RSC Advances

RSCPublishing

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *RSC Advances*, 2013, **3**, 9201

Received 16th January 2013,
Accepted 30th April 2013

DOI: 10.1039/c3ra41912f

www.rsc.org/advances

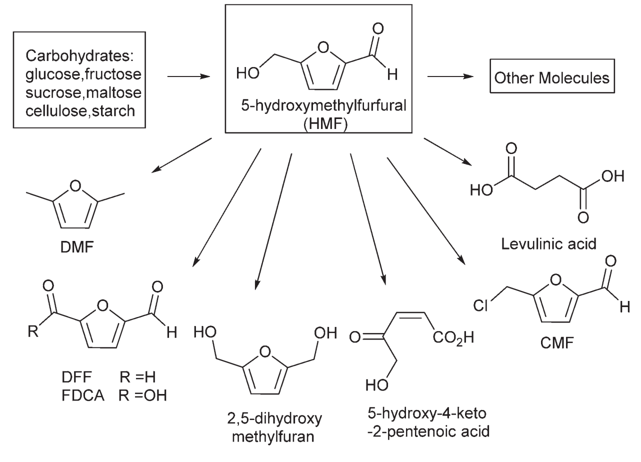
Conversion of carbohydrates into 5-hydroxymethylfurfural using polymer bound sulfonic acids as efficient and recyclable catalysts†

Zhang Zhang,* Bin Du, Li-Jia Zhang, Yu-Xia Da, Zheng-Jun Quan, Liang-Jie Yang and Xi-Cun Wang*

52–94% yields of 5-hydroxymethylfurfural (HMF) from carbohydrates such as monosaccharides, disaccharides and polysaccharides were achieved using PEG-OSO$_3$H or PS-PEG-OSO$_3$H as reusable catalysts in a DMSO/H$_2$O reaction system. Using polymer-supported catalysis, corn stover could also be effectively transformed into HMF and furfural.

At the beginning of the 21st century, the utilization of renewable raw material will gain significant importance in the industrial conversion of chemicals. This is a consequence of diminishing fossil fuel reserves, which will urge the development of new methodologies to make use of sustainable sources for chemical production in the near future.[1] Since biomass is renewable and abundant in nature, it is a promising alternative for the sustainable supply of valuable intermediates and platform chemicals to the chemical industry.[2]

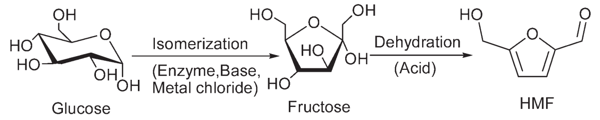
Carbohydrates are among the most abundant organic compounds on earth and represent the majority of the world's annually renewable biomass. Sources of carbohydrates include conventional forestry, wood processing by-products, agricultural crops and surpluses, and plants grown on degraded soils. The bulk of the carbohydrate-biomass comprises monosaccharides (*e.g.* glucose and fructose), disaccharides (*e.g.* sucrose and maltose) and polysaccharides (*e.g.* starch and cellulose), which by Brønsted or Lewis acid catalyst hydrolysis form 5-hydroxymethylfurfural.[3] HMF has been hailed as the central biorenewable chemical from which liquid fuel and other important chemicals can be produced.[4] HMF is very useful, not only as an intermediate for the production of the biofuel dimethylfuran (DMF) and other molecules, but also for important molecules such as levulinic acid (LA), 2,5-furandicarboxylic acid (FDCA), 2,5-diformylfuran (DFF), 2,5-dihydroxymethylfuran, 5-chloromethyl furfural (CMF) and 5-hydroxy-4-keto-2-pentenoic acid (Scheme 1).[5] Numerous important scientific groups are carrying out studies on the synthesis and applications of HMF and its derivatives. Glucose conversion to HMF proceeds *via* two steps: isomerization of glucose to fructose, followed by dehydration of fructose to HMF in the presence of enzyme, metal chloride or base catalysts[6–10] (Scheme 2). Among these catalysts, metal chlorides are favored because they effectively catalyze isomerization and dehydration. Zhao *et al.* have shown that using CrCl$_2$ in ionic liquid leads to HMF yields of 67% at 100 °C.[10a] Hu and co-workers reported a catalytic conversion of glucose using SnCl$_4$, in which HMF was formed in 64% yield.[10b] Interestingly, Kerton transformed chitosan into HMF using SnCl$_4$·5H$_2$O as a catalyst in microwave irradiation and the yield of HMF was only 10%.[11] Abu-Omar and partners have employed AlCl$_3$·6H$_2$O as a catalyst to obtain HMF from carbohydrates in AlCl$_3$·6H$_2$O–NaCl–H$_2$O/THF biphasic medium.[12] Sn–Mont catalyst was found to efficiently convert carbohydrates into HMF by Wang *et al.*[13] These catalyst systems, however, have drawbacks, as Cr and Sn are toxic, ionic liquids and expensive due to several separation processes. The biphasic medium is harsh while the Sn–Mont



Scheme 1 5-Hydroxymethylfurfural (HMF) as a bio-platform molecule.

Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education, Gansu Key Laboratory of Polymer Materials, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu 730070, P. R. China. E-mail: wangxicun@nwnu.edu.cn; zhangz@nwnu.edu.cn; Fax: +86-931-7971971; Tel: +86-931-7971971

† Electronic supplementary information (ESI) available: experimental section and experimental data. See DOI: 10.1039/c3ra41912f



Scheme 2 Schematic representation of glucose to HMF with an acid catalyst.

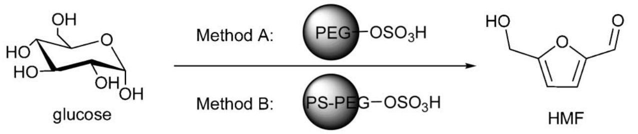
catalyst preparation is complex and their application on an industrial scale remains prohibitive.

In recent years, an abundant and cheap catalyst was widely used in many organic reactions. For instance, Fu *et al.*[14] reported that Fe_3O_4-SBA-SO_3H (a magnetic solid acid) could be used as a cheap and nontoxic catalyst for fructose dehydration into HMF. However, there is still no report on using the polymer bound sulfonic acids to catalyze the dehydration of carbohydrates towards HMF. The utility of polymer-supported acid catalysts is well-recognized because of their ease of workup and separation of products and catalysts, from an economical point of view, and in application to industrial processes.[15] We previously reported the preparation and utilization of polyethylene glycol (PEG)-bound sulfonic acid (PEG-OSO_3H)[16] and polystyrene-poly (ethylene glycol) (PS-PEG) resin-supported sulfonic acid (PS-PEG-OSO_3H)[17] in the Biginelli reaction, the Beckmann rearrangement and other multicomponent reactions.[18] We found that these two polymer bound catalysts are mild, non-volatile and non-corrosive organic acids[19] and can efficiently convert carbohydrates to HMF in a one-pot fashion. In this report, we describe a one-pot synthesis of HMF from carbohydrate and lignocellulosic biomass using these polymer bound sulfonic acids catalysts in a DMSO/H_2O medium.

Glucose can be obtained from starch, cellulose, sucrose, maltose, and even biomass. Therefore, we initially chose the reaction of glucose as a typical reaction to optimize the reaction conditions (Scheme 3).

We began by exploring the reactivity of glucose with PEG-OSO_3H as a catalyst. The reaction was performed in the presence of 2 mmol glucose, 0.3 g lithium chloride (LiCl), 0.7 g PEG-OSO_3H (0.23 mmol –SO_3H), 2 mL H_2O and 4 mL various solvents (water, *n*-butyl alcohol, THF, DMA, DMF, DMSO, 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM]PF_6, glycerol and PEG-300) in Fig. 1. From the results we can see that the reaction did not occur when only water, glycerol or PEG-300 was used as the solvent and good HMF yields (35–76%) were obtained in organic solvents. The highest yield of HMF (76%) was obtained in DMSO because it favours the furanoid form and the side reactions are remarkably suppressed.[20] Lower yields were obtained when the load of catalyst was reduced, such as 0.4 g (0.13 mmol) of catalyst, yielding the product HMF in 65% yield. Subsequently, we investigated different temperatures and found that the temperature has a significant effect on the yield of HMF. In the temperature range 80–140 °C, the maximum yield occurred at 120 °C. At lower temperatures (80–110 °C) and higher temperatures (130–140 °C), the yield of HMF was low. The main reason was that the isomerization and dehydration reactions of glucose were accelerated by increasing the temperature, which was favorable to achieving a high yield. However, the side reactions were also enhanced by rising temperature. The competition of the two opposite factors led to the largest yield at 120 °C.

In addition, various co-catalysts were investigated; the results are summarized in Fig. 2. We can see from Fig. 2 that glucose is converted to HMF in higher yields from metal chloride (LiCl, NaCl, KCl, $NiCl_2$, $CrCl_2$, $BiCl_3$, $CuCl_2$, $ZnCl_2$, $FeCl_3 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and $FeCl_3/CuCl_2$). Increased yields up to 76% can be obtained through catalysis by LiCl. However, metal catalysts (Se, Sn, Fe, Cu and Cu/Fe) showed a lower yield (*e.g.* Cu gave 31% yield). We also investigated two kinds of rare earth metal (Rb_2O and Nb_2O_5), for which no product was found. The existence of LiCl gave HMF in higher yield; this improvement might very well be attributed to the decrease in pH upon introduction of LiCl (pH = 3.0–3.6 *versus* pH = 2.0–2.4). In the acid medium, it promoted



Scheme 3 Conversion of glucose into HMF catalyzed by polymer-bound sulfonic acids.

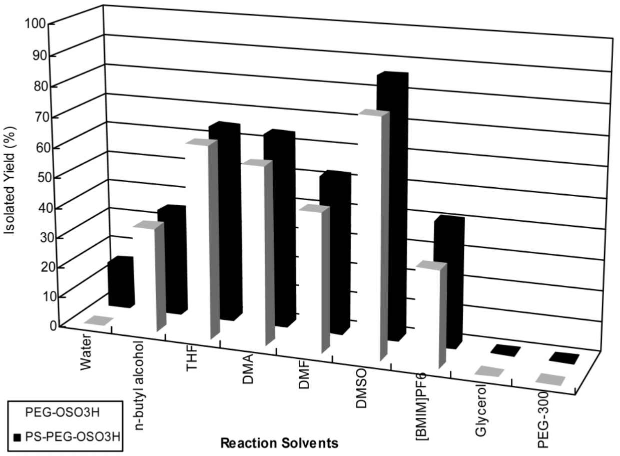


Fig. 1 Effect of different solvents on the yield of HMF from glucose.

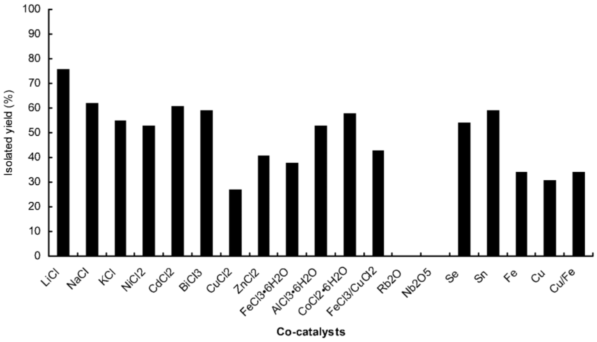


Fig. 2 The yield of HMF from glucose by various co-catalysts in H_2O/DMSO systems.

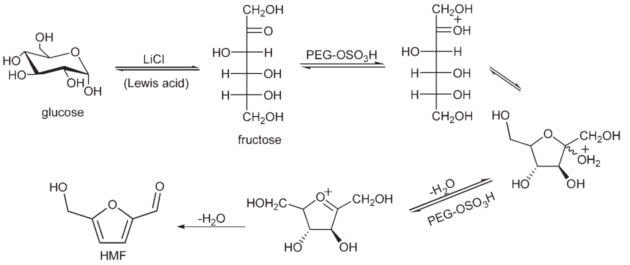


Fig. 3 Possible reaction mechanism for glucose isomerisation to fructose following dehydration to HMF on PEG-OSO_3H catalyst.

isomerization of glucose to fructose, followed by dehydration of fructose to HMF as shown in Fig. 3. The influence of the amount of LiCl in the system on dehydration of glucose to HMF was investigated at 120 °C; the yield of HMF increased to a maximum of 76% with an increase in the amount of LiCl from 0 to 0.3 g and then slowly decreased to 60% with a further increase in the amount of LiCl from 0.3 to 1.0 g. Thus, we decided to use 2 mmol of glucose, 0.3 g LiCl, PEG-OSO_3H (0.7 g, 0.23 mmol), in H_2O (2 mL) and DMSO (4 mL) at 120 °C for 1.5 h as the optimal reaction conditions for the preparation of HMF.

The reaction between glucose (2 mmol), LiCl (0.3 g) and H_2O (2 mL) using PS-PEG-OSO_3H 0.2 g (0.66 mmol) as the catalyst in various solvents was tested. As shown in Fig. 1, the yield of HMF was increased and the best yield (84%) of HMF was obtained by carrying out the reaction at 120 °C. It can be indicated that high polarity solvents (such as THF and DMSO) are more effective than the non-polar solvents. When the load of catalyst PS-PEG-OSO_3H was reduced to 0.1 g (0.33 mmol), the yield of HMF was 77%. Thus, we decided to use 0.2 g (0.66 mmol) catalyst in subsequent reactions. The ratio of substrates and temperatures were also screened and we found that the optimal reaction conditions for the preparation of HMF were glucose (2 mmol), LiCl (0.3 g), H_2O (2 mL), DMSO (4 mL) and PS-PEG-OSO_3H (0.2 g, 0.66 mmol) in DMSO at 120 °C for 1 h.

Recyclability is of great importance for applying a catalyst in industrial processes. The reusability of the catalysts PEG-OSO_3H and PS-PEG-OSO_3H were studied in this work and evaluated through seven repeated reactions (Table 1). Firstly, the catalytic activity and repeatability of PEG-OSO_3H was tested in the reaction for glucose, the yields of HMF were 76%, 72%, 64%, 58%, 50%, 43% and 38%, respectively. After the reaction, the catalyst was extracted by dichloromethane. The white PEG-OSO_3H catalyst can be obtained by adding cooled diethyl ether into the concentrated organic phase. The recovered catalyst can be used directly in the next run.

Table 1 Recycling study of PEG-OSO_3H and PS-PEG-OSO_3H for glucose converted into HMF

PEG-OSO_3H[a]	No.	Fresh	1	2	3	4	5	6
	m g^{-1}	0.70	0.68	0.60	0.57	0.53	0.48	0.43
	Recovery (%)[b]	—	97	88	81	76	69	61
	Yield (%)[c]	76	72	64	58	50	43	38
PS-PEG-OSO_3H[d]	No.	Fresh	1	2	3	4	5	6
	m g^{-1}	0.20	0.19	0.18	0.16	0.15	0.13	0.12
	Recovery (%)[e]	—	95	90	80	75	65	60
	Yield (%)[f]	84	77	69	60	52	46	41

[a] Reaction conditions: molar ratio of glucose/PEG-OSO_3H/LiCl = 2 : 0.23 : 7), H_2O (2 mL), DMSO (4 mL), 120 °C, 1.5 h. [b] Based on 0.7 g PEG-OSO_3H. [c] Isolated yield based on glucose. [d] Reaction conditions: molar ratio of glucose/PS-PEG-OSO_3H/LiCl = 2 : 0.66 : 7), H_2O (2 mL), DMSO (4 mL), PS-PEG-OSO_3H (0.2 g, 0.66 mmol), 120 °C, 1 h. [e] Based on 0.2 g PS-PEG-OSO_3H. [f] Isolated yield based on glucose.

The recyclability of PS-PEG-OSO_3H was also investigated in the same reaction. To recover the catalyst, the resulting mixture after reaction was filtered, the PS-PEG-OSO_3H was filtered off, washed with EtOH (3 × 10 mL) and dried at 50 °C. The used catalyst was added to the new substrates directly for the next run. The highest yield of HMF (84%) was obtained from fresh one. Subsequently, the yield of HMF was checked in recycle 1 to recycle 6 (77%, 69%, 60%, 52%, 46%, 41%, respectively), and the results are shown in Table 1.

These results indicate that the polymer bound sulfonic acids catalysts exhibited excellent activity for glucose conversion. However, the PS-PEG-OSO_3H catalyst showed a higher activity than the PEG-OSO_3H catalyst. The poor activity of PEG-OSO_3H might very well be attributed to the gradual leaching of its surface –SO_3H groups in every repeatable process.

The excellent activity of polymer bound sulfonic acid catalysts in synthesizing HMF from glucose opens up the possibility of using more complex carbohydrates, such as disaccharides (sucrose and maltose) and polysaccharides (starch and cellulose) as renewable raw materials. Herein, sucrose, maltose, starch and cellulose could be converted into HMF with our catalysts and the yields of HMF were lower than monosaccharide (glucose and fructose). Moderate to good yields of HMF were obtained from glucose, fructose, sucrose, maltose, starch and cellulose using PEG-OSO_3H (yield: 78%, 90%, 75%, 67%, 60%, and 52%, respectively) or PS-PEG-OSO_3H as the catalyst (yield: 86%, 94%, 76%, 68%, 66%, and 54%, respectively). The results are illustrated in Table 2.

Finally, we applied the polymer bound sulfonic acid catalysts to the raw biomass variant. When corn stover was treated with PS-PEG-OSO_3H at 130 °C for 6 h, a mixture, which contained HMF and furfural in a ratio of 15 : 82 with 3% of other side products, was obtained in 36% yield (w/w). It is notable that the major product was furfural, which is also an important chemical and synthetic material,[21,22] and can be obtained from corn stover under these reaction conditions. Furfural can be the starting material for the synthesis of a series of derivatives including furfuryl alcohol, furoic acid, furan, tetrahydrofuran, 2-methyltetrahydrofuran, and related resins.

Conclusions

Glucose or glucose-based carbohydrates were efficiently transformed into HMF co-catalyzed by polymer bound sulfonic acids

Table 2 Carbohydrate conversion and HMF yield catalyzed by the polymer bound sulfonic acid catalysts

	PEG-OSO_3H[a]			PS-PEG-OSO_3H[b]		
Carbohydrates	Con.[c] (%)	HPLC yield (%)	Isolated yield (%)	Con. (%)	HPLC yield (%)	Isolated yield (%)
Glucose	99	78	76	98	86	84
Fructose	>99	90	85	99	94	91
Sucrose	98	75	71	97	76	73
Maltose	98	67	64	98	68	63
Starch	99	60	52	98	66	55
Cellulose	98	52	47	96	54	50

[a] Reaction conditions: carbohydrates (2.0 mmol), LiCl (0.3 g), H_2O (2 mL), DMSO (4 mL), PEG-OSO_3H (0.7 g, 0.23 mmol), 120 °C, 1.5 h.
[b] Reaction conditions: carbohydrates (2.0 mmol), LiCl (0.3 g), H_2O (2 mL), DMSO (4 mL), PS-PEG-OSO_3H (0.2 g, 0.66 mmol), 120 °C, 1 h.
[c] Detected by HPLC.

with LiCl. It displayed high activity and good yield. For glucose, the yield of HMF can mount to 86% in DMSO/H_2O mixed systems. It is confirmed that the key to successfully achieving the direct conversion of the carbohydrates to HMF is that the catalytic system contains both Brønsted acid (polymer bound sulfonic acids) and Lewis acid (LiCl) sites and combines the isomerization process with the dehydration step in a one-pot reaction system. Hence, our chemical process uses simple, inexpensive catalysts to transform carbohydrates into a valuable product in an ample yield. Due to its economy, non-corrosive, highly effective and high reusability, this catalyst system has excellent potential for the conversion of biomass into biofuels and platform chemicals.

Experimental procedure

D-Glucose, D-fructose, sucrose, maltose and starch were purchased from J&K Scientific Ltd (Beijing, China), α-cellulose was obtained from Aladdin Reagent Co., Ltd (Shanghai, China). All chemicals were analytical grade, and used as received without further purification, Corn stover was obtained from our test field. PEG-OSO_3H[16] and PS-PEG-OSO_3H[17] were prepared according to our previous procedures.

All reaction products were analyzed by HPLC with a Kromasil-C_{18}-5μ column at 30 °C, P98-I pump, UV98-I detector at 254 nm. Acetonitrile and water (45 : 90) were used as the mobile phase at a flow rate of 0.8 mL min^{-1}. HMF was quantified with calibration curves generated from commercially available standards. Following a typical experimental procedure for the glucose reaction: A mixture of glucose (2 mmol), LiCl (0.3 g) and PS-PEG-OSO_3H (0.2 g, 0.66 mmol –SO_3H) in DMSO aqueous solution was stirred at 120 °C for 1 h. After completion monitored by TLC, the resulting mixture was diluted with a known mass of deionized water. The concentrations of products were calculated from HPLC-peak integrations and were used to calculate molar yield, and 86% yield of HMF was achieved. ^1H NMR (400 MHz, $CDCl_3$): 3.00 (s, 1H, OH), 4.72 (s, 2H, CH_2), 6.52 (d, J = 3.6 Hz, 1H, Furan-H-4), 7.23 (d, J = 3.6 Hz, 1H, Furan-H-3), 9.58 (s, 1H, CHO) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): 57.39 (CH_2), 109.93, 123.18 (Ar), 152.15 (Ar), 160.83 (Ar), 177.69 (CHO) ppm. FTIR (KBr) (ν, cm^{-1}): 1026 (C–O–C), 1520 (C=C), 1674 (–CHO), 2992, 2908 (–CH_2), 3412 (–OH). HRMS (ESI†): calculated for $C_6H_6O_3$: $[M + H]^+$ 127.0390; found: 127.0392. See ESI† for further experimental details.

Acknowledgements

We are thankful for the financial support from the National Nature Science Foundation of China (Nos. 20902073 and 21062017), the Natural Science Foundation of Gansu Province (No. 1208RJYA083), and the Scientific and Technological Innovation Engineering program of Northwest Normal University (Nos. nwnu-kjcxgc-03-64, nwnulkqn-10-15).

Notes and references

1 Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982–985.
2 Y. Román-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933–1937.
3 J. N. Chheda, Y. Román-Leshkov and J. A. Dumesic, *Green Chem.*, 2007, **9**, 342–350.
4 (*a*) A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411–2502; (*b*) A. A. Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, *Green Chem.*, 2011, **13**, 754–793.
5 (*a*) J. M. R. Gallo, D. M. Alonso, M. A. Mellmer and J. A. Dumesic, *Green Chem.*, 2013, **15**, 85–90; (*b*) M. Balakrishnan, E. R. Sacia and A. T. Bell, *Green Chem.*, 2012, **14**, 1626–1634; (*c*) A. A. Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, *Green Chem.*, 2011, **13**, 754–793; (*d*) Z. T. Du, J. P. Ma, F. Wang, J. X. Liu and J. Xu, *Green Chem.*, 2011, **13**, 554–557.
6 R. L. Huang, W. Qi, R. X. Su and Z. M. He, *Chem. Commun.*, 2010, **46**, 1115–1117.
7 A. Takagaki, M. Ohara, S. Nishimura and K. Ebitani, *Chem. Commun.*, 2009(41), 6276–6278.
8 M. Watanabe, Y. Aizawa, T. Iida, T. M. Aida, C. Levy, K. Sue and H. Inomata, *Carbohydr. Res.*, 2005, **340**, 1925–1930.
9 (*a*) Y. Roman-Leshkov, M. Moliner, J. A. Labinger and M. E. Davis, *Angew. Chem., Int. Ed.*, 2010, **49**, 8954–8957; (*b*) H. Jadhav, C. M. Pedersen, T. Sølling and M. Bols, *ChemSusChem*, 2011, **4**, 1049–1051; (*c*) R. S. Assary and L. A. Curtiss, *J. Phys. Chem. A*, 2011, **115**, 8754–8760.
10 (*a*) H. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, **316**, 1597–1600; (*b*) S. Hu, Z. Zhang, J. Song, Y. Zhou and B. Han, *Green Chem.*, 2009, **11**, 1746–1749; (*c*) B. R. Caes, M. J. Palte and R. T. Raines, *Chem. Sci.*, 2013, **4**, 196–199.
11 K. W. Omari, J. E. Besaw and F. M. Kerton, *Green Chem.*, 2012, **14**, 1480–1487.

12 Y. Yang, C. W. Hu and M. M. Abu-Omar, *Green Chem.*, 2012, **14**, 509–513.

13 J. J. Wang, J. W. Ren, X. H. Liu, J. X. Xi, Q. E. Xia, Y. H. Zu, G. Z. Lu and Y. Q. Wang, *Green Chem.*, 2012, **14**, 2506–2512.

14 Z. Z. Yang, J. Deng, T. Pan, Q. X. Guo and Y. Fu, *Green Chem.*, 2012, **14**, 2986–2989.

15 L. A. Thompson and J. A. Ellman, *Chem. Rev.*, 1996, **96**, 555–600.

16 X. C. Wang, Z. J. Quan, F. Wang, M. G. Wang, Z. Zhang and Z. Li, *Synth. Commun.*, 2006, **36**, 451–456.

17 Z. J. Quan, Y. X. Da, Z. Zhang and X. C. Wang, *Catal. Commun.*, 2009, **10**, 1146–1148.

18 X. C. Wang, L. Li, Z. J. Quan, H. P. Gong, H. L. Ye and X. F. Cao, *Chin. Chem. Lett.*, 2009, **20**, 651–655.

19 (*a*) A. Hasaninejad, A. Zare, M. Shekouhy and J. Ameri-Rad, *Green Chem.*, 2011, **13**, 958–964; (*b*) A. Hasaninejad, A. Zare and M. Shekouhy, *Tetrahedron*, 2011, **67**, 390–400.

20 (*a*) J. J. Wang, W. J. Xu, J. W. Ren, X. H. Liu, G. Z. Lu and Y. Q. Wang, *Green Chem.*, 2011, **13**, 2678–2681; (*b*) M. Bicker, D. Kaiser, L. Ott and H. Vogel, *J. Supercrit. Fluids*, 2005, **36**, 118–126; (*c*) F. W. Lichtenthaler and S. Ronninger, *J. Chem. Soc., Perkin Trans.*, 1990, **2**, 1489–1497.

21 H. Guo and G. Yin, *J. Phys. Chem. C*, 2011, **115**, 17516–17522.

22 J.-P. Lange, E. V. D. Heide, J. A. Buijtenen and R. Price, *ChemSusChem*, 2012, **5**, 150–166.