ARTICLES

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# Efficient dehydration of carbohydrates to 5-hydroxymethylfurfural in ionic liquids catalyzed by tin(IV) phosphonate and zirconium phosphonate

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In this work, we synthesized tin(IV) phosphonate (SnBPMA) and zirconium phosphonate (ZrBPMA) by the reaction of SnCl<sub>4</sub>·5H<sub>2</sub>O or ZrOCl<sub>2</sub>·8H<sub>2</sub>O with *N*,*N*-bis(phosphonomethyl)aminoacetic acid, which was synthesized from a biomaterial glycine through a Mannich-type reaction. The SnBPMA and ZrBPMA were very efficient heterogeneous catalysts for the dehydration of fructose to produce 5-hydroxymethylfurfural (HMF), and the SnBPMA had higher activity than the ZrBPMA. The effects of solvents, temperature, reaction time, and reactant/solvent weight ratio on the reaction catalyzed by SnBPMA were investigated. It was demonstrated that the yield of HMF could reach 86.5% with 1-ethyl-3-methylimidazolium bromide ([Emim]Br) as solvent, and the SnBPMA and SnBPMA/[Emim]Br catalytic system could be reused five times without considerable reduction in catalytic efficiency. Further study indicated that the SnBPMA and ZrBPMA in [Emim]Br were also effective for the dehydration of sucrose and inulin to produce HMF with satisfactory yields.

fructose, inulin, sucrose, dehydration, 5-hydroxymethylfurfural, heterogeneous catalysts

# 1 Introduction

In recent years, transformation of biomass into liquid fuels and valuable intermediates has received much attention [1–7]. Among the processes of biomass conversion, dehydration of carbohydrates to produce 5-hydroxymethylfurfural (HMF) is one of the most important routes because HMF is considered to be a platform molecule for the production of high value chemicals and biofuels [8, 9].

Up to now, many efforts have been devoted to the dehydration of carbohydrates to produce HMF efficiently. Various catalysts, including homogeneous and heterogeneous catalysts, have been developed for the dehydration reactions. Homogeneous catalysts include Lewis acids [10–12], boric acid [13, 14], heteropoly acids [15, 16], ionic liquids (ILs) [17, 18], and so on. Some heterogeneous catalysts have also been used for the dehydration of carbohydrates, such as mesoporous niobium phosphate [19], cellulose-derived amorphous carbon [20, 21] and ionic liquids supported on silica nanoparticles [22], etc. In general, the homogeneous catalysts are more effective, but the separation of the catalysts from the reaction mixture is difficult. The heterogeneous catalysts are more easily recovered, but the efficiency is usually lower.

Recently, mesoporous metal phosphonate hybrid materials have attracted much interest because they can be used in adsorption, separation, solar light utilization and catalysts [23, 24]. In addition, organics with different functional groups can be introduced into the metal phosphonates structure by introducing desired organic compounds into a phosphonic acid. Among various applications, using meso-

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porous phosphonate materials as catalysts is very attractive. Many reactions have been conducted using metal phosphonates as the catalysts or the supports, such as synthesis of adipic acid [25], methanolysis of sunflower oil [26], biodiesel synthesis [27], etc.

As discussed above, many catalysts have been developed for the dehydration reaction of carbohydrates to produce HMF. However, it is still highly desirable to develop efficient and cheap heterogeneous catalysts for producing HMF from carbohydrates. In this work, we synthesized SnBPMA and ZrBPMA using *N*,*N*-bis(phosphonomethyl)aminoacetic acid (H<sub>5</sub>BPMA) synthesized from Mannich-type reaction of glycine, which is a biomaterial (Scheme 1) [28, 29]. It was found that SnBPMA and ZrBPMA were very active, selective, and stable for the dehydration reactions of some carbohydrates to produce HMF and could be easily recovered and reused.



Scheme 1 Mannich-type reaction for synthesis of *N*,*N*-bis(phosphon-omethyl)aminoacetic acid from glycine.

# 2 Experimental Section

# 2.1 Materials

Fructose, sucrose, inulin, and phosphorous acid were all A.R. grade and were purchased from Alfa Aesar. Glycine, formaldehyde (37%-40% water solution), hydrochloric acid (38% water solution), ZrOCl<sub>2</sub>·8H<sub>2</sub>O, SnCl<sub>4</sub>·5H<sub>2</sub>O, dimethylacetamide (DMA) and dimethylsulfoxide (DMSO) were A.R. grade and were obtained from Beijing Chemical Reagent Company. The ionic liquids 1-ethyl-3-methylimidazo-lium bromide ([Emim]Br) and 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF<sub>4</sub>) were provided by Lanzhou Greenchem ILS, LICP, CAS, China, and their purity was > 99%. All chemicals were used as received.

#### 2.2 Catalyst characterization

FT-IR spectra were recorded on Bruker Tensor 27 IR spectrometer and the sample was prepared by the KBr pellet method. Scanning electron microscopy (SEM) images were taken using a Hitachi S-4300 instrument (Japan) operated at 15 kV. The BET surface area measurement and pore analysis were carried out by N<sub>2</sub> adsorption at 77 K with Micromeritics ASAP 2020 V3.00 H (USA) surface area analyser. X-ray diffraction (XRD) measurements were conducted on an X-ray diffractometer (D/MAX-RC, Japan) operated at 40 kV and 200 mA with Cu K $\alpha$  ( $\lambda$  = 0.154 nm) radiation. XPS measurements were carried out on an ESCAL Lab 220i-XL specrometer at a pressure of ~3 × 10<sup>-9</sup>

mbar using Al K $\alpha$  as the excitation source (hv = 1486.6 eV) and operated at 15 kV and 20 mA.

#### 2.3 Analysis methods for the product

The amount of HMF was analyzed by HPLC with Supelcosil LC-18 5im column, Shimadzu LC-15C pump, Shimadzu UV-Vis SPD-15C detector at 282 nm. Before analyzed, the reaction mixture was diluted to 1000 mL. Methanol/water solution (50/50, v/v) was used as the mobile phase at a flow rate of 0.8 mL/min.

#### 2.4 Catalyst synthesis

# *N*,*N*-*Bis*(phosphonomethyl)aminoacetic acid [(H<sub>2</sub>O<sub>3</sub>PCH<sub>2</sub>)<sub>2</sub>-*N*CH<sub>2</sub>CO<sub>2</sub>H] (H<sub>5</sub>BPMA)

The H<sub>3</sub>BPMA with a functional carboxylate group was prepared by a Mannich-type reaction (Scheme 1). In the reaction, glycine (15.2 g, 0.2 mol) was mixed with hydrochloric acid (50 mL), deionized water (50 mL) and phosphorous acid (65.6 g, 0.8 mol) in a flask of 500 mL. The mixture was allowed to reflux at 120 °C for 1 h, then formaldehyde (100 g) was added over a period of 1h, and the mixture was then refluxed for other three hours. The water was removed under reduced pressure to get a white powder, which was dissolved in water (20 mL) and recrystallized by adding acetone (500 mL). The H<sub>5</sub>BPMA was collected by filtration and washed using acetone and dried at room temperature.

Preparation of  $Zr[(O_3PCH_2)_2NCH_2CO_2H]$  (ZrBPMA) and  $Sn[(O_3PCH_2)_2NCH_2CO_2H]$  (SnBPMA)

 $H_3BPMA$  (5.26 g, 20 mmol) was dissolved in  $H_2O$  (300 mL) at room temperature with stirring, then ZrOCl<sub>2</sub>·8H<sub>2</sub>O (6.44 g, 20 mmol) or SnCl<sub>4</sub>·5H<sub>2</sub>O (7.0 g, 20 mmol) was added to this solution. Immediately white precipitate was formed and the reaction mixture was stirred for three days. The white precipitate was separated by filtration, thoroughly washed with  $H_2O$ , ethanol, ethyl ether and dried at 80 °C under vacuum for 12 h.

# 2.5 Catalytic reaction

# Conversion of carbohydrates into HMF

In a typical experiment, known amounts of carbohydrate, catalyst, and solvent were loaded into a flask of 10 mL sealed with a glass stopper. The reaction mixture was stirred at a fixed temperature for desired time. Then the mixture was cooled to room temperature immediately. The samples were analyzed by HPLC to obtain the yields. Each reaction was repeated at least two times. In the experiments to test the reusability of catalyst SnBPMA, 5 mL of water was added into the reaction system after the reaction. Then the catalyst was recovered by centrifugation, washed with water, ethanol and ethyl ether. After dried under vacuum for 12 h at 60 °C, the catalyst was reused for the next run by adding new carbohydrates. In the experiments to test the reusability

of SnBPMA/[Emim]Br catalytic system, 1 mL of water was added into the reaction system after the reaction. Then the mixture was extracted with ether ( $4 \times 50$  mL) to remove the HMF produced. After extraction, the water in the SnBP-MA/[Emim]Br mixture was removed under reduced pressure at 80 °C, and the SnBPMA/[Emim]Br mixture was then used directly for the next run by adding new carbohydrates.

# Calculation of 5-HMF yield.

The yield of 5-HMF was calculated by the following equation: 5-HMF yield (mol%) =  $\frac{\text{Moles of 5-HMF formed}}{\text{Moles of carbohydrate used}} \times 100\%$ 

# 3 Results and Discussion

# 3.1 Catalyst characterization

The FT-IR spectra of the SnBPMA and ZrBPMA are

presented in Figure 1(a) and 1(b), respectively. The broad band at 3400 cm<sup>-1</sup> corresponds to the surface-adsorbed water. For the SnBPMA in Figure 1(a), the bands at 1170 and 1032 cm<sup>-1</sup> are attributed to weak P–C stretching vibrations and P–O bending vibration, respectively. The peak at 1687 cm<sup>-1</sup> is assigned to the COOH group. For the ZrBPMA in Figure 1(b), the band at 1043 cm<sup>-1</sup> is the P–O bending vibration. Meanwhile, the band of the COOH group at 1641 cm<sup>-1</sup> is also observed in the ZrBPMA spectrum.

The scanning electron microscopy (SEM) was used to characterize the SnBPMA and ZrBPMA. It can be known from the SEM images shown in Figure 2 that the materials were featureless with a size of submicron.

The power XRD patterns of the SnBPMA and ZrBPMA are shown in Figure 3. It can be known that the catalysts had no X-ray crystal structures. Meanwhile, each XRD pattern showed one broad diffraction peak, which indicated amorphous framework walls of the obtained materials.



Figure 1 The FT-IR spectra of the SnBPMA (a) and ZrBPMA (b).





Figure 2 The SEM images of the SnBPMA (a) and ZrBPMA (b).



Figure 3 The Powder X-ray diffraction patterns of the SnBPMA (a) and ZrBPMA (b).

XPS spectra were also taken to investigate the chemical state of the SnBPMA and ZrBPMA (Figure 4). For SnBP-MA, the Sn 3d signal of SnBPMA is composed of two single peaks located at 487.5 eV for Sn 3d<sub>5/2</sub> and 496.5 eV for Sn  $3d_{3/2}$ , which are characteristic of Sn<sup>4+</sup>. The binding energy of P 2p at 134.0 eV is characteristic of P<sup>5+</sup>. The broad C 1s line might be fitted by three components situated at the binding energies of 284.8 eV, 286.8 eV and 288.7 eV, which may correspond to the C species of C-H or C-C, C-N or C-P and COOH bonds, respectively. For ZrBPMA, the Zr 3d signal of ZrBPMA is composed of two single peaks located at 182.4 eV for Zr 3d<sub>5/2</sub> and 184.7 eV for Zr  $3d_{3/2}$ , which are characteristic of  $Zr^{4+}$ . The binding energy of P 2p at 132.5 eV is characteristic of  $P^{5+}$ . The broad C 1s line might be fitted by three components situated at the binding energies of 284.8 eV, 286.5 eV and 288.5 eV, which may correspond to the C species of C-H or C-C, C-N or C-P and COOH bonds, respectively.

The textural parameters of the SnBPMA and ZrBPMA obtained from  $N_2$  adsorption/desorption isotherms are presented in Table 1. The results indicate that the SnBPMA synthesized was porous with an average pore diameter of 24.2 nm. The SnBPMA exhibited a BET surface area of 34.0 m<sup>2</sup>/g with a pore volume of 0.21 cm<sup>3</sup>/g. Meanwhile, ZrBPMA is also porous with an average pore diameter of 18.0 nm and it exhibited a BET surface area of 85.8 m<sup>2</sup>/g with a pore volume of 0.37 cm<sup>3</sup>/g.

# 3.2 Activity of the catalysts in [Emim]Br

The activity of various catalysts for the dehydration of fructose (Scheme 2) was tested at 373 K in [Emim]Br, and the results are summarized in Table 2. Although the dehydration reaction could be proceeded without catalysts in [Emim]Br, the yield of HMF was very low (Entry 1). According to the experimental data, the two heterogeneous



Figure 4 The XPS spectra of Sn 3d (a), P 2p (b), C 1s (c) regions of the SnBPMA and Zr 3d (d), P 2p (e), C 1s (f) regions of the ZrBPMA.

Table 1 The surface area, pore volume and average pore diameter of the materials

Sample <sup>a)</sup>	BET surface area <sup>b)</sup> (m <sup>2</sup> /g)	Pore volume <sup>c)</sup> (cm <sup>3</sup> /g)	Pore diameter <sup>c)</sup> (nm)
SnBPMA	34.0	0.21	24.2
ZrBPMA	85.8	0.37	18.0

a) The sample was degassed at 100 °C for 12 h; b) surface area based on multipoint BET method; c) pore volume and pore diameter based on BJH method.



Scheme 2 Dehydration of fructose to produce HMF.

Table 2 Dehydration of fructose catalyzed by various catalysts <sup>a)</sup>

Entry	Catalyst	Conversion (%)	Yield (%)
1	None	26	19.1
2	SnCl <sub>4</sub> ·5H <sub>2</sub> O	98	76.4
3	ZrOCl <sub>2</sub> ·8H <sub>2</sub> O	99	82.3
4	ZrBPMA	90	70.0
5	SnBPMA	93	83.3

a) Reaction conditions: 0.1 g fructose, 25 mg catalyst, 1 g [Emim]Br, reaction time 1 h, reaction temperature 373 K.

catalysts (ZrBPMA and SnBPMA) had similar catalytic activity with the homogeneous lewis acid catalysts (SnCl<sub>4</sub>·5H<sub>2</sub>O and ZrOCl<sub>2</sub>·8H<sub>2</sub>O) and the SnBPMA had a higher activity than ZrBPMA under the same condition. According to the results of Wang *et al.* [19], both the Lewis and Brönsted acid sites in the phosphate salts can promote the dehydration of fructose to HMF. The high catalytic activity of the ZrBPMA and SnBPMA was due to the Brönsted acid group COOH and Lewis acid nature of Sn<sup>4+</sup> and Zr<sup>4+</sup>, which coexisted in the heterogeneous catalysts. Further more, we chose SnBPMA as catalyst to study the effects of various conditions on the reaction, and the results are discussed in the following.

#### 3.3 Effect of solvents

Several commonly used solvents were chose to investigate the solvent effects on the reaction using the SnBPMA as the catalyst and the results are shown in Figure 5. The reaction did not occur when water was used as the reaction solvent. While in dimethylacetamide (DMA) and dimethylsulfoxide (DMSO), the yields of HMF were 0.8% and 19.1%, respectively. We also studied the reaction in different ionic liquids [Emim]BF<sub>4</sub> and [Emim]Br. It can be known from Figure 5 that a HMF yield of 83.3% was achieved in [Emim]Br while the yield is 4.3% in [Emim]BF<sub>4</sub>. Compared with SnCl<sub>4</sub> in [Emim]BF<sub>4</sub> [11], SnBPMA in [Emim]BF<sub>4</sub> was less efficient because the structures of SnBPMA and SnCl<sub>4</sub> are different, and they showed different performances in the same IL. The [Emim]Br may interact with fructose and the intermediates through hydrogen bonding and show nucleophilic effect to activate fructose and stabilize intermediates, which is favorable to producing HMF [30, 31]. This could be the main reason that the best reaction activity and selectivity was achieved in [Emim]Br.

### **3.4 Influence of reaction temperature and time**

Figure 6 shows the effect of reaction temperature on the dehydration of fructose to produce HMF in [Emim]Br catalyzed by SnBPMA at 353 K and 373 K. It can be seen that the yield at 373 K was higher than at 353 K because the dehydration reaction was accelerated by increasing temperature, which was favorable to achieving higher yield in a short reaction time.

When the reaction was conducted at 373 K, the yield increased dramatically with time at the beginning, and reached the maximum (86.5%) at 1.5 hours with a fructose conversion of 98%. Then the yield decreased slightly with prolonged time, which may be due to the rehydration of the HMF produced. When the reaction was 353 K, the reaction reached equilibrium at 3 hours with the yield of 83.0% and a fructose conversion of 99%.

# 3.5 Influence of substrate/solvent weight ratio

The dependence of HMF yield on the fructose/[Emim]Br weight ratio was also investigated and the results are demonstrated in Figure 7. In the experiment, the weight ratio of substrate to the catalyst was fixed at 4. When the fructose/[Emim]Br weight ratio was increased from 0.05:1



**Figure 5** Effect of different solvents on the yield of HMF. Reaction conditions: 0.1 g fructose, 25 mg SnBPMA, 1 g solvent, reaction temperature 373 K, reaction time 1 h.



Figure 6 Influence of reaction temperature and reaction time on the reaction. Reaction conditions: 0.1 g fructose, 25 mg SnBPMA, 1 g [Em-im]Br.

to 0.1:1, the HMF yield increased slightly from 82.9% to 86.5%. As the fructose/[Emim]Br weight ratio increased from 0.1:1 to 0.15:1, the HMF yield was independent of the ratio. However, when the fructose/[Emim]Br weight ratio increased from 0.15:1 to 0.3:1, the HMF yield decreased substantially to 69.7%. Therefore, the suitable fructose/[Emim]Br weight ratio for our catalytic system was from 0.1:1 to 0.15:1.

#### 3.6 Reusability of catalyst

The reusability of SnBPMA and SnBPMA/[Emim]Br catalyst system was studied in this work and the results are presented in Table 3. Obviously, the decrease of the activity of SnBPMA was not considerable after reused five times. In the reusing, the activity decrease of the catalyst/[Emim]Br system was less than that the catalyst, which may be due to less loss of the catalyst in the separation process when the SnBPMA/[Emim]Br system was reused. The SnBPMA recovered from SnBPMA/[Emim]Br system after reused five times was also characterized by FT-IR, XPS, XRD and SEM, and the results are shown in Figure 8. It can be known by comparing Figures 1–4 and 8 that the properties of the SnBPMA were not changed after reused, which is consistent



**Figure 7** Influence of fructose/[Emim]Br weight ratio on the yield of HMF. Reaction conditions: reaction temperature 373 K, reaction time 1.5 h.

Table 3 The reusability of the SnBPMA and SnBPMA/[Emim]Br system a)

Run	Yield (%)		
	SnBPMA	SnBPMA/[Emim]Br system	
1	84.0	84.0	
2	82.0	83.1	
3	79.3	82.6	
4	79.5	82.3	
5	78.8	82.9	

a) Reaction conditions: 0.5 g fructose, 125 mg catalyst, 5 g [Emim]Br, reaction time 1.5 h, reaction temperature 373 K.



Figure 8 The characterization of the catalyst SnBPMA after reused five times. (a) FT-IR, (b) XPS Sn 3d, (c) XPS P 2p, (d) XPS C 1s, (e) XRD and (f) SEM.

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with that fact that the yields of the products in different runs were nearly unchanged, as shown in Table 3.

# 3.7 Dehydration of other carbohydrates

The SnBPMA/[Emim]Br catalytic system was also used to catalyze the dehydration of other carbohydrates, and the results are illustrated in Figure 9. As expected, the sucrose and inulin with fructose unit in the molecular structures gave moderate HMF yield of 45.3% and 48.8%, respectively. When the yields of HMF reached maximum, the conversions of sucrose and inulin were 99% and 97%, respectively. Reaction times for reaching the maximum HMF yield from sucrose and inulin were 2 hours and 3 hours, respectively.

# 3.8 Comparison of catalytic activity between SnBPMA and ZrBPMA

The activity of the catalysts for different carbohydrates was studied under the same reaction conditions and the results are shown in Table 4. It can be concluded that catalysts were active for all the carbohydrates tested, and the SnBPMA had higher activity than ZrBPMA.

# 4 Conclusions

In summary, porous SnBPMA and ZrBPMA have been synthesized and used as the heterogeneous catalysts for dehydration of some carbohydrates to produce HMF using



**Figure 9** Dehydration of different carbohydrates. Reaction conditions: 0.1 g carbohydrates, 25 mg SnBPMA, 1 g [Emim]Br, reaction temperature 373 K.

**Table 4** The catalytic activities of the SnBPMA and ZrBPMA for different carbohydrates  $^{a)}$ 

Entry	Substrate	Time T (h)	Temperature	Yield (%)	
			(K)	SnBPMA	ZrBPMA
1	Fructose	3	353	83.0	54.2
2	Fructose	1.5	373	86.5	78.1
3	Inulin	3	373	48.7	42.1
4	Sucrose	3	373	45.3	40.1

a) Reaction conditions: 0.1 g substrate, 25 mg catalyst, 1 g [Emim]Br.

[Emim]Br as the solvent. High yield of 86.5% has been achieved from dehydration of fructose in [Emim]Br catalyzed by the SnBPMA. The SnBPMA and SnBPMA/ [Emim]Br catalytic system can be reused five times without considerable reduction in the reaction activity and selectivity. In addition, the catalysts can also be used to promote the dehydration of sucrose and inulin to produce HMF efficiently. We believe that the simple, efficient, and easily recyclable catalytic system has potential application for producing HMF from dehydration of carbohydrates.

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- Tuck CO, Pérez E, Horváth IT, Sheldon RA, Poliakoff M. Valorization of biomass: Deriving more value from waste. *Science*, 2012, 337: 695–699
- 2 Alonso DM, Wettstein SG, Dumesic JA. Bimetallic catalysts for upgrading of biomass to fuels and chemicals. *Chem Soc Rev*, 2012, 41: 8075–8098
- 3 Gallezot P. Conversion of biomass to selected chemical products. *Chem Soc Rev*, 2012, 41: 1538–1558
- 4 Long JX, Li XH, Wang LF, Zhang N. Ionic liquids: Efficient solvent and medium for the transformation of renewable lignocellulose. *Sci China Chem*, 2012, 55: 1500–1508
- 5 Stark A, Sellin M, Ondruschka B, Massonne K. The effect of hydrogen bond acceptor properties of ionic liquids on their cellulose solubility. *Sci China Chem*, 2012, 55: 1663–1670
- 6 Fang DW, Li M, Ge RL, Zang SL, Yang JZ, Gao YA. Density estimated physicochemical properties of alanine-based ionic liquid [C<sub>7</sub>mim][Ala] and its application in selective transesterification of soybean oil. *Sci China Chem*, 2012, 55: 1677–1682
- 7 Deng TY, Sun JY, Liu HC. Cellulose conversion to polyols on supported ru catalysts in aqueous basic solution. *Sci China Chem*, 2010, 53: 1476–1480
- 8 Qi XH, Watanabe M, Aida TM, Smith RL. Synergistic conversion of glucose into 5-hydroxymethylfurfural in ionic liquid–water mixtures. *Bioresource Technol*, 2012, 109: 224–228
- 9 Zhang ZH, Liu B, Zhao ZB. Conversion of fructose into 5-HMF catalyzed by GeCl<sub>4</sub> in DMSO and [Bmim]Cl system at room temperature. *Carbohyd Polym*, 2012, 88: 891–895
- 10 Zhang ZH, Wang Q, Xie HB, Liu WJ, Zhao ZB. Catalytic conversion of carbohydrates into 5-hydroxymethylfurfural by germanium(IV) chloride in ionic liquids. *ChemSusChem*, 2011, 4: 131–138
- 11 Hu SQ, Zhang ZF, Song JL, Zhou YX, Han BX. Efficient conversion of glucose into 5-hydroxymethylfurfural catalyzed by a common lewis acid SnCl<sub>4</sub> in an ionic liquid. *Green Chem*, 2009, 11: 1746– 1749
- 12 Yang Y, Hu CW, Abu-Omar MM. Conversion of carbohydrates and lignocellulosic biomass into 5-hydroxymethylfurfural using AlCl<sub>3</sub>·6H<sub>2</sub>O catalyst in a biphasic solvent system. *Green Chem*, 2012, 14: 509–513
- 13 Ståhlberg T, Rodriguez-Rodriguez S, Fristrup P, Riisager A. Metal-free dehydration of glucose to 5-(hydroxymethyl)furfural in ionic liquids with boric acid as a promoter. *Chem Eur J*, 2011, 17: 1456–1464
- 14 Hansen TS, Mielby J, Riisager A. Synergy of boric acid and added salts in the catalytic dehydration of hexoses to 5-hydroxymethylfurfural in water. *Green Chem*, 2011, 13: 109–114
- 15 Zhao S, Cheng MX, Li JZ, Tian J, Wang XH. One pot production of 5-hydroxymethylfurfural with high yield from cellulose by a bronsted–lewis-surfactant-combined heteropolyacid catalyst. *Chem Commun*, 2011, 47: 2176–2178

- 16 Zhang YM, Degirmenci V, Li C, Hensen EJM. Phosphotungstic acid encapsulated in metal–organic framework as catalysts for carbohydrate dehydration to 5-hydroxymethylfurfural. *ChemSusChem*, 2011, 4: 59–64
- 17 Qu YS, Huang CP, Song YL, Zhang J, Chen BH. Efficient dehydration of glucose to 5-hydroxymethylfurfural catalyzed by the ionic liquid, 1-hydroxyethyl-3-methylimidazolium tetrafluoroborate. *Bioresource Technol*, 2012, 121: 462–466
- 18 Tong XL, Ma Y, Li YD. An efficient catalytic dehydration of fructose and sucrose to 5-hydroxymethylfurfural with protic ionic liquids. *Carbohyd Res*, 2010, 345: 1698–1701
- 19 Zhang Y, Wang JJ, Ren JW, Liu XH, Li XC, Xia YJ, Lu GZ, Wang YQ. Mesoporous niobium phosphate: An excellent solid acid for the dehydration of fructose to 5-hydroxymethylfurfural in water. *Catal Sci Technol*, 2012, 2: 2485–2491
- 20 Qi XH, Guo HX, Li LY, Smith RL. Acid-catalyzed dehydration of fructose into 5-hydroxymethylfurfural by cellulose-derived amorphous carbon. *ChemSusChem*, 2012, 5: 2215–2220
- 21 Wang JJ, Xu WJ, Ren JW, Liu XH, Lu GZ, Wang YQ. Efficient catalytic conversion of fructose into hydroxymethylfurfural by a novel carbon-based solid acid. *Green Chem*, 2011, 13: 2678–2681
- 22 Sidhpuria KB, Daniel-da-Silva AL, Trindade T, Coutinho JAP. Supported ionic liquid silica nanoparticles (SILnPs) as an efficient and recyclable heterogeneous catalyst for the dehydration of fructose to 5-hydroxymethylfurfural. *Green Chem*, 2011, 13: 340–349
- 23 Iremonger SS, Liang JM, Vaidhyanathan R, Martens I, Shimizu GKH, Daff TD, Aghaji MZ, Yeganegi S, Woo TK. Phosphonate monoesters as carboxylate-like linkers for metal organic frameworks. *J Am Chem Soc*, 2011, 133: 20048–20051
- 24 Ma TY, Lin XZ, Zhang XJ, Yuan ZY. High surface area titanium

phosphonate materials with hierarchical porosity for multi-phase adsorption. *New J Chem*, 2010, 34: 1209–1216

- 25 Dutta A, Pramanik M, Patra AK, Nandi M, Uyama H, Bhaumik A. Hybrid porous tin(IV) phosphonate: An efficient catalyst for adipic acid synthesis and a very good adsorbent for CO<sub>2</sub> uptake. *Chem Commun*, 2012, 48: 6738–6740
- 26 Jiménez-Morales I, Santamaría-González J, Maireles-Torres P, Jiménez-López A. Mesoporous tantalum phosphate as acidic catalyst for the methanolysis of sunflower oil. *Appl Catal B-Environ*, 2012, 123–124: 316–323
- 27 Pramanik M, Nandi M, Uyama H, Bhaumik A. Organic-inorganic hybrid porous sulfonated zinc phosphonate material: Efficient catalyst for biodiesel synthesis at room temperature. *Green Chem*, 2012, 14: 2273–2281
- 28 Song JL, Mao JG, Sun YQ, Clearfield A. Novel hybrid porous 3d networks of Lead(II) diphosphonate and triphosphonate containing 1,3,5-benzenetricarboxylate. *Eur J Inorg Chem*, 2003, 2003: 4218– 4226
- 29 Mao JG, Wang ZK, Clearfield A. Building layered structures from hydrogen bonded molecular units and 1D metal phosphonate chains: Synthesis, characterization and crystal structures of *N*,*N*<sup>\*</sup>-dimethyl-*N*,*N*<sup>\*</sup> -ethylenediamine-bis(methylenephosphonic acid), its Ni(II) and Pb(II) complexes. *J Chem Soc*, *Dalton T*, 2002, 2: 4541–4546
- 30 Lai LK, Zhang YG. The effect of imidazolium ionic liquid on the dehydration of fructose to 5-hydroxymethylfurfural, and a room temperature catalytic system. *ChemSusChem*, 2010, 3: 1257– 1259
- 31 Tong XL, Li YD. Efficient and selective dehydration of fructose to 5-hydroxymethylfurfural catalyzed by brønsted-acidic ionic liquids. *ChemSusChem*, 2010, 3: 350–355