DOI: 10.1002/cssc.201402131



Poly-benzylic Ammonium Chloride Resins as Solid Catalysts for Fructose Dehydration

Siew Ping Teong, Guangshun Yi, Xueqin Cao, and Yugen Zhang*^[a]

5-hydroxymethylfurfural (HMF) is one of the most promising platform molecules, and can be converted into a variety of interesting chemicals. The production of HMF is essentially targeted at bulk chemicals downstream, such as chemicals for the fuels and plastics industries. One critical challenge in HMF production processes is the link to further value-adding reactions in a simple and efficient way (e.g., fewer isolation and purification steps). Herein, a novel poly-benzyl ammonium chloride (PBnNH₃Cl) resin is developed as a highly efficient and stable catalyst for dehydration of carbohydrates into HMF. In the isopropanol system, PBnNH₃Cl produces high purity HMF that is suitable as feedstock for oxidation to 2,5-furandicarboxylic acid (FDCA). The excellent catalytic properties together with its easy synthesis, low cost, and nontoxic nature make this poly-ammonium resin a promising catalyst for the development of new and efficient processes for biomass-based chemicals.

The depletion of fossil fuels and their negative impact on the environment promote the search for renewable carbon resources, such as biomass, to use in the production of chemicals and fuels.^[1,2] Recently, great efforts have been devoted towards converting biomass into 5-hydroxymethylfurfural (HMF), a versatile and key intermediate in biofuel chemistry and the petrochemical industry.^[3,4] However, the high production costs of HMF are a major drawback preventing the application of this biomass-based compound. The development of sustainable, large-scale chemical biomass processing methods is critical for their efficient utilization.^[5] Biomass-derived HMF is most commonly obtained by the dehydration of carbohydrates with acidic catalysts.^[6,7] Mineral acids formed the first generation of catalysts for carbohydrate dehydration reactions, and are currently still widely used.^[7] Owing to their corrosive and nonrecyclable nature, however, large-scale production processes using mineral acid catalysts would put a heavy burden on the environment. In pursuit of economical, simple, efficient, and environmentally friendly HMF production process, various heterogeneous catalysts have been tested under different conditions, such as acidic carbons,^[8] zeolites,^[9] functionalized silica,^[10] functionalized metal-organic frameworks (MOFs),^[11]

_	
[a]	S. P. Teong, Dr. G. Yi, Dr. X. Cao, Dr. Y. Zhang
	Institute of Bioengineering and Nanotechnology
	31 Biopolis Way, The Nanos #04-01
	Singapore 138669 (Singapore)
	Fax: (+ 65) 6478-9080
	E-mail: ygzhang@ibn.a-star.edu.sg
	Supporting Information for this article is available on the WWW under
	http://dx.doi.org/10.1002/cssc.201402131.

Wiley Online Library © 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

heteropolyacids (HPAs),^[12] and porous TiO₂/TiPO₄.^[13,14] Among these heterogeneous catalysts, ion-exchange resins (such as Amberlyst-15) are most widely used and have been tested in almost all types of carbohydrate dehydration systems.^[14,15] Indeed, Amberlyst resins as acidic catalysts are cost-efficient and accessible. They can dehydrate fructose into HMF in high yields (>90%), in high-boiling-point polar aprotic solvent systems, such as DMSO or ionic liquids. Generally, solid catalysts often suffer from low stability. They may partially lose their acidic sites or change from their original structure during the reaction, which may lead to catalyst deactivation.

Recently, the use of low-boiling-point, readily available, and cost-efficient solvents in HMF production has attracted more attention owing to the ease of HMF isolation.^[16] Single-phase, low-boiling-point (environmentally benign) solvent systems may provide new opportunities for large-scale economically viable processes.^[17] Our group has developed an isopropanolmediated reaction system for the production of HMF from fructose. High HMF yields (>80%) were achieved by using this system with HCl as catalyst.^[18] To avoid the use of corrosive HCl as catalyst and allow for more efficient solvent/catalyst recycling, Amberlyst-15 was tested as acidic heterogeneous catalyst in isopropanol for fructose dehydration. However, this led to low HMF selectivity and poor recyclability. We thus screened other Brønsted-acid catalysts in isopropanol, and found that the weak acid ammonium chloride can produce high yields of HMF in this solvent.^[19] This stimulated us to screen other ammonium salts as well, as shown in Scheme 1. We found that



Scheme 1. Ammonium salts screened for dehydration of fructose into HMF in isopropanol. General conditions: fructose (0.18 g), catalyst (10 mol%), isopropanol (2 mL), 120 °C, 2 h.

benzyl ammonium chloride gave a very good yield of HMF (up to 80% in 5 h). Ionic-liquid ammonium salts have been used as medium for HMF production with other catalysts.^[20] The dissociation of HCl from benzyl ammonium chloride is believed to be a key factor for the catalytic activity of these salts. The equilibrium between ammonium salt and HCl/amine in this system also makes it a potentially recyclable catalyst. These prelimina-

ry results encouraged us to develop a polystyrene-based benzyl ammonium chloride (P-Bn-NH₃Cl) as new heterogeneous catalyst for HMF production.

Herein, we report a polystyrene-based benzyl ammonium chloride resin as catalyst for biomass dehydration to HMF. The poly-benzyl ammonium chloride catalyst demonstrates high selectivity and recyclability for the dehydration of fructose to highly pure HMF, suitable as feedstock for further oxidation to 2,5-furandicarboxylic acid (FDCA).

The ammonium resins were synthesized from poly-benzyl chloride (P-BnCl) using either aqueous NH_3 (CPN-) or urea (CPU-) as the ammonia source (Scheme 2). Catalysts with different ammonium loadings were synthesized and tested for catalytic activity. The compositions of the resins were characterized by elemental analysis (Supporting Information, Table S1).



Scheme 2. Synthesis of a poly-benzyl ammonium chloride resin.

In a control experiment without addition of catalyst, no yield of HMF could be detected, indicating that autocatalysis does not take place under the investigated conditions. Generally, the results showed that ammonium resins demonstrate good activity towards dehydration of fructose to HMF in isopropanol (Supporting Information, Table S2). All catalysts gave promising HMF yields, and the formation of HMF-isopropyl ether (as a minor product) was also observed in certain conditions. Polymeric catalysts with different ammonium loadings demonstrated different activities, however, no simple linear relationship could be established. Both BnNH₃Cl and BnCl play a role in this reaction and they may have a synergistic effect on the HMF yield. Multiple BnCl groups may interact with carbohydrates to bind fructose onto the catalytic resin surface by hydrogenbonding,^[21] while BnNH₃Cl acts as catalytic site when HCl dissociates to catalyze the formation of HMF from fructose (Scheme 3). This synergy could explain the catalytic performance of the bifunctional PBnNH₃Cl resin. This hypothesis was further confirmed by screening ammonium resins with different BnNH₃Cl/BnCl molar ratios: the BnNH₃Cl/BnCl ratio is an important factor and the optimum percentage ratio is 21% BnNH₃Cl and 79% BnCl (Figure 1).

Notably, poly-benzyl chloride itself (Figure 1 and Supporting Information, Table S2) also showed some catalytic activity in this system. This activity is due to an attack by isopropanol (a nucleophile) onto benzyl chloride, giving benzyl ether and HCI in the process. This was further confirmed by a control experiment with benzyl chloride in isopropanol under the same reaction conditions as those in which benzyl ether was detected. (Supporting Information, Scheme S1 and Figure S1)

Based on the data obtained, the best catalyst (CPN3) with the optimum ratio ($BnNH_3CI/BnCI = 21:79$) was selected for fur-



Scheme 3. Synergy between benzyl chlorides and ammonium chlorides in the catalytic dehydration of fructose.



Figure 1. Effect of the ratio of $BnNH_3Cl/BnCl$ of $PBnNH_3Cl$ on HMF yield. Conditions: fructose (0.18 g), catalyst (0.14 g), isopropanol (5 mL), 120 °C, 2 h.

ther optimization. As shown in Figure 2 below, the HMF yield generally increased with time initially and then slowly decreased, probably due to formation of humins. When the catalyst loading was increased from 1 mol% (ammonium chloride-to-fructose) to 5 mol%, the reaction time to reach maximum yield was shortened from 11 h to 8 h (yields of 66% and 71%, respectively). When the reaction temperature was increased to 140°C, the reaction rate apparently increased and a high yield of HMF (71%) was achieved in 3 h. The effect of the water content of the system was also evaluated. Small amounts of water in the system (3 vol%) were found to improve HMF yield to 77% (Figure 1 b). This could be of great advantage during solvent recycling in real applications.

The stability of this ammonium resin was then investigated in a fructose dehydration process in isopropanol at 140 °C for 3 h (Figure 3). To recycle the catalyst, it was simply washed with methanol and dried for the next run. A slight drop in HMF yield was observed for the 5th run, which could be due to chloride loss during the recycling process (Supporting Information, Figure S2). However, after washing the catalyst with dilute HCI solution, high HMF yields were maintained for up to at least 8 runs. A hot filtration experiment showed that the reaction was catalyzed by heterogeneous ammonium chloride (see Supporting Information). Generally, the ammonium resin catalyst demonstrates good recyclability in this reaction (Figure 3). Interestingly, the selectivity towards HMF generally increased in subsequent runs, probably due to the relocation of acidic sites on the surface of polymer. The recyclability of the entire

CHEMSUSCHEM COMMUNICATIONS





Figure 2. Reaction conditions for dehydration of fructose to HMF catalyzed by PBnNH₃Cl in isopropanol. (a) Effect of catalyst loading and reaction temperature on HMF yield. (b) Effect of water content on HMF yield. Conditions (unless otherwise stated): fructose (0.18 g), CPN3 (0.07 g, 5 mol%), isopropanol (5 mL), 140 °C, 3 h.

system was further demonstrated on a gram scale, for both catalyst and solvent (Figure 3 b). The catalyst was collected by filtration and isopropanol was simply collected by evaporation, and were re-used directly for the next run. The HMF yield could successfully be maintained at a high level in this recycling system.

To further test the potential application of this ammonium resin/isopropanol system, polysaccharide inulin and a raw biomass material, Jerusalem artichoke tuber (JAT), were dehydrated in this system. JAT is an abundant, easy, and fast-growing biomass with a composition that is rich in inulin/fructose.^[22] To our delight, HMF yields of 80% and 63% were achieved from inulin and JAT, respectively. The complex matrix of the raw biomass did not affect the catalytic system (Scheme 4a, b).

HMF is an important intermediate in the step from biomass to chemicals. An important step after biomass dehydration is to convert HMF into industrial bulk chemicals. Impurities in the fresh HMF from biomass pose a critical challenge, because these impurities could seriously affect the subsequent conversion reaction. In fact, isolation and purification of HMF is a major bottleneck for its large-scale production.^[3,23] However, we demonstrate herein that the ammonium resin/isopropanol system can minimize this issue and that fresh HMF obtained from this system can be converted to 2,5-furandicarboxylic acid (FDCA) with Au/HT (HT=hydrotalcite) catalyst in quantitative yield. As shown in Scheme 4c, after the fructose dehydra-

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Figure 3. Catalyst recycling experiments. (a) Recycled catalysts were washed with methanol and dried for subsequent run. The catalyst was re-acidified at the 5th run. Reaction conditions: fructose (0.18 g), CPN3 (0.07 g, 5 mol%), isopropanol (5 mL), 140 °C, 3 h. (b) Both catalyst and solvent were recycled. The reaction scale was increased by a factor of 5.

tion step, isopropanol was evaporated (for recycling) and the remaining dark-brown solid was extracted with water. The aqueous solution of HMF was transferred to the reactor for the second step: oxidization catalyzed by Au/HT. Using standard conditions reported in earlier literature,^[24] the reaction was completed in 4 h and, most importantly, an excellent yield of FDCA (>98%) was achieved (Scheme 4c). A kinetics study of the oxidization reaction was conducted for fructose-based HMF from both HCl and ammonium-resin catalyst systems. The conversion into FDCA when using HMF obtained from the ammonium resin system proved much faster than the same reaction using HMF obtained from the HCl catalyst system (Figure 4). This suggests that HMF produced by using the ammonium catalyst has a higher purity and therefore is more suitable to use as platform for further reaction steps. This entire fructose-to-FDCA system is less energy intensive and avoids the use of large amounts of extracting solvent and corrosive catalyst, which are detrimental to the environment and industrial processes.

The ammonium resin is an efficient and stable catalyst for fructose dehydration in isopropanol. For comparison, other solid-acid catalysts, such as sulfonic acid functionalized catalysts (Amberlyst), zeolites (H-M, H-beta, H-ZSM-5, H-Y), Lewis acids, and niobic compounds (HNb_3O_8), have also been screened in the conversion of fructose to HMF in isopropanol.



Scheme 4. (a) Dehydration of inulin to HMF in PBnNH₃Cl/isopropanol. (b) Dehydration of Jerusalem artichoke biomass to HMF in PBnNH₃Cl/isopropanol. (c) Two-step conversion of fructose into FDCA, in 74% overall yield.



Figure 4. Kinetic study of HMF oxidation with fresh HMF produced from different catalyst systems.

The ammonium resin gave the highest yield among those catalysts (Supporting Information, Table S3). Although Lewis acids (such as Sn-beta) and niobic acid have been shown to be active and selective in aqueous media,^[25] they are almost inert in isopropanol, probably because they are less acidic in alcohol than in water. Furthermore, the ammonium resin catalyst also gave high HMF yields in other solvent systems, for example, 73% of HMF yield was obtained in DMSO at 140°C for 3 h. Amberlyst resins are not suitable for use in aqueous-NaCl/organic biphasic systems owing to ion exchange effects, while the dehydration of fructose to HMF in an aqueous medium (water/butanol biphasic system) worked well using the ammonium resin (68% selectivity, Supporting Information, Table S3). The high selectivity, good recyclability, and tolerance make P-Bn-NH₃Cl resin a promising heterogeneous catalyst for fructose dehydration.

In conclusion, a poly-benzyl ammonium chloride resin is demonstrated to be a highly efficient catalyst for dehydration of fructose to HMF. The PBnNH₃Cl/iso-PrOH system offers selectivity and recyclability for the dehydration of fructose to HMF. The HMF produced in this system is of high quality, can be easily separated, and is suitable as feedstock for further oxidation to 2,5-furandicarboxylic acid (FDCA). A two-step reaction to convert fructose to FDCA was carried out in a simple and efficient manner, achieving a high overall yield (74%). Polysaccharide (inulin) and raw biomass (Jerusalem artichoke) could be dehydrated in this system, achieving good yields of HMF. These excellent catalytic properties, together with its easy synthesis, low cost, and nontoxic nature, make this poly-ammonium resin a very promising catalyst for the dehydration of carbohydrates.

Experimental Section

General Information: All solvents and chemicals used were obtained from commercial suppliers, unless otherwise indicated. NMR spectra were recorded on Bruker AV-400 (400 MHz) instrument. Progress of the reaction (conversion) was typically monitored by using a SU-300 Sugar Analyzer (TOA-DKK Corp.). Poly-benzyl chloride (P-BnCl) was purchased from Aldrich (Product No.: 63868). HMF yield was analyzed by both NMR and HPLC (Agilent Technologies, 1200 series). HPLC working conditions: column (Agilent Hi-Plex H, 7.7×300 mm, 8 μ m), solvent 10 mm H₂SO₄, flow rate 0.7 mLmin⁻¹, 25 °C, UV detector: 280 nm. The retention time of HMF is 36.5 min.

Catalyst synthesis: For catalysts CPN2 and CPN3, P-BnCl resin (1 g, 5.5 mmol Clg⁻¹) and aq. NH₃ (2.75 mmol and 4.68 mmol respectively) in DMF (15 mL) were stirred at $80\,^\circ\text{C}$ for 24 h. The resins were washed with DMF (15 mL \times 5), DMF/H₂O (1:1 v/v, 15 mL \times 5), MeOH (10 mL \times 5), filtered and dried under vacuum at 50 °C for 24 h. For CPN5, P-BnCl resin (1 g) and aq. NH₃ (600 mmol) were stirred at 120 $^{\circ}$ C for 48 h. The resins were washed with H₂O, acetone, filtered, and dried under vacuum at 50 °C for 24 h. For CPU5, P-BnCl resin (1 g), urea (1.67 g, 27.8 mmol) and H_2O (1 mL, 55.5 mmol) were stirred in CH₃CN (20 mL) at 120 $^{\circ}$ C for 48 h. The resins were washed with H₂O, acetone, filtered, and dried under vacuum at 50 $^\circ\text{C}$ for 24 h. After synthesis, the catalysts were stirred in dilute HCl (5 M, 28 mL) solution for 1 h, washed with MeOH, filtered, and dried under vacuum at 50 °C for 6 h. The ammonium loading was analyzed by elemental analysis (Supporting Information, Table S1). The catalyst has the same morphology as purchased P-BnCl resin. No Brunauer-Emmett-Teller (BET) parameters could be measured for both catalyst and original P-BnCl resin.

^{© 2014} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Fructose dehydration to HMF in isopropanol: To a 15 mL sealed tube equipped with stirrer bar, fructose (0.18 g, 1 mmol), isopropanol (5 mL) and CPN3 (0.07 g, 5 mol%) were added. The reaction mixture was stirred at 140 °C for 3 h and then cooled to room temperature. The catalyst was filtered, washed with methanol, and the combined filtrate was concentrated under reduced pressure to obtain the crude HMF product. Mesitylene (0.06 g, 0.5 mmol) was added as an internal standard and the composition was analyzed by NMR. For the large-scale reaction, fructose (0.90 g, 5 mmol), isopropanol (25 mL), and CPN3 (0.35 g, 5 mol%) were stirred at 140 °C for 3 h.

Recycling experiments: After performing the dehydration reaction as described above, the washed catalyst was simply dried under vacuum at 50 °C for 2 h and used directly for next batch of reaction. For catalyst regeneration (after the fourth run), the catalyst was stirred in dilute HCl (1 m, 1.50 mL) solution for 1 h, washed with MeOH, filtered, and dried under vacuum at 50 °C for 6 h. For large scale recycling experiment, the catalyst was recycled as described above. The solvent was collected via evaporation and used directly for subsequent runs.

Catalytic reaction from HMF to FDCA: The reaction was conducted by using a method reported in literature with Na₂CO₃ as base. Au/HT was prepared according to a literature method (Supporting Information, Figure S3).^[1] HMF produced from fructose (1 mmol) was extracted in 10 mL H₂O. Au/HT (0.25 g) and Na₂CO₃ (1 mmol) were added into the water solution. With oxygen gas bubbling, the solution was heated to 95 °C and kept at that temperature for 1–7 h. The solution was diluted for HPLC analysis. For product isolation, the aqueous solution was adjusted to pH 1, where FDCA was precipitated from the solution. The precipitate was filtered and washed with ethanol.

Acknowledgements

This work was supported by the Institute of Bioengineering and Nanotechnology (Biomedical Research Council, the Agency for Science, Technology and Research (A*STAR), Singapore), and the Biomass-to-Chemicals Program (Science and Engineering Research Council, A*STAR, Singapore).

Keywords: biomass · carbohydrates · heterogeneous catalysis · oxidations · solid acids

- a) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 2007, *107*, 2411; b) P. Gallezot, *Green Chem.* 2007, *9*, 295; c) C. H. Christensen, J. Rass-Hansen, C. C. Marsden, E. Taarning, K. Egeblad, *Renewable Chem. Ind.* 2008, *1*, 283; d) D. Tilman, R. Socolow, J. A. Foley, J. Hill, E. Larson, L. Lynd, S. Pacala, J. Rrilly, T. Searchinger, C. Somerville, R. Williams, *Science* 2009, *325*, 270; e) X. Li, D. Wu, T. Lu, G. Yi, H. Su, Y. G. Zhang, *Angew. Chem. Int. Ed.* 2014, *53*, 4200–4204; *Angew. Chem.* 2014, *126*, 4284–4288.
- [2] a) J. P. Holdren, Science 2007, 315, 737; b) B. Kamm, Angew. Chem. Int. Ed. 2007, 46, 5056; Angew. Chem. 2007, 119, 5146; c) F. W. Lichtenthaler, Biorefineries—Industrial Processes and Products, Wiley-VCH, Weinheim, 2006.
- [3] G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, *Science* 2005, 308, 1446.
- [4] Selected reviews for HMF production and HMF chemistry: a) B. F. M. Kuster, *Starch/Staerke* 1990, *42*, 314; b) L. Cottier, G. Descotes, *Trends Heterocycl. Chem.* 1991, *2*, 233; c) J. Lewkowski, *ARKIVOC* 2001, *2*, 17; d) C. Moreau, M. N. Belgacem, A. Gandini, *Top. Catal.* 2004, *27*, 11; e) A. Boisen, T. B. Christensen, W. Fu, Y. Y. Gorbanev, T. S. Hansen, J. S. Jensen, S. K. Klitgaard, S. Pedersen, A. Riisager, T. Stahlberg, J. M. Woodley, *Chem. Eng. Res. Des.* 2009, *87*, 1318; f) Y. G. Zhang, J. Y. G. Chan, *Energy*

Environ. Sci. **2010**, *3*, 408–417; g) J. C. Serrano-Ruiz, R. M. West, J. A. Dumesic, *Annu. Rev. Chem. Biomol. Eng.* **2010**, *1*, 79; h) A. A. Rosatella, S. P. Simeonov, R. F. M. Frade, C. A. M. Afonso, *Green Chem.* **2011**, *13*, 754; i) X. L. Tong, Y. Ma, Y. D. Li, *Appl. Catal. A* **2010**, *385*, 1; j) S. Dutta, *RSC Adv.* **2012**, *2*, 12575; k) A. M. Ruppert, K. Weinberg, R. Palkovits, *Angew. Chem. Int. Ed.* **2012**, *51*, 2564; *Angew. Chem.* **2012**, *124*, 2614; l) S. P. Teong, G. Yi, Y. G. Zhang, *Green Chem.* **2014**, *16*, 2015–2026.

- [5] C. O. Tuck, E. Perez, I. T. Horvath, R. A. Sheldon, M. Poliakoff, *Science* 2012, 337, 695.
- [6] a) J. J. Bozell, Science 2010, 329, 522; b) J. N. Chheda, Y. Roman-Leshkov, J. A. Dumesic, Green Chem. 2007, 9, 342–350; c) C. Moreau, A. Finiels, L. Vanoye, J. Mol. Catal. A 2006, 253, 165–169; d) L. Lai, Y. G. Zhang, ChemSusChem 2010, 3, 1257; e) S. Lima, P. Neves, M. M. Antunes, M. Pillinger, N. Ignatyev, A. A. Valente, Appl. Catal. A 2009, 363, 93; f) Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, Nature 2007, 447, 982; g) M. Chidambaram, A. Bell, Green Chem. 2010, 12, 1253; h) Q. X. Bao, K. Qiao, D. Tomida, C. Yokoyama, Catal. Commun. 2008, 9, 1383; i) A. I. Torres, P. Daoutidis, M. Tsapatsis, Energy Environ. Sci. 2010, 3, 1560; j) S. Q. Hu, Z. F. Zhang, J. L. Song, Y. X. Zhou, B. X. Han, Green Chem. 2009, 11, 1746; k) J. Y. G. Chan, Y. G. Zhang, ChemSusChem 2009, 2, 731.
- [7] 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.
- [8] a) J. Wang, W. Xu, J. Ren, X. Liu, G. Lu, Y. Wang, *Green Chem.* 2011, *13*, 2678; b) C. Tian, Y. Oyola, K. M. Nelson, S.-H. Chai, X. Zhu, J. C. Bauer, C. J. Janke, S. Brown, Y. Guo, S. Dai, *RSC Adv.* 2013, *3*, 21242.
- [9] a) E. Nikolla, Y. Román-Leshkov, M. Moliner, M. E. Davis, ACS Catal. 2011, 1, 408–410; b) V. V. Ordomsky, J. Van der Schaaf, J. C. Schouten, T. A. Nijhuis, J. Catal. 2012, 287, 68–75.
- [10] A. J. Crisci, M. H. Tucker, M.-Y. Lee, S. G. Jang, J. A. Dumesic, S. L. Scott, ACS Catal. 2011, 1, 719–728.
- [11] a) Y. Zhang, V. Degirmenci, C. Li, E. J. M. Hensen, *ChemSusChem* 2011, *4*, 59–64; b) V. Degirmenci, E. A. Pidko, P. C. M. M. Magusin, E. J. M. Hensen, *ChemCatChem* 2011, *3*, 969–972.
- [12] a) Q. Zhao, L. Wang, S. Zhao, X. Wang, S. Wang, *Fuel* **2011**, *90*, 2289–2293; b) K. Shimizu, H. Furukawa, N. Kobayashi, Y. Itayab, A. Satsumaa, *Green Chem.* **2009**, *11*, 1627–1632; c) J. Tian, J. H. Wang, S. Zhao, C. Jiang, X. Zhang, X. H. Wang, *Cellulose* **2010**, *17*, 587–594; d) S. Zhao, M. Cheng, J. Li, J. Tian, X. Wang, *Chem. Commun.* **2011**, *47*, 2176–2178.
- [13] a) S. De, S. Dutta, A. K. Patra, B. S. Rana, A. K. Sinha, B. Saha, A. Bhaumik, *Appl. Catal. A* **2012**, *385*, 435–436; b) A. Dutta, A. K. Patra, S. Dutta, B. Saha, A. Bhaumik, *J. Mater. Chem.* **2012**, *22*, 14094.
- [14] M. J. Climent, A. Corma, S. Iborra, Green Chem. 2011, 13, 520-540.
- [15] a) A. Takagaki, M. Ohara, S. Nishimura, K. Etibani, Chem. Commun. 2009, 6225-6227; b) C. Aellig, I. Hermans, ChemSusChem 2012, 5, 1737.
- [16] a) M. H. Tucker, A. J. Crisci, B. N. Wigington, N. Phadke, R. Alamillo, J. Zhang, S. L. Scott, J. A. Dumesic, ACS Catal. 2012, 2, 1865; b) M. Ohara, A. Takagaki, S. Nishimura, K. Ebitani, Appl. Catal. A 2010, 383, 149–155.
- [17] a) J. Jeong, C. A. Antonyraj, S. Shin, S. Kim, B. Kim, K. Lee, J. K. Cho, J. Ind. Eng. Chem. 2013, 19, 1106–1111; b) J. M. R. Gallo, D. M. Alonso, M. A. Mellmer, J. A. Dumesic, Green Chem. 2013, 15, 85–90; c) M. H. Tucker, R. Alamillo, A. J. Crisci, G. M. Gonzalez, S. L. Scott, J. A. Dumesic, ACS Sustainable Chem. Eng. 2013, 1, 554–560.
- [18] L. Lai, Y. G. Zhang, ChemSusChem 2011, 4, 1745.
- [19] D. W. Brown, A. J. Floyd, R. G. Kinsman, Y. Roshan-Ali, J. Chem. Technol. Biotechnol. 1982, 32, 920.
- [20] Q. Cao, X. Guo, J. Guan, X. Mu, D. Zhang, Appl. Catal. A 2011, 403, 98– 103.
- [21] L. Shuai, X. Pan, Energy Environ. Sci. 2012, 5, 6889-6894.
- [22] L. K. Zhou, A. Q. Wang, C. Z. Li, M. Y. Zheng, T. Zhang, ChemSusChem 2012, 5, 932.
- [23] M. Kröger, U. Prusse, K. D. Vorlop, Top. Catal. 2000, 13, 237.
- [24] a) S. E. Davis, L. R. Houk, E. C. Tamargo, A. K. Datye, R. J. Davis, *Catal. Today* 2011, *160*, 55; b) N. K. Gupta, S. Nishimura, A. Takagaki, K. Ebitani, *Green Chem.* 2011, *13*, 824–827.
- [25] F. Wang, H.-Z. Wu, C.-L. Liu, R.-Z. Yang, W.-S. Dong, Carbohydr. Res. 2013, 368, 78–83.

Received: March 2, 2014 Published online on June 5, 2014

^{© 2014} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim