

Carbohydrates

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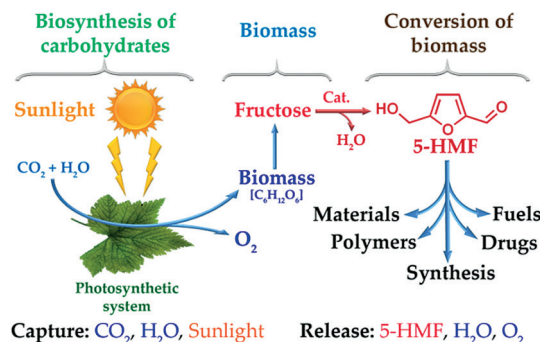
Critical Influence of 5-Hydroxymethylfurfural Aging and Decomposition on the Utility of Biomass Conversion in Organic Synthesis

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Abstract: Spectral studies revealed the presence of a specific arrangement of 5-hydroxymethylfurfural (5-HMF) molecules in solution as a result of a hydrogen-bonding network, and this arrangement readily facilitates the aging of 5-HMF. Deterioration of the quality of this platform chemical limits its practical applications, especially in synthesis/pharma areas. The model drug Ranitidine (Zantac®) was synthesized with only 15 % yield starting from 5-HMF which was isolated and stored as an oil after a biomass conversion process. In contrast, a much higher yield of 65 % was obtained by using 5-HMF isolated in crystalline state from an optimized biomass conversion process. The molecular mechanisms responsible for 5-HMF decomposition in solution were established by NMR and ESI-MS studies. A highly selective synthesis of a 5-HMF derivative from glucose was achieved using a protecting group at O(6) position.

5-Hydroxymethylfurfural (5-HMF) is a well-established platform chemical with numerous opportunities in organic chemistry,^[1] materials science,^[2] biofuels,^[3] and sustainable chemical industry.^[4] An unquestionable advantage of 5-HMF is its direct preparation from biomass, for which the estimated global net primary production is nearly 1.05×10^{14} kg fixed carbon per year.^[5] A practically important factor is the nearly equal contribution from marine and terrestrial primary biomass producers.^[5] The overall process starts with production of carbohydrate biomass and involves capture of sunlight, CO₂, and H₂O, and release of O₂ (Scheme 1). The next stage is conversion of carbohydrates into sugar monomers, followed by catalytic synthesis of 5-HMF with water as the only side product. The overall process is highly efficient and completely environmentally benign. Capture of CO₂, H₂O, and sunlight is accompanied by release of 5-HMF, H₂O and O₂.^[6]

A number of different catalytic systems have been reported for the preparation of 5-HMF from carbohydrates.^[1–7] Use of fructose and glucose as monomeric sugars, as well as cellulose as a raw carbohydrate material, has been

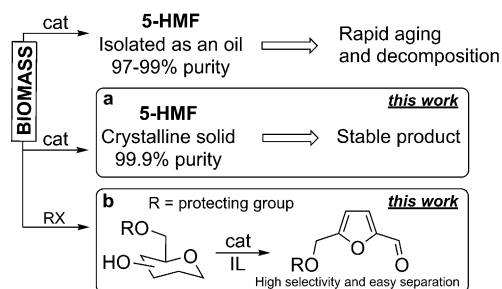


Scheme 1. The use of solar energy for biomass-derived chemical production of 5-HMF.

demonstrated.^[8,9] However, in the vast majority of cases, 5-HMF was isolated as an oil of varying purity (mostly 90–98 %), whereas isolation of solid 5-HMF is rarely described.^[10]

In the present study, we found a critical difference between 5-HMF prepared as an oil compared to a crystalline solid. Degradation during the isolation and storage of 5-HMF in an oil form critically reduces the advantages of this platform chemical. Even 97–99 % pure 5-HMF is susceptible to rapid aging and decomposition upon storage in an oil form (Scheme 2). Such rapid degradation and aging of 5-HMF imposes an unavoidable obstacle which drastically complicates its practical utilization as a platform chemical in organic synthesis and industrial applications.

In this work, the process of 5-HMF aging was studied in detail, and the nature of the decomposition was revealed. Understanding the nature of the process made it possible to develop an efficient procedure for the synthesis of crystalline 5-HMF from fructose and cellulose with greater than 99.9 % purity using a simple and recyclable catalytic system (Sche-



Scheme 2. Possible pathways of biomass conversion and critical role of product purity in the synthetic utility of 5-HMF.

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me 2a). A new approach was developed for the conversion of less reactive glucose. A simple protection of the O(6)-position in glucose increased the selectivity of the reaction and simplified product separation (Scheme 2b). Preparation of the drug Ranitidine was used as a model synthetic application, and a significant increase in yield was observed when using crystalline 5-HMF as the starting material instead of the oil form (65 % versus 15 %).

5-HMF was synthesized from fructose using the known catalytic system with H_2SO_4 as a catalyst and [BMIM][Cl], an ionic liquid, as the reaction medium.^[11] Transformation of fructose into 5-HMF under these reaction conditions proceeded with high conversion (90–99 %) and good yield (80–90 %). Isolation of 5-HMF was performed by extraction with ethyl acetate followed by purification by filtration through silica gel (see the Supporting Information). The product was obtained as a yellow or light orange oil of 97–99 % purity.

5-HMF, isolated as an oil, was dried and stored at room temperature. The color of the stored sample changed from light yellow to dark brown over 2 weeks of storage. Small aliquots were taken and subjected to NMR analysis, which clearly revealed the formation of another compound (Figure 1A). 2D DOSY NMR spectroscopy showed a decreased self-diffusion coefficient for the newly formed compound (Figure 1B), and indicated that the molecule was larger than 5-HMF. The compound was isolated, and the structure was unambiguously established as a 5-HMF dimer by X-Ray analysis (Figure 1C). 5-HMF intermolecular etherification took place with a yield of approximately 50 % after two weeks of storage.

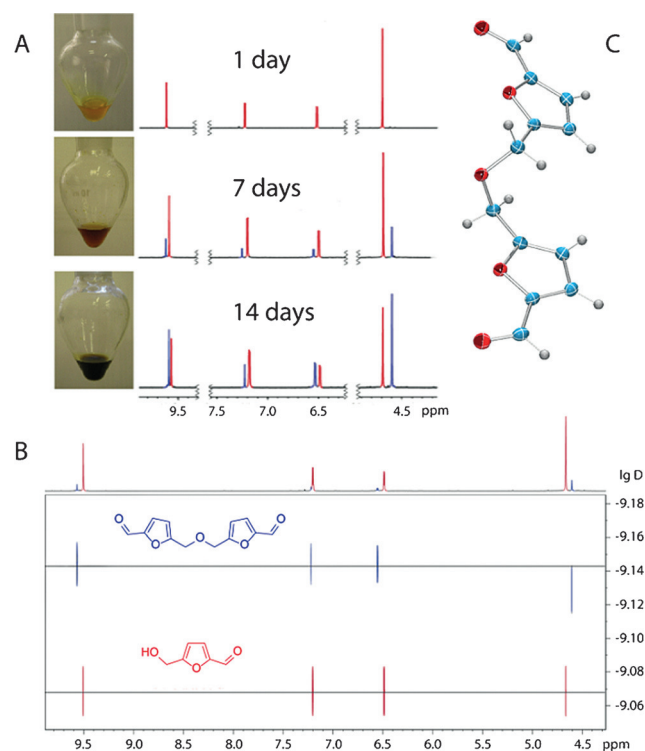


Figure 1. A) ^1H NMR monitoring of 5-HMF stored at RT as an oil. B) ^1H DOSY study of the stored 5-HMF sample. C) Molecular view of 5-HMF dimer determined by X-ray analysis.

In addition to the 5-HMF dimer, an HPLC-ESI-MS study of the aging process revealed a number of other decomposition products. Oligomerization of 5-HMF readily took place and resulted in the formation of several higher molecular weight compounds with three to ten furan cores. The structures of the degradation products, suggested on the basis of MS and MS/MS data, can be found in the Supporting Information.

Apparently, prolonged storage of 5-HMF resulted in decomposition, thus leading to formation of the dimer and larger oligomers. We propose that the aging process is facilitated by the impurities remaining after synthesis of 5-HMF. In the studied system, the presence of acidic impurities, remaining after the catalytic transformation, may be a reason for the oligomerization process. Even 97–99 % pure 5-HMF in the oil state was found to undergo rapid aging.

Many organic compounds are synthesized and stored as oils. Generally, having 97–99 % purity is usually sufficient for synthetic applications and provides the required stability upon storage. In this regard, the observed behavior of 5-HMF in the oil form is somewhat unusual. To evaluate 5-HMF behavior in a solution and in the neat oil state, we conducted an NMR analysis of samples with varying concentrations.

The measurement of self-diffusion coefficients (D) with increasing concentration revealed a rapid nonlinear decrease of D (Figure 2). For comparison, the self-diffusion coefficient of the covalently linked 5-HMF dimer was also recorded. At about 1 M concentration, the self-diffusion coefficient of the 5-HMF dimer was comparable to the corresponding value recorded for pure 5-HMF. Slow self-diffusion of 5-HMF in solution indicated strong noncovalent interactions between 5-HMF molecules and formation of larger aggregates. The process took place even at low concentration of 5-HMF in diluted solutions. Further increase of the 5-HMF concentration led to rapid growth of the molecular network in solution and a large decrease in mobility. To gain insight into the nature of the solution of 5-HMF, we carried out 2D NOESY experiments. Even at 5–10 vol % concentration, intermolecular NOE contacts were present in the spectrum, thus confirming the possibility of intermolecular bonding

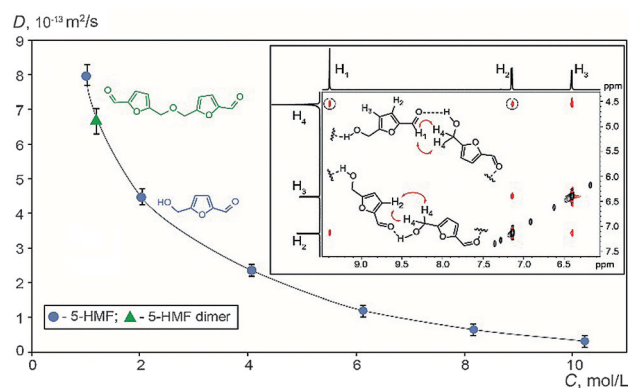


Figure 2. Self-diffusion coefficients for 5-HMF and covalent dimer at various concentrations. The insert shows the NOE spectrum of 5-HMF at 20 vol % (2.05 M) concentration (for $\blacktriangle$, the concentration based on the number of furan fragments was 1.1 M; see Supporting Information for details).

(Figure 2; the insert). The NOESY NMR spectrum of the neat 5-HMF exhibited NOE correlations between every pair of non-equivalent protons, suggesting the existence of a more closely packed arrangement of molecules connected by a hydrogen-bonding network (see the Supporting Information).

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 5-HMF in the neat oil state exhibited rather narrow lines with full width at half maximum (FWHM) at less than 10 Hz, which corresponds to T_2^* relaxation times in the range of 50–70 ms. This range is close to the typical values for tissues and other specimens with constrained molecular mobility.

As determined by NMR spectroscopy, aggregation of 5-HMF in solution leads to the formation of a self-organized network. The close arrangement of the molecules in the network is favorable for dimerization and further oligomerization. This observation may explain unique properties of 5-HMF and its tendency toward rapid aging and decomposition. In fact, dimerization and oligomerization takes place in already geometrically preorganized system, thus the oligomerization process can be very facile. In such a supramolecular network of molecules in solution, a much stronger influence of the acidic impurities and other reaction conditions should be observed. In the crystalline form, molecules of 5-HMF also exhibit intermolecular hydrogen bonds,^[12] however restricted molecular mobility ensures stability of crystallized 5-HMF.

For monitoring carbohydrate conversion and 5-HMF decomposition processes, we developed a straightforward procedure for the analysis of 5-HMF-containing systems using NMR spectroscopy directly in ionic liquids (see the Supporting Information). Spectral analysis of the reaction mixture provided a reliable picture of catalytic performance and eliminated the influence of product decomposition during isolation. A number of optimizations were carried out and revealed a strong influence of water on the reaction yield and selectivity. To achieve selective conversion of carbohydrates into 5-HMF, continuous removal of excess of water was essential.^[9] Conventional stirring of the reaction mixture using a magnetic stirrer bar or mechanical stirrer did not give desired efficiency of the catalytic process, even under vacuum (see Figure S4 in the Supporting Information). However, continuous surface renewal during exposure to vacuum substantially improved the reaction outcome. Continuous surface renewal was efficiently achieved using a rotary evaporator for the synthesis of 5-HMF. Carrying out the synthetic procedure in the rotary evaporator simplified the reaction setup and product isolation. Solvent recycling during the extraction process was carried out using the same rotary evaporator. This option is a convenient and affordable reactor which allows the dehydration reaction to proceed in a vacuum under very efficient surface-renewing mixing conditions (see Figure S4).

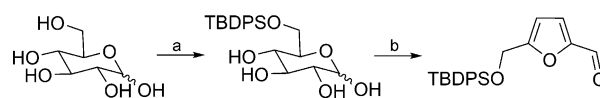
Use of a large amount of the catalyst and heating above 80 °C led to a decrease in the yield of 5-HMF as a result of the formation of byproducts. Another important factor was the ratio between the amounts of the carbohydrate substrate and ionic liquid. The concentration of the dissolved carbohydrate affected the viscosity of the reaction mixture and influenced

the contribution of the side-reactions. Under the optimized reaction conditions efficient recycling was demonstrated: $(82 \pm 10)\%$ yield was observed in 15 cycles (see Figure S2). In all cycles, 99% pure 5-HMF was obtained, and it formed crystals upon cooling. Also, it could be recrystallized to obtain the crystalline product with greater than 99.9% purity (see the Supporting Information). The reaction was successfully carried out with fructose and cellulose as starting materials and led to 85 and 50% yields of 5-HMF, respectively. Storage of crystalline 5-HMF for 1 month at room temperature did not lead to product decomposition, and the compound remained pure as confirmed by NMR and MS analysis. These results are in sharp contrast to the behavior of oily 5-HMF, in which aging and decomposition rapidly took place in a short period of time.

The observed strong influence of water can be explained by taking into account the molecular arrangement of 5-HMF in solution (Figure 2) as it may facilitate the side-reactions. Continuous removal of water during synthesis decreased the effect of the product degradation process and increased the yield. The studied catalytic system utilized an important advantage of ionic liquids—low vapor pressure and high thermal stability combined with unique molecular level properties.^[13]

The selectivity of 5-HMF formation from glucose is much lower as compared to fructose because of harsh reaction conditions and decomposition of 5-HMF during the synthetic process.^[8,9] As we established, the fact can be associated with the formation of oligomeric products resulting from hydrogen-bonding networks involving 5-HMF. In such a case protection of O(6)-position of the carbohydrate (which is involved in hydrogen-bonding to the hydroxymethyl group in 5-HMF) should effect side-reactions.

Indeed, the concept is very practical since O(6)-protected glucose is easily accessible (Scheme 3). We have found that 6-O-TBDPS-D-glucopyranose undergoes conversion into 5-



Scheme 3. Highly selective conversion of O-protected D-glucopyranose to O-protected 5-HMF. a) TBDPSCl, DMAP, Py, RT, 24 h; b) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, [BMIM][Cl], methyl isobutyl ketone, 120 °C, 1 h. BMIM = 1-*n*-butyl-3-methylimidazolium, DMAP = 4-(*N,N'*-dimethylamino)pyridine, Py = pyridine, TBDPS = Ph_2tBuSi .

(TBDPS-oxymethyl)furfural using a known CrCl_3 catalyst. The product was obtained in 81% yield upon isolation. For comparison, conversion of unprotected glucose with the same catalytic system results in much lower yields of 40–50%.^[11a] In some cases high yields were observed according to NMR and HPLC analyses.^[1–8] However, the yield of pure isolated 5-HMF can be significantly lower because of degradation during the isolation process. In such a case, handling O-protected sugar can noticeably improve the process.

The absence of a free hydroxy group prevents formation of a hydrogen-bonding network, thus suggesting a plausible influence on oligomerization during the conversion process.

In addition, 5-(TBDPS-oxymethyl)furfural was extracted from the reaction mixture much more easily as compared to 5-HMF, presumably because of the lower polarity of the former. Improved separation is an important advantage in the case of ionic liquid media.

The resulting O-protected 5-HMF is a stable compound which can be stored at room temperature for a long time without significant decomposition. The TBDPS-group is easily removed to obtain 5-HMF in a pure crystalline form. The presence of protecting group also extends possible synthetic applications for stepwise selective transformations involving reaction of the aldehyde group as a first step.^[14]

5-HMF obtained by the developed procedure was utilized in the synthesis of the histamine H₂-receptor antagonist Ranitidine (trade name of the drug is Zantac®) using the modified synthetic scheme suggested by Mascall and Dutta.^[15] Starting from crystalline 5-HMF, this valuable pharmaceutical product was obtained in five steps with an overall yield of 65 % and the purity of synthesized Ranitidine was 99.9 % (see the Supporting Information for details). An identical yield of Ranitidine was obtained starting from crystalline 5-HMF stored for one month. In contrast, a small 15 % yield of Ranitidine was obtained using one-month-old oily 5-HMF.

Rapid aging of 5-HMF in the oil form diminishes the utility of this valuable building block in synthetic applications. Moreover, a more resource-demanding separation procedure based on chromatography may be required at intermediate stages to remove byproducts. It should be noted that the presence of the dimer and oligomers in the aged 5-HMF resulted in several parallel pathways during the synthetic process. Indeed, the dimer and oligomers showed similar reactivity compared to the parent 5-HMF and readily participated in the same reactions. Overall, storage of 5-HMF in an oil state and related aging processes make it impractical for synthetic applications.

To summarize, synthesis of 5-HMF from fructose was carried out under vacuum with surface-renewing mixing conditions which removed water from the reaction mixture. Under the optimized reaction conditions, pure 5-HMF was obtained in high yields and excellent selectivity using an easily available recyclable catalytic system. The synthetic procedure, as well as the subsequent 5-HMF isolation, were carried out in a rotary evaporator without the need for special equipment.

The degradation and aging of 5-HMF were studied by NMR and MS methods and confirmed the formation of dimers and oligomers during storage. Self-organization of 5-HMF in solution and formation of a hydrogen-bonded network greatly facilitated the oligomerization process, especially in the presence of acidic impurities. The process is readily facilitated at higher concentrations of 5-HMF and affects neat 5-HMF stored in the oil state. Crystalline 5-HMF was found to be superior for storage and practical synthetic applications, while preparation and usage of 5-HMF as an oil should be avoided. Biomass conversion with crystalline 5-HMF as a platform chemical provides excellent synthetic opportunities.

A new approach was developed to achieve high selectivity in the conversion of less reactive glucose. Disruption of the

hydrogen-bonding network with a simple protecting group avoids decomposition during the synthesis and facilitates extraction from the reaction mixture. Thus, conversion of glucose resulted in a high yield of isolated 5-HMF (> 80 %) under readily available catalytic conditions. The synthesized O-protected 5-HMF is a stable product and can be stored without a need of extensive purification.

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- [1] a) R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.* **2013**, *113*, 1499; b) M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* **2014**, *114*, 1827; c) A. Grossmann, S. Bartlett, M. Janeczek, J. T. Hodgkinson, D. R. Spring, *Angew. Chem. Int. Ed.* **2014**, *53*, 13093; *Angew. Chem.* **2014**, *126*, 13309; d) A. A. Rosatella, S. P. Simeonov, R. F. M. Frade, C. A. M. Afonso, *Green Chem.* **2011**, *13*, 754; e) C. Chatterjee, F. Pong, A. Sen, *Green Chem.* **2015**, *17*, 40; f) J. Lewkowski, *ARKIVOC* **2005**, *2001*, 17; g) J. A. S. Coelho, A. F. Trindade, V. André, M. Teresa Duarte, L. F. Veiros, C. A. M. Afonso, *Org. Biomol. Chem.* **2014**, *12*, 9324; h) W. P. Dijkman, D. E. Groothuis, M. W. Fraaije, *Angew. Chem. Int. Ed.* **2014**, *53*, 6515; *Angew. Chem.* **2014**, *126*, 6633; i) H. G. Cha, K.-S. Choi, *Nat. Chem.* **2015**, *7*, 328; j) T. Buntara, S. Noel, P. H. Phua, I. Melián-Cabrera, J. G. de Vries, H. J. Heeres, *Angew. Chem. Int. Ed.* **2011**, *50*, 7083; *Angew. Chem.* **2011**, *123*, 7221.
- [2] a) Y. Y. Gorbanev, S. K. Klitgaard, J. M. Woodley, C. H. Christensen, A. Riisager, *ChemSusChem* **2009**, *2*, 672; b) A. S. Amarasekara in *Renewable Polymers: Synthesis Processing, and Technology* (Ed.: V. Mittal), Wiley, Hoboken, **2012**, pp. 398–428; c) S. Subbiah, S. P. Simeonov, J. M. S. S. Esperança, L. P. N. Rebelo, C. A. M. Afonso, *Green Chem.* **2013**, *15*, 2849; d) T. Xiang, X. Liu, P. Yi, M. Guo, Y. Chen, C. Wesdemiotis, J. Xu, Y. Pang, *Polym. Int.* **2013**, *62*, 1517; e) G. Yi, S. P. Teong, X. Li, Y. Zhang, *ChemSusChem* **2014**, *7*, 2131; f) F. Menegazzo, T. Fantinel, M. Signoretto, F. Pinna, M. Manzoli, *J. Catal.* **2014**, *319*, 61; g) X. Kong, Y. Zhu, H. Zheng, F. Dong, Y. Zhu, Y.-W. Li, *RSC Adv.* **2014**, *4*, 60467; h) J. J. Pacheco, J. A. Labinger, A. L. Sessions, M. E. Davis, *ACS Catal.* **2015**, *5*, 5904; i) W.-J. Liu, H. Jiang, H.-Q. Yu, *Chem. Rev.* **2015**, *115*, 12251; j) E. de Jong, M. A. Dam, L. Sipos, G.-J. M. Gruter, in *Biobased Monomers, Polymers, and Materials* (Eds.: P. B. Smith, R. A. Gross), American Chemical Society, Washington, DC, **2012**, pp. 1–13; k) A. Scott, *Chem. Eng. News* **2016**, *94*, 15.
- [3] a) Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature* **2007**, *447*, 982; b) T. Thananathanachon, T. B. Rauchfuss, *Angew. Chem. Int. Ed.* **2010**, *49*, 6616; *Angew. Chem.* **2010**, *122*, 6766; c) M. Balakrishnan, E. R. Sacia, A. T. Bell, *Green Chem.* **2012**, *14*, 1626; d) L. Hu, G. Zhao, W. Hao, X. Tang, Y. Sun, L. Lin, S. Liu, *RSC Adv.* **2012**, *2*, 11184; e) A. D. Sutton, F. D. Waldie, R. Wu, M. Schlaf, L. A. Pete Silks, J. C. Gordon, *Nat. Chem.* **2013**, *5*, 428; f) D. Liu, E. Y.-X. Chen, *ChemSusChem* **2013**, *6*, 2236; g) B. Saha, C. M. Bohn, M. M. Abu-Omar, *ChemSusChem* **2014**, *7*, 3095; h) L. Hu, L. Lin, S. Liu, *Ind.*

- Eng. Chem. Res.* **2014**, *53*, 9969; i) B. R. Caes, R. E. Teixeira, K. G. Knapp, R. T. Raines, *ACS Sustainable Chem. Eng.* **2015**, *3*, 2591; j) A. Bohre, S. Dutta, B. Saha, M. M. Abu-Omar, *ACS Sustainable Chem. Eng.* **2015**, *3*, 1263; k) J. D. Lewis, S. Van de Vyver, A. J. Crisci, W. R. Gunther, V. K. Michaelis, R. G. Griffin, Y. Román-Leshkov, *ChemSusChem* **2014**, *7*, 2255.
- [4] a) S. Krawielitzki, T. M. Kläusli, *Ind. Biotechnol.* **2015**, *11*, 6; b) T. Ståhlberg, W. Fu, J. M. Woodley, A. Riisager, *ChemSusChem* **2011**, *4*, 451; c) S. P. Teong, G. Yi, Y. Zhang, *Green Chem.* **2014**, *16*, 2015.
- [5] C. B. Field, M. J. Behrenfeld, J. T. Randerson, P. Falkowski, *Science* **1998**, *281*, 237.
- [6] a) P. M. Donate, *Chem. Biol. Technol. Agric.* **2014**, *1*, 4; b) A. Mukherjee, M.-J. Dumont, V. Raghavan, *Biomass Bioenergy* **2015**, *72*, 143.
- [7] a) J. J. Bozell, G. R. Petersen, *Green Chem.* **2010**, *12*, 539; b) M. E. Zakrzewska, E. Bogel-Lukasik, R. Bogel-Lukasik, *Chem. Rev.* **2011**, *111*, 397; c) T. Wang, M. W. Nolte, B. H. Shanks, *Green Chem.* **2014**, *16*, 548; d) M. Dashtban, A. Gilbert, P. Fatehi, *RSC Adv.* **2014**, *4*, 2037; e) E. Nikolla, Y. Román-Leshkov, M. Moliner, M. E. Davis, *ACS Catal.* **2011**, *1*, 408.
- [8] a) Y. Román-Leshkov, J. N. Chheda, J. A. Dumesic, *Science* **2006**, *312*, 1933; b) S. P. Simeonov, J. A. S. Coelho, C. A. M. Afonso, *ChemSusChem* **2012**, *5*, 1388; c) V. Choudhary, S. H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N. S. Marinkovic, A. I. Frenkel, S. I. Sandler, D. G. Vlachos, *J. Am. Chem. Soc.* **2013**, *135*, 3997; d) E. A. Khokhlova, V. V. Kachala, V. P. Ananikov, *ChemSusChem* **2012**, *5*, 783; e) S. Despax, C. Maurer, B. Estrine, J. Le Bras, N. Hoffmann, S. Marinkovic, J. Muzart, *Catal. Commun.* **2014**, *51*, 5; f) A. Chinnappan, A. H. Jadhav, H. Kim, W.-J. Chung, *Chem. Eng. J.* **2014**, *237*, 95; g) Y. Xiao, Y.-F. Song, *Appl. Catal. A* **2014**, *484*, 74; h) C. M. Cai, N. Nagane, R. Kumar, C. E. Wyman, *Green Chem.* **2014**, *16*, 3819; i) J. Chen, K. Li, L. Chen, R. Liu, X. Huang, D. Ye, *Green Chem.* **2014**, *16*, 2490; j) J. B. Binder, R. T. Raines, *J. Am. Chem. Soc.* **2009**, *131*, 1979.
- [9] a) I.-J. Kuo, N. Suzuki, Y. Yamauchi, K. C.-W. Wu, *RSC Adv.* **2013**, *3*, 2028; b) H. Li, Q. Zhang, X. Liu, F. Chang, D. Hu, Y. Zhang, W. Xue, S. Yang, *RSC Adv.* **2013**, *3*, 3648; c) B. R. Caes, M. J. Palte, R. T. Raines, *Chem. Sci.* **2013**, *4*, 196; d) Y. Qu, Q. Wei, H. Li, P. Oleskowicz-Popiel, C. Huang, J. Xu, *Bioresour. Technol.* **2014**, *162*, 358; e) S. Xiao, B. Liu, Y. Wang, Z. Fang, Z. Zhang, *Bioresour. Technol.* **2014**, *151*, 361; f) A. M. da Costa Lopes, R. Bogel-Lukasik, *ChemSusChem* **2015**, *8*, 947; g) Y. Zhang, J. Pan, Y. Shen, W. Shi, C. Liu, L. Yu, *ACS Sustainable Chem. Eng.* **2015**, *3*, 871; h) L. Zhou, Y. He, Z. Ma, R. Liang, T. Wu, Y. Wu, *Carbohydr. Polym.* **2015**, *117*, 694; i) R. Carrasquillo-Flores, M. Kåldström, F. Schüth, J. A. Dumesic, R. Rinaldi, *ACS Catal.* **2013**, *3*, 993; j) A. S. Kashin, K. I. Galkin, E. A. Khokhlova, V. P. Ananikov, *Angew. Chem. Int. Ed.* **2016**, *55*, 2161; *Angew. Chem.* **2016**, *128*, 2201.
- [10] a) M. L. Mednick, *J. Org. Chem.* **1962**, *27*, 398; b) B. F. M. Kuster, *Starch/Stärke* **1990**, *42*, 314; c) D. J. Liu, E. Y.-X. Chen, *ACS Catal.* **2014**, *4*, 1302.
- [11] a) H. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science* **2007**, *316*, 1597; b) Q. Cao, X. Guo, S. Yao, J. Guan, X. Wang, X. Mu, D. Zhang, *Carbohydr. Res.* **2011**, *346*, 956.
- [12] T. Shalumova, J. M. Tanski, *Acta Crystallogr. Sect. E* **2010**, *66*, o2266.
- [13] a) R. Hayes, G. G. Warr, R. Atkin, *Chem. Rev.* **2015**, *115*, 6357; b) H. Tadesse, R. Luque, *Energy Environ. Sci.* **2011**, *4*, 3913; c) M. V. Fedorov, A. A. Kornyshev, *Chem. Rev.* **2014**, *114*, 2978; d) A. A. Kornyshev, *J. Phys. Chem. B* **2007**, *111*, 5545; e) G. Feng, X. Jiang, R. Qiao, A. A. Kornyshev, *ACS Nano* **2014**, *8*, 11685; f) J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508; g) N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123; h) R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792; i) A. Kuchenbuch, R. Giernoth, *ChemistryOpen* **2015**, *4*, 677; j) R. Giernoth, *Angew. Chem. Int. Ed.* **2010**, *49*, 2834; *Angew. Chem.* **2010**, *122*, 2896.
- [14] Representative examples are shown in the Supporting Information (Scheme S2).
- [15] M. Mascal, S. Dutta, *Green Chem.* **2011**, *13*, 3101.

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