HD under the attack of the activated Ru–H, respectively.

3.5. The Separation of DMF from the Crude Hydrogenation Mixture. As stated in the Introduction, DMF is a promising renewable liquid fuel with excellent physicochemical properties, and it will play a very important role in the transportation sector in the near future. In the process of HMF hydrogenation, the products are very complicated. How to separate DMF from the complicated products is the prerequisite for the practical application of DMF. Therefore, in addition to getting a higher DMF yield, exploring a simple and efficient method for DMF separation is also a necessary step for the practical application of DMF.

In the present work, HD, HA, FA, and THFA with yields of 1.2, 1.7, 0.8, and 0.5% are the main byproducts, and their boiling points, 191, 139, 171, and 178 °C, are very high, respectively. However, the boiling points of THF, DMF, and H₂O with 66, 94, and 100 °C are relatively low; thus, it can be seen that the boiling points among the main byproducts, THF and DMF, are largely different and a combination of atmospheric distillation and vacuum distillation could be applied to separate DMF. As can be seen from Scheme 3, after reaction, the catalyst of Ru/C was first separated by filtration, and then, the filtrate was distilled at 66 °C to recover THF. Subsequently, the remanent filtrate was further distilled in a vacuum at 75 °C to get a mixture of DMF and H₂O. The main byproducts HD, HA, FA, and THFA, possessing high boiling points, were very difficult to be distilled out of the mixture. Due to the immiscibility between DMF and H₂O, the mixture of DMF and H₂O would be automatically layered and the upper layer was the separated DMF. The GC analysis of the separated DMF (Figure S3, Supporting Information) demonstrated that the purity of DMF was improved to 98.9% from 94.7%, and the recovery of DMF could also be achieved to 95%, indicating that the combination of atmospheric distillation and vacuum distillation was a very effective method for the separation of DMF from the hydrogenation mixture in the present work. Furthermore, another two points should be pointed out: (i) The physicochemical properties of DMF and DMTHF are very similar; therefore, a very small amount of DMTHF with 1.1% was contained in the separated DMF; however, the presence of DMTHF would not affect the usage of DMF if DMF was used as liquid fuel. (ii) The separated DMF was confirmed to be in accordance with the authentic DMF in the chemical structures determined by GC-MS (Figure S4, Supporting Information), FT-IR (Figure S5, Supporting Information), ¹³C NMR (Figure S6, Supporting Information), and ¹H NMR (Figure S7, Supporting Information) and the physical properties such as the appearance, boiling point, liquid density, refractive index, and water solubility (Table S1, Supporting Information).

3.6. Transformation of Biomass-Derived Carbohydrates into DMF. In addition to pure HMF, a variety of

biomass-derived carbohydrates was also used for the synthesis of DMF (Table 6). First, a mixture of 100 mg of carbohydrate, 40 mg of cellulose-derived sulfonated carbonaceous catalyst (CCC),³¹ and 1 g of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was stirred at 160 °C for 15 min. At the end of the reaction, the reaction mixture was immediately quenched to room temperature in an ice–water bath and then 4 mL of deionized water was added to the reaction mixture to reduce the viscosity of [BMIM]Cl, which was further centrifuged at 10 000 rpm for 5 min to separate CCC. Subsequently, HMF was extracted from the reaction mixture by 5 mL of THF for 10 times, dehydrated by anhydrous sodium sulfate, and then analyzed by GC. The yields of HMF with 82.5, 47.4, 63.2, 46.8, 45.1, 43.9, and 41.6% were obtained when fructose, glucose, sucrose, maltose, cellobiose, starch, and cellulose were used, respectively. Eventually, the extracted HMF was hydrogenated in the presence of THF over Ru/C under the same reaction conditions as the above hydrogenation reactions. Gratifyingly, more than 82% DMF yields were achieved, demonstrating that the source of HMF had very little effect on the synthesis of DMF in the presence of THF and Ru/C. In other words, a combination of THF and Ru/C in the present work was also suitable for the direct hydrogenation of carbohydrate-derived HMF into DMF, which is favorable for the practical production of DMF from a variety of biomass-derived carbohydrates. Moreover, in the light of our previous reported results^{31–35} and the results from this research, a technology roadmap for the transformation of biomass-derived carbohydrates into DMF was drafted (Scheme 4) to provide the theoretical reference and technical support for the practical production of DMF in the near future.

4. CONCLUSIONS

In summary, an excellent DMF yield of 94.7% from HMF was achieved over Ru/C in the presence of THF at 200 °C for 2 h, which is a high value under relatively mild reaction conditions. Moreover, Ru/C exhibited good stability and catalytic activity, and it could be recycled at least six times after a simple regeneration process. Furthermore, a plausible mechanism involving an aldehyde group, a hydroxyl group, and a furan ring for the selective hydrogenation of HMF into DMF and a simple procedure containing atmospheric distillation and vacuum distillation for the separation of DMF from the crude hydrogenation mixture were proposed. More importantly, a combination of Ru/C and THF was also effective for the direct hydrogenation of HMF produced from a variety of biomass-derived carbohydrates such as fructose, glucose, sucrose, maltose, cellobiose, starch, and cellulose into DMF.

■ ASSOCIATED CONTENT

■ Supporting Information

Figure S1 showing a GC chromatogram for the hydrogenation of HMF; Figure S2 showing a GC-MS chromatogram for the hydrogenation products of HMF; Figure S3, S4, S5, S6, and S7 showing a GC chromatogram, a GC-MS chromatogram, a FT-IR spectrum, a ¹³C-NMR spectrum, and a ¹H-NMR spectrum of the separated DMF, respectively; and Table S1 showing a comparison of physical properties between the separated and authentic DMF. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the National Basic Research Program of China (2010CB732201), the National Natural Science Foundation of China (21106121), the Provincial R&D Program from Economic and Trade Committee of Fujian Province of China (1270-K42004), the Key Programs for Cooperation Between Universities and Enterprises in Fujian Province (2013NS011), and the Fundamental Research Funds for the Central Universities (2010121077).

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