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An integrated process for the production of 2,5-dimethylfuran from fructose†

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2,5-Dimethylfuran was successfully produced in 92% overall yield from fructose in 1-butanol through a combination of dehydration over Amberlyst-15 and hydrogenolysis over the Ru–Sn/ZnO catalyst. The environmental favorability of this process, and its unprecedented efficiency, makes it promising from both a green chemistry and an industrial perspective.

Renewable biofuels have recently attracted much interest due to the depletion of non-renewable fossil fuels.[1] Among the various renewable biofuels, 2,5-dimethylfuran (DMF) is particularly promising because its properties compare favorably to those of gasoline, including its boiling point, high energy density, high research octane number, and immiscibility with water.[2] DMF is generally produced by the dehydration of fructose to form 5-hydroxymethylfurfural (HMF) and the subsequent conversion of HMF by hydrogenolysis of the two outlying C–O bonds.[3]

Unfortunately, a cost-effective method for selectively producing HMF from fructose in high yields is not straightforward, although there are some start-up companies that produce HMF on an industrial scale. Aqueous reactions tend not to proceed well due to the rehydration of HMF to form levulinic acid and formic acid, as well as the condensation of HMF and/or fructose to form insoluble humin polymers.[4] Research has therefore focused on the use of organic solvents such as dimethylsulfoxide (DMSO) and ionic liquids;[5] however, these solvents are not easily separable from the desired HMF product, thereby complicating the product recovery. HMF yield is improved in a biphasic reaction system of water/1-butanol (BuOH), comprising homogeneous HCl as a catalyst and NaCl as an electrolyte. This is due to the immediate extraction of HMF produced in an aqueous phase into an organic phase with BuOH, which prevents HMF rehydration and condensation. However, the yield using this system is less than 70%. In addition, the use of heterogeneous catalysts is not possible, owing to the presence of NaCl.[3]

The hydrogenolysis of HMF, meanwhile, has been most successfully achieved when using bifunctional catalytic systems that can both hydrogenate and deoxygenate; Cu–Ru/C, Ru/Co_3O_4, Zn-assisted Pd/C, and Ni-W_2C/C have all been widely studied.[6] It has been reported that these catalysts selectively hydrogenate the formyl and hydroxyl groups of HMF without excessively opening the furan ring. Recently, Schüth *et al.* reported that PtCo bimetallic nanoparticles in hollow carbon spheres can efficiently convert HMF to DMF, giving a 98% yield.[7]

Despite these improvements, these studies are limited by the fact that they do not account for the difficulty of isolating HMF in the first step of the reaction scheme. An integrated catalytic system that can be more directly applied to DMF production could resolve this issue. Dumesic *et al.* recently proposed a revised process where fructose is dehydrated to HMF by Amberlite-70 in gammavalerolactone (GVL), giving a yield of 71%.[8] The resulting solution could then be directly applied to DMF production by using a Ru–Sn/C catalyst. Rauchfuss *et al.* developed a one-pot process for the production of DMF from fructose using formic acid as an acid catalyst, a hydrogen source, and a deoxygenation agent.[9] However, the overall yield of this process is less than 50%, which is unsatisfactory for industrial applications.

Herein, we propose a green and integrated process for the high-yield production of DMF from fructose, which is based on a two-step heterogeneous catalytic reactions (Fig. 1). In this integrated process, fructose is first dehydrated to HMF over Amberlyst-15 in BuOH, which is a sustainable solvent that can be produced from a variety of waste biomass sources.[10] The HMF in the resulting mixture is then converted to DMF by vapor-phase hydrogenolysis over the Ru–Sn/ZnO catalyst.

HMF was initially synthesized by using Amberlyst-15 in various solvents. The reactions were carried out using a high

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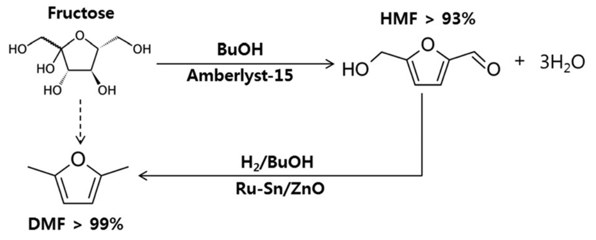

Fig. 1 Two-step reaction scheme for the production of DMF from fructose.

concentration of fructose (15 wt%) and at ambient pressure. The results are summarized in Table 1.

When water was used as the solvent, the maximum HMF yield was 60% after 3 h. As the reaction progressed further, the HMF yield decreased despite an increase in fructose conversion. The HMF yield was negligible after 6 h, although the fructose conversion reached 100% (Fig. 2). This indicated that the rate of humin formation from HMF exceeded the rate of HMF formation later on in the reaction. The yield improved significantly when water was replaced with DMSO or GVL; these solvents resulted in HMF yields of 78 and 76% and fructose conversions of 98 and 86%, respectively. Interestingly, BuOH gave the highest HMF yield of 93%, with 96% fructose conversion. Note that these results were obtained at a high fructose concentration of 15 wt% and without the use of ionic liquids. As seen in water, the HMF yield in BuOH decreased as the reaction progressed further. This likely resulted from an increased water concentration from fructose dehydration, which implied that a concurrent removal of water should improve the yield.

Table 1 Catalytic activity of fructose dehydration in various solvents[a]

Solvent	Time/h	Fructose conversion (%)	HMF selectivity (%)	HMF yield (%)
BuOH	5	96	97	93
DMSO	5	98	80	78
Water	3	73	60	60
GVL	5	86	88	76

[a] Reaction conditions: Amberlyst-15 1.0 g, fructose 15 g, solvent 85 g, temperature 100 °C.

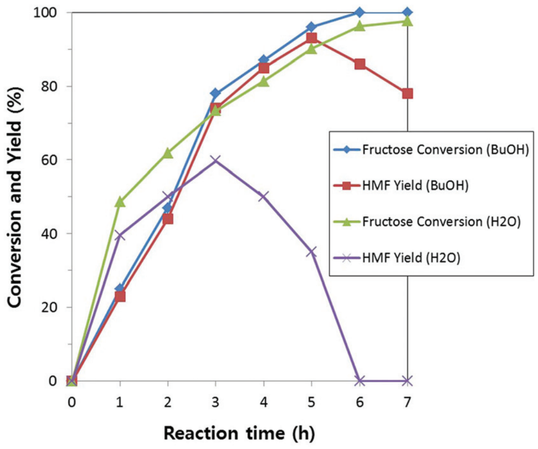

Fig. 2 Reaction profiles of fructose dehydration in different solvents. Reaction conditions: Amberlyst-15 1.0 g, fructose 15 g, solvent 85 g, and temperature 100 °C.

After 5 h, the mixture was cooled to room temperature. Interestingly, this caused the unreacted fructose to crystallize, allowing for its removal along with the catalyst by filtration. Since fructose is highly soluble in water, the catalyst could be recycled by simply washing the solids with water and drying at 100 °C. This recycled catalyst showed a nearly identical performance for up to five cycles (Fig. S1†). In addition, the SO_3H density of the catalyst, which was measured by the acid–base back titration, as well as the BET surface area and pore volume, which were measured by N_2 physisorption at −196 °C, were similar to the original catalyst.

We then aimed to produce DMF directly using this solution. The isolation of DMF from BuOH should be significantly easier than the isolation of HMF, because DMF has a lower boiling point and a higher thermal stability than BuOH. Ru–Sn/ZnO was selected as the catalyst for this step, because it was effective and selective for the hydrogenation of butyric acid, and had good chemical stability in our previous work.[11] This catalyst contained 1.4 wt% Ru and had a Ru/Sn molar ratio of 0.5, and was prepared using a sequential coprecipitation–deposition method. In this catalyst, Sn was found to exist as a part of a Ru intermetallic alloy such as Ru_3Sn_7 on ZnO. DMF production was carried out at atmospheric pressure, and the catalytic activities are presented in Table 2.

When the BuOH mixture was used, Ru–Sn/ZnO provided a DMF yield of 90% and an HMF conversion of 93% at a weight hourly space velocity (WHSV) of 0.5 h^{-1}. The main by-products, determined by gas chromatography, were 5-methylfurfuryl alcohol (MFA), 2,5-dihydroxymethylfuran (DHMF), and 5-methylfurfural (MF). Neither humin formation nor BuOH degradation was observed. However, DMSO was not suitable under these reaction conditions, owing to its instability at high temperatures.

The activity of this catalyst was then compared to those of other Ru-based catalysts. Ru/ZnO gave a DMF yield of only 61% at 91% HMF conversion, while yielding 10% MFA and 17% DHMF as the major byproducts. Ru/C and Ru/Al_2O_3, meanwhile, provided DMF yields of 64 and 62%, respectively, at an HMF conversion of 100%. Previous reports indicated that DMF is produced from HMF by an initial reaction with hydrogen, with further hydrogenation yielding MFA before yielding the final product.[12] In the Ru-based vapor-phase reactions conducted, DHMF appears to be the initial intermediate, since MF concentrations were negligible at WHSV values higher than 1.0 h^{-1}. Likewise, the large amounts of DHMF formed over Ru/ZnO, Ru/C, and Ru/Al_2O_3 suggested that the deoxygenation of DHMF to form MFA is much slower than the hydrogenation of HMF to form DHMF. Interestingly, both DHMF and MFA yields were negligible over Ru–Sn/ZnO. In this case, the acidic

Table 2 Catalytic activity of HMF/BuOH hydrogenolysis over various catalysts[a]

			Product yield (%)				
Catalyst	WHSV (h^{-1})	HMF conversion (%)	DMF	MFA	DHMF	MF	Unknown
Ru–Sn/ZnO	0.5	93[b]	90.0	1.2	0.6	0.3	0.9
	0.5	98[c]	94.5	1.0	0.8	0.6	1.1
	0.5	98[d]	95.0	0.9	0.6	0.4	1.0
	0.2	100[c]	99.0	0.4	0.4	0.1	0.1
	1.0	91[c]	78.0	9.0	1.0	0.6	2.4
5% Ru/ZnO	0.5	91[c]	61.0	10.0	17.0	0.9	2.1
5% Ru/C	0.5	100[c]	64.0	6.0	27.0	1.1	1.9
5% Ru/Al_2O_3	0.5	100[c]	62.0	8.0	26.0	1.4	2.6

[a] Reaction conditions: 240 °C, 1 atm, catalyst 1.0 g, HMF 12 wt% in BuOH, H_2 flow rate 20 ml min^{-1}, and reaction time 100 h. [b] As-synthesized HMF feed before purification. [c] As-synthesized HMF feed after purification. [d] Pure HMF feed.

properties of the Sn cation, which are induced by the electronic interactions with Ru metal in the Ru–Sn alloy on ZnO, might activate and polarize the OH group in DHMF, yielding MFA and then DMF shortly thereafter.[13] The overall scheme and relative kinetics are summarized in Fig. 3.

The activity of the Ru–Sn/ZnO catalyst was also evaluated using pure HMF in BuOH under the same reaction conditions. In this case, the DMF yield and HMF conversion were increased to 95 and 98%, respectively. The lower performance observed for the impure feed was likely due to humin formation from residual fructose on the catalyst surface. To resolve this, the as-synthesized HMF was purified by washing with an aqueous NaCl solution (30wt%). Notably, the use of the resulting HMF feed showed a performance that was almost identical to the pure feed.

Next, the effect of the HMF flow rate on the catalytic activity was investigated. Notably, a WHSV of 0.2 h^{-1} resulted in a DMF yield of 99% and an HMF conversion of 100%, with negligible humin formation. However, increasing the WHSV to 1.0 h^{-1} decreased the DMF yield and HMF conversion to 78 and 91%, respectively. This decrease was mainly due to increased MFA production, which indicated that there were an insufficient number of active sites to effect a full conversion at such a high flow rate. In addition, the humin formation was more significant due to the condensation of unreacted HMF.

Catalyst stability is as important as activity in a continuous heterogeneous catalytic process. Therefore, the long-term stability of the catalyst in the system in question was investigated (Fig. 4). Notably, the catalyst maintained a nearly perfect performance for more than 300 h. In addition, the catalyst stability was confirmed by studying the used catalyst by X-ray diffraction (XRD) and transmission electron microscopy (TEM) (Fig. S2†). In particular, the XRD pattern of the used catalyst was almost identical to that of the fresh one, with Ru_3Sn_7 peaks present in both samples and with similar relative intensities between both sets. Thermogravimetric analysis (TGA) showed that the used catalyst underwent a 5 wt% greater weight loss than the fresh one up to 300 °C. However, after washing, the TGA pattern of the used catalyst was nearly identical to that of the fresh one (Fig. S3†); this indicated that the coke deposition on the Ru–Sn/ZnO surface was not significant.

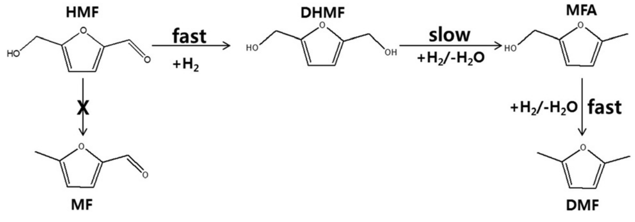

Fig. 3 DMF production pathway from HMF.

We also carried out a batch-type hydrogenolysis at 180 °C and an H_2 pressure of 10 bar using the as-synthesized HMF in BuOH over the Ru–Sn/ZnO catalyst. The as-synthesized feed gave a DMF yield of 90% at an HMF conversion of 94% after a reaction time of 2 h. After purification of the feed, the DMF yield and HMF conversion were increased to 95 and 97%, respectively. There was no leaching of the active sites during the HMF hydrogenation in the liquid phase, which was confirmed by inductively coupled plasma atomic emission ana-

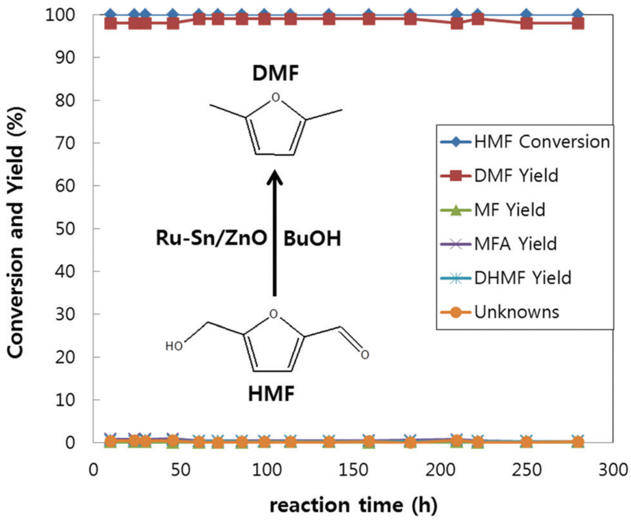

Fig. 4 Long-term catalytic activity for the hydrogenolysis of HMF/BuOH. Reaction conditions: 240 °C, 1 atm, catalyst 1.0 g, HMF 12 wt% in BuOH, H_2 flow rate 20 ml min^{-1}, and WHSV 0.2 h^{-1}.

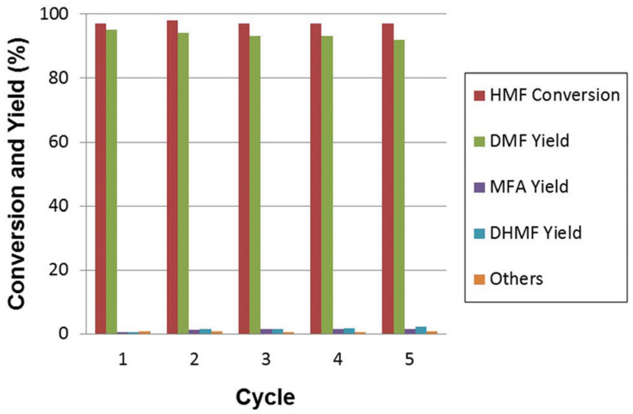

Fig. 5 Catalytic activity for the batch-type hydrogenolysis of HMF/BuOH. Reaction conditions: 180 °C, H_2 pressure 10 bar, catalyst 1.0 g, HMF 12 wt% in BuOH 100 g, and reaction time 2 h.

lysis of the product mixture. The recycled catalyst showed a nearly identical performance up to five cycles (Fig. 5). Therefore, the complete reaction from fructose to DMF could be conducted in one pot by changing the reaction conditions.

Conclusions

DMF was selectively produced from fructose through a two-step reaction in BuOH. Fructose was dehydrated to HMF with over 93% yield using Amberlyst-15; the resulting solution was then directly transformed to DMF at over 99% yield by vapor-phase hydrogenolysis over Ru–Sn/ZnO. Both catalysts could be used for extended periods of time. A simple washing with water after the first reaction allowed for the facile isolation of both the catalyst and the unreacted substrate. The recyclability, efficiency, and extended operation afforded by this process make it particularly favorable environmentally and industrially, and establish it as a new method for the production of DMF as a fossil fuel alternative.

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Notes and references

1 G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044; A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411; B. Kamm, *Angew. Chem., Int. Ed.*, 2007, **46**, 5056; J. J. Bozell and G. R. Petersen, *Green Chem.*, 2010, **12**, 539; D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493; J. C. Serrano, R. Luque and A. Sepulveda-Escribano, *Chem. Soc. Rev.*, 2011, **40**, 5266; B. Kamm and M. Kamm, *Appl. Microbiol. Biotechnol.*, 2004, **64**, 137.

2 T. Thananatthanachon and T. B. Rauchfuss, *Angew. Chem., Int. Ed.*, 2010, **49**, 6616; S. Zhong, R. Daniel, H. Xu, J. Zhang, D. Turner, M. L. Wyszynski and P. Richards, *Energy Fuels*, 2010, **24**, 2891.

3 Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982; Q. Zhao, L. Wang, S. Zhao, X. Wang and S. Wang, *Fuel*, 2011, **90**, 2289.

4 H. E. Van Dam, A. P. G. Kieboom and H. Van Bekkum, *Starch*, 1986, **38**, 95; R.-J. V. Putten, J. C. Waal, E. D. Jong, C. B. Rasrendra, H. J. Heeres and J. G. Vries, *Chem. Rev.*, 2013, **113**, 1499; P. P. Upare, J.-W. Yoon, M. Y. Kim, H.-Y Kang, D. W. Hwang, Y. K. Hwang, H. H. Kung and J.-S. Chang, *Green Chem.*, 2013, **15**, 2935.

5 A. A. Rosatell, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, *Green Chem.*, 2011, **13**, 754; M. E. Zakrzewska, E. Bogel-Łukasik and R. Bogel-Łukasik, *Chem. Rev.*, 2011, **111**, 397.

6 Y.-B. Huang, M.-Y. Chen, L. Yan, Q.-X. Guo and Y. Fu, *ChemSusChem*, 2014, **7**, 1068; Y. Zu, P. Yang, J. Wang, X. Liu, J. Ren, G. Lu and Y. Wang, *Appl. Catal., B*, 2014, **146**, 244; B. Saha, C. M. Bohn and M. M. Abu-Omar, *ChemSusChem*, 2014, **7**, 3095; J. Jae, W. Zheng, R. F. Lobo and D. G. Vlachos, *ChemSusChem*, 2013, **6**, 1158.

7 G. H. Wang, J. Hilgert, F. H. Richter, F. Wang, H.-J. Bongard, B. Splietho, C. Weidenthaler and F. Schüth, *Nat. Mater.*, 2014, **13**, 293.

8 J. M. R. Gallo, D. M. Alonso, M. A. Mellmer and J. A. Dumesic, *Green Chem.*, 2013, **15**, 85.

9 T. Thananatthanachon and T. B. Rauchfuss, *Angew. Chem., Int. Ed.*, 2010, **122**, 6766.

10 B. G. Harvey and H. A. Meylemans, *J. Chem. Technol. Biotechnol.*, 2011, **86**, 2; P. Dürre, *Biotechnol. J.*, 2007, **12**, 1525; V. Garciaa, J. Pakkilaa, H. Ojamob, E. Muurinena and R. L. Keiski, *Renewable Sustainable Energy Rev.*, 2011, **5**, 964.

11 J.-M. Lee, P. P. Upare, J.-S. Chang, Y. K. Hwang, J. H. Lee, D. W. Hwang, D.-Y. Hong, S. H. Lee, M. G. Jeong, Y. D. Kim and Y.-U. Kwon, *ChemSusChem*, 2014, **7**, 2998.

12 M. Chidambaram and A. T. Bell, *Green Chem.*, 2010, **12**, 1253; L. Hu, X. Tang, J. Xu, Z. Wu, L. Lin and S. Liu, *Ind. Eng. Chem. Res.*, 2014, **53**, 3056.

13 B. A. Riguetto, C. E. C. Rodrigues, M. A. Morales, E. Baggio-Saitovitch, L. Gengembre, E. Payen, C. M. P. Marques and J. M. C. Bueno, *Appl. Catal., A*, 2007, **318**, 70.