Cite this: Green Chem., 2011, 13, 1503

www.rsc.org/greenchem

# COMMUNICATION

# Direct transformation of cellulose into 5-hydroxymethyl-2-furfural using a combination of metal chlorides in imidazolium ionic liquid<sup>†</sup>

Bora Kim,<sup>a</sup> Jaewon Jeong,<sup>a</sup> Dohoon Lee,<sup>a</sup> Sangyong Kim,<sup>a</sup> Hyo-Jin Yoon,<sup>b</sup> Yoon-Sik Lee<sup>b</sup> and Jin Ku Cho\*<sup>a</sup>

*Received 9th February 2011, Accepted 29th March 2011* DOI: 10.1039/c1gc15152e

Direct transformation of cellulose into HMF was carried out using a combination of metal chlorides in ionic liquid [EMIM]Cl. From high throughput screening of various metal chlorides, a combination of CrCl<sub>2</sub> and RuCl<sub>3</sub> was found as the most effective catalyst. HMF was directly afforded from cellulose in nearly 60% yield. Gram scale-up synthesis of HMF was successfully performed from cellulose using CrCl<sub>2</sub> and RuCl<sub>3</sub>. Furthermore, lignocellulosic raw material reed could be directly converted into HMF and furfural in reasonable yields under these conditions.

Over the past 150 years, humankind has consumed carbon sources in a mostly irreversible manner, which resulted in diminishing reserves of fossil fuels and global warming by CO<sub>2</sub> emission.1 This issue is prompting us to replace fossil-based resources with renewable and sustainable ones.<sup>2</sup> With this in mind, plentiful biomass has the potential as a renewable carbon source for transportation fuels and chemicals. Actually, bioethanol produced from corn or sugarcane is used as a transportation fuel in some countries. There are, however, many arguments that such a use of crop-based feedstock could bring a food shortage problem. In an effort to overcome this dispute, cellulose derived from naturally grown lignocellulosic biomass currently attracts much attention as a promising carbon source due to its abundance and limited share of cultivated land. Until now, studies have mainly focused on the efficient depolymerization of cellulose into monomeric glucose, because cellulose itself is too complex and its crystalline structure (formed by internal hydrogen bonds) is chemically and biologically too stable to convert.<sup>3</sup> However, the depolymerization step of cellulose into glucose still remains an expensive and energy-intensive process.

5-Hydroxymethyl-2-furfural (HMF) is a template compound to synthesize a broad range of chemicals and fuels.<sup>4</sup> Although HMF can be obtained by straightforward dehydration of ketosetype hexose forming 5-membered ring such as fructose,<sup>5</sup> ketosetype carbohydrates are not abundant in nature and most of them are sourced from agricultural feedstock. Recently, a remarkable study by Zhang's group found that aldose-type glucose could be converted into HMF in record yield using Cr(II) or Cr(III) metal catalysts in imidazolium ionic liquid and they revealed that the Cr metal could assist an isomerization from C1-aldose to C2-ketose by a specific coordination to the hemiacetal portion of aldose.6 More recently, HMF synthesis from glucose was also accomplished by common Lewis acid, SnCl<sub>4</sub> in 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMim]BF<sub>4</sub>) instead of Cr metal catalyst,7 effective bulky NHC (N-heterocyclic carbene) metal ligands,8 and an integration of enzymatic and chemical conversion.9 Furthermore, some efforts to utilize cellulose as a starting material for direct synthesis of HMF by means of a mixed catalyst using Brønsted acid and Lewis acid10 and a microwave-assisted conversion11 were tried. Herein, we report an effective direct transformation of cellulose into HMF using a combination of metal catalysts screened in a combinatorial manner (Scheme 1).



Scheme 1 Direct transformation of cellulose into HMF using a combination of metal catalysts in imidazolium ionic liquid.

In terms of chemical pathway, a direct transformation of cellulose into HMF involves three reactions corresponding to (1) hydrolysis of polymeric cellulose into mono-saccharide such as glucose, so called saccharification, (2) isomerization from aldose-type sugar to ketose-type one, allowing five-membered ring formation, and (3) dehydrations of ketose-type (or furanose-type if cyclized) sugar to generate final product, HMF (Scheme 2). It means that various functions of catalysts

<sup>&</sup>lt;sup>a</sup>Green Chemistry & Engineering R&D Department, Cleaner Production Technology Division, Korea Institute of Industrial Technology (KITECH), 35-3, Hongcheon-Ri, Ipchang-Myeon, Cheonan-Si, Chungnam, 330-825, South Korea. E-mail: jkcho@kitech.re.kr; Fax: +82-41-589-8580; Tel: +82-41-589-8665

<sup>&</sup>lt;sup>b</sup>School of Chemical and Biological Engineering, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul, 151-742, South Korea. E-mail: yslee@snu.ac.kr; Fax: +82-2-876-9625; Tel: +82-2-880-7073 † Electronic supplementary information (ESI) available: Detailed experimental and analytical procedures, seven figures including UV and RI HPLC traces, standard curve for quantification of HMF and total reducing sugars, NMR and MS spectra of synthetic HMF. See DOI: 10.1039/c1gc15152e



Scheme 2 Chemical pathway of direct transformation of cellulose into HMF.

should be simultaneously required for direct transformation of cellulose into HMF.

In an initial attempt for the ability to transform cellulose into HMF directly, a wide range of single metal chlorides including CrCl<sub>2</sub>, MnCl<sub>2</sub>, FeCl<sub>2</sub>, FeCl<sub>3</sub>, CoCl<sub>2</sub>·6H<sub>2</sub>O (simply called CoCl<sub>2</sub> in the following), NiCl<sub>2</sub>, CuCl<sub>2</sub>, ZnCl<sub>2</sub>, MoCl<sub>3</sub>, VCl<sub>3</sub>, RuCl<sub>3</sub> were assayed under imidazolium-type ionic liquid, ethylmethylimdazolium chloride ([EMIM]Cl) that is class of solvents capable of dissolving cellulose.12 When reactions were carried out using single metal chloride at 90 °C for 2 h, HMF yields obtained from all the reactions were less than 15% (blue bars in Fig. 1).13 Although it was reported that HMF synthetic yield from glucose, using CrCl<sub>2</sub> in [EMIM]Cl under these conditions was approximately 70%,6 only 7.4% of HMF was obtained from cellulose. It indicates that CrCl<sub>2</sub> is the most powerful metal chloride to catalyze the isomerization of aldose-type glucose to ketose-type fructose (second step in Scheme 2) but it is not effective to hydrolyze cellulose into glucose. Expecting enhancement of catalytic activity in hydrolysis and dehydration



Fig. 1 High throughput screening of single metal catalyst for direct transformation of cellulose into HMF under [EMIM]Cl (conditions: each metal catalyst (10 mol%), cellulose (50 mg), [EMIM]Cl (500 mg)); blue bars: 90 °C, 2 h; green bars: 120 °C, 2 h; red bars: 120 °C, 4 h and comparison of solvents including [EMIM]Cl, cholic acid/citric acid ([CA]/[CA] = 2/1), DMSO for HMF synthesis from cellulose using CrCl<sub>2</sub> at 120 °C for 4 h (inner box).

steps, the reaction was tried at a temperature above the boiling point of water (120  $^{\circ}$ C).

The results were positive to some extent. In most cases using CrCl<sub>2</sub>, MnCl<sub>2</sub>, FeCl<sub>2</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, ZnCl<sub>2</sub>, higher yields of HMF were synthesized at 120 °C than at 90 °C (green bars in Fig. 1). Particularly, CrCl<sub>2</sub> gave more than two times of HMF yield (7.4% to 19%) when temperature was increased from 90 °C to 120 °C. As a next attempt, reactions were carried out for longer reaction time (4 h) and HMF yield was increased to 27.1% in the presence of CrCl<sub>2</sub>. Meanwhile, a similar or less amount of HMF was obtained in the presence of other metal chlorides. It was believed that the produced HMF was consumed due to subsequent reaction into levulinic acid by deformylation for an extended reaction time. In another attempt, direct transformation of cellulose into HMF was tried under choline chloride (CC)/citric acid (CA) known as renewable material based ionic liquid<sup>14</sup> and DMSO using CrCl<sub>2</sub> at 120 °C for 4 h. In both cases, HMF yields were, however, less than 5% (inner box in Fig. 1).

Based on the above results, we realized that direct transformation of cellulose into HMF in the presence of single metal chloride was unable to afford a yield over 30%. Therefore, in order to enhance the ability of depolymerizing cellulose, additional metal chlorides were applied. Cu,15 Fe,16 Ru17 metal chlorides were employed based on the recent results about hydrolytic efficiency of cellulose into glucose and CuCl<sub>2</sub>, FeCl<sub>2</sub>, FeCl<sub>3</sub>, RuCl<sub>3</sub> was used in combination with CrCl<sub>2</sub> under [EMIM]Cl (molar ratio between two metal chlorides is  $CrCl_2$ :  $MCl_n = 4:1$ ). Reactions were carried out at 120 °C for 2 h. As expected, HMF yields were improved and all the yields of HMF were more than 37%. No additional water was required for the depolymerization of cellulose into glucose. Especially when RuCl<sub>3</sub> was added to CrCl<sub>2</sub>, HMF was obtained in nearly 60% yield. However, after the reaction progressed over 4 h, HMF yield was diminished. It was thought to be due to the same reasons previously mentioned (Fig. 2).



**Fig. 2** Direct transformation of cellulose into HMF using two metal chloridesin [EMIM]Cl (conditions: metal chlorides (10 mol% to cellulose, total equivalent of two metal chlorides), cellulose (50 mg), [EMIM]Cl (500 mg)); green bars: 120 °C, 2 h; red bars: 120 °C, 4 h.

Next, the effect of molar ratio of  $CrCl_2$  and  $RuCl_3$  was investigated. A series of molar ratios from 10:1 ( $CrCl_2:RuCl_3$ ) to 1:4 ( $CrCl_2:RuCl_3$ ) were screened. The reactions were carried out at 120 °C for 2 h. From the results, a molar ratio of CrCl<sub>2</sub> greater than 50% was required for efficient transformation into HMF, and a molar ratio of 4:1 (CrCl<sub>2</sub>:RuCl<sub>3</sub>) showed the best performance (Fig. 3). In a practical aspect, the amount of precious metal ruthenium can be reduced to a molar ratio of 6:1 (CrCl<sub>2</sub>:RuCl<sub>3</sub>) with which HMF was still obtained in over 50% yield. In addition, gram scale-up tests and time course experiments of HMF synthesis from cellulose using CrCl<sub>2</sub> and RuCl<sub>3</sub> were performed. In a 250 mL round-bottomed flask were placed CrCl<sub>2</sub> and RuCl<sub>3</sub> (8 mol% of CrCl<sub>2</sub> and 2 mol% of RuCl<sub>3</sub> to cellulose) and [EMIM]Cl (40 g), the mixture was elevated to 90 °C and stirred for 40 min. After cooling to room temperature, 4 g of cellulose was added into the reaction mixture and then it was re-elevated to 120 °C and stirred in a temperature-controlled oil bath with magnetic stirring. The reaction was a little bit lagging at the initial stage because of heat transferring time occurring from scale-up. Nevertheless, maximum yield of HMF could be achieved in approximately 60% after 3 h (Fig. 4) and yield of total reducing sugars titrated from DNS (3,5-



Fig. 3 HMF yields according to molar ratio of two metal chlorides (conditions: metal chlorides (10 mol% to cellulose, total equivalent of two metal chlorides), cellulose (50 mg), [EMIM]Cl (500 mg), 120  $^{\circ}$ C, 2 h).



**Fig. 4** Scale-up and time course experiment of direct transformation of cellulose into HMF using  $CrCl_2/RuCl_3$  in [EMIM]Cl (conditions: metal chlorides (10 mol% to cellulose, total equivalent of  $CrCl_2$  and  $RuCl_3$  in molar ratio of 4 : 1), cellulose (4 g), [EMIM]Cl (40 g), 120 °C).

dinitrosalicylic acid) was 14%.<sup>18</sup> As previously found in screening experiments, prolonged reaction led to exacerbation of HMF yields due to subsequent deformylation of produced HMF into levulinic acid, which could be confirmed from refractive index HPLC analysis (see Fig. S3 in ESI<sup>†</sup>).

Finally, the reaction was applied to the conversion of lignocellulosic raw material. Reed (*Phragmites communis*, Trin.) naturally grown all over Korea was chosen as a model lignocellulosic raw material.<sup>19</sup> Under the conditions using  $CrCl_2/RuCl_3$ (4:1) in [EMIM]Cl at 120 °C for 2 h, reed was converted into HMF and furfural in 41% and 26% of yields, respectively, based on glucan and xylan contents.

## Conclusions

In conclusion, the effective catalytic conditions using  $CrCl_2$ and  $RuCl_3$  in imidazolium ionic liquid to transform cellulose into HMF was found by high throughput screening of various metal chlorides. Under these conditions, gram scale-up synthesis of HMF was successfully performed and lignocellulosic raw material, reed could be directly converted into HMF and furfural in reasonable yields.

#### Acknowledgements

This work was supported by the Korea Ministry of Environment as "Converging technology project (202–091–002)" and we acknowledge Dr Jung Kon Kim in Rural Development Administration of Korea for generous supply of lignocellulosic raw materials.

### Notes and references

- (a) A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484; (b) G. Stephanopoulos, *Science*, 2007, **315**, 801; (c) Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982.
- 2 (a) J. N. Chheda, G. W. Huber and J. A. Dumesic, Angew. Chem., Int. Ed., 2007, 46, 7164; (b) A. Corma, S. Iborra and A. Velty, Chem. Rev., 2007, 107, 2411.
- 3 (a) Q. Gan, S. J. Allen and G. J. Taylor, J. Chem. Technol. Biotechnol., 2005, 80, 688; (b) J. F. Saeman, Ind. Eng. Chem., 1945, 37, 43; (c) N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Y. Lee, M. Holtzapple and M. Ladisch, Bioresour. Technol., 2005, 96, 673; (d) G. Sanchez, L. Pilcher, C. Roslander, T. Modig, M. Galbe and G. Liden, Bioresour. Technol., 2004, 93, 249.
- 4 (a) T. Werpy, G. Petersen, A. Aden, J. Bozell, J. Holladay, J. White and A. Manheim, *Top value-added chemicals from biomass, volume I: Results of screening for potential candidates from sugars and synthesis* gas; *Report DOE/GO-102004-1992*, Office of Scientific and Technical Information, U.S. Department of Energy, Oak Ridge, TN, 2004; (b) G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, **308**, 1446; (c) J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2007, **46**, 7164.
- 5 Y. Román-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, 312, 1937.
- 6 H. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, **316**, 1597.
- 7 S. Hu, Z. Zhang, J. Song, Y. Zhou and B. Han, *Green Chem.*, 2009, **11**, 1746.
- 8 G. Yong, Y. Zhang and J. Y. Ying, Angew. Chem., Int. Ed., 2008, 47, 9345.
- 9 R. Huang, W. Qi, R. Su and Z He, Chem. Commun., 2010, 1115.

- 10 (a) J. B. Binder and R. T. Raines, J. Am. Chem. Soc., 2009, 131, 1979; (b) S. Zhao, M. Cheng, J. Li, J. Tian and X. Wang, Chem. Commun., 2011, 47, 2176.
- 11 Z. Zhang and Z. K. Zhao, Bioresour. Technol., 2010, 101, 1111.
- 12 R. C. Remsing, R. P. Swatloski, R. D. Rogers and G. Moyna, *Chem. Commun.*, 2006, 1271.
- 13 HMF yields were determined from HPLC peak area at 280 nm using standard curve ready-made with authentic HMF (For detailed analytical procedure, see ESI†); HMF yields obtained from MoCl<sub>3</sub>, VCl<sub>3</sub>, RuCl<sub>3</sub>were not shown in Fig. 1 due to their negligible yields less than 5%.
- 14 S. Hu, Z. Zhang, Y. Zhou, B. Han, H. Fan, W. Li, J. Song and Y. Xie, *Green Chem.*, 2008, **10**, 1280.
- 15 Y. Su, H. M. Brown, X. Huang, X. Zhou, J. E. Amonette and Z. C. Zhang, *Appl. Catal.*, A, 2009, 361, 117.
- 16 F. Tao, H. Song and L. Chou, ChemSusChem, 2010, 3, 1298.
- 17 (a) A. Fukuoka and P. L. Dhepe, Angew. Chem., Int. Ed., 2006, 45, 5161; (b) H. Kobayashi, T. Komanoya, K. Hara and A. Fukuoka, ChemSusChem, 2010, 3, 440.
- 18 G. L. Miller, Anal. Chem., 1959, 31, 426.
- 19 The components of reed used in this experiment are 40.0% glucan, 22.0% xylan, 26.1% lignin, and 5.2% ashes.