

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

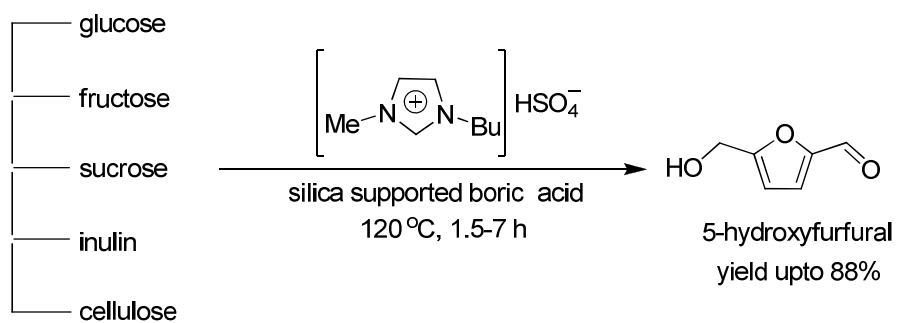
You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Silica-Supported Boric Acid Assisted Conversion of Mono- and Poly-saccharides to 5-Hydroxymethylfurfural in Ionic Liquid

Mayanka Walia, Upendra Sharma, Vijai K. Agnihotri,* Bikram Singh*

Graphical abstract



Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Silica-Supported Boric Acid Assisted Conversion of Mono- and Poly-saccharides to 5-Hydroxymethylfurfural in Ionic Liquid[†]

Mayanka Walia,^{a,b} Upendra Sharma,^{a,c} Vijai K. Agnihotri,^{*a,b} Bikram Singh^{*a,b}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Silica-supported boric acid has been prepared and applied as heterogeneous catalyst for the direct conversion of inexpensive and biorenewable mono- and polysaccharides to 5-hydroxymethylfurfural (HMF) in ionic liquid under much milder conditions. Fructose, glucose, sucrose, inulin, and cellulose were successfully converted to HMF with moderate to excellent conversion. The catalyst and the solvent system can be recycled up to four consecutive cycles without a significant loss in conversion.

Introduction

In response to the presently existing threats regarding the global warming's caused by greenhouse gas emissions as well as continuous depletion of fossil fuel reserves, much effort has been devoted to the development of technologies that facilitate the conversion of renewable biomass resources into transportation fuels and chemical intermediates (e.g. alcohols, aldehydes, acids).¹ Therefore, there is an urgent need for the development of cost-effective processes by which these bio-sustainable substrates can be transformed into value added chemicals. Nature produces more than 75% of carbohydrates from the total biomass out of which less than 5% used in food and non-food sectors.² Carbohydrate-based biomass, a widely distributed and inexpensive resource, constitutes one of the most abundant groups of organic compounds.³ The potentiality of these compounds as the sustainable substitutes is well recognized for building blocks derived from petrochemicals in the production of plastics and fine chemicals.⁴ One molecule of particular interest, 5-hydroxymethylfurfural (HMF) has been identified as one of the most promising platform compounds, which undergo a variety of reactions and form a series of derivatives which can be converted into a wide range of industrially important chemicals, such as alternative biofuels, diesel fuel additives, solvents and biopolymers.^{5,6,7} Conventionally, HMF is produced from the acid-catalyzed dehydration of C6-sugars (*i.e.*, hexoses) by eliminating three moles of water molecules at an elevated temperature.⁸ Fructose is produced from glucose isomerisation whereas glucose is generally produced by hydrolysis of starch, which is a main constituent of food material such as potato, rice, and maize.⁹ Therefore, non-digestible carbohydrate resources such as cellulose, hemicelluloses, lignin and inulin are the ideal substrates for the production of HMF.^{10,11} But it is more difficult to produce HMF from glucose and its polymer since the isomerisation step *i.e.*, glucose to fructose conversion is the main step in HMF

production from glucose and its polymers.¹² HMF can be produced by Ionic liquid-assisted dehydration of sugars and carbohydrates has been of high interest during recent years.¹³ Ionic liquids are presented as promising solvents as they are capable of dissolving cellulose and other biomass components and can significantly improve the selectivity as well as the yield of HMF assertively.¹⁴

Recently, various catalytic methods have been developed for the production of HMF from carbohydrates.⁴ Mostly, Lewis acid catalysts have been applied for the conversion of saccharides to HMF in various ionic liquids.¹⁵ Zhang's group has reported conversion of sugar to HMF with 68-70% yield in a system consisting of 1-ethyl-3-methyl-imidazolium chloride [emim]Cl and a CrCl₂ catalyst.¹⁶ HMF synthesis from glucose was also accomplished by common Lewis acid, SnCl₄ in 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim] BF₄)¹⁷ and bulky NHC (*N*-heterocyclic carbene) metal ligands.¹⁸ One report also available by using dimethylacetamide (DMA), NaBr, a Lewis acid and CrCl₂ with a significant enhancement of HMF yield up to 81%.¹⁹ HMF has also been synthesized from fructose by using bronsted acidic ionic liquids as a catalyst with yield up to 72%.²⁰ Acidic ionic liquid 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate has been also used as a catalyst for HMF conversion from fructose with 100% conversion and 95% yield.²¹ 1-Methylimidazolium-based and *N*-methylmorpholinium-based protic ionic liquids has also been employed as a catalyst for the conversion of fructose and sucrose to HMF with 74.8% and 47.5% respectively.²² For the HMF preparation from fructose, effect of ionic liquids with different cations and anions has also been studied.²³ The production of HMF from glucose in 63% yield was also reported using enzyme by two step method.²⁴ First step involved isomerisation of glucose to fructose in the presence of glucose isomerase and borate ions, followed by the acid catalyzed dehydration of fructose to HMF using HCl as a catalyst in a biphasic system. Other reports on HMF production showed the HMF yields of 42% at a 73% conversion by combining a solid acid catalyst, amberlyst-15 and a solid base catalyst, Mg-Al hydrotalcite, in *N,N*-dimethylformamide,²⁵ Glucose dehydration in water by using CrCl₂-Im-SBA-15 as a catalyst yield 50% of HMF.²⁶ HMF yields of 57% at 79% conversion of glucose using a Lewis acidic Sn-Beta zeolite and HCl in a water/NaCl/THF biphasic reaction system²⁷ and HMF yield of 61% from glucose using AlCl₃·6H₂O as the catalyst in a biphasic system.²⁸ HMF production from cellulose has also been studied by using mesoporous titania

(MTN) and zirconia (MZrN) nanoparticles with 18.2% and 29.2% yield.²⁹ However, most of these methods required use of toxic and expensive metal catalysts, strong acids and most importantly resulted in low HMF yield. Ionic liquids [mmim]HSO₄, [mmbim]HSO₄, [hmbim]HSO₄ and [psmbim]HSO₄ have also been studied as a catalyst for the conversion of fructose to HMF using DMSO as a solvent.³⁰ Most of these methods are applicable for the mono saccharides such as fructose and glucose but non-digestible carbohydrate resources such as cellulose, hemicelluloses, lignin and inulin are the ideal substrates for the production of HMF. There is a strong desire for the development of general method for this transformation without using any toxic or strong acid catalyst.

In recent years, boric acid has been used in organic synthesis because it is commercially available, moisture and air stable, non toxic, environmentally benign, cheap and easy to handle. The operational simplicity and non corrosiveness of boric acid makes it as an attractive catalyst. Boric acid has been reported for the conversion of fructose and glucose into HMF with low yield.^{31, 32}

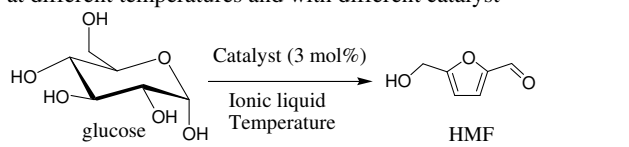
Using the catalytic system, boric acid/NaCl, and methyl isobutyl ketone as extractive solvent, a yield of 60% in HMF was achieved from fructose, while only 14% was obtained from glucose. Ionic liquids have remarkable unique properties such as high thermal stability and high solubilising ability, which enable carbohydrates to be dissolved at high concentration³³ and serving as solvents that are potentially recyclable. Therefore ionic liquids are growing as a most preferred reaction media for the synthesis of HMF from sugars.³⁴ Nevertheless, the existing processes suffered from limited substrates scope, longer reaction time and most importantly lower yield of HMF. To the best of our knowledge, there is no report available in literature for the conversion of carbohydrate to HMF with much improved conversion by using silica supported boric acid (SSBA) as a heterogeneous catalyst. Surface-catalyzing dehydration of carbohydrates on supported boric acid can decrease product contamination and aid the development of greener route in HMF synthesis. To circumvent the aforementioned limitations, herein, we report mild silica supported boric acid promoted conversion of carbohydrates to HMF in ionic liquid.

Results and Discussion

In continuation to our previous study, silica supported boric acid was prepared by the similar strategy and characterized accordingly.³⁵ We began our investigation for the HMF formation taking glucose as a model substrate. For the conversion HMF from glucose, firstly glucose isomerised to fructose and then there is elimination of three water molecules (Scheme 1). When the reaction was carried out at 90 °C with SSBA or at 120 °C without SSBA, traces of HMF was obtained as the desired product (Table 1, entry 1 and 3). Increasing the reaction temperature to 120 °C resulted in complete conversion of glucose after 3 h as observed by thin layer chromatography (TLC) (Table 1, entry 2); 81% GC conversion (isolated yield 60%) of HMF was observed for glucose. No product was observed when silica gel and boric acid were used separately instead of SSBA clearly demonstrating the catalytic role of SSBA (Table 1, entries 4 and 5). When the reaction was performed using ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF₄, 1, 3-dimethylimidazolium hydrogen carbonate solution [50% solution in MeOH: H₂O (2: 3)] [1,3-dimim]HCO₃ and water as a solvent; no reaction was observed in any of the case (Table 1, entries 6-8). When the reaction was performed using sodium tetraborate with

ionic liquid 1-butyl-3-methylimidazolium hydrogen sulphate [bmim]HSO₄, only 10% conversion was observed (Table 1, entry 9). These results showed that the H₃BO₃-SiO₂ in conjunction with ionic liquid [bmim]HSO₄ is the proficient catalytic system for HMF production from carbohydrates.

Table 1: Conversion of glucose to HMF in different ionic liquids, at different temperatures and with different catalyst^a



Entry	Catalyst	Solvent	Temperature (°C)	Yield(%) ^b
1	SSBA	[bmim]HSO ₄ ^c	90	traces
2	SSBA	[bmim]HSO ₄	120	81
3	[bmim]HSO ₄	120	traces
4	Boric acid	[bmim]HSO ₄	120	nd
5	Silica gel (60-120)	[bmim]HSO ₄	120	nd
6	SSBA	[bmim]BF ₄ ^d	120	nd
7	SSBA	[1,3-dimim]HCO ₃ ^e	120	nd
8	SSBA	H ₂ O	120	traces
9	Sodium tetraborate	[bmim]HSO ₄	120	10

^a reaction conditions: glucose (100 mg), ionic liquid (1g), catalyst (15 mg, 0.02 mmol of boric acid), 120 °C, 3 h

^bGC based conversion after derivatization to corresponding acetyl derivative

^c1-butyl-3-methylimidazolium hydrogen sulphate

^d1-butyl-3-methylimidazolium tetrafluoroborate

^e1, 3-dimethylimidazolium hydrogen carbonate solution [50% solution in MeOH: H₂O (2: 3)]

nd: not detected

In the present study, we have also investigated the most preferred reaction conditions for the production of HMF taking different mono-, di- and polysaccharides as test substrates (Table 2). In case of fructose excellent GC conversion 88% was obtained at 90 °C even in short reaction time *i.e.* 1.5 h. The product (HMF) was isolated by column chromatography using ethyl acetate: methanol (9.5: 0.5) as a solvent. The purified product was identified on the basis of HRMS and NMR data. HRMS calculated for C₆H₇O₃ is 127.0395 and observed as 127.0404.

Although in case of other carbohydrates such as sucrose, inulin and cellulose, higher conversion was observed at 120 °C than at 90 °C. Interestingly, the present catalytic conditions were found to be highly efficient for the conversion of the disaccharide sucrose and afforded HMF in 80% conversion; just 3 h were required for its transformation. When the reaction was carried out without catalyst, 72% of HMF conversion was observed in case of fructose, however no reaction was observed in case of glucose and sucrose without catalyst.

Further to examine the applicability of our catalyst, the same reaction was carried out with biopolymers; inulin and cellulose. For the direct transformation of inulin (polymer of fructose) into HMF involves two reactions. First step for the hydrolysis of inulin into monosaccharide, fructose and second step involves the dehydration of fructose to final product,¹¹ HMF. From the GC

data using internal standard, it was observed that inulin completely hydrolyzed to its monomer, which in turn converted to the final product HMF with 88% GC conversion. Whereas in case of cellulose (polymers of glucose), direct conversion involves three reactions *i.e.* Firstly, hydrolysis into monosaccharide glucose, second reaction involves isomerisation from aldose-type sugar (glucose) to ketose-type sugar (fructose) and finally, exclusive formation of HMF occurs by the dehydration of this ketose-type sugar, fructose.¹² For the conversion of cellulose, 0.04 mmol of SSBA was used and 18% of HMF conversion was observed.

Table 2: Applicability of catalytic system, [bmim]HSO₄ + H₃BO₃-SiO₂ for the conversion of different saccharides to HMF^a

Substrate	Product	Time/h	Yield(%) ^b
Fructose ^c	HMF	2	72
Fructose	HMF	1.5	88
Glucose	HMF	3	81
Sucrose	HMF	3	80
Inulin	HMF	5	88
Cellulose ^d	HMF	7	18

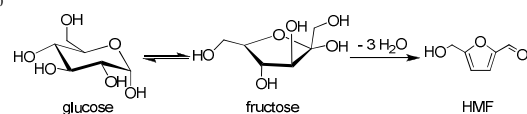
^aReaction conditions: carbohydrate (100 mg), ionic liquid (1g), catalyst (15 mg, 0.02 mmol of boric acid), 120 °C, 1.5-7 h

^bGC based conversion

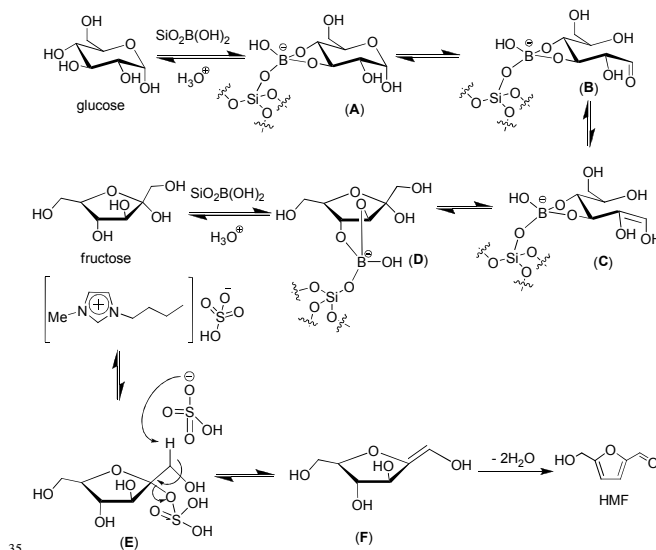
^cwithout SSBA

^dcatalyst (25 mg, 0.04 mmol of boric acid)

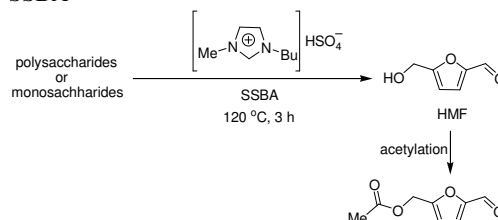
Regarding the mechanistic study of the reaction, we propose similar type of mechanism as reported earlier (Scheme 2).³² Possibly silica support increases the Lewis acid character of boric acid which increases its reactivity for the isomerisation of glucose into fructose and also helps in the hydrolysis of glycosidic linkage of di or polysaccharides.



Scheme 1: Dehydration of glucose into HMF.



Scheme 2: Proposed mechanism for the formation of HMF using SSBA



Scheme 3: Catalytic conversion of saccharides into HMF and subsequent acetylation

Recyclability of the Catalytic System

Recyclability of the [bmim]HSO₄ + H₃BO₃-SiO₂ catalytic system was carried out after the product HMF was separated from the reaction mixture by extracting five times with ethyl acetate. Product was separately derivatized by acetylation (Scheme 3) for GC analysis every time. After each run, HMF was extracted with ethyl acetate and the catalytic system ([bmim]HSO₄ + H₃BO₃-SiO₂) was dried under vacuum before using for the next. The catalytic system can be recycled for four times without any significant decrease in the conversion of HMF (Fig 1).

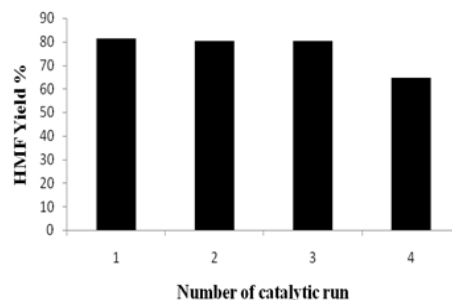


Fig. 1 Recycling of [bmim]HSO₄ and catalyst for the dehydration reaction. Reaction conditions for each run: Glucose (100 mg, 0.55 mmol), catalyst (15 mg, 0.02 mmol recycled) [bmim]HSO₄ (1 g, recycled), reaction time = 3 h, temperature = 120 °C.

Therefore, silica-supported boric acid catalyst has been established as a promising catalyst for carbohydrates because of its high efficient activity, long catalyst life, reusability and easy recovery. However, this method of HMF production will only be industrial useful if it is scalable.

Conclusion

In conclusion, an efficient catalytic system has been developed for the excellent conversion of carbohydrates to HMF. The catalytic system in combination with ionic liquid is applicable for mono-, di- and polysaccharides and can be recycled up to four times. Therefore, this could be an effective and environmentally safe catalytic system for the conversion of carbohydrates to HMF as there is no use of strong and toxic acids.

Experimental

General information: Fructose, glucose, sucrose, boric acid, silica and cellulose were purchased from S.D. Fine-Chem. Ltd (Mumbai, India). Ionic liquid, [bmim]HSO₄, [bmim]BF₄, [1,3-dimim]HCO₃, HMF, inulin and sodium tetraborate were purchased from Sigma-Aldrich. All other chemicals used were of analytical grade and purchased from Merck India Ltd. Reaction mixture analyses were performed on Shimadzu GC 2010, AOC-20i auto-sampler coupled with a DB-5 capillary column, (30 m x 0.25 mm i.d., 0.25 μm) and FID. The initial temperature of column was 40 °C held for 5 min. and programmed to 230 °C at 4 °C/min., then held for 5 min. at 230 °C; the sample injection volume was 2 μl in HPLC grade dichloromethane. Helium was used as carrier gas at a flow rate of 1.1 ml min⁻¹ on split mode (1:50). Products identified by GC, were confirmed by analysis of monosaccharides and HMF standards. HMF was also isolated by column chromatography and identified by ¹H and ¹³C NMR (Bruker Avance-300 spectrometer) and mass spectroscopic techniques.

General experimental procedure:

Synthesis of silica-supported boric acid (SSBA): Boric acid (3.0 g) with 60 ml water was taken in a 250 ml round bottom flask and heated to 60-80 °C. To this, silica gel (60-120 mesh, 27.0 g) was added gradually with constant stirring and refluxed for 5 h. Water was evaporated under vacuum and the residue was stirred at 100 °C for 6-7 h under vacuum to give free flowing white powder.³⁵

Typical procedure for the conversion of saccharides to HMF:

A mixture of saccharide (100 mg) and H₃BO₃-SiO₂ (15 mg, 0.02 mmol of boric acid) was heated in ionic liquid [bmim]HSO₄ (1g) at 120 °C for 3 h under nitrogen atmosphere. After the reaction, the reaction flask was cooled in an ice bath; the reaction mixture was acetylated³⁶ *in situ* with pyridine: acetic anhydride (1:1, v/v) for 16 h at room temperature (Scheme 3). After acetylation reaction, water was added and the product was extracted with the ethyl acetate. The derivatised product mixture was analysed by GC and hexadecane used as the internal standard. In case of cellulose, after the completion of acetylation reaction, final product was extracted with ethyl acetate; the aqueous layer was dried and weighed. HMF conversion was calculated on the basis of the initial substrate amount and the amount of the product.

$$\text{yield of HMF} = \frac{\text{amount of HMF}}{\text{starting amount of cellulose}} \times 100$$

The product (HMF) was isolated by column chromatography. The purified product was identified on the basis of HRMS and NMR data. ¹H NMR (MeOD) δ_H: 7.38 (1H, d, J = 3.5 Hz, H-3), 6.59 (1H, d, J=3.5 Hz, H-4), 9.54 (1H, s, H-6), 4.62 (2H, s, H-7). ¹³C NMR δ_C = 123.7 (C-3), δ_C = 109.8 (C-4), δ_C = 178.4 (C-6), δ_C = 56.6 (C-7), δ_C = 152.8 (C-2), δ_C = 162.2 (C-5)³⁷.

Acknowledgments

The authors are grateful to the Director, CSIR-IHBT Palampur (HP), India for continuous encouragement and for providing necessary facilities during the course of the investigation.

^aAcademy of Scientific & Innovative Research; CSIR-Institute of Himalayan Bioresource Technology, Palampur, Himachal Pradesh-176 061, INDIA

^bNatural Plant Products Division, CSIR-Institute of Himalayan Bioresource Technology, Palampur, Himachal Pradesh-176 061, INDIA

^cPresent address: Indian Institute of Technology Bombay, Powai, 400 076, India

E-mail: kantvijai@yahoo.com, bikram_npp@rediffmail.com

[†]IHBT communication no. 3575

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

Notes and references

- 1 P. M. Arvela, E. Salminen, T. Riittonen, P. Virtanen, N. Kumar and J. P. Mikkola, *International Journal of Chemical Engineering*, 2012, Volume 2012, Article ID 674761, 10 pages. doi:10.1155/2012/674761.
- 2 S. H. Mushrif, S. Caratzoulas and D. G. Vlachos, *Phys. Chem. Chem. Phys.*, 2012, **14**, 2637-2644.
- 3 O. O. James, S. Maity, L. A. Usman, K. O. Ajanaku, O. O. Ajani, T. O. Siyanbola, S. Sahuc and R. Chaubey R (2010) *Energy Environ. Sci.*, 2010, **3**, 1833-1850.
- 4 J. N. Chheda, Y. R Leshkov and J. A. Dumesic, *Green Chem.*, 2007, **9**, 342-350.
- 5 S. Zhu, Y. Tong, Y. Lv and Y. Wu, *Bioresources*, 2012, **7**, 3-4.
- 6 S. Lima, A. Fernandes, M. M. Autunes, M. Pillinger, F. Ribeiro and A. A. Valente, *Catal Lett* 2010, **135** 41-47.
- 7 S. Dutta, S. De, B. Saha, *ChemPlusChem*, **77**, 259-272.
- 8 A. A. Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, *Green Chem.*, 2011, **13**, 754-793.
- 9 P. L. Dhepe and A. Fukuoka, *ChemSusChem*, 2008, **1**, 969-975.
- 10 P. L. Dhepe and R. Sahu, *Green Chem.*, 2010, **12**, 2153-2156.
- 11 X. Qi, M. Watanabe, T. M. Aida and Jr. R. L. Smith, *Green Chem.*, 2010, **12**, 1855-1860.
- 12 B. Kim, J. Jeong, D. Lee, S. Kim, H. Y. Yoon, Y. S. Lee and J. K. Cho, *Green Chem.*, 2011, **13**, 1503-1506.
- 13 S. Murugesana and R. J. Linhardt, *Curr. Org. Synth.*, 2005 **2**: 437-451.
- 14 P. Mäki-Arvela, I. Anugwom, P. Virtanen, R. Sjöholm and J. P. Mikkola, *Ind. Crop. Prod.*, 2010, **32**, 175-201.
- 15 M. E. Zakrzewska, E. Bogel-Lukasik and R. Bogel-Lukasik, *Chem. Rev.*, 2010, **111**, 397-417.
- 16 H. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, **316**, 1597-1600.
- 17 S. Hu, Z. Zhang, J. Song, Y. Zhou and B. Han, *Green Chem.*, 2009, **11**, 1746-1749.
- 18 G. Yong, Y. Zhang and J. Y. Ying, *Angew Chem. Int. Ed.*,

- 2008, **47**, 9345-9348.
- 19 J. B. Binder and R. T. Raines, *J. Am. Chem. Soc.*, 2009, **131**, 1979-1985.
- 20 X. Tong and Y. Li, *ChemSusChem*, 2010, **3**, 350-355.
- 5 21 F. Tao, H. Song and L. Chou, *RSC advances*, 2011, **1**, 672-676.
- 22 X. Tong, Y. Ma and Y. Li, *Carbohydr. Res.*, 2010, **345**, 1698-1701
- 23 C. Shi, Y. Zhao, J. Xin, J. Wang, X. Lu, X. Zhang and S. Zhang, *Chem. Commun.*, 2012, **48**, 4103-4105.
- 10 24 R. Huang, W. Qi, R. Su and Z. He, *Chem. Commun.*, 2010, 1115-1117
- 25 A. Takagaki, M. Ohara, S. Nishimura and K. Ebitani, *Chem. Commun.*, 2009, 6276-6278.
- 15 26 E. Nikolla, Y. Román-Leshkov, M. Moliner and M. E. Davis, *ACS Catal.*, 2011, **1**, 408-410.
- 27 V. Degirmenci, E. A. Pidko, P. C. M. M. Magusin, E. J. M. Hensen, *ChemCatChem*, 2011, **3**, 969-972.
- 28 Y. Yang, C. Hu and M. M. Abu-Omar, *Green Chem.*, 2012, **14**, 509-513.
- 20 29 D. A. Kotadia and S. S. Soni., *Catal. Sci. Technol.*, 2013, **3**, 469-474.
- 30 T. S. Hansen, J. Mielby and A. Riisager, *Green Chem.*, 2011, **13**, 109-114.
- 25 31 I. J. Kuo, N. Suzuki, Y. Yamauchi and K. C. W. Wu, *RSC Advances*, 2013, **3**, 2028-2034.
- 32 T. Ståhlberg, S. R. Rodriguez, P. Fristrup and A. Riisager, *Chem. Eur. J.*, 2011, **17**, 1456-1464.
- 33 T. Ståhlberg, W. Fu, J. M. Woodley and A. Riisager, *Chemsuschem*, 2011, **4**, 451-458.
- 30 34 L. J. A. Conceição, B. L. Ewa and B. L. Rafał, *RSC Advances*, 2012, **2**, 1846-1855.
- 35 V. Kumar, U. Sharma, P. K. Verma, N. Kumar and B. Singh, 2011, *Chem. Pharm. Bull.*, **59**, 639-645.
- 35 36 M. V. Macron, L. C. Vriesmann, G. Wosiacki, E. B. Carnerio and C. L. O. Petkowicz, *Polímeros: Ciência e Tecnologia*, 2005, **15**, 127-129.
- 37 A. S. Amarasekara, L. D. Williams and C. C. Ebde, *Carbohydr Res.*, 2008, **343**, 3021-3024.

40

45