View Article Online
View Journal

Green Chemistry

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

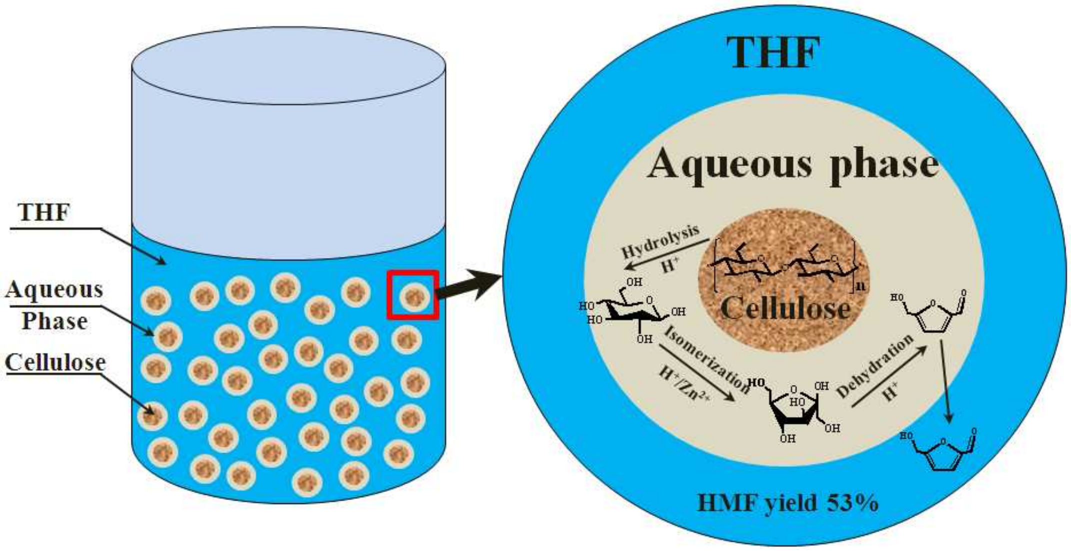
RSC Publishing

www.rsc.org/greenchem

Registered Charity Number 207890

Entry for the Table of Contents:

In a biphase system consisted of tetrahydrofuran (THF) and aqueous solution with high volume ratio, the cellulose particles and the aqueous solution were highly dispersed into the organic phase under stirring. For the hydrophilcity of cellulose, its surface was covered by the aqueous solution to form an aqueous film. The high concentration of $NaHSO_4$ (1.5mol/L) and $ZnSO_4$ (2.3mol/L) in the aqueous film could efficiently catalyze the degradation of cellulose into 5-hydroxymethylfurfural (HMF), and the formed HMF could efficiently spread into the organic phase to prevent its further decomposition. High HMF yield of 53mol% was obtained accompanied with 96% conversion of cellulose in 60mins.



High Yield Production of 5–Hydroxymethylfurfural from Cellulose by High Concentration of Sulfates in Biphasic System

Ning Shi[a,b], Qiying Liu[a], Tiejun Wang[a], Longlong Ma[a,]*, Qi Zhang[a]

[a]*Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, 510640, P. R. China and*

[b]*University of Chinese Academy of Sciences, Beijing, 100049, P. R. China*

Abstract: High 5–hydroxymethylfurfural (HMF) yield of 53mol% was obtained by direct degradation of cellulose in a biphasic system with concentrated $NaHSO_4$ and $ZnSO_4$ as co-catalyst, accompanied with 96% of cellulose conversion in 60min. The high concentration of catalyst in the aqueous solution and the high volume ratio of organic phase to aqueous phase were responsible for the excellent performance. Depolymerization of cellulose presented as the rate-determine step, and the formed glucose could be efficiently converted by concentrated catalysts in the aqueous solution, leading to low concentration of glucose in the solution, thus suppressed the side reactions such as humins and char formation.

Keywords: concentrated sulfates, cellulose, 5-hydroxymethyfurfural, biphasic system, aqueous film

Corresponding author:

Longlong Ma, Tel: +86-20-87057673, Fax: +86-20-87057673, E-mail: mall@ms.giec.ac.cn.

Tiejun Wang, Tel: +86-20-87057751, Fax: +86-20-87057737, E-mail: wangtj@ms.giec.ac.cn.

1. Introduction

With the consumption of fossil fuels and the increasing concern of environmental problem, production of liquid fuel and fine chemicals from renewable biomass has attracted widespread attention[1]. 5-hydroxymethylfurfural (HMF), which can be obtained from lignocellulosic biomass, is considered to be a key platform chemical for production of a variety of downstream chemicals and biofuels[1-2].

Recently, great progresses have been approached on HMF production from the cheap and abundant glucose in ionic liquids, polar aprotic solvents and biphasic systems[3]. Chromium-contained catalysts are employed in most of work for the excellent catalytic activity of ion Cr^{m+} on isomerization of glucose[4], which is generally regarded as a main obstacle for HMF production from glucose based substrates. Some other metal chlorides, such as $ZnCl_2$, $GeCl_4$, $SnCl_4$, $AlCl_3$ are also reported to be efficient for isomerization of glucose[5]. Work of combining Lewis and Brønsted acid for HMF production from glucose are also reported. $AlCl_3$-HCl, $ZnCl_2$-HCl, $CrCl_3$-HCl, (Sn-Beta)-HCl were reported to be efficient on HMF production from glucose[6]. High HMF yield of 81% was achieved in $BMIM^+Cl^-$ ionic liquid with the NHC/Cr catalyst (NHC=N-heterocyclic carbene)[7].

Though high yield of HMF have been approached from glucose and fructose, directly degradation of wildly existed cellulose into HMF is more feasible for commercial. However, the recalcitrant of cellulose and the multiple side-reactions[8] occurred during the process make the one-pot synthesis of HMF from cellulose a significant challenge. Under the same condition, the yield of HMF obtained from glucose was 61mol% but from cellulose was only 37mol%[5d]. Systems employing ionic liquid solvents and polar aprotic solvents are reported to be efficient for this process, with chromium chloride as catalyst. Binder and his co-worker obtained high HMF yield of 54mol% from cellulose in the DMA-LiCl solvent with $CrCl_3$ and HCl as co-catalyst[9]. Yu et al. obtained high HMF yield of 62mol% in ionic liquid 1-butyl-3-methylimidazolium chloride with $CrCl_3$/LiCl as catalyst[4e]. Zhang et al. reported the formation of 55mol% HMF from cellulose using two metal chloride catalysts ($CuCl_2$ and $CrCl_2$) in in 1-ethyl-3-methylimidazolium chloride[10]. Nevertheless, the high cost of ionic liquids, the high energy consumption in HMF separating process and the toxic chromium-contained catalysts all make the process impracticable for industrialization. On the contrary, water-contained biphasic systems, which afford the function of simultaneously producing HMF in aqueous phase and extracting HMF into organic phase to prevent its further degradation, are proved to be more cost effective[11]. Recently, some alkylphenol solvents, which could be obtained from the lignin, are proved to be efficient as extract solvent in the biphasic system, making the HMF production with biphasic system feasible for commercial[6b,11]. However, the HMF yield obtained from cellulose in the biphasic system kept low compared to that obtained in the ionic liquid and polar aprotic solvents[5d].

Herein, we developed a cost-effective method for high yield production of HMF from micro-crystal cellulose in a biphasic system consisted of tetrahydrofuran (THF) and water, concentrated $NaHSO_4$ and $ZnSO_4$ were employed as co-catalysts.

2. Experimental section

2.1 Chemicals

Glucose (99%), fructose (99%), cellobiose (99%), soluble starch (AR), micro-crystalline cellulose (90 μm) (extra pure graded), 5-hydroxymethylfurfural (HMF) (98%), formic acid (98%) and levulinic acid (99%) were purchased from Shanghai crystal pure reagent Co., LTD and used without further purification. $NaHSO_4$ and $ZnSO_4$ (analytical pure level) were purchased from Tianjin Fu Chen chemical reagent factory. Tetrahydrofuran (THF) was purchased from Tianjin Fu Yu fine chemical Co., LTD.

2.2 Degradation of cellulose to HMF

Degradation of cellulose was carried out in a 100 ml stainless steel reactor with a teflon inner. In a typical experiment, 1.0 g cellulose, 4 ml deionized water, 40 ml THF and a certain of catalysts were loaded into the reactor. High purity N_2 was used to remove air inside the reactor and pressurize the system to 3.0 MPa. Then the reaction system was heated to target temperature with heating rate of 5K/min and kept at the temperature for a certain period. After reaction, solid residues were collected by filtration with a 0.45 μm membrane. The liquid products in both aqueous solution and organic solution were analyzed by GC-MS and HPLC instrument. The collected solid residues were washed with water and dried at 378K with 3 hours for TG analysis, SEM analysis, elemental analysis and FT-IR analysis. For the catalyst reuse process, the aqueous solution containing catalyst was separated for recycle.

2.3 Analysis of liquid products

The qualitative analysis of HMF, furfural and levulinic acid were determined by a GC-MS instrument (HP5890; MSD, HP5972A) equipped a DB-5MS capillary column (30 m×0.25 mm×0.25 μm). The oven temperature was retained at 40 °C for 4 min, then ramped to 250 °C at 10 °C/min, and held at this final temperature for 3 min.

The concentration of cellobiose, D-glucose, D-fructose, HMF, furfural and levulinic acid in the solution were quantified using HPLC equipped with a Hewlett Packard 1050 pump and a Biorad Aminex HPX-87H organic acid column. A Waters 410 refractive index detector (operated at 45 °C) was equipped for detecting of cellobiose, D-glucose, D-fructose and levulinic acid while a UV detector (with the wavelength of 284 nm) was equipped for detecting of HMF and furfural. The mobile phase was an aqueous solution of sulfuric acid (5 mM) at the flow rate of 0.55 mL/min and the column was kept at 50 °C. Quantification of products was determined by external standard method based on the average peak area of each product under three parallel HPLC measurements of each experiment. All liquid samples obtained after each experiments were diluted 50 times by pure water before analysis.

The mole yield of the product i was calculated by the following formula, assuming the molecular weight of the constructed D-glucose unit of cellulose being 162:

$$\mathrm{Y(mol\%)} = \frac{[Concen.(org) \times Vol(org) + Concen.(aqu) \times Vol(aqu)]/M_i}{Grams\ of\ cellulose\ loaded/162}$$

M_i is the molar mass of each material, its value is 126, 96, 116 for HMF, furfural and levulinic acid, respectively.

2.4 Characterization of the solid residue

The cellulose conversion was measured by weighting the solid residue and thermogravimetric (TG) analysis of the solid residue. Thermogravimetric (TG) analysis were implemented on a NETZSCH-STA 409PC DSC-SP thermal analyzer with 5-10mg of sample by increasing the temperature from 40 °C to 500 °C at 10 °C/min under an air flow rate of 30 mL/min.

The morphology of cellulose and solid residues (SEM image) were observed using a scanning electron microscope (HITACHI S-4800).

Elemental analysis of the solid residue was performed on a Vario EL Z CHN elemental analyzer under 0.12MPa He and 0.2MPa of O_2 at 1145 °C, with a TCD detector.

The Brunauer–Emmet–Teller (BET) surface area (S_{BET}) of the cellulose was analyzed by the adsorption and desorption isotherms of nitrogen at -196°C using a ASIQMO002-2 analyzer (Quantachrome, US). The samples were degassed under vacuum at 80°C for 16 h prior to measurement.

The structures of the solids were analyzed by FT-IR with an IR Prestige-21 spectrometer (Shimadzu) with scanning from the wavenumbers of 4000 to 400 cm^{-1} at 2 cm^{-1} resolution. Samples for FT-IR analysis were prepared by mixing the sample powders with KBr and compacting into thin slice.

3. Results and discussion

Here we employed high volume ratio of THF solvent to water as 10:1. Because water is mutually soluble with THF, no aqueous phase was formed with none salt addition. With the addition of salts, the aqueous solutions were formed with volume of 0.2-1.5ml, which were much lower than the volume of water added (Table 1). The strong acidic $NaHSO_4$ was very efficient on the degradation of cellulose in this system. Little HMF was formed accompanied with great deal of unreacted cellulose without of $NaHSO_4$ (Table 1, Entry 1-2), but high HMF yield of 36.7mol% was obtained by increasing the usage of $NaHSO_4$ to 1.8mmol (Table 1, Entry 4). However, excessive of H^+ significantly decreased HMF yields accompanied with the formation of levulinic acid (LA), which is a degradation product of HMF (Table 1, Entry 5). The excellent performance with single $NaHSO_4$ indicated that the H^+ offered by $NaHSO_4$ was active for all reactions involved (hydrolysis of cellulose, isomerization of glucose and dehydration of fructose). Zn^{2+} is reported to be efficient for isomerization of glucose to fructose via 1,2-hydride shift[12], so here we investigated the impact of $ZnSO_4$ on HMF production in this reaction system. Addition of $ZnSO_4$ greatly increase the HMF yield (Table 1, Entry 6-12), and the highest yield of 53.2mol% was obtained with 1.8mmol $NaHSO_4$ and 2.8mmol $ZnSO_4$ as co-catalysts (Table 1, Entry 8). We also noticed that the volumes of aqueous solutions increased with the addition of $ZnSO_4$, so we propose that $ZnSO_4$ could also have the function of adjusting the acidity of aqueous solution and increasing its volume. The HMF yield obtained here was comparable with that of 62mol% obtained in the ionic liquid with $CrCl_3$ as catalyst[4e], and much higher than the 37mol% obtained from biphasic system with $AlCl_3$ as catalyst[5d]. Experiment for catalysts recycle was conducted by separating the aqueous phase, but the HMF yield decreased to 41.3mol%, which could be attributed to the fact that a certain of catalysts were dissolved in the organic solvent (Table 1, Entry 13).

Some byproducts were also detected. Furfural (FF) was formed in all the reaction with the yield of below 5mol%, and the furfural formation mechanism was discussed elsewhere[13] (Scheme1). Addition of the transparent organic filtrate into pure water formed a turbid liquid, indicating that THF-soluble but water-insoluble polymer existed in the organic solvent. Comparing the FT-IR spectrum of this polymer with that of humins reported by other literature[14], we concluded that the THF-soluble polymer was humins (Figure 1). SEM image showed that this THF-soluble humins was spherical with the size of 1~3um (Figure 2e). Several work also reported that humins could be dissolve in some organic solvents[14b, 15].

Brownish black solid residues were detected in all reactions. Effect of reaction time on the yield of HMF, glucose and solid residue was conducted (Figure 3). The slight decreasing of HMF yield after 60min indicated that HMF was relatively stable in this system. Only ignorable amounts of glucose were formed during the process, suggesting that this reaction system was very efficient for glucose conversion. Lowest residue weight of 8.0wt.% was obtained at 50min, indicating that more that 92% of cellulose was converted. The weight of solid residue began to increase after 50min, suggesting the formation of solid humins[8d,14b,16]. Because humins was formed in the residue, it's not precise to determine the conversion of cellulose by simply weighing the collected solid residue. TG of the solid residues showed two weight losses (Figure 4), the former weight loss was assigned to the cellulose decomposition, while the latter weight loss was due to decomposition of humins. Coupling of the TG behaviors and the weight of residues, we concluded that about 96% of cellulose was converted in 60min. The SEM images showed that the cellulose was compact while the residue was loose and porous (Figure 2). The elemental analysis showed that the solid residues contained about 62 wt.% carbon and 30 wt.% oxygen, which was similar with humins[14] (Table 2).

The water amounts could greatly influence the HMF yield (Table 3). Because the salts are insoluble in the THF solvent, the salts presented as solid in THF solvent with no water was added. Insoluble salts were detected with less than 4ml of water addition, indicating that the aqueous solutions were saturated with these catalysts. Relatively low HMF yield of 37.7mol% was obtained with 1ml of water addition (Table 3, Entry 14), but the HMF yield increased with increasing of water addition. Highest yield of HMF was obtained with 4ml of water addition. With 8ml of water addition, only 1.7ml of the aqueous phase was formed accompanied with completely dissolving of all salts, while the HMF yield decreased to 41.8mol% (Table 3, Entry 17). However, further increasing the water addition to 16ml, the volume of aqueous solution even decreased to 1.4ml, and HMF yield greatly decreased to 8.2mol% accompanied with more than 80wt.% of unreacted cellulose (Table 3, Entry 18). The remarkable decreasing of HMF yield with 16ml of water addition was due to that the solubility of catalyst in the water-THF mixture increased with

16ml of water addition, leading to the sharp decreasing of catalyst concentration and poor performance on cellulose degradation. Here, the salts had functions of catalyzing the degradation of cellulose and decreasing the miscibility of water with THF.

As mentioned above, under the conditions of 1-4ml of water addition, the aqueous solutions were saturated with catalysts. High concentration of the catalysts in aqueous solution was responsible for the excellent performance of this reaction system. Adding 4ml of water into the mixture of 1.8mmol $NaHSO_4$, 2.8mmol $ZnSO_4$ and 40ml THF formed only 1.2ml of aqueous phase and 43.2ml of organic phase, so the concentration of $NaHSO_4$ and $ZnSO_4$ in the aqueous phase was 1.5mol/L of and 2.3mol/L, respectively. The high concentration of catalyst was efficient for hydrolysis of cellulose and decomposition of glucose. Especially, Deng et al. reported that the concentrated Zn^{2+} in the aqueous solution could incompletely coordinate with the hydroxyl group of saccharides to catalyze the converting of saccharides[17]. Directly degradation of cellulose to HMF involves the steps of hydrolysis of cellulose to glucose and decomposition of glucose to HMF. As the active energy of hydrolysis of cellulose (about 180kJ/mol) is much higher than that of glucose decomposition HMF (about 135kJ/mol)[8c,18], hydrolysis of cellulose presents as the rate-determining step. In this reaction, when cellulose was hydrolyzed, the formed glucose was quickly consumed by the abundant H^+ and the Zn^{2+} in the aqueous solution to form HMF, which reduced the glucose concentration in aqueous solution (Figure 3), thus significantly suppressed the side reactions of glucose such as condensation with HMF into humins[8d,14b] , carbonization into char or reverse into oligosaccharides[8c].

High volume ratio of organic phase to the aqueous phase was another key factor for the excellent performance of this reaction system. As the volume of organic phase was more than 25 times of that of aqueous phase, both the catalyst-contained aqueous solution and the cellulose particles were highly dispersed in the organic phase under stirring. Because the surface of cellulose is abundant of hydroxyl groups, and the polarity of aqueous solvent (10.2) is much stronger than that of THF solvent (4.2), so the surface of cellulose is likely to be covered by aqueous solution instead of THF. Assuming that the surface of cellulose is totally covered by the aqueous solution, we could calculate that the thickness of aqueous film is 1.7um because the volume of aqueous phase is 1.2ml and the surface of cellulose is $0.7m^2/g$ (determined by the BET analysis of cellulose). This thin aqueous film containing high concentration of catalysts could efficiently catalyze the depolymerization of cellulose and dehydration of saccharides, and the formed HMF molecule could easily spread into the organic phase to prevent it from further degradation (Figure 5). Here, the organic phase acts not only as HMF protector but also as the dispersing agent to disperse the cellulose particles and catalyst-contained aqueous solution, while water acts both as the reactant to hydrolyze the cellulose and as the solvent to dissolve the catalysts. A similar reaction system was reported by Zhao and his co-worker, in which the surfactant in the micellar catalyst $Cr[(DS)H_2PW_{12}O_{40}]_3$ could overcome the diffusion problem in this solid-solid reaction for hydrolysis of cellulose, and the HMF formed on the surface of catalyst could efficiently spread into the major aqueous solution to avoid its further degradation[19]. The system in this work was similar with their system at the following two points: first, the catalyst could easily contact with the surface of cellulose and efficiently catalyze the depolymerization of cellulose; second, the formed HMF could easily spread into the major solvent to improve its stability.

The performances of the system at temperature from 413K to 453K were studied (Figure 6).

The low temperature of 413K leaded to low HMF yield of 35.8mol% accompanied with 41.6% of unreacted cellulose while the high temperature of 453K leaded to the increasing yield of levulinic acid, which decreased the yield of HMF.

The reaction system showed excellent performance on synthesis of HMF from cellulose, but showed relatively poor performance with the soluble sugars (glucose, cellobiose and starch) as the feedstock. After 45min, the conversion of all these reactants had reached 100%, but less than 40mol% of HMF were obtained accompanied with about 20-40wt.% of black residue formation (Table 4, Entry 19-22). SEM image of the black residue showed that the residue was irregular particle with size of larger than 10um, which was very different from the strip-shaped unreacted cellulose and the spherical THF-soluble humins (Figure 2). The FT-IR spectrums of the black residue and THF-soluble humins were similar, the absorption peaks at 1604, 1510 and 1395 cm^{-1} indicated that furan ring existed in both solids[14a] (Figure 1). However, an obvious difference was observed. Contrary to humins, the relative intensity of the peak at 1706 cm^{-1} was stronger than that at $1672cm^{-1}$, indicating fewer C=O bonds were conjugated with the C=C bonds in this black char[20]. Compared with literature[20], we concluded that this black residue was char instead of humins[14]. Generally, char is formed under some extreme conditions, such as high temperature[21], high acidic environment or high concentration of soluble saccharides[20,22]. Here, the formation of char is ascribed to the high acidity of aqueous solution and high concentration of soluble saccharides. Because these substrates (glucose, cellobiose and starch) are hardly dissolve in THF, when 1g glucose was added into the reaction solution (4ml H_2O,1.8mmol $NaHSO_4$, 2.8mmol $ZnSO_4$, 40ml THF), its concentration in the aqueous solution was as high as 40wt.%. Insoluble saccharides were detected with 1g cellobiose or starch addition, indicating that the aqueous solutions were saturated with them. The high acidity of aqueous solution and the concentrated saccharides could obviously lead to char formation. Because high concentration of glucose could be favor for the reverse reaction to form oligosaccharides[8c], we proposed that the char was formed by directly dehydration of oligosaccharides. Relatively higher HMF yields and lower char yields were obtained with lower glucose dosage, and the HMF yield of 45.2mol% was approached with 0.2g of glucose dosage (Table 4, Entry 23-24). This is accord with the former report that ignorable char was detected with low glucose concentration, but plenty of char was formed with high concentration of glucose[22].

High HMF concentration in the solution is desired for its practical applications.[23] Herein, we explored improving HMF concentration by improving the reactant dosage. High HMF yield of 42.5mol% was obtained with 5g of cellulose, indicating that the reaction system was also efficient with high ratio of cellulose to aqueous solution (Table 5, Entry 25). With the increasing of the cellulose dosage, the yield of HMF decreased gradually while the weight of solid residue increased, this is due to that high concentration of HMF is favor for the HMF concentration reaction [8d] (Table 5). High HMF concentration of 5.9 wt.% was obtained with 15 g cellulose loading, but the HMF yield decreased to 22.6mol% under this condition (Table 5, Entry 30). Obtaining high concentration of HMF with high selectivity is the following challenge for commercial production of HMF.

4 Conclusions

In summary, a biphasic system consisted of THF and concentrated $NaHSO_4$-$ZnSO_4$ aqueous solution was developed for efficiently degradation of cellulose into HMF. High HMF yield of 53% was obtained accompanied with 96% conversion of cellulose in 60min. High concentration of catalyst in the aqueous phase and high volume ratio of organic phase to aqueous phase were the main factors for the excellent performance. High HMF concentration of 5.9 wt.% in the organic phase was approached by increasing the cellulose loading. In this system, THF was employed as the major solvent, which does have some disadvantages, such as the high cost and the environmental effect. However, we should also notice that the low boiling point of THF could make the distillation process much less energy consumption. If an abundant, green and low-boiling point solvent could be developed to replace THF, this system could step much closer to industrialization.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Basic Research Program of China (2012CB215304), the Natural Science Foundation of China (51161140331) and the International Co-operation Project of Ministry of Science and Technology of China (2012DFA61080).

References

(1) J. C. Serrano-Ruiz and J. A. Dumesic, *Energ. Environ. Sci*., **2011**, *4*, 83.

(2) (a) S. Dutta, S. De and B. Saha, *Chempluschem*, **2012**, *77*, 259; (b) A. A.Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M.Afonso, *Green Chem*., **2011**, *13*, 754.

(3) A.Takagaki, S. Nishimura and K. Ebitani, *Catal. Surv. Asia*, **2012**, *16*, 164.

(4) (a) H. B. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, **2007**, *316*, 1597; (b) Z. H. Zhang and Z. B. K. Zhao, *Bioresource Technol*., **2010**, *101*, 1111; (c) B. Kim, J. Jeong, D. Lee, S. Kim, H. J. Yoon, Y. S. Lee and J. K. Cho, *Green Chem*., **2011**, *13*, 1503; (d) X. H. Qi, M. Watanabe, T. M. Aida and R. L. Smith, *Cellulose*, **2011**, *18*, 1327; (e) H. B.Yu, P. Wang, S. H. Zhan and S. Q. Wang, *Bioresource Technol*, **2011**, *102*, 4179.

(5) (a) T. M. Chen and L. Lin, *Research Progress in Paper Industry and Biorefinery (4th Isetpp), Vols 1-3* **2010**, 1421; (b) J. Q. Bond, D. M. Alonso, D. Wang, R. M. West and J. A. Dumesic, *Science*, **2010**, *327*, 1110; (c) H. B. Xie, Z. H. Zhang, Q. A. Wang, W. J. Liu and Z. B. Zhao, *ChemSusChem*, **2011**, *4*, 131; (d) Y. Yang, C. W. Hu and M. M. Abu-Omar, *Green Chem*, **2012**, *14*, 509.

(6) (a) M. E. Davis, E. N. Nikolla, Y. Roman-Leshkov and M. Moliner, *Acs Catal*., **2011**, *1*, 408 (b) Y. J. Pagan-Torres, T. F. Wang, J. M. R. Gallo, B. H. Shanks and J. A. Dumesic, *Acs Catal*., **2012**, *2*, 930; (c) C. H. Chung, J. A. Chun, J. W. Lee, Y. B. Yi and S. S. Hong, *Korean J. Chem. Eng*., **2010**, *27*, 930.

(7) G. Yong, Y. G. Zhang and J. Y. Ying, *Angew. Chem. Int. Edit*., **2008**, *47*, 9345.

(8) (a) H. J. Heeres, B. Girisuta and L. P. B. M. Janssen, *Chem. Eng. Res. Des*., **2006**, *84*, 339; (b) H. J. Heeres, C. B. Rasrendra, I. G. B. N. Makertihartha and S. Adisasmito, *Topics in Catalysis*, **2010**, *53*, 1241; (c) H. M. Pilath, M. R. Nimlos, A. Mittal, M. E. Himmel and D. K. Johnson, *J. Agric. Food Chem.* **2010**, *58*, 6131; (d) S. J. Dee and A. T. Bell, *ChemSusChem*, **2011**, *4*, 1166.

(9) J. B. Binder and R. T. Raines, *J Am Chem Soc* **2009**, *131*, 1979.

(10) Z. C. Zhang, S. Yu, H. M. Brown, X. W. Huang, X. D. Zhou and Amonette, J. E. *Appl. Catal. A-Gen*., **2009**, *361*, 117.

(11) (a) J. A. Dumesic and Y. Roman-Leshkov, *Topics in Catalysis*., **2009**, *52*, 297; (b) Y. Roman-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, **2006**, *312*, 1933.

(12) R. W. Nagorski and J. P. Richard, *J. Am. Chem. Soc*., **2001**, *123*, 794.

(13) F. M. Jin and H. Enomoto, *Energ. Environ. Sci*., **2011**, *4*, 382.

(14) (a) M. Zhang, H. Yang, Y. N. Liu, X. D. Sun, D. K. Zhang and D. F. Xue, *Nanoscale Res. Lett*., **2012**, *7*; (b) I. V. Sumerskii, S. M. Krutov and M. Y. Zarubin, *Russ. J Appl. Chem+*., **2010**, *83*, 320.

(15) D. M. Alonso, S. G. Wettstein, M. A. Mellmer, E. I. Gurbuz and J. A. Dumesic, *Energ. Environ. Sci*.,**2013**, *6*, 76.

(16) (a) B. Girisuta, L. P. B. M. Janssen and H. J. Heeres, *Green. Chem*., **2006**, *8*, 701; (b) X. Hu, C. Lievens, A. Larcher and C. Z. Li, *Bioresource Technol*., **2011**, *102*, 10104.

(17) T. S. Deng, X. J. Cui, Y. Q. Qi, Y. X. Wang, X. L. Hou and Y. L. Zhu, *Chem. Commun*., **2012**, *48*, 5494.

(18) (a) J. F. Saeman, *Ind. Eng. Chem*., **1945**, *37*, 43; (b) C. B. Rasrendra, J. N. M. Soetedjo, I. G. B. N. Makertihartha, S. Adisasmito and H. J. Heeres, *Topics in Catalysis*, **2012**, *55*, 543.

(19) S. Zhao, M. X. Cheng, J. Z. Li, J. A. Tian and X. H. Wang, *Chem. Commun*., **2011**, *47*, 2176.

(20) A. Chuntanapum and Y. Matsumura, *Ind. Eng. Chem. Res.*; **2010**, *49*, 4055.
(21) S. D. Yin, Y. L. Pan and Z. C. Tan, *Int. J. Green Energy*, **2011**, *8*, 234.
(22) Z. W. Srokol and G. Rothenberg, *Topics in Catalysis*, **2010**, *53*, 1258.
(23) Q. Cao, X. C. Guo, J. Guan, X. D. Mu and D. K. Zhang, *Appl. Catal.*, *A-Gen.* **2011**, *403*, 98.

Table 1 Performance of combined metal sulfates in direct degradation of cellulose to HMF [a]

Entry	Catalyst (mmol)		Volume of aqueous solvent (ml)	Product yield (mol%)		
	$NaHSO_4$	$ZnSO_4$		HMF	FF	LA
1	-	-	0	<0.5	<0.5	<0.5
2	-	2.8	1.0	0.7	<0.5	<0.5
3	0.9	-	0.2	29.8	<0.5	<0.5
4	1.8	-	0.3	36.7	1.7	<0.5
5	2.7	-	0.4	28.4	1.3	10.4
6	1.8	0.5	0.5	45.7	2.1	<0.5
7	1.8	1.0	0.8	48.7	2.7	<0.5
8	1.8	2.8	1.2	53.2	1.7	<0.5
9	1.8	3.5	1.4	48.1	1.3	<0.5
10	1.8	4.2	1.5	47.8	1.5	0.7
11	2.3	2.8	1.5	47.4	2.1	6.8
12	2.7	2.8	1.5	45.9	2.0	12.9
13 [b]	1.8	2.8	1.2	41.3	1.6	<0.5

[a] Reaction condition: 1g cellulose; THF 40 ml and H_2O 4ml; reaction temperature 433 K; reaction time 60 min.

[b] The aqueous phase containing catalyst was separated from Entry 8 with 2.8ml of extra water addition.

HMF, 5-hydromethylfurfural; FF, furfural; LA, levulinic acid.

Table 2 Elemental analysis of cellulose and solid residues with different reaction time

Materials	Elements percentage (wt.%)		
	C	H	O
Cellulose	44.1	5.9	50.0
Residue 60	61.6	6.7	31.8
Residue 120	63.6	6.5	29.9

Residue 60 and Residue 120 represented the solid residues collected after 60 min and 120 min of reaction time, respectively. Reaction condition: 1 g cellulose; 40 ml THF and 4 ml H_2O; 1.8mmol $NaHSO_4$ and 2.8mmol $ZnSO_4$; reaction temperature 433 K.

Table 3 Impact of water addition on the HMF yield from cellulose [a]

Entry	Water addition	Catalyst solution	Volume of solvent (ml)[b]		HMF Yield (wt%)	Residue (wt%)
			Aqueous solvent	Organic solvent		
14	1	P.D. [c]	0.2	40.8	37.7	10.3
15	2	P.D.	0.5	41.4	47.6	9.7
16	4	P.D.	1.2	43.2	53.2	8.1
17	8	C.D. [d]	1.7	46.3	41.8	17.2
18	16	C.D.	1.4	55.1	8.2	85.6

[a] Reaction condition: 1g cellulose; 40 ml THF; 1.8mmol $NaHSO_4$ and 2.8mmol $ZnSO_4$; temperature, 433 K; reaction time, 60 min.

[b] The volume of each solvents were measured at 298K;

[c] P.D. stands for partially dissolved;

[d] C.D. stands for completely dissolved;

1 Table 4 Comparison of direct degradation of glucose, starch and cellobiose to HMF [a]

Entry	Substrate	Substrate usage (g)	Time (min)	Conversion (%)	Product yield (mol%)			Black Char (wt.%)
					HMF	FF	LA	
19	Glucose	1.0	30	98.4	35.7	0.5	<0.5	21.7
20	Glucose	5.0	30	95.5	24.1	0.6	<0.5	36.3
21	Starch	1.0	45	100	16.9	0.7	<0.5	24.1
22	Cellobiose	1.0	45	100	17.6	1.5	<0.5	23.8
23	Glucose	0.5	30	99.1	40.9	0.6	<0.5	14.3
24	Glucose	0.2	30	100	45.2	<0.5	<0.5	10.9

2 [a] Reaction condition: 4ml H_2O; 40ml THF; 1.8 mmol $NaHSO_4$ and 2.8 mmol $ZnSO_4$; reaction

3 temperature 433 K,.

Table 5 Effect of cellulose dosage on HMF yield and concentration in direct degradation of cellulose [a]

Entry	Cellulose dosage(g)	Ratio (g/ml) [b]	Reaction time(min)	Product yield(mol%)			HMF concentration (wt%)	Residue (wt%)
				HMF	FF	LA		
25	5	4.2	60	42.5	1.2	<0.5	3.3	12.2
26	10	8.3	60	35.0	2.1	1.4	5.0	17.1
27	11	9.2	60	33.5	2.6	1.9	5.2	19.4
28	12	10.0	60	31.8	1.9	3.3	5.4	21.2
29	13	10.8	60	24.9	2.2	4.8	5.5	25.4
30	15	12.5	90	22.6	2.7	5.7	5.9	30.7

[a] Reaction condition: 4ml H_2O; 40ml THF; 1.8mmol $NaHSO_4$ and 2.8mmol $ZnSO_4$; reaction temperature, 433K.

[b] Ratio of cellulose to aqueous solution.