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Efficient Conversion of Fructose to 5-Hydroxymethylfurfural Catalyzed by Sulfated Zirconia in Ionic Liquids

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ABSTRACT: An efficient process was developed for the dehydration of fructose to 5-hydroxymethylfurfural (5-HMF) in the ionic liquid (IL) 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) by using sulfated zirconia as catalyst. A fructose conversion of 95.8% with a 5-HMF yield of 88.4% was achieved in 30 min reaction time at 100 °C. The IL and sulfated zirconia could be recycled and exhibited constant activity for 6 successive trials, and 5-HMF yields of above 60% could be kept up to 10 trials. The proposed process of using an IL with sulfated zirconia solid catalyst greatly reduces the reaction temperature required over previous works for converting fructose to 5-HMF.

1. INTRODUCTION

The efficient utilization of biomass has recently received considerable attention as a promising alternative for the sustainable supply of fuel and valuable chemicals.[1] Among the many possible biomass-derived chemicals, 5-Hydroxymethylfurfural (5-HMF) is considered to be a significant intermediate for a wide variety of chemical and alternative fuels,[2] and the production of 5-HMF from carbohydrates such as glucose and fructose has been investigated by many researchers.[3−6] Although glucose is the most abundant monosaccharide in nature, the most effective method for the preparation of 5-HMF is the acid-catalyzed dehydration of fructose, and this process has received increasing attention.[1,7−25] Homogenous acids, such as mineral acids, have been employed broadly in the studies[1,15−17,26], and they are effective and give 5-HMF yields of 40−60% for relatively high fructose conversions (70−90%).[27] However, mineral acids have serious drawbacks in terms of separation and recycling in addition to equipment corrosion. On the other hand, heterogeneous catalysts such as H-form zeolites can be recycled with no material corrosion and have high selectivity (60−90%), but only low fructose conversion (30−60%) even at reaction times as long as 2 h.[19,28,29]

Sulfated zirconia is a well-known solid acid catalyst that has been used for various acid catalyzed reactions such as alkylation, acylation, esterification, etherification, nitration, and oligomerization.[30−32] In our previous work,[9] sulfated zirconia was prepared by impregnation with H_2SO_4, and was characterized using Brunauer−Emmett−Teller (BET) surface area, X-ray diffraction (XRD), thermogravimetry and differential thermal analysis (TG-DTA), and FT-IR techniques. The prepared sulfated zirconia was evaluated as a catalyst for the dehydration of fructose to 5-HMF in aqueous solution and acetone-dimethylsulfoxide (DMSO) mixtures. The sulfated zirconia was proven to be an effective catalyst for producing 5-HMF from fructose in organic solvent but shows low catalytic activity in water solvent, and a fructose conversion of 93.6% with 5-HMF yield of 72.8% could be obtained at high reaction temperature of 180 °C for 20 min reaction time in acetone-DMSO mixtures. Although good results were attained in acetone-DMSO solvents, the usage of DMSO has some negative environmental risk, and the high reaction temperature means that high-pressure apparatuses have to be employed and more energy is consumed for reaction. Thus, we searched for a greener solvent and to reduce the reaction temperature.

Ionic liquids (ILs) are considered as a sort of promising solvent with some unusual properties, such as nonflammability, high thermal and chemical stability, negligible vapor pressure, and adjustable solvent power for organic substances.[33] In this work, we investigated the dehydration of fructose to 5-HMF catalyzed by sulfated zirconia in ILs. With the given catalytic process and fructose as the starting material, a 5-HMF yield of 88.4% could be achieved at a low reaction temperature of 100 °C for a reaction time of 30 min.

2. EXPERIMENTAL SECTION

2.1. Material. Fructose (99%), 5-hydroxymethylfurfural, and sulfuric acid (1 M) were purchased from Wako Pure Chemical Company (Osaka). Zirconium hydroxide was purchased from Nakalai Tesque Company (Tokyo). 1-Butyl-3-methyl imidazolium chloride ([BMIM][Cl]), 1-ethyl-3-methyl imidazolium chloride ([EMIM][Cl]), 1-Hexyl-3-methyl imidazolium chloride ([HexylMIM][Cl]), 1-ethyl-3-methyl imidazolium hydrogen sulfate ([EMIM][HSO_4], 1-butyl-3-methyl imidazolium hydrogen sulfate ([BMIM][HSO_4], and 1-butyl-3-methyl imidazolium acetate ([BMIM][Ac]) were purchased from Sigma-Aldrich Company; all of them were used as received.

2.2. Catalyst Preparation. Sulfated zirconia was prepared as described in our previous paper.[9] Briefly, zirconium hydroxide was mixed with 1 M H_2SO_4 and vigorously stirred at room temperature for 3 h. The suspension was centrifuged, and the deposition at the bottom of the centrifugal tube was dried at 60 °C overnight in a vacuum-dry oven, and further calcined at

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600 °C for 3 h. The characterization of sulfated zirconia by XRD, FT-IR, TG-DTA, and BET surface area was presented in ref 9.

2.3. General Procedure for the Conversion of Fructose to 5-HMF. The experimental procedure is similar to that used in related papers.[9,12,13,34] In a typical reaction, 0.05 g of fructose was dissolved in 1 g of [BMIM][Cl] first, and 0.02 g sulfate zirconia was added. The reaction mixture was heated to 100 °C by microwave heating and kept for 30 min. Zero time was taken to be when the temperature reached the given temperature. After the desired reaction time elapsed, each sample was diluted with 10 g of ultra pure water before analysis. In the case of the recycling of IL and catalyst, 5-HMF was extracted out from the mixture 5 times with 6 mL of ethyl acetate after 0.5 g of water was added. After extraction, the IL was heated at 60 °C for 24 h in a vacuum oven to remove water and residual ethyl acetate. The IL was then used directly for the next run by adding fructose.

2.4. Analysis. A high performance liquid chromatograph equipped with a refractive index detector (HPLC-RI, SH 1011 column) was employed for the analysis of products. Column oven temperature was 60 °C, and mobile phase was a 0.5 mM sulfuric acid aqueous solution with a flow rate of 1 mL/min.

The fructose conversion (mol %), the 5-HMF yield (mol %), and the selectivity (mol %) were calculated on a carbon basis as shown below.

Fructose conversion (mol %)

$$X = \left(1 - \frac{\text{Fructose concentration in product}}{\text{Fructose concentration in the loaded sample}}\right) \times 100\% \quad (1)$$

5-HMF yield (mol %)

$$Y = \frac{\text{moles of carbon in 5-HMF}}{\text{moles of carbon loaded as fructose}} \times 100\% \quad (2)$$

5-HMF selectivity (mol %)

$$S = \frac{\text{yield of 5-HMF}}{\text{Fructose conversion}} \times 100\% \quad (3)$$

3. RESULTS AND DISCUSSION

3.1. Catalytic Conversion of Fructose to 5-HMF by SO_4^{2-}/ZrO_2 in Various ILs. First, fructose conversion into 5-HMF catalyzed by SO_4^{2-}/ZrO_2 was studied in a series of ILs, namely, [BMIM][Cl], 1-ethyl-3-methyl imidazolium chloride ([EMIM][Cl]), 1-hexyl-3-methyl imidazolium chloride ([HexylMIM][Cl]), 1-ethyl imidazolium hydrogen sulfate ([EMIM][HSO_4]), 1-butyl-3-methyl imidazolium hydrogen sulfate ([BMIM][HSO_4]), and 1-butyl-3-methyl imidazolium acetate ([BMIM][Ac]). They include three neutral ILs ([BMIM][Cl], [EMIM][Cl], and [HexylMIM][Cl]), two Brønsted acidic ILs ([EMIM][HSO_4] and [BMIM][HSO_4]), and one basic IL ([BMIM][Ac]). Results are given in Figure 1, where it can be seen that the conversion of fructose to 5-HMF catalyzed by SO_4^{2-}/ZrO_2 in the neutral ILs was very effective, and high fructose conversions of 88.4−100% with 81.9−89.0% of 5-HMF yields were achieved for 30 min at 100 °C. The Brønsted acidic ILs were very effective for fructose conversion (ca. 100%), but only 35.6% and 43.0% of 5-HMF yields were obtained in [EMIM][HSO_4] and [BMIM][HSO_4], respectively. We think that the strong acidity of the acidic ILs led to the formation of insoluble humins and reduced the 5-HMF yields, which was verified from the observation of black solid

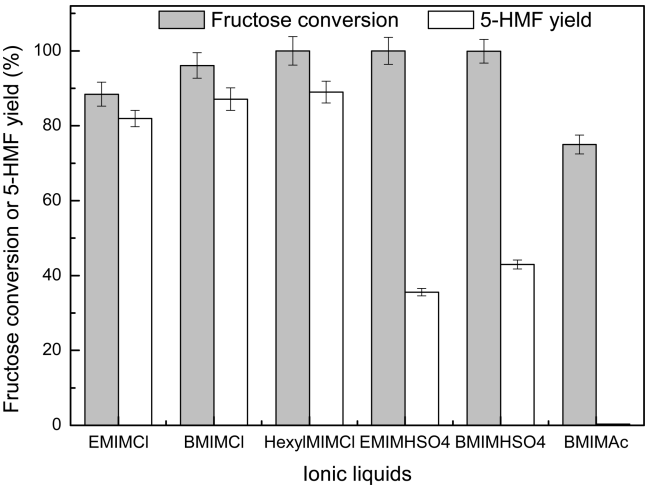

Figure 1. Conversion of fructose to 5-HMF in various ILs in the presence of sulfate zironia (0.05 g of fructose, 1 g of ILs, 0.02 g of SO_4^{2-}/ZrO_2, 100 °C, 30 min).

formed in the reaction. For basic IL [BMIM][Ac], although a fructose conversion of 75% was achieved, no 5-HMF formation was obtained. It seems that the basic solvent inhibited the formation of 5-HMF from fructose even in the presence of solid acid catalyst, which should be probably due to the neutralization of the acid sites in the sulfated zirconia by the basic IL.

3.2. Comparison between ZrO_2 and SO_4^{2-}/ZrO_2 for Fructose Conversion into 5-HMF. Since [BMIM][Cl] is one of the most common ILs, which is used broadly as the starting material for the production of other ILs, and it is the cheapest IL among [BMIM][Cl], [HexylMIM][Cl], and [EMIM][Cl], we selected [BMIM][Cl] as the IL for this study.

To investigate the effect of impregnation of ZrO_2 with H_2SO_4 on its catalytic activity, the formation of 5-HMF from fructose in [BMIM][Cl] catalyzed by untreated zirconia and sulfated zirconia was studied, and the results are presented in Figure 2. It shows that for the given reaction conditions, the dehydration of fructose can proceed in [BMIM][Cl] in the presence of ZrO_2 or SO_4^{2-}/ZrO_2, but the usage of SO_4^{2-}/ZrO_2 effectively promoted the reaction rate. A fructose conversion of 60.2% and a 5-HMF yield of 54.9% were obtained for ZrO_2 for a 30 min reaction time. While in the case of sulfated zirconia, for the same reaction conditions, the corresponding values increased to 95.8% and 88.4%, respectively. Compared with ZrO_2, SO_4^{2-}/ZrO_2 had higher catalytic activity for fructose conversion into 5-HMF but with almost similar 5-HMF selectivity of between 88 and 93%. The increase in catalytic activity of SO_4^{2-}/ZrO_2 in acid-catalyzed dehydration of fructose can be attributed to the increase in acid sites in SO_4^{2-}/ZrO_2 compared with that in ZrO_2. The increase in acid sites in sulfated zirconia was confirmed by the FT-IR spectrum of SO_4^{2-}/ZrO_2 presented in our previous work.[9]

3.3. Effect of Catalyst Dosage. Figure 3 shows the effect of the catalyst dosage on fructose conversion and 5-HMF yield. The amount of sulfated zironia used was 0.01, 0.02, 0.05, and 0.1 g, respectively. When 0.01 g of catalyst was used, 83.7% of fructose was converted at 100 °C for 30 min reaction time and a 5-HMF yield of 74.9% was obtained. When catalyst dosage increased to 0.02 g, fructose conversion and 5-HMF yield increased to 96.1% and 87.1%, respectively. However, when the amount of catalyst was increased from 0.02 to 0.1 g, there was little change in

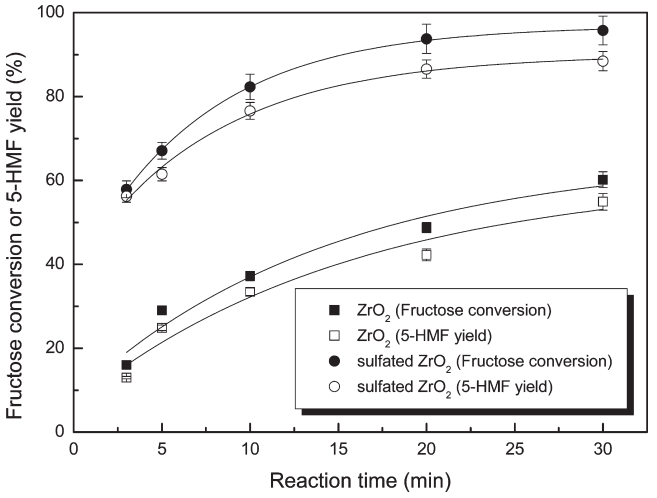

Figure 2. Comparison between ZrO_2 and SO_4^{2-}/ZrO_2 on fructose conversion into 5-HMF (0.05 g of fructose, 1 g of [BMIM][Cl], 0.02 g of ZrO_2 or SO_4^{2-}/ZrO_2, 100 °C).

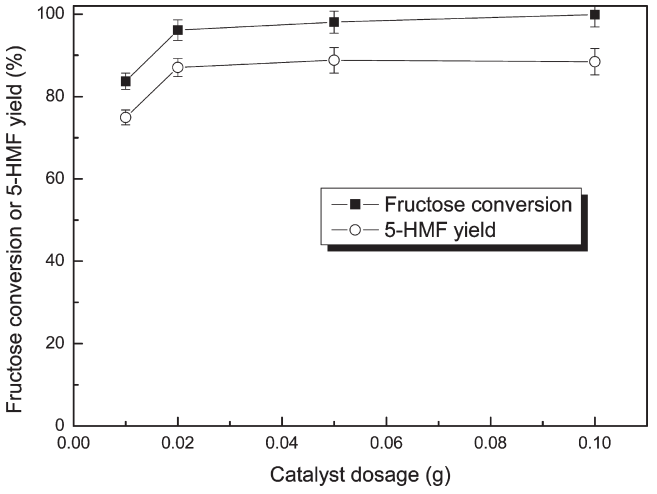

Figure 3. Effect of catalyst dosage on the fructose conversion into 5-HMF (0.05 g of fructose, 1 g of [BMIM][Cl], 100 °C, 30 min).

fructose conversion and 5-HMF yield. As the fructose conversion and 5-HMF yield did not change with further catalyst dosage over 0.02 g, this implies that there are sufficient catalytic sites available for the substrate fructose (0.278 mmol) in the system and almost all of the fructose was converted in the presence of over 0.02 g catalyst at the experimental conditions.

3.4. Effect of Reaction Temperature. Figure 4 shows the influence of the temperature on the reaction with respect to the fructose conversion and 5-HMF yield, and the experiments were conducted at 90, 100, 110, and 120 °C. It can be seen that the reaction temperature had a large effect both on the fructose conversion and 5-HMF yield. When reaction temperature was 90 °C, the fructose conversion was 83.6% with 76.9% of 5-HMF yield for 60 min reaction time. When the temperature increased to 100 °C, the fructose conversion and 5-HMF yield increased to 95.8% and 88.4%, respectively, for 30 min reaction time. Conversion of fructose and yield of 5-HMF reached 97.3% and 86.3%, respectively, for 10 min reaction time at 120 °C. The 5-HMF yield always increased with increasing reaction time for all

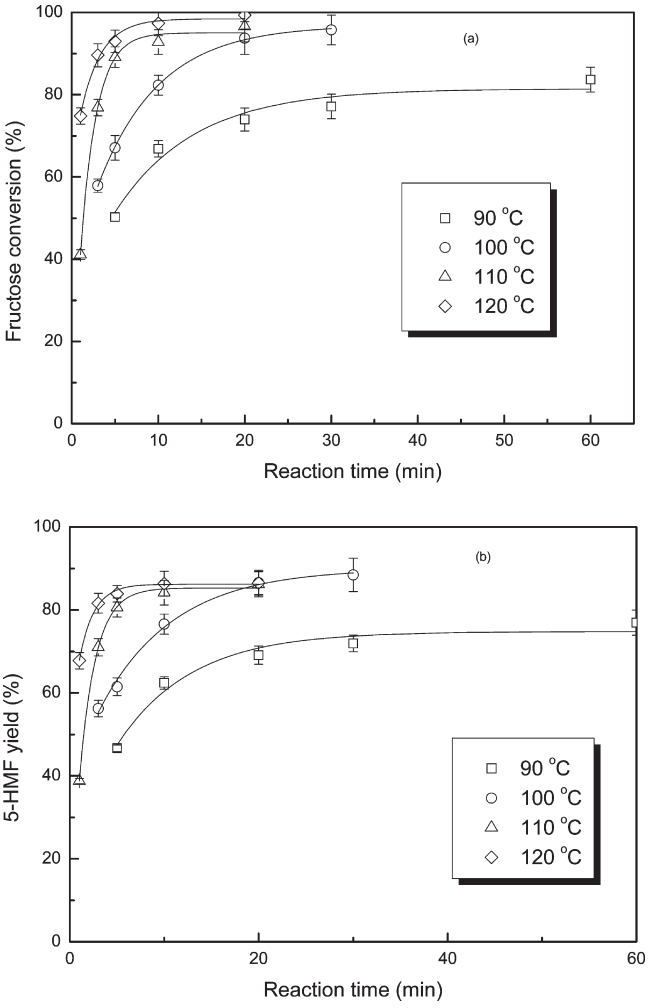

Figure 4. Effect of reaction temperature on the Fructose conversion into 5-HMF (0.05 g of Fructose, 1 g of [BMIM][Cl], 0.02 g of SO_4^{2-}/ZrO_2).

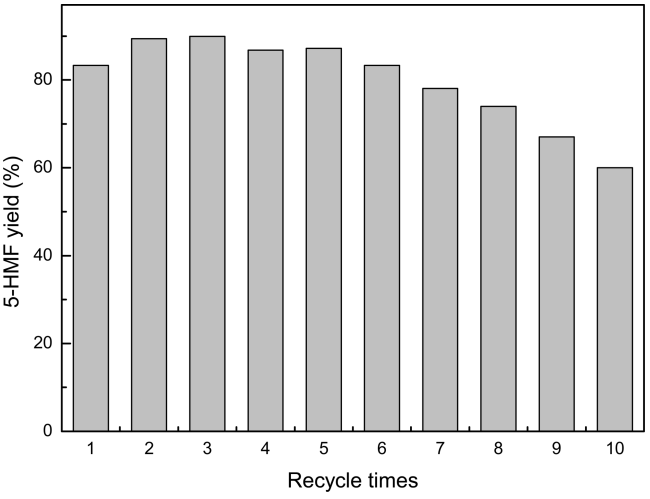

Figure 5. Recycle of [BMIM][Cl] and catalyst (100 °C, 0.05 g (0.278 mmol) fructose, 1 g of [BMIM][Cl], 0.02 g of SO_4^{2-}/ZrO_2, 30 min).

temperatures. The use of IL as solvent in the acid catalytic dehydration of fructose catalyzed by sulfated zirconia significantly

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reduced the temperature required for the reaction compared with aqueous or organic solvents.[9,32] In our previous work, 93.6% of fructose was converted and 72.8% of 5-HMF yield was obtained at 180 °C for 20 min in 70:30 (w/w) acetone-DMSO mixture in the presence of the same catalyst.[9] Yang et al. studied the fructose conversion into 5-HMF in DMSO using SO_4^{2-}/ZrO_2 as catalyst, and got a 5-HMF yield of 68.2% at 130 °C for 4 h.[32] Compared with this work, the reaction temperature could be reduced to 100 °C for higher 5-HMF yield and selectivity at equal or shorter reaction times.

3.5. Recycling of IL and Catalyst. Figure 5 gives the results for the recycling of [BMIM][Cl] and sulfated zirconia. The reuse of the IL and catalyst was tried for 10 times to study its stability and activity. Experiments were conducted at 100 °C for a reaction time of 30 min. The product 5-HMF was separated from the solvent mixture after reaction by extracting 5 times with 6 mL of ethyl acetate after 0.5 g of water was added. We examined the amount of 5-HMF in ethyl acetate that represents the total amount of 5-HMF obtained after separation. It can be seen from Figure 5 that the recycled IL and catalyst gave comparable amounts of 5-HMF showing that the IL and catalyst retained a very high activity for the conversion of fructose into 5-HMF up to 6 trials, and then 5-HMF yields decreased gradually, but still kept above 60% until recycled 10 times. The decrease in catalytic activity should be attributed to the decreasing of acid sites in the catalyst because of the occupation by byproducts and the drop of SO_4^{2-} from the catalyst. In some cases, the 5-HMF yield in the recycled IL was even higher than that in the fresh IL, which might be due to the retention of some 5-HMF and unreacted fructose in the previous cycle. To quantify the 5-HMF and fructose remaining in the reaction mixture before recycling, we did a duplicate experiment and analyzed the reaction mixture after the extraction of 5-HMF was completed, and the residual amounts of 5-HMF (0.001 mmol, 4% yield) and fructose (0.0014 mmol, 5% yield) were obtained.

4. CONCLUSIONS

Solid acid catalyst sulfated zirconia was prepared by impregnation with H_2SO_4, and was employed in the catalytic conversion of fructose to 5-HMF in IL [BMIM][Cl]. The sulfated zirconia was shown to have higher catalytic activity over untreated ZrO_2 for the 5-HMF formation from fructose, and a high fructose conversion of 95.8% with a 5-HMF yield of 88.4% could be achieved in the presence of sulfated zirconia at 100 °C for 30 min reaction time. Compared with the previous work where water or organic solvents was used as reaction media, the reaction temperature in this work could be reduced from 180 to 100 °C for higher 5-HMF yield and selectivity at equal reaction times. The IL [BMIM][Cl] and sulfated zirconia could be recycled up to 6 times without loss of activity after the product 5-HMF was separated with ethyl acetate.

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REFERENCES

(1) Roman-Leshkov, Y.; Chheda, J. N.; Dumesic, J. A. Phase modifiers promote efficient production of hydroxymethylfurfural from fructose. *Science* **2006**, *312* (5782), 1933–1937.

(2) Lewkowski, J. Synthesis, chemistry and applications of 5-hydroxymethyl-furfural and its derivatives. *Arkivoc* **2001**, *2*, 17–54.

(3) Zakrzewska, M. E.; Bogel-Lukasik, E.; Bogel-Lukasik, R. Ionic Liquid-Mediated Formation of 5-Hydroxymethylfurfural-A Promising Biomass-Derived Building Block. *Chem. Rev.* **2011**, *111* (2), 397–417.

(4) Stahlberg, T.; Rodriguez-Rodriguez, S.; Fristrup, P.; Riisager, A. Metal-Free Dehydration of Glucose to 5-(Hydroxymethyl)furfural in Ionic Liquids with Boric Acid as a Promoter. *Chem.—Eur. J.* **2011**, *17* (5), 1456–1464.

(5) James, O. O.; Maity, S.; Usman, L. A.; Ajanaku, K. O.; Ajani, O. O.; Siyanbola, T. O.; Sahu, S.; Chaubey, R. Towards the conversion of carbohydrate biomass feedstocks to biofuels via hydroxylmethylfurfural. *Energy Environ. Sci.* **2010**, *3* (12), 1833–1850.

(6) Rosatella, A. A.; Simeonov, S. P.; Frade, R. F. M.; Afonso, C. A. M. 5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications. *Green Chem.* **2011**, *13* (4), 754–793.

(7) Lai, L. K.; Zhang, Y. G. The Effect of Imidazolium Ionic Liquid on the Dehydration of Fructose to 5-Hydroxymethylfurfural, and a Room Temperature Catalytic System. *ChemSusChem* **2010**, *3* (11), 1257–1259.

(8) Sievers, C.; Musin, I.; Marzialetti, T.; Olarte, M. B. V.; Agrawal, P. K.; Jones, C. W. Acid-Catalyzed Conversion of Sugars and Furfurals in an Ionic-Liquid Phase. *ChemSusChem* **2009**, *2* (7), 665–671.

(9) Qi, X. H.; Watanabe, M.; Aida, T. M.; Smith, R. L. Sulfated zirconia as a solid acid catalyst for the dehydration of fructose to 5-hydroxymethylfurfural. *Catal. Commun.* **2009**, *10* (13), 1771–1775.

(10) Binder, J. B.; Raines, R. T. Simple Chemical Transformation of Lignocellulosic Biomass into Furans for Fuels and Chemicals. *J. Am. Chem. Soc.* **2009**, *131* (5), 1979–1985.

(11) Qi, X. H.; Watanabe, M.; Aida, T. M.; Smith, R. L. Catalytical conversion of fructose and glucose into 5-hydroxymethylfurfural in hot compressed water by microwave heating. *Catal. Commun.* **2008**, *9* (13), 2244–2249.

(12) Qi, X. H.; Watanabe, M.; Aida, T. M.; Smith, R. L. Catalytic dehydration of fructose into 5-hydroxymethylfurfural by ion-exchange resin in mixed-aqueous system by microwave heating. *Green Chem.* **2008**, *10* (7), 799–805.

(13) Qi, X. H.; Watanabe, M.; Aida, T. M.; Smith, R. L. Selective conversion of D-fructose to 5-hydroxymethylfurfural by ion-exchange resin in acetone/dimethyl sulfoxide solvent mixtures. *Ind. Eng. Chem. Res.* **2008**, *47* (23), 9234–9239.

(14) Zhao, H. B.; Holladay, J. E.; Brown, H.; Zhang, Z. C. Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural. *Science* **2007**, *316* (5831), 1597–1600.

(15) Roman-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature* **2007**, *447* (7147), 982–985.

(16) Chheda, J. N.; Roman-Leshkov, Y.; Dumesic, J. A. Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides. *Green Chem.* **2007**, *9* (4), 342–350.

(17) Bicker, M.; Kaiser, D.; Ott, L.; Vogel, H. Dehydration of D-fructose to hydroxymethylfurfural in sub- and supercritical fluids. *J. Supercrit. Fluid* **2005**, *36* (2), 118–126.

(18) Benvenuti, F.; Carlini, C.; Patrono, P.; Galletti, A. M. R.; Sbrana, G.; Massucci, M. A.; Galli, P. Heterogeneous zirconium and titanium catalysts for the selective synthesis of 5-hydroxymethyl-2-furaldehyde from carbohydrates. *Appl. Catal., A* **2000**, *193* (1−2), 147–153.

(19) Carlini, C.; Giuttari, M.; Galletti, A. M. R.; Sbrana, G.; Armaroli, T.; Busca, G. Selective saccharides dehydration to 5-hydroxymethyl-2-furaldehyde by heterogeneous niobium catalysts. *Appl. Catal., A* **1999**, *183* (2), 295–302.

(20) Kuster, B. F. M. 5-Hydroxymethylfurfural (HMF). A review focussing on its manufacture. *Starch* **1990**, *42*, 314–321.

(21) Asghari, F. S.; Yoshida, H. Dehydration of fructose to 5-hydroxymethylfurfural in sub-critical water over heterogeneous zirconium phosphate catalysts. *Carbohydr. Res.* **2006**, *341* (14), 2379–2387.

(22) Benoit, M.; Brissonnet, Y.; Guelou, E.; Vigier, K. D.; Barrault, J.; Jerome, F. Acid-Catalyzed Dehydration of Fructose and Inulin with Glycerol or Glycerol Carbonate as Renewably Sourced Co-Solvent. *ChemSusChem* **2010**, *3* (11), 1304–1309.

(23) Asghari, F. S.; Yoshida, H. Kinetics of the decomposition of fructose catalyzed by hydrochloric acid in subcritical water: Formation of 5-hydroxymethylfurfural, levulinic, and formic acids. *Ind. Eng. Chem. Res.* **2007**, *46* (23), 7703–7710.

(24) Tong, X. L.; Li, Y. D. Efficient and Selective Dehydration of Fructose to 5-Hydroxymethylfurfural Catalyzed by Bronsted-Acidic Ionic Liquids. *ChemSusChem* **2010**, *3* (3), 350–355.

(25) Hu, S. Q.; Zhang, Z. F.; Zhou, Y. X.; Han, B. X.; Fan, H. L.; Li, W. J.; Song, J. L.; Xie, Y. Conversion of fructose to 5-hydroxymethylfurfural using ionic liquids prepared from renewable materials. *Green Chem.* **2008**, *10* (12), 1280–1283.

(26) Hansen, T. S.; Woodley, J. M.; Riisager, A. Efficient microwave-assisted synthesis of 5-hydroxymethylfurfural from concentrated aqueous fructose. *Carbohydr. Res.* **2009**, *344* (18), 2568–2572.

(27) Asghari, F. S.; Yoshida, H. Acid-catalyzed production of 5-hydroxymethyl furfural from D-fructose in subcritical water. *Ind. Eng. Chem. Res.* **2006**, *45* (7), 2163–2173.

(28) Carlini, C.; Patrono, P.; Galletti, A. M. R.; Sbrana, G. Heterogeneous catalysts based on vanadyl phosphate for fructose dehydration to 5-hydroxymethyl-2-furaldehyde. *Appl. Catal., A* **2004**, *275* (1−2), 111–118.

(29) Watanabe, M.; Aizawa, Y.; Iida, T.; Aida, T. M.; Levy, C.; Sue, K.; Inomata, H. Glucose reactions with acid and base catalysts in hot compressed water at 473 K. *Carbohydr. Res.* **2005**, *340* (12), 1925–1930.

(30) Tyagi, B.; Mishra, M. K.; Jasra, R. V. Solvent free isomerisation of longifolene with nano-crystalline sulphated zirconia. *Catal. Commun.* **2006**, *7* (1), 52–57.

(31) Yu, S.; Brown, H. M.; Huang, X. W.; Zhou, X. D.; Amonette, J. E.; Zhang, Z. C. Single-step conversion of cellulose to 5-hydroxymethylfurfural (HMF), a versatile platform chemical. *Appl. Catal., A* **2009**, *361* (1−2), 117–122.

(32) Yan, H. P.; Yang, Y.; Tong, D. M.; Xiang, X.; Hu, C. W. Catalytic conversion of glucose to 5-hydroxymethylfurfural over SO42-/ZrO2 and SO42-/ZrO2-Al2O3 solid acid catalysts. *Catal. Commun.* **2009**, *10* (11), 1558–1563.

(33) Kroon, M. C.; Toussaint, V. A.; Shariati, A.; Florusse, L. J.; van Spronsen, J.; Witkamp, G. J.; Peters, C. J. Crystallization of an organic compound from an ionic liquid using carbon dioxide as anti-solvent. *Green Chem.* **2008**, *10* (3), 341–344.

(34) Qi, X. H.; Watanabe, M.; Aida, T. M.; Smith, R. L. Fast transformation of glucose and di-/polysaccharides into 5-hydroxymethylfurfural by microwave heating in an ionic liquid/catalyst system. *ChemSusChem* **2010**, *3* (9), 1071–1077.