Carbohydrate Research 345 (2010) 1846-1850

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Production of 5-hydroxymethylfurfural in ionic liquids under high fructose concentration conditions

Changzhi Li^a, Zongbao K. Zhao^{a,b,*}, Aiqin Wang^a, Mingyuan Zheng^a, Tao Zhang^{a,*}

^a Dalian Institute of Chemical Physics, CAS, 457 Zhongshan Road, Dalian 116023, PR China ^b Dalian National Laboratory for Clean Energy, Dalian 116023, PR China

ARTICLE INFO

Article history: Received 25 May 2010 Received in revised form 30 June 2010 Accepted 4 July 2010 Available online 30 July 2010

Keywords: 5-Hydroxymethylfurfural Ionic liquid Fructose Dehydration Bio-based product

ABSTRACT

Acid-promoted, selective production of 5-hydroxymethylfurfural (HMF) under high fructose concentration conditions was achieved in ionic liquids (ILs) at 80 °C. A HMF yield up to 97% was obtained in 8 min using 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl) catalyzed with 9 mol % hydrochloric acid. More significantly, an HMF yield of 51% was observed when fructose was loaded at a high concentration of 67 wt % in [C₄mim]Cl. Water content below 15.4% in the system had little effect on HMF yield, whereas a higher water content was detrimental to both reaction rate and HMF yield. In situ NMR analysis suggested that the transformation of fructose to HMF was a highly selective reaction that proceeded through the cyclic fructofuranosyl intermediate pathway. This work increased our capacity to produce HMF, and should be valuable to facilitate cost-efficient conversion of biomass into biofuels and bio-based products.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Studies on the efficient use of renewable resources such as carbohydrates for the generation of biofuels and chemicals are currently being intensified worldwide.^{1,2} One particular compound, 5-hydroxymethylfurfural (HMF), a dehydration product of hexoses, has attracted significant attention (Scheme 1). HMF can be further transformed into levulinic acid and 2,5-disubstituted furan derivatives, the latter being potential building blocks for the production of plastics and fine chemicals.³ Moreover, HMF can be converted into biofuel molecules 2,5-dimethylfuran⁴ and other liquid alkanes that can be, for example, in diesel engines. Therefore, advances in HMF production will be of a great significance for the transformation of biomass into bio-based chemicals and biofuels.

HMF has been produced under various conditions catalyzed by mineral acids,^{5,6} organic acids,⁷ zeolites,⁸ and strong acidic resins^{9,10} in different solvents, including water, organic solvents, organic/water mixtures, and supercritical solvents.¹¹ However, most of these systems are inadequate in terms of hexose conversion, product selectivity, and catalyst recycling. Recent studies by Dumesic and co-workers,⁴ Qi¹⁰ and Amarasekara et al.¹² in organic solvent (dimethylsulfoxide (DMSO), acetone, and butanol) systems or biphasic systems showed that HMF could be produced in moderate to high yields over various catalysts and that the product could be separated by extraction.

Ionic liquid (IL) systems have also been reported for HMF production. Moreau and co-workers⁹ reported dehydration of fructose in 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim]-BF₄) and 1-butyl-3-methyl imidazolium hexafluorophosphate $([C_4 mim]PF_6)$ with a moderate HMF yield of 50%. Subsequently, the same authors used the protic IL 1-H-3-methyl imidazolium chloride as a dual solvent and catalyst for the dehydration of fructose.¹³ Zhang¹⁴ and Raines¹⁵ showed that CrCl₂ and CrCl₃ were efficient catalysts for the conversion of carbohydrates to HMF in ILs. Accordingly, we achieved the direct conversion of cellulose to HMF in an isolated yield of 60% in IL under microwave irradiations in the presence of CrCl₃.¹⁶ Similarly, microwave irradiation was also used rather than the conventional heating modes used elsewhere to enhance the reaction rate and to improve HMF yield.¹⁷ Very recently, HMF production at room temperature was achieved by Qi and his co-workers, where 5 wt % fructose in IL/organic solvent mixture was treated with an unspecified resin to give HMF in high yields.¹⁸

It should be pointed out that the majority of previous studies on HMF production used low initial hexose concentrations (usually $\leq 10 \text{ wt \%}$). Therefore, it remains necessary to develop new chemistry for the dehydration of hexoses with much lower solvent consumption. In this paper, we report our results on acid-catalyzed dehydration of fructose to HMF in high isolated yields at 80 °C in ILs. More importantly, this strategy is effective under high fructose concentration conditions. Our method is expected to progress the HMF production technology further toward a large-scale application.





^{*} Corresponding authors. Tel./fax: +86 411 84379211 (Z.K.Z.).

E-mail addresses: zhaozb@dicp.ac.cn (Z.K. Zhao), taozhang@dicp.ac.cn (T. Zhang).

^{0008-6215/\$ -} see front matter \odot 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.carres.2010.07.003



Scheme 1. General transformation pathway of fructose.

2. Experimental

2.1. Materials and instruments

Fructose was purchased from Sigma (St. Louis, USA), and was dried under vacuum at 80 °C for 24 h before use. *N*-Methylimidazole (99%) was obtained from J&K Chemical Ltd (Beijing, China). 1-Chlorobutane (98%), 1-chlorohexane (99%), and 1-bromobutane (99%) were purchased from ABCR Gmbh & Co. (Karlsruhe, Germany) and were freshly distilled before use. Hydrochloric acid (36 wt %), sulfuric acid (98 wt %), nitric acid (65–68 wt %), phosphoric acid (85 wt %), maleic acid (99%), acetic acid (99%), citric acid (99%), allyl chloride (95%), pyridine (99%), and other chemicals were all supplied by local suppliers. Unless otherwise specified, acids were directly used as received. NMR spectra were measured with a Bruker DRX-400 spectrometer (400 MHz for ¹H, 100 MHz for ¹³C).

2.2. Preparation of ionic liquids

1-Butyl-3-methylimidazolium chloride ([C_4 mim]Cl), 1-butyl-3-methylimidazolium bromide ([C_4 mim]Br), 1-ethyl-3-methyl-imidazolium bromide ([C_2 mim]Br), *N*-butyl pyridinium chloride ([C_4 Py]Cl), 1-allyl-3-methylimidazolium chloride ([Amim]Cl), 1-butyl-3-methylimidazolium bisulfate ([C_4 mim]HSO₄), 1-(4-sulfobutyl)-3-methylimidazolium bisulfate ([Sbmim]HSO₄), 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4 mim]BF₄), 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4 mim]PF₆), and 1-hexyl-3-methylimidazolium chloride ([C_6 mim]Cl), were prepared according to the methods described in our previous work.¹⁹ All IL samples were dried under vacuum at 90 °C for 3 d before use.

2.3. Typical procedure for fructose dehydration

After an appropriate amount of fructose was dissolved in $[C_4mim]Cl$ (4.0 g) at 80 °C, hydrochloric acid (9 mol %, based on fructose) was added. The reaction mixture was stirred at 80 °C; samples were withdrawn at various time intervals, weighed (recorded as M_1 , usually 50 mg), quenched with cold water, and subjected to analysis. Alternatively, the entire reaction mixture was loaded on silica gel and purified by column chromatography (ethyl acetate/petroleum ether = 1: 10 to 1: 1) to afford HMF as a yellow oil, which was transformed to a yellow solid upon storage below 0 °C. ¹H NMR (400 Hz, CDCl₃): δ 9.70 (s, 1H), 7.35 (d, J = 2.8 Hz, 1H), 6.65 (d, J = 2.8 Hz, 1H), 4.84 (s, 2H). ¹³C NMR (100 Hz, CDCl₃): δ 178.2, 161.2, 152.8, 123.4, 110.5, 58.0.

2.4. HMF quantification procedure

The water-quenched samples were neutralized with 0.5 mol/L NaOH and centrifuged at 10,000 rpm for 5 min to give the supernatant (volume recorded as V_1), from which a sample (25 μ L) was pipetted and diluted with deionized water to a final volume of 4.025 mL. The HMF concentration was measured on a JASCO V-530 Model spectrophotometer (JASCO Inc., Japan) at 282 nm using

the standard curve method. The mass of HMF $(M_{\rm H})$ was calculated as follows,

$$M_{\rm H}~({\rm mg}) = {\rm HMF~concentration}(\times 10^{-3}~{\rm mg}/{\rm mL}) \times 4.025~({\rm mL})$$

$$\times (V_1/0.025) \times (M_0/M_1)$$

The yield of HMF was calculated as follows,

HMF yield = $M_{\rm H}/({\rm initial \ fructose \ mass} \times 0.7) \times 100\%$

In which, $M_{\rm H}$ is the mass of HMF, V_1 is the volume of the sample, M_0 is the total mass of the reaction solution, and M_1 is the mass of sample.

The results obtained by this quantification assay were in good agreement with the isolated yields achieved by column chromatography on silica gel.

2.5. Fructose quantification procedure

Fructose concentration was determined through DNS method described elsewhere.²⁰

3. Results and discussion

3.1. Preliminary dehydration of fructose in ILs

The dehydration of 10 wt % fructose in [C₄mim]Cl in the presence of 9 mol % hydrochloric acid was studied initially. The reaction was completed in 8 min at 80 °C and HMF was obtained in 97% yield (Table 1, entry 1). By comparison, performing the same reaction without acid resulted in a HMF yield of only 65% after 900 min (entry 2). The dehydration reaction catalyzed with nitric acid (5 min) and sulfuric acid (3 min) (both with an H⁺ concentration close to 9 mol % of fructose) at 80 °C afforded HMF in 93% and 91% yields, respectively (entries 3 and 4), indicating that strong mineral acids were near equally effective. This suggests that a catalytic amount of strong mineral acids in [C₄mim]Cl is an excellent system for the selective dehydration of fructose to HMF. Interestingly, the reaction was quite slow in the presence of a weaker acid, phosphoric acid (entry 5), indicating that the nature of the acid played an important role. We found that organic acids also catalyzed the reaction effectively. Under otherwise identical conditions, the HMF yield was 88% after 50 min in the presence of 7.6 mol % maleic acid (entry 6) and 78% after 720 min in the presence of acetic acid (entry 7).

Excellent results in $[C_4mim]Cl$ encouraged us to test other ILs. As shown in Table 1, regardless of the type of cation in the IL, the reactions catalyzed with hydrochloric acid in halide anion-containing ILs, $[C_4mim]Br$, $[C_4Py]Cl$, $[C_2mim]Cl$, [Amim]Cl, and $[C_6mim]Cl$, afforded reasonably high HMF yields, although the optimal reaction time varied (entries 8–12). However, reactions in acidic ILs [Sbmim]HSO₄ and $[C_4mim]HSO_4$ tended to form insoluble products. On the other hand, if [Sbmim]HSO₄ or $[C_4mim]HSO_4$ was applied as a catalyst at 5 mol % loading, the HMF yields reached over 80% within 30 min (entries 13 and 14). These results indicate that [Sbmim]HSO₄ and $[C_4mim]HSO_4$ behaved as strong acids, and likely promoted extensive side reactions when used as

1	84	18
---	----	----

Entry	Solvent	Catalyst	Cat. amount (mmol)	R ^b (%)	Time (min)	Yield (%
1	[C₄mim]Cl	HCl	0.20	9	8	97 (95)
2	[C ₄ mim]Cl	No	_	_	900	65
3	[C ₄ mim]Cl	HNO ₃	0.20	9	5	93
4	[C ₄ mim]Cl	H_2SO_4	0.10	9	3	91
5	[C ₄ mim]Cl	H_3PO_4	0.09	12	720	67
6	[C₄mim]Cl	Maleic acid	0.17	7.6	50	88
7	[C ₄ mim]Cl	Acetic acid	0.17	7.6	720	78
8	[C4mim]Br	HCl	0.20	9	11.5	95 (92)
9	[C ₄ Py]Cl	HCl	0.10	4.5	10	97
10	[Amim]Cl	HCl	0.20	9	25	96
11	[C ₂ mim]Br	HCl	0.20	9	2	88
12	[C ₆ mim]Cl	HCl	0.20	9	360	85
13	[C₄mim]Cl	[C ₄ mim]HSO ₄	0.17	5	30	80
14	[C ₄ mim]Cl	[Sbmim]HSO ₄	0.13	5	26	91
15	[C ₄ mim]PF ₆	HCl	0.20	9	60	8
16	[C ₄ mim]BF ₄	HCl	0.20	9	60	5

 Table 1

 Dehvdration of fructose in ILs with different catalysts^a

^a Reaction conditions: 4.0 g ionic liquid, 0.4 g fructose, 80 °C. The yields relate to the time required to achieve maximum yields and the data in parenthesis were the isolated yields.

^b *R* was defined as the theoretically calculated molar percentage of H⁺ in the catalyst based on fructose.

the reaction media. It should be noted that ILs with poor coordination ability,²¹ for example, [C₄mim]PF₆ and [C₄mim]BF₄, were inert (entries 15 and 16). This was probably because PF₆⁻ and BF₄⁻ were less competent than halide anions in providing a hydrogen-bonding network^{22,23} for the dehydration reaction.

It should be pointed out that other common hexoses, such as glucose and mannose, gave significantly lower yields under identical conditions used for the entry 1 of Table 1. These results were in accordance with the fact that alternative catalysts are required to promote isomerization of these sugars into ketosugar to facilitate HMF production.¹⁶

3.2. Effect of water on the reaction

One product of HMF formation is water which can react with HMF or other reaction intermediates, leading to levulinic acid or complex products. Because the reaction was carried our in ILs, a non-aqueous environment, the initial water concentration in the solution may be a sensitive issue. To address this concern, we ran the reactions in the presence of various amounts of water. As illustrated in Figure 1, when water was added at 8.3 wt % in the system, the dehydration reaction proceeded more slowly, yet a



Figure 1. Results of fructose dehydration using various initial amounts of water. Conditions: 1.0 g [C₄mim]Cl, 0.1 g fructose, 5 mg HCl, 80 °C.

similar HMF yield was achieved in 30 min (Fig. 1, line 2 vs line 1). When water was included at 15.3 wt %. HMF was obtained in ca. 92% yield within 40 min (line 3). Thus, a small amount of water had little effect on HMF yield, although the dehydration reaction slowed down. Indeed, our results under high fructose concentration conditions also support such a conclusion (vide infra). When the initial water content was 31.2 wt %, the dehydration reaction was noticeably slower. The HMF yield was reduced to 72% after 60 min and fructose conversion was 75%; whereas a 92% HMF yield with a 94% fructose conversion was achieved after 180 min (line 4). If the water content reached 47.5 wt %, the HMF yield and fructose conversion were 28% and 29%, respectively, after 60 min. However, when the reaction time was prolonged to 420 min, the HMF yield and fructose conversion were 80% (line 5) and 85%, respectively. These results clearly suggest that excess water reduced the dehydration reaction rate. but had little effect on HMF selectivity.

3.3. Dehydration under high fructose concentration

A high substrate concentration is usually preferred in terms of process economics. Although a number of HMF production strategies have been available,²⁴ few of them have satisfactory selectivity and/or yield at high fructose concentrations. Qi et al.²⁵ achieved 54% HMF yield when 20 wt % fructose was treated at 150 °C for 5 min in the presence of an ion-exchange resin in an acetone/water mixture (Table 2, entry 1). Dumesic³ and co-workers also showed relatively good results in this area. They performed the same reaction in H₂O-salt/organic solvent systems with 30 wt % fructose at 180 °C and attained 55-66% HMF yield (entries 2 and 3). Further, the same author²⁶ used a complicated two-phase reaction system including 0.25 mol L⁻¹ hydrochloric acid to process 50 wt % fructose at 180 °C for 3 min, giving a fructose conversion of 90% and a HMF yield of 70% (entry 4). Because water was used as a co-solvent and the reactions were carried out at a relatively high temperature, it seems that ca. 20% fructose was lost under those conditions. In contrast, dehydration of 33 wt % fructose in [C₄mim]Cl gave HMF in 82% yield after 35 min in the presence of 9 mol % hydrochloric acid at 80 °C (entry 5). Our experiments with initial fructose concentrations at 43, 50, and 67 wt % produced HMF in 76%, 67%, and 51% yields, although the reaction times were longer when the substrate concentrations were higher (Table 2, entries 6-8). Obviously, our strategy offered an opportunity to use a high fructose concentration under mild conditions without significantly compromising the HMF yield. Because a higher substrate

The results of fructose dehydration promoted by various catalytic systems ^a									
	Entry	Solvent system	Catalyst	Fructose concn (wt %)	Temperature (°C)	Time (min)	Conversion (%)	Yield (%)	Ref.
	1	Acetone/H ₂ O	IER ^b	20	150	5	89	54	25
	2	H ₂ O-salt/butanol	HCl	30	180	3	80	66	3
	3	H ₂ O-salt/MIBK ^c	HCl	30	180	3	72	55	3
	4	WDPMB ^d	HCl	50	180	3	90	70	26
	5	[C ₄ mim]Cl	HCl	33	80	35	90	82	This work
	6	[C4mim]Cl	HCl	43	80	46	86	76	This work
	7	[C ₄ mim]Cl	HCl	50	80	55	78	67	This work
	8	[C₄mim]Cl	HCl	67	80	120	67	51	This work

Table 2

^a Unless otherwise specified, the reactions in this work were performed by using a set amount of fructose in 4.0 g of [C₄mim]Cl catalyzed by 9 mol % hydrochloric acid at 80 °C; The yields relate to the time required to achieve maximum yields.

Ion-exchange resin Dowex 50wx8.

^c MIBK is methyl isobutyl ketone.

^d Water/DMSO/poly(1-vinyl-2-pyrrolidinone)/MIBK/2-butanol mixture.

concentration can greatly reduce solvent use, this method is expected to have great potential in terms of improved process economics and environmental friendliness.

3.4. Reaction mechanism considerations

Various kinetic studies on the acid-catalyzed dehydration of fructose have been reported in the literature. Two major routes were considered; the open-chain pathway⁸ through two 1,2-eliminations and one 1,4-elimination of water and the cyclic fructofuranosyl intermediate pathway.²² Although evidence exists to support both mechanisms, it is clear that the reaction intermediates and HMF could be further converted into other products by means of processes such as fragmentation, condensation, rehydration, and/or additional dehydration reactions. To look in more detail at the dehydration in ILs, we monitored the time course of the fructose dehydration reaction in $[C_4mim]Cl$ at 80 °C by in situ NMR analysis.

Figure 2a shows a time-progression stack of ¹H NMR spectra of fructose dehydration where the initial fructose concentration was 50 wt %. The strong peaks at around 9.89, 8.36, 4.85, and 4.62 ppm are assigned to $[C_4 mim]Cl$; the relatively lower peaks between 4.0 and 5.4 ppm are those of fructose; the peaks at 10.20, 8.10, and 7.23 ppm are typical signals of HMF. The spectra recorded after 1.0 min at 80 °C (t = 1.0 min) showed mainly fructose and [C₄mim]Cl signals and only a trace amount of HMF was present. At t = 5.0 min, the three peaks in the low-field region at 10.20 (s), 8.10 (d, J = 3.3 Hz) and 7.23 (d, J = 3.2) ppm became higher and in the meantime, the fructose signals at 3.8-5.4 ppm decreased, indicating the formation of HMF. With the reaction time increased further, stronger HMF signals, accompanied by weaker fructose signals were observed. It should be pointed out that no discernible by-product signal was observed during the whole process and the spectra recorded after 60 min showed only HMF and [C₄mim]Cl signals, indicating that the dehydration reaction was highly selective.

The ¹³C NMR spectra (Fig. 2b) show similar results. The two alkene peaks at 156 and 146 ppm and a peak in the carbonyl region at 173 ppm are assigned to HMF, while the peaks between 60 and 100 ppm belong to the cyclic form of fructose. With increased reaction time, stronger HMF signals accompanied by weaker fructose signals were detected. It is interesting to note that during the whole process, no discernible carbonyl signal was present at ca. 180 ppm, indicating that the linear form of fructose was negligible in [C₄mim]Cl at 80 °C. Thus, acid-catalyzed formation of HMF in ILs may proceed through the cyclic fructofuranosyl pathway, as described elsewhere.²

Although an exact explanation for the exceptional effectiveness of IL for the conversion of fructose remains elusive, we can offer



Figure 2. In situ ¹H NMR spectra (a) and ¹³C NMR spectra (b) of the transformation of 50 wt % fructose catalyzed by 9 mol % HCl in 1.0 g [C₄mim]Cl at 80 °C.

some insights into the reaction. First, water-associated side reactions (e.g., HMF hydrolysis and water reacting with by-products/ intermediates) may be greatly suppressed because ILs can "fix" water molecule through strong hydrogen-bonding interactions between the -OH unit from water and halide anions in the system.^{22,23} In this regard, water in amounts up to 15.3 wt % showed limited influence on the dehydration reaction. This may also be the reason that the system involving the organic solvent DMSO gave better results compared with those performed in an aqueous system.⁴ Second, the high viscosity of the ILs may also assist the reaction. Because fructose dehydration is a unimolecular reaction, while most side reactions involve multiple reactants, a solvent system with a higher viscosity should favor the former reaction but disfavor the latter due to mass transfer effects. Because HMF is relatively labile under acidic conditions and elevated temperatures, conditions used in most previous works may have been too harsh to avoid substantial side reactions.^{8,9} In contrast, the reactions in this work were performed at 80 °C in the presence of a catalytic amount of acid, a mild condition where HMF per se is stable so that the reaction could be sustained for a longer time, providing an opportunity to work with high initial fructose concentrations. Taken together, our system ensured efficient and selective conversion of concentrated fructose into HMF by suppressing side reactions.

4. Conclusions

We showed that acids in dialkylimidazolium halide ILs were efficient for the dehydration of fructose into HMF at 80 °C under high fructose concentration conditions. In situ NMR analysis suggests that the reaction followed a highly selective, cyclic fructofuranosyl intermediate pathway, with no discernible formation of byproducts. We believe that side reactions were suppressed because the system had a low free water concentration and a high viscosity. Our efforts in HMF production at high substrate concentration are expected to be valuable in facilitating a cost-efficient conversion of biomass into biofuels and bio-based products.

Acknowledgments

Supports from the National High Technology Research and Development Program of China (No. 2007AA05Z403), the National

Basic Research Program of China (2009CB226102), and the Knowledge Innovation Program of CAS (No. KGCX2-YW-336) are gratefully acknowledged.

References

- 1. Corma, A.; Iborra, S.; Velty, A. Chem. Rev. 2007, 107, 2411-2502.
- 2. Asghari, F. S.; Yoshida, H. Carbohydr. Res. 2010, 345, 124-131.
- Chheda, J. N.; Roman-Leshkov, Y.; Dumesic, J. A. Green Chem. 2007, 9, 342–350.
 Román-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. Nature 2007, 447, 982–985
- 5. Chheda, J. N.; Dumesic, J. A. Catal. Today 2007, 123, 59–70.
- 6. Moye, C. J. Aust. J. Chem. 1966, 19, 2317-2320.
- 7. Kuster, B. F. M. Starch 1990, 42, 314-321.
- Moreau, C.; Durand, R.; Razigade, S.; Duhamet, J.; Faugeras, P.; Rivalier, P.; Ros, P.; Avignon, G. Appl. Catal., A 1996, 145, 211–224.
- 9. Lansalot-Matras, C.; Moreau, C. Catal. Commun. 2003, 4, 517-520.
- Qi, X.; Watanabe, M.; Aida, T. M.; Smith, R. L. Ind. Eng. Chem. Res. 2008, 47, 9234–9239.
- 11. Asghari, F. S.; Yoshida, H. Carbohydr. Res. 2006, 341, 2379-2387.
- Amarasekara, A. S.; Williams, L. D.; Ebede, C. C. Carbohydr. Res. 2008, 343, 3021–3024.
- 13. Moreau, C.; Finiels, A.; Vanoye, L. J. Mol. Catal. A: Chem. 2006, 253, 165-169.
- 14. Zhao, H.; Holladay, J. E.; Brown, H.; Zhang, Z. C. Science 2007, 316, 1597-1600.
- 15. Binder, J. B.; Raines, R. T. J. Am. Chem. Soc. 2009, 131, 1979–1985.
- 16. Li, C. Z.; Zhang, Z.; Zhao, Z. K. Tetrahedron Lett. 2009, 50, 5403-5405
- 17. Hansen, T. S.; Woodley, J. M.; Riisager, A. Carbohydr. Res. 2009, 344, 2568-2572.
- 18. Qi, X.; Watanabe, M.; Aida, T. M.; Smith, R. L. ChemSusChem 2009, 2, 944-946.
- 19. Li, C. Z.; Wang, Q.; Zhao, Z. K. Green Chem. 2008, 10, 177-182.
- 20. Miller, G. L. Anal. Chem. **1959**, 31, 426–428.
- Remsing, R. C.; Swatloski, R. P.; Rogers, R. D.; Moyna, G. Chem. Commun. 2006, 1271–1273.
- 22. Wishart, J. F. Energy Environ. Sci. 2009, 9, 956-961.
- Hanke, C. G.; Atamas, N. A.; Lynden-Bell, R. M. Green Chem. 2002, 4, 107–111.
 Chheda, J. N.; Huber, G. W.; Dumesic, J. A. Angew. Chem., Int. Ed. 2007, 46, 7164–
- 7183.
- 25. Qi, X.; Watanabe, M.; Aida, T. M. Green Chem. 2008, 10, 799-805.
- 26. Román-Leshkov, Y.; Chheda, J. N.; Dumesic, J. A. Science 2006, 312, 1933–1937.