RSC Advances

PAPER

View Article Online
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Cite this: *RSC Adv.*, 2014, 4, 4194

Efficient production of 5-hydroxymethylfurfural and alkyl levulinate from biomass carbohydrate using ionic liquid-based polyoxometalate salts†

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Received 7th October 2013
Accepted 5th December 2013

DOI: 10.1039/c3ra45632c

www.rsc.org/advances

Direct conversion of fructose into 5-hydroxymethylfurfural (HMF) and alkyl levulinate is achieved by making use of ionic liquid-based polyoxometalate salts (IL-POMs) as solid acid catalysts. Among these solid acids, phosphotungstic acid-derived IL-POM shows the highest catalytic performance in both the HMF and ethyl levulinate (EL) formation. A study for optimizing the reaction conditions such as the reaction time and the temperature has been performed. High HMF and EL yields of up to 99% and 82%, respectively, are obtained from fructose under the investigated conditions. Moreover, the generality of the catalyst is further demonstrated by processing representative di- and polysaccharides such as sucrose and inulin with good yields to HMF (76% from inulin and 48% from sucrose) and EL (67% from inulin and 45% from sucrose), again under mild conditions, thereby eliminating the separate hydrolysis step before the dehydration reaction. The catalyst recycling experiment indicates that the adsorption and accumulation of oligomeric products on the catalyst surface results in a partial deactivation of catalyst. The mechanism research reveals that a major pathway for EL formation involves a fructose-to-HMF transformation followed by HMF etherification and rehydration of HMF-ether to give EL. The research highlights an efficient, environment-friendly and recyclable solid acid for biomass valorization.

Introduction

Catalytic routes to fuels and chemicals from sustainable feedstock have attracted much attention over the last few years, owning to diminishing fossil reserves as well as degradation of the environment.[1–3] Renewable and carbon-neutral biomass provides an abundant alternative to fossil resources for the sustainable production of fuels and chemicals; particularly, biomass carbohydrate is one of the largest components of woody biomass. Current research in this area has led to significant progress in exploring efficient routes for the conversion of carbohydrate into biomass-based platform chemical compound. Among these platform molecules, 5-hydroxymethylfurfural (HMF)[4,5] and alkyl levulinates[6] are of particular interest due to their versatile functions and benign properties.

As a sustainable precursor for petrochemical industry and biofuel chemistry, HMF is obtained mainly by dehydration of biomass-based carbohydrate, especially monosaccharide fructose,[7,8] using a variety of mineral acids,[9] organic acids,[10] acidic resins,[11] oxides,[12] phosphates,[13] and zeolites[14] as catalysts. Dehydration was carried out in many solvents including water, organic solvents, and biphasic mixed systems.[15] Recently, the synthesis of HMF was developed rapidly with acidic ionic liquids (ILs) as catalysts or in ILs.[16]

In addition to HMF, alkyl levulinate is well known to have widespread applications as odorous substances, plasticizing agents, and fuel additives.[6,17,18] Generally, the synthetic routes for alkyl levulinate from biomass feedstock involve typically either the esterification of levulinic acid with alcohol[19] or a direct acid-catalyzed alcoholysis of biomass-based feedstocks such as furfuryl alcohol[20–22] and monosaccharide.[23–27] The former route requires acid catalyst such as mineral liquid acid or solid acid for esterification of levulinic acid with corresponding alcohol. The one-step, direct alcoholysis of biomass feedstock to alkyl levulinate is preferable, as it avoids the isolation and purification steps of the intermediate levulinic acid. Moreover, the latter route shows a minimized wastewater as well as higher grade products over the route of esterification of levulinic acid.

In recent years, solid acid catalysts for direct production of alkyl levulinate through biomass carbohydrate have undergone an impressive development. Zhao and co-workers made impressive progress on the direct alkyl levulinate production from furfuryl alcohol using methylimidazolebutylsulfate

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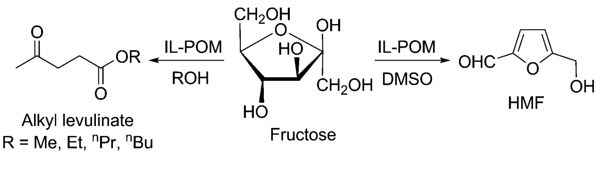
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ra45632c

phosphotungstate ($[MIMBS]_3PW_{12}O_{40}$) as solid acid catalyst.[21] The plausible reaction pathway of furfuryl alcohol alcoholysis was subsequently revealed by Dumesic *et al.*[20] Riisager and co-workers did nice work on a direct conversion of mono- and disaccharides to ethyl levulinate (EL) with sulfonic acid-functionalized ILs[23] and sulfonic acid-functionalized SBA-15[24] as catalysts. Lin and Liu reported a direct conversion of glucose to EL over sulfated zirconia catalysts with a moderate yield of 30% at 200 °C.[25,26] Tominaga group reported mixed-acid systems of Lewis and Brønsted acids for direct synthesis of methyl levulinate from cellulose.[27] Recently, we achieved a direct conversion of fructose into HMF and alkyl levulinate by using poly(*p*-styrenesulfonic acid)-grafted multi-walled carbon nanotubes as solid acid catalyst.[8] Therefore, a study on developing various kinds of green and efficient acid catalysts is very important.

In recent years, solid acids, especially IL-based polyoxometalate salts (IL-POMs), have attracted much attention due to the flexible adaptability of both the inorganic and the organic groups.[21,28–30] Tethering organic groups to POMs can realize heterogenization of heteropolyacid (HPA)-promoted reactions, which has become an attractive topic for catalyst recycling. In particular, IL-cations with varieties of structures and properties can be applied to organic blocks to modify POM catalysts with their acidity, polarity, solubility, redox properties and surface structures. Herein we report on the behaviour of a series of IL-POMs as solid acid catalysts for the fructose dehydration to HMF and one-pot conversion of fructose into alkyl levulinate (Scheme 1). The HPA and IL used in IL-POMs, the catalyst loading and the reaction temperature were found to have significant effects on these catalytic systems. Under the optimal conditions, high yields of HMF and EL of up to 99 and 82% were obtained, respectively, from direct fructose conversion. Moreover, in comparison with commonly used monocationic IL-POMs, dicationic IL-POMs in this research allow greater variety and control of the properties of an IL-POM, including its higher melting point and lower solubility in the reaction system, which achieves its heterogenization and recycling. In addition, by using preferred reaction conditions for representative di- and polysaccharides such as sucrose (from sugarcane) and inulin (from chicory), that are abundantly available, renewable and inexpensive, we can directly process these saccharides with good yields to HMF (76% from inulin and 48% from sucrose) and EL (67% from inulin and 45% from sucrose) by using IL-POMs as catalysts. Notably, these processes thereby eliminate the need to obtain simple carbohydrate molecules by acid hydrolysis as a separate processing step. The catalyst system described in this article thus achieves an integrated chemical process where multi-step reactions are consolidated in one pot without isolation of intermediate of monosaccharides, and with excellent efficiency.



Scheme 1 Conversion of fructose into HMF and alkyl levulinate.

Experimental

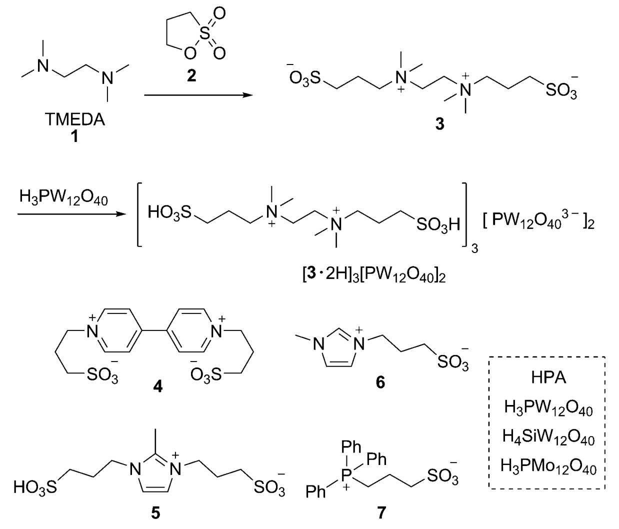
Materials

Unless otherwise stated, all chemicals in this work were commercial available and used without further purification. Keggin-type phosphotungstic acid ($H_3PW_{12}O_{40}$), silicotungstic acid ($H_4SiW_{12}O_{40}$), phosphomolybdic acid ($H_3PMo_{12}O_{40}$), fructose, glucose, sucrose, methanol, ethanol, diethyl ether, and petroleum ether were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, PR China). Inulin, cellobiose, cellulose, 5-hydroxymethylfurfural, ethyl levulinate, methyl levulinate, *n*-propyl levulinate, *n*-butyl levulinate, *n*-propanol, *n*-butanol, dimethyl sulfoxide, toluene, tetramethylethylenediamine (TMEDA), 1,3-propanesulfonate, 1-methylimidazole, 2-methylimidazole, 4,4′-bipyridine, triphenylphosphine, methyl hexadecanoate (internal standard), and sodium ethoxide were purchased from Aladdin Industrial Inc. (Shanghai, PR China). Hydrogen gas (>99.999%) and nitrogen gas (>99.999%) were obtained from Huate Co. Ltd (foshan, PR China). De-ionized pure water from Millipore-Milli Q Plus System was used as solvent.

Catalyst preparation

The ILs **3–7** were prepared according to literature procedure with slight modifications (Scheme 2) (see the ESI for details†).

The IL-POMs were prepared by the treatment of ILs **3–7** with HPA in water. In a typical synthetic procedure of $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$, IL **3** (0.36 g, 1 mmol) dissolved in water (5 mL) was slowly dropped into the aqueous solution (5 mL) of $H_3PW_{12}O_{40}$ (1.92 g, 0.67 mmol) under vigorous stirring. When it finished, the mixture continued to stir at room temperature for 24 hours. Water was removed under vacuum, and the final product, $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$ was obtained as a white solid and characterized by FT-IR spectroscopy. $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$: FT-IR (KBr): $\nu = 1482$ (C–H), 1228, 1155 (S═O), 1080, 1041 ($P–O_a$), 981



Scheme 2 Synthesis of IL-POMs.

(W–O$_d$), 978 (W = O$_d$), 899, 811 cm^{-1} (P–O$_{b/c}$). The other IL-POMs were prepared following the same procedures as for [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$.

General procedure for the reaction

Fructose conversion into HMF. In a typical run, fructose (50 mg), [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$ (25 mg) and DMSO (2 mL) were added to an Ace pressure tube. The mixture was heated at 100 °C with vigorous stirring for 1.0 h. After the reaction, the mixture was filtered and then decanted into a volumetric flask using water as diluents, and analyzed by high-performance liquid chromatography (HPLC). HMF: ^{1}H NMR (400 MHz, D$_2$O) δ 9.33 (s, 1H), 7.40 (d, J = 3.6 Hz, 1H), 6.55 (d, J = 3.1 Hz, 1H), 4.57 (s, 2H). ^{13}C {^{1}H} NMR (101 MHz, D$_2$O) δ 180.5, 161.3, 151.8, 126.8, 110.9, 56.0. IR (KBr, cm^{-1}): ν = 3377 (O–H), 1670 (C=O). Mass spectrum (EI) m/z 126 (M$^+$).

Fructose conversion into EL. In a typical run, fructose (50 mg), [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$ (50 mg) and ethanol (4 mL) were added to an Ace Pressure Tube. The mixture was heated at 120 °C with vigorous stirring for 12 h. After the reaction, the mixture was filtered and analyzed by GC, GC-MS and HPLC. EL: ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.12 (q, J = 7.1 Hz, 2H), 2.74 (t, J = 6.5 Hz, 2H), 2.56 (t, J = 6.6 Hz, 2H), 2.18 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 206.7, 172.7, 60.6, 37.9, 29.8, 27.9, 14.1. FT-IR (KBr, cm^{-1}): ν = 1726 (C=O). Mass spectrum (EI) m/z 144 (M$^+$).

Analytic methods

1H NMR spectra were recorded on a Bruker AVANCE Digital 400 MHz spectrometer at 25 °C with D$_2$O or CDCl$_3$ as solvent. IR spectra were measured on a Bruker Tensor 27 FT-IR spectrometer as KBr pellets. The HPLC analysis was performed on Shimadzu LC-20AT equipped with a UV-Vis/refractive index detector and a Shodex Sugar SP-0810 column (ø 8 × 300 mm). H$_2$SO$_4$ (0.005 M) solution was used as the mobile phase at a flow rate of 0.5 mL min^{-1}, and the column temperature was maintained at 50 °C. The amounts of fructose and HMF were calculated based on external standard curves constructed with authentic standards. The GC analysis was performed by Agilent 6890 or Shimadzu 2010 equipped with a flame ionization detector (FID) and a KB-5 capillary column (internal diameter 0.32 mm, length 30 m) using nitrogen as the carry gas. The GC-MS analysis was performed by Trace GC-MS 2000 as well as by comparing the retention times to respective standards in GC traces. The operating conditions for GC and GC-MS were as follows: injector port temperature, 260 °C; column temperature, initial temperature 50 °C (2 min), gradient rate 30 °C min (7 min), final temperature 260 °C (3 min), flow rate 75 mL min^{-1}. The amounts of products were calculated based on internal standard curves constructed with authentic standards.

Results and discussion

Conversion of fructose into HMF

Table 1 Dehydration of fructose to HMF catalyzed by various catalysts[a]

Run	Catalyst	Conversion [%]	Yield [%]
1	[**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$	>99	92
2	[**4**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$	>99	92
3	[**5**·H]$_3$[PW$_{12}$O$_{40}$]	>99	91
4	[**6**·H]$_3$[PW$_{12}$O$_{40}$]	>99	90
5	[**7**·H]$_3$[PW$_{12}$O$_{40}$]	>99	90
6	[**3**·2H]$_2$[SiW$_{12}$O$_{40}$]	>99	90
7	[**4**·2H]$_2$[SiW$_{12}$O$_{40}$]	>99	89
8	[**5**·H]$_4$[SiW$_{12}$O$_{40}$]	>99	88
9	[**6**·H]$_4$[SiW$_{12}$O$_{40}$]	>99	86
10	[**7**·H]$_4$[SiW$_{12}$O$_{40}$]	>99	83
11	[**3**·2H]$_3$[PMo$_{12}$O$_{40}$]$_2$	>99	48
12	[**4**·2H]$_3$[PMo$_{12}$O$_{40}$]$_2$	>99	42
13	[**5**·H]$_3$[PMo$_{12}$O$_{40}$]	>99	38
14	[**6**·H]$_3$[PMo$_{12}$O$_{40}$]	>99	39
15	[**7**·H]$_3$[PMo$_{12}$O$_{40}$]	>99	40

[a] *Reaction conditions*: fructose (50 mg, 0.28 mmol), catalyst (2.5 mol% relative to fructose), DMSO (2 mL), 100 °C, 1.0 h.

Table 1 shows the dehydration of fructose to HMF in DMSO at 100 °C for 1 h with different IL-POMs as solid acid catalysts (Scheme 1). Generally, tungsten IL-POMs (IL = **3**–**7**), such as IL-H$_3$[PW$_{12}$O$_{40}$] and IL-H$_4$[SiW$_{12}$O$_{40}$], showed excellent to good activity toward the fructose dehydration with HMF yield ranging from 92 to 83% (Table 1, Runs 1–10). In the case of molybdenum IL-POMs, the HMF was obtained with very low yields (Table 1, Runs 11–15). The main by-products in the fructose dehydration reaction were polymeric humans, which were not observed in HPLC analyses. Currently, humins could not be quantified according to their composition.[31] The influence of various HPAs in the IL-POM on fructose dehydration thus revealed that with a same IL organic cation, the catalytic activities were in the order of IL-H$_3$[PW$_{12}$O$_{40}$] > IL-H$_4$[SiW$_{12}$O$_{40}$] $\gg$ IL-H$_3$[PMo$_{12}$O$_{40}$], which is in accordance with that of the Brønsted acidity of HPAs.[32] In addition to relatively lower acid strength, lower thermal stability, and higher oxidation potential of [PMo$_{12}$O$_{40}$]$^{3+}$ cation compared with tungsten heteropolyacid cations ([PW$_{12}$O$_{40}$]$^{3+}$ and [SiW$_{12}$O$_{40}$]$^{4+}$) are presumably related to low catalytic performance of IL-H$_3$[PMo$_{12}$O$_{40}$].[32] Nevertheless, for the IL-POMs with the same heteropolyanion, various protonated IL cation groups have very limited influence on the catalytic activity of IL-POMs.

The influence of catalyst loading amounts on the fructose-to-HMF transformation was investigated by varying the amount of [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$ ranging from blank to 5 mol% based on fructose used (Fig. 1). As expected, the more catalyst there is, the higher both the conversion of fructose and the yield of HMF are. The conversion of fructose is enhanced from 24% to 100% in 30 min. The yields of HMF could reach to maxima of 93% with 5 mol% of catalyst. Under the investigated reaction conditions, 2.5 mol% of catalyst was required to reach a complete conversion of fructose within 30 min with an HMF yield of 90% (Fig. 1). The increase in the HMF yield with an increasing catalyst dosage should be attributable to an increase in the availability and number of catalytically active sites of [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$ during dehydration of fructose.

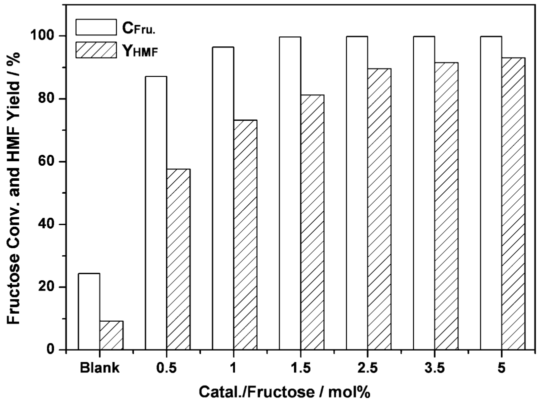


Fig. 1 Influence of the catalyst amount on fructose dehydration. (*Reaction conditions*: fructose, 50 mg, 0.28 mmol; catalyst, specified amount of $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$; DMSO, 2 mL; 100 °C; 30 min.)

Fig. 2 shows the influence of reaction temperature and time on the dehydration of fructose catalyzed by $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$ using DMSO as solvent. Both the conversion of fructose and the yield of HMF increased with reaction time at all temperatures investigated. The yield of HMF increased slowly to 55% after 60 min at 60 °C, while it increased quickly to 97% after 15 min at 100 °C, confirming that increasing the reaction temperature promotes the conversion of fructose to HMF. Moreover, an HMF yield of 99% with a full fructose conversion was obtained in DMSO using $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$ as catalyst at 100 °C after a reaction time of 30 min (Fig. 2).

It is well known that the presence of DMSO can stabilize the HMF and increase its selectivity and yield;[33,11b] however, this approach necessitates energy intensive isolation procedures owning the high boiling point of DMSO.[34] Recently, phosphotungstic acid/metal–organic framework hybrid (PTA/MOFs) was developed as a novel solid acid catalyst for fructose dehydration to HMF in 1-ethyl-3-methylimidazolium chloride (EMIMCl).[35] In addition, the catalytic conversion of fructose into HMF in a two-phase reactor system of water and methylisobutylketone (MIBK) was explored with solid $Ag_3PW_{12}O_{40}$ as catalyst.[36] The above researches thus developed POM-based catalyst system for fructose-to-HMF transformation with IL or bi-phase solvent as an alternative to DMSO.

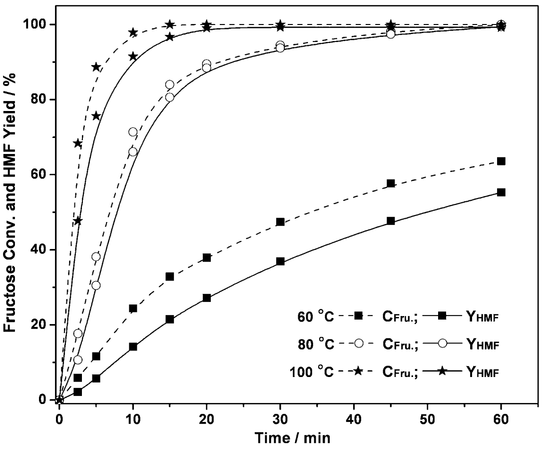


Fig. 2 Influence of the temperature and time on fructose dehydration to HMF. *Reaction conditions*: fructose (20 mg, 0.11 mmol) and $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$ (10 mg, 2.5 mol% relative to fructose) in DMSO (1 mL).

Conversion of fructose into alkyl levulinate

In addition to fructose-to-HMF transformation, in order to explore the application scope of IL-POM catalyst, a one-pot conversion of fructose into alkyl levulinates was investigated (Scheme 1). Table 2 shows the one-pot conversion of fructose into ethyl levulinate (EL) catalyzed by various IL-POMs at 120 °C in ethanol (Scheme 1). Initial experiments were performed with IL-$H_3[PW_{12}O_{40}]$ (IL = **3–7**) as solid acid catalyst. In all these reactions EL was found to be the predominant product with a yield ranging from 80 to 74% (Table 2, Runs 1–5). The main by-products in the reaction were HMF, 5-ethoxymethylfurfural (EMF), and 2-(diethoxymethyl)-5-(ethoxymethyl)furan (DEEF), which were observed in GC and GC-MS analyses (Fig. S4†). To evaluate the influence of the HPA on the formation of EL, IL-$H_4[SiW_{12}O_{40}]$ (IL = **3–7**) and IL-$H_3[PMo_{12}O_{40}]$ (IL = **3–7**) were introduced into the reaction as catalyst as well. The IL-$H_4[SiW_{12}O_{40}]$ gave a relatively lower EL yield than the corresponding IL-$H_3[PW_{12}O_{40}]$ analogue (Table 2, Runs 1–10). In the case of IL-$H_3[PMo_{12}O_{40}]$, the observed EL yields were remarkably inferior under the investigated conditions (Table 2, Runs 11–15). The influence of various HPAs in the IL-POMs on fructose alcoholysis to EL revealed a similar trend to fructose-to-HMF transformation.

When $H_3PW_{12}O_{40}$ was used as a catalyst, an EL yield of 84% with a full fructose conversion was obtained (Table 2, Run 16). However, in this system, $H_3PW_{12}O_{40}$ behaved homogeneously

Table 2 Conversion of fructose into alkyl levulinate catalyzed by various catalysts[a]

Run	Catalyst	R	*T* [°C]	Conversion [%]	Yield [%]
1	$[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$	Et	120	>99	80
2	$[\mathbf{4}\cdot 2H]_3[PW_{12}O_{40}]_2$	Et	120	>99	76
3	$[\mathbf{5}\cdot H]_3[PW_{12}O_{40}]$	Et	120	>99	79
4	$[\mathbf{6}\cdot H]_3[PW_{12}O_{40}]$	Et	120	>99	76
5	$[\mathbf{7}\cdot H]_3[PW_{12}O_{40}]$	Et	120	>99	74
6	$[\mathbf{3}\cdot 2H]_2[SiW_{12}O_{40}]$	Et	120	>99	72
7	$[\mathbf{4}\cdot 2H]_2[SiW_{12}O_{40}]$	Et	120	>99	67
8	$[\mathbf{5}\cdot H]_4[SiW_{12}O_{40}]$	Et	120	>99	67
9	$[\mathbf{6}\cdot H]_4[SiW_{12}O_{40}]$	Et	120	>99	66
10	$[\mathbf{7}\cdot H]_4[SiW_{12}O_{40}]$	Et	120	>99	60
11	$[\mathbf{3}\cdot 2H]_3[PMo_{12}O_{40}]_2$	Et	120	>99	33
12	$[\mathbf{4}\cdot 2H]_3[PMo_{12}O_{40}]_2$	Et	120	>99	30
13	$[\mathbf{5}\cdot H]_3[PMo_{12}O_{40}]$	Et	120	>99	47
14	$[\mathbf{6}\cdot H]_3[PMo_{12}O_{40}]_2$	Et	120	>99	28
15	$[\mathbf{7}\cdot H]_3[PMo_{12}O_{40}]_2$	Et	120	>99	32
16	$H_3PW_{12}O_{40}$	Et	120	>99	84
17	$[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$	Me	100	>99	75
18	$[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$	^{n}Pr	120	>99	83
19	$[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$	^{n}Bu	120	>99	77

[a] *Reaction conditions*: fructose (50 mg, 0.28 mmol), catalyst (5.0 mol% relative to fructose), alcohol (4 mL), 12 h.

Table 3 Recycling of $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$ in the fructose conversion into EL[a]

Run	Number of previous cycles	Conversion [%]	Yield [%]
1	0	>99	80
2	1	>99	78
3	2	>99	73
4	3	>99	68
5	4	>99	62

[a] *Reaction conditions*: fructose (50 mg, 0.28 mmol), $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$ (50 mg, 5.0 mol% relative to fructose), ethanol (4 mL), 120 °C, 12 h.

in the ethanol, and the separation and recovery of the $H_3PW_{12}O_{40}$ from the reaction medium was problematic. On the other hand, all of the dicationic IL-POMs (IL = **3–5**) developed in this research are insoluble in ethanol leading to heterogeneous catalysis, which can be readily recovered and reused. Therefore, in contrast to the HPA, the propylsulfonic acid group in the organic cation of IL-POMs provides the active acid site which is responsible for catalytic performance. Whereas, owing to high valence and large volume, the heteropolyanions of IL-POMs can trap the ILs and show a high melting point as well as low solubility.[28]

In addition to EL, in order to explore the scope of this method (Scheme 1), the preparations of methyl levulinate, *n*-propyl levulinate, and *n*-butyl levulinate were achieved as well with corresponding alkyl alcohol as solvent (Table 2, Runs 17–19). Previously, $[MIMBS]_3PW_{12}O_{40}$ was used as solid acid catalyst for alcoholysis of furfuryl alcohol to give alkyl levulinate. Methyl levulinate and *n*-propyl levulinate were obtained with yields of 5% and 80%, respectively.[21] In our case, yields of 75% for methyl levulinate, and 83% for *n*-propyl levulinate were achieved by direct alcoholysis of fructose, further indicating a clean and facile catalytic process.

In order to demonstrate the reusability of catalyst, a five-cycle experiment of the $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$ was investigated for the fructose-to-EL transformation as described in Table 3. The $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$ catalyst was recovered by filter, washed with ethanol and then recycled for further reaction. The yield of EL decreased from 80% to 62%, indicating that the catalyst partially lost activity during the reaction process. A similar phenomena of catalyst deactivation was also previously reported study by Zhao[21] and us.[8,37] It is important to note that the reusability of $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$ is still higher than that achieved with regards to $[MIMBS]_3PW_{12}O_{40}$. A fast deactivation process of furfuryl alcohol conversion into *n*-butyl levulinate was observed with $[MIMBS]_3PW_{12}O_{40}$ as catalyst. The catalyst recycling showed sharply decreased yields of *n*-butyl levulinate from 83 to 65% for the second run.[21]

As illustrated in Fig. 3, the profile of FT-IR spectra for the recovered $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$ after the fifth run was well consistent with that of the fresh one. Both the fresh and the recovered $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$ show characteristic bands corresponding to $[\mathbf{3}\cdot 2H]^{2+}$ (1481 cm^{-1} assigned to CH_3, 1227–1153 cm^{-1} assigned to SO_3) and $[PW_{12}O_{40}]^{3-}$ species (observed from 1080 to 811 cm^{-1}) (Fig. S1†). Notably, the spectrum of the recovered catalyst shows peaks at 1717 and 1623 cm^{-1}, assigned to the stretching frequencies of C=O groups (Fig. 3b). This indicated the presence of organic carbonyl species on the surface of $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$ after reuse. Therefore, our results suggest that the adsorption and accumulation of oligomeric products on the catalyst surface, presumably blocking acidic catalytic sites, was the main reason for the partial deactivation of $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$.

Reaction pathways for the $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$-catalyzed fructose-to-EL transformation in ethanol were further investigated using liquid chromatography-mass spectrometry (LC-MS) and gas chromatography-mass spectrometry (GC-MS). From LC-MS and GC-MS analysis, three species of HMF (*m*/*z* 126.1), EMF (*m*/*z* 154.0), and DEEF (*m*/*z* 228.1) were observed to be formed and later consumed in the interval of time, suggesting an intermediate behavior; whereas, EL (*m*/*z* 144.0) was observed to increase with time (Fig. S4†). The GC analysis and a plausible pathway for EL formation are shown in Fig. 4 and Scheme 3, respectively.

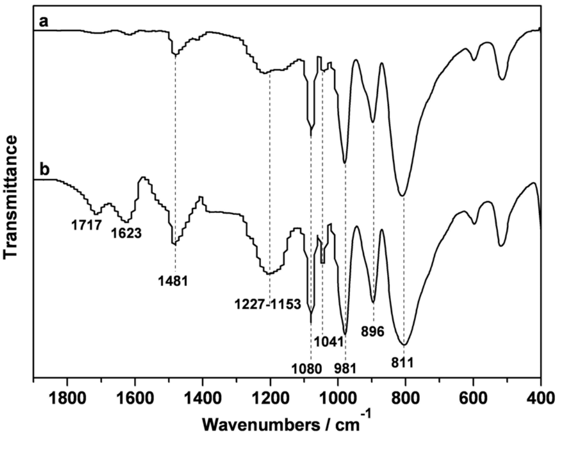


Fig. 3 FT-IR of (a) the fresh $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$, and (b) the recovered $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$ after a five-cycle in the fructose conversion into EL.

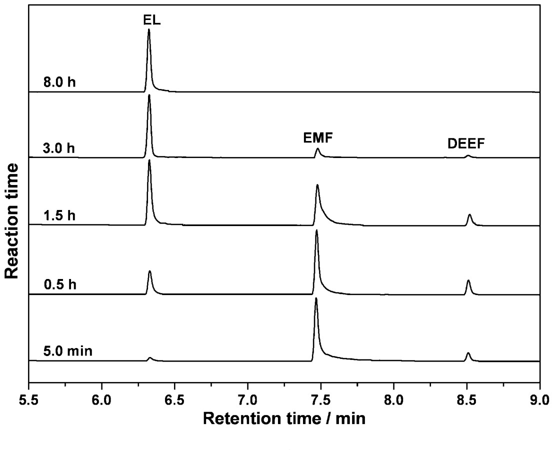
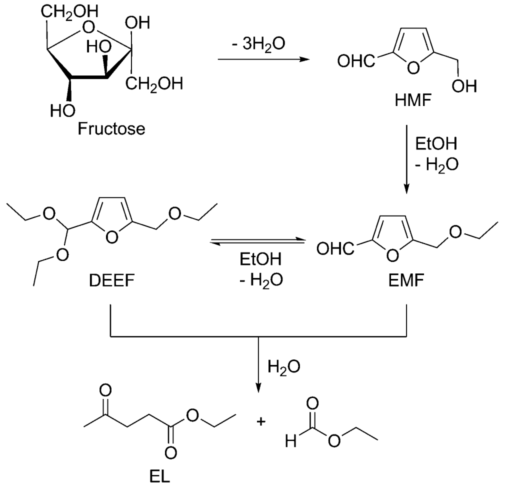


Fig. 4 GC analysis of EL formation (*Reaction conditions*: fructose, 50 mg, 0.28 mmol; $[\mathbf{3}\cdot 2H]_3[PW_{12}O_{40}]_2$, 50 mg, 5.0 mol%; ethanol, 4 mL; 120 °C).



Scheme 3 Plausible pathway for the formation of EL from fructose.

In principle, our reported results seemed to agree with the mechanism of fructose alcoholysis proposed by Riisager and co-workers with sulfonic acid-functionalized ILs as catalysts.[23] According to the literature, a plausible major pathway for EL formation involves a fructose-to-HMF transformation followed by HMF etherification and rehydration of HMF-ether to give EL (Scheme 3). Moreover, in our case, EMF was seen to be in a reversible equilibrium with DEEF *via* acetalisation, the rehydration of DFFE was presumably another minor pathway to form EL (Fig. 4 and Scheme 3). When xylose and furfural were subjected to the reaction conditions, the expected product EL was unobserved. However, EL was quantitatively obtained with furfuryl alcohol or HMF as starting materials, respectively. These results thus further indicate that the etherification step of HMF to EMF plays a key role for EL formation.

Fig. 5 shows the influences of temperature and time on the conversion of the fructose into EL in the presence of ethanol with $[3\cdot2H]_3[PW_{12}O_{40}]_2$ as solid catalyst. The conversion of fructose increased with time at all temperatures investigated (Fig. 5a). Moreover, with a fixed reaction time point, the fructose conversion increased as the temperature increased. The conversion of fructose increased slowly to 97% after 24 h at 80 °C, while it increased quickly to 99% after 1 h at 140 °C.

As shown in Scheme 3, both HMF and EMF are "intermediates" to the final product EL, the influences on both the formation and consumption of HMF (Fig. 5b) and EMF (Fig. 5c) were observed as well during the conversion of the fructose into EL. Generally, the HMF yields increased as the temperature increased with a maximum of 74% at 120 °C (Fig. 5b). A further increased temperature to 140 °C, however, led to a slightly reduced HMF yield to 58%, indicating acid catalyzed HMF degradation under higher reaction temperature. The reaction times for maximum yields of "intermediate" HMF are different, based on the different reaction temperatures; that is, the higher the temperature is, the shorter the reaction time needs to be. At the higher temperature of 120 °C, the yields of HMF reach maximum values of 74% in 5 min. The HMF yields decrease to 33% at 100 °C in the same time and reach a maximum of 64% in

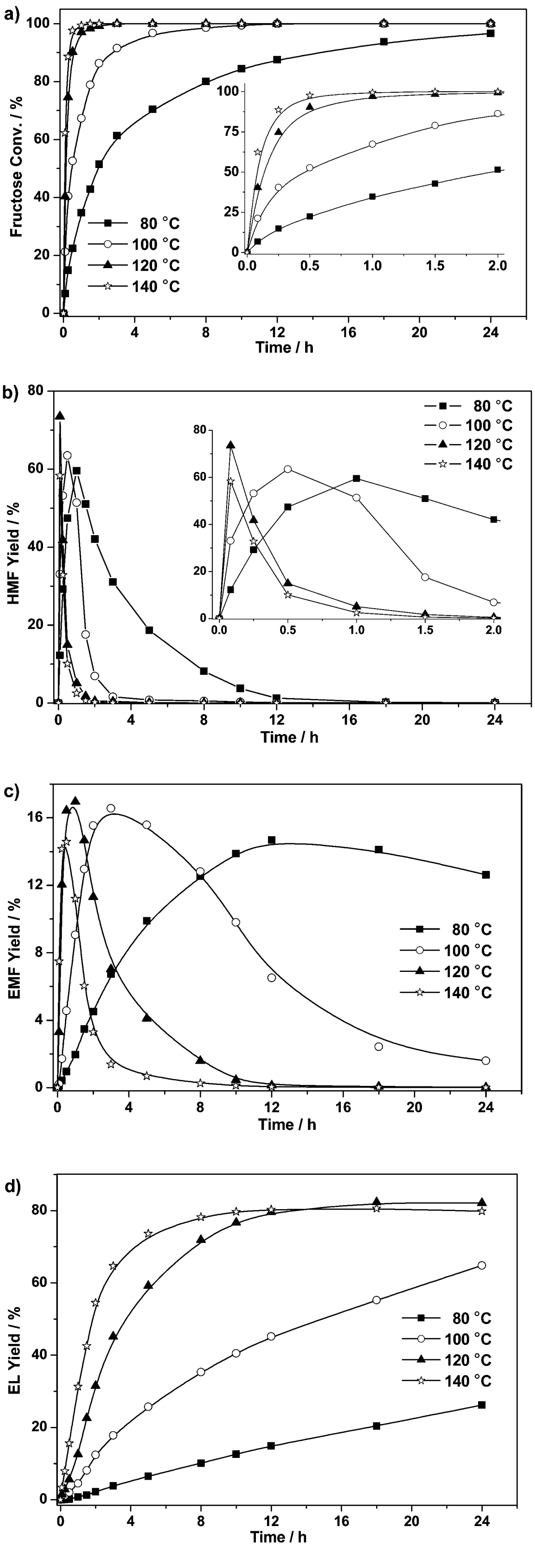


Fig. 5 Influence of the reaction temperature and time on fructose conversion into EL. (a) The conversion of fructose, (b) the yield of HMF, (c) the yield of EMF, (d) the yield of EL. (*Reaction conditions*: fructose, 50 mg, 0.28 mmol; $[3\cdot2H]_3[PW_{12}O_{40}]_2$, 50 mg, 5.0 mol%; ethanol, 4 mL; specified temperature).

30 min. For a reaction temperature of 80 °C, the reaction time was much longer to 60 min as the yields of HMF reach maximum values.

The effect of the reaction temperature on EMF is similar to that of HMF (Fig. 5c). With the HMF as the "intermediate" for the subsequently generated EMF, the reaction time was, however, much longer as the yields of EMF reach maximum values than that of HMF. For example, the yields of HMF reach maximum values of 74% in 5 min at 120 °C. After 60 min, the second transformation of the HMF to EMF reaches a maximum yield of EMF at 17%.

In the case of final production EL, as discussed in Scheme 3, the one-pot conversion of fructose with ethanol requires the formation of HMF firstly and EMF secondly, which then was converted into the final product EL. When the reaction was carried out at 80 °C, the rate for the EL formation was rather slow (Fig. 5d). Even with a prolonged reaction time, we only obtained EL in a low yield of 26% within 24 h. Moreover, EMF remained unchanged at 80 °C within 24 h under the investigated conditions (Fig. 5c), indicating that the EMF-to-EL transformation was difficult at 80 °C. When the reaction temperature was elevated to 100 °C, both the EMF conversion (Fig. 5c) and the EL yield (Fig. 5d) enhanced significantly. In comparison with the reaction at 80 °C, the yield of EL within 24 h increased sharply, from 26% to 65%. When the reaction temperature was further increased to 120 °C, its influence was much more obvious. As shown in Fig. 5c and d, intermediate EMF was almost completely converted into the product EL in a yield of 80% within just 12 h at 120 °C. A further increased temperature to 140 °C led to a reduced reaction time to 10 h to reach a full conversion of EMF with the EL yield of 80%. Fig. 5d further reveals higher EL yields at 120 °C after 13.5 h than in the case of 140 °C, presumably owing to an acid catalyzed EL degradation under higher reaction temperature as a prolonged reaction time. The above results demonstrated that the optimal reaction temperature for the one-pot fructose conversion into EL was 120 °C with a maximum EL yield of 82% and an optimal reaction time of 18 h.

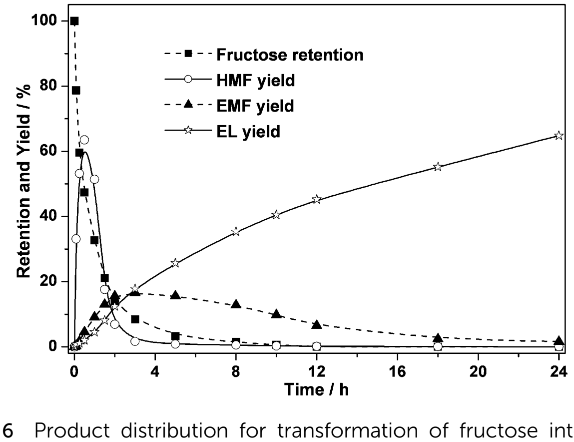


Fig. 6 Product distribution for transformation of fructose into EL. (*Reaction conditions*: fructose, 50 mg, 0.28 mmol; [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$, 50 mg, 5.0 mol% relative to fructose; ethanol, 4 mL; 100 °C).

Fig. 6 shows a typical reaction profile obtained using [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$ for the catalytic transformation of the fructose to EL at 100 °C, which further reveals the influences of reaction time on EL formation. Fructose is immediately converted to HMF. The yield of HMF has a maximum value of 64% after 30 min. After 3 hours, the second transformation of the HMF to EMF reaches a maximum yield of 17%. After this time, the yield of EMF decreases with the concomitant production of EL. Therefore, the yield trends of both HMF and EMF increase first, and then decrease with reaction time. However, both the fructose conversions and EL yields increase as the reaction time. These results further suggest that the conversion of fructose to EL is going stepwise with observed HMF and EMF as the "intermediates".

Conversion of other feedstocks to HMF and EL

Besides fructose, the [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$ catalyst was further extended to fructose based di- and polysaccharides such as sucrose and inulin, and the results of HMF and EL formations are presented in Table 4. Both sucrose and inulin are the most abundant and renewable saccharides. When inulin was used, the HMF yield reached 76%, which is higher than the HMF yield of 48% obtained from sucrose (Table 4, Runs 1–2). According to the literature, one molecule of inulin contains one molecule of glucose and 1–59 molecules of fructose; whereas, one molecule of sucrose is composed of one molecule of glucose and one molecule of fructose.[38,39] Thus much higher HMF yield was obtained from inulin. These results further indicate that [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$ effectively promotes the hydrolysis of sucrose and inulin under mild conditions. When glucose, cellobiose, and α-cellulose were subjected to our reaction conditions, the HMF yield was remarkably inferior (Table 4, Runs 3–5). This result clearly indicates that only fructose in sucrose and inulin was converted to HMF, and [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$, functions as Brønsted acid, can hardly promotes the isomerization of glucose to fructose.

In the case of EL production, the catalyst [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$ yielded EL of 67% from inulin (Table 4, Run 6), 45% from

Table 4 Conversion of other feedstocks to HMF[a] and EL[b] catalyzed by [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$

Run	Substrate	*T* [°C]	*t* [h]	Yield [%]
1[a]	Inulin	120	2	76
2	Sucrose	120	2	48
3	Glucose	120	2	18
4	Cellobiose	150	2	30
5	α-Cellulose	150	2	10
6[b]	Inulin	120	12	67
7	Sucrose	120	12	45
8	glucose	120	24	7
9	Glucose	150	24	20
10	Cellobiose	150	24	18
11	α-Cellulose	150	24	14

[a] *Reaction conditions*: HMF production (Run 1–5), substrate (50 mg), [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$, (25 mg), DMSO (1 mL). [b] EL production (Run 6–11), substrate (50 mg), [**3**·2H]$_3$[PW$_{12}$O$_{40}$]$_2$ (50 mg), ethanol (4 mL).

sucrose (Table 4, Run 7), and only 7% from glucose (Table 4, Run 8), respectively. Even under the conditions of increased reaction temperature and prolonged reaction time, the EL yield, obtained from glucose, cellobiose, and α-cellulose, were still remarkable inferior (Table 4, Runs 9–11). Both sucrose and inulin can be readily obtained from biomass such as sugarcane sugarbeet, chicory, and cassava. For these reason, this process is an economically viable and environmentally attractive route to produce HMF and EL as sustainable chemicals using renewable biomass as the raw material in one-pot reaction under reasonably mild reaction conditions.

Conclusions

In conclusion, IL-POMs are prominent solid acid catalysts for one-pot conversion of fructose into HMF and alkyl levulinate. The catalytic activities of IL-POMs for fructose dehydration to HMF as well as fructose alcoholysis to EL followed the order of their acid strength. A major pathway for EL formation involves a fructose-to-HMF transformation followed by HMF etherification and rehydration of HMF-ether to give EL. After the reaction, the catalyst can easily be separated from the reaction mixture for reuse. Moreover, the developed method herein provides a catalytic process for converting abundant, cheap and renewable di- and polysaccharide such as sucrose and inulin to biomass-based fine chemicals HMF and EL using recoverable and cheap IL-POMs as catalysts. In addition, these processes eliminate the need to obtain simple monosaccharide molecules by acid hydrolysis as a separate processing step. Therefore, solid acids IL-POMs are a step toward the more economical production of HMF and EL through the processing of inexpensive, abundantly available and renewable biomass feedstocks.

Acknowledgements

This work was supported by National Natural Science Foundation of China (21172219 and 21207039), National Basic Research Program of China (973 Program, 2012CB215304), Scientific Research Foundation for the Returned Overseas Chinese Scholars (State Education Ministry), and Guangdong Natural Science Foundation (S2013010012986 and S2011010002274).

Notes and references

1 P. Gallezot, *Chem. Soc. Rev.*, 2012, **41**, 1538–1558.

2 A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411–2502.

3 G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044–4098.

4 A. A. Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, *Green Chem.*, 2011, **13**, 754–793.

5 R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres and J. G. de Vries, *Chem. Rev.*, 2013, **113**, 1499–1597.

6 J. Zhang, S. B. Wu, B. Li and H. D. Zhang, *ChemCatChem*, 2012, **4**, 1230–1237.

7 A. Ranoux, K. Djanashvili, I. W. C. E. Arends and U. Hanefeld, *ACS Catal.*, 2013, **3**, 760–763.

8 R. L. Liu, J. Z. Chen, X. Huang, L. M. Chen, L. L. Ma and X. J. Li, *Green Chem.*, 2013, **15**, 2895–2903.

9 Y. Román-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933–1937.

10 F. S. Asghari and H. Yoshida, *Ind. Eng. Chem. Res.*, 2006, **45**, 2163–2173.

11 (*a*) Z.-Z. Yang, J. Deng, T. Pan, Q.-X. Guo and Y. Fu, *Green Chem.*, 2012, **14**, 2986–2989; (*b*) K.-I. Shimizu, R. Uozumi and A. Satsuma, *Catal. Commun.*, 2009, **10**, 1849–1853; (*c*) J. N. Chheda and J. A. Dumesic, *Catal. Today*, 2007, **123**, 59–70; (*d*) X. H. Qi, M. Watanabe, T. M. Aida and R. L. Smith, Jr, *Green Chem.*, 2008, **10**, 799–805.

12 M. Watanabe, Y. Aizawa, T. Iida, R. Nishimura and H. Inomata, *Appl. Catal., A*, 2005, **295**, 150–156.

13 Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982–985.

14 V. V. Ordomsky, J. van der Schaaf, J. C. Schouten and T. A. Nijhuis, *J. Catal.*, 2012, **287**, 68–75.

15 F. W. Lichtenthaler, *Acc. Chem. Res.*, 2002, **35**, 728–737.

16 (*a*) D. A. Kotadia and S. S. Soni, *Catal. Sci. Technol.*, 2013, **3**, 469–474; (*b*) H. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, **316**, 1597–1600; (*c*) T. Ståhlberg, W. J. Fu, J. M. Woodley and A. Riisager, *ChemSusChem*, 2011, **4**, 451–458; (*d*) T. Okano, K. Qiao, Q. X. Bao, D. Tomida, H. Hagiwara and C. Yokoyama, *Appl. Catal., A*, 2013, **451**, 1–5.

17 A. Lee, N. Chaibakhsh, M. B. A. Rahman, M. Basri and B. A. Tejo, *Ind. Crops Prod.*, 2010, **32**, 246–251.

18 A. Demirbas, *Appl. Energy*, 2011, **88**, 17–28.

19 F. Su, L. Ma, D. Y. Song, X. H. Zhang and Y. H. Guo, *Green Chem.*, 2013, **15**, 885–890.

20 G. M. G. Maldonado, R. S. Assary, J. A. Dumesic and L. A. Curtiss, *Energy Environ. Sci.*, 2012, **5**, 8990–8997.

21 Z. H. Zhang, K. Dong and Z. B. Zhao, *ChemSusChem*, 2011, **4**, 112–118.

22 J.-P. Lange, W. D. van de Graaf and R. J. Haan, *ChemSusChem*, 2009, **2**, 437–441.

23 S. Saravanamurugan, O. N. Van Buu and A. Riisager, *ChemSusChem*, 2011, **4**, 723–726.

24 S. Saravanamurugan and A. Riisager, *Catal. Commun.*, 2012, **17**, 71–75.

25 L. C. Peng, L. Lin, J. H. Zhang, J. B. Shi and S. J. Liu, *Appl. Catal., A*, 2011, **397**, 259–265.

26 L. C. Peng, L. Lin, H. Li and Q. L. Yang, *Appl. Energy*, 2011, **88**, 4590–4596.

27 K.-I. Tominaga, A. Mori, Y. Fukushima, S. Shimada and K. Sato, *Green Chem.*, 2011, **13**, 810–812.

28 Y. Leng, J. Wang, D. R. Zhu, X. Q. Ren, H. Q. Ge and L. Shen, *Angew. Chem., Int. Ed.*, 2008, **48**, 168–171.

29 R. Kreiter, M. D. A. Rietkerk, H. L. Castricum, H. M. van Veen, J. E. ten Elshof and J. F. Vente, *ChemSusChem*, 2009, **2**, 158–160.

30 (*a*) Z. Sun, M. X. Cheng, H. C. Li, T. Shi, M. J. Yuan, X. H. Wang and Z. J. Jiang, *RSC Adv.*, 2012, **2**, 9058–9065; (*b*) K. X. Li, L. Chen, H. L. Wang, W. B. Lin and Z. C. Yan,

Appl. Catal., A, 2011, **392**, 233–237; (*c*) M. J. dos Reis, V. Prévot, F. Leroux, F. Silvério and J. B. Valim, *J. Porous Mater.*, 2010, **17**, 443–451.

31 (*a*) X. H. Qi, H. X. Guo, L. Y. Li and R. L. Smith Jr, *ChemSusChem*, 2012, **5**, 2215–2220; (*b*) K.-I. Shimizu, R. Uozumi and A. Satsuma, *Catal. Commun.*, 2009, **10**, 1849–1853.

32 (*a*) I. V. Kozhevnikov, *Appl. Catal., A*, 2003, **256**, 3–18; (*b*) M. N. Timofeeva, *Appl. Catal., A*, 2003, **256**, 19–35.

33 J. N. Chheda, Y. Román-Leshkov and J. A. Dumesic, *Green Chem.*, 2007, **9**, 342–350.

34 (*a*) F. W. Lichtenthaler and S. Röninger, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1489–1497; (*b*) Z. Huang, W. Pan, H. Zhou, F. Qin, H. Xu and W. Shen, *ChemSusChem*, 2013, **6**, 1063–1069.

35 Y. M. Zhang, V. Degirmenci, C. Li and E. J. M. Hensen, *ChemSusChem*, 2011, **4**, 59–64.

36 C. Y. Fan, H. Y. Guan, H. Zhang, J. H. Wang, S. T. Wang and X. H. Wang, *Biomass Bioenergy*, 2011, **35**, 2659–2665.

37 J. Z. Chen, S. P. Wang, J. Huang, L. M. Chen, L. L. Ma and X. Huang, *ChemSusChem*, 2013, **6**, 1545–1555.

38 S. Sirisansaneeyakul, N. Worawuthiyanan, W. Vanichsriratana, P. Srinophakun and Y. Chisti, *World J. Microbiol. Biotechnol.*, 2007, **23**, 543–552.

39 Y. Yang, M. M. Abu-Omar and C. W. Hua, *Appl. Energy*, 2012, **99**, 80–84.