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Efficient catalytic conversion of the fructose into 5-hydroxymethylfurfural by heteropolyacids in the ionic liquid of 1-butyl-3-methyl imidazolium chloride

Yaping Xiao [1], Yu-Fei Song *

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

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ABSTRACT

The heteropolyacids (HPAs) of $H_3PW_{12}O_{40}$ (PW_{12}) and $H_4SiW_{12}O_{40}$ (SiW_{12}) have been demonstrated to be effective catalysts for promoting dehydration of the fructose to 5-hydroxymethylfurfural (5-HMF) in the presence of the ionic liquid of 1-butyl-3-methyl imidazolium chloride ([BMIM]Cl) as green solvent. The 5-HMF can be obtained with both the yield and selectivity of 99% at 80 °C in only 5 min. The activation energy of 31.88 kJ mol^{-1} by applying the [BMIM]Cl/PW_{12} system for dehydration of the fructose is much lower than those reported in the literature. Moreover, the used ionic liquid of [BMIM]Cl and HPAs could be recycled and reused with only slight decrease of reactivity for at least ten times. Compared with those systems reported so far, the [BMIM]Cl/PW_{12} and [BMIM]Cl/SiW_{12} exhibit higher yield, shorter reaction time, lower temperature for catalytic conversion of the fructose to 5-HMF, and they are environmental-friendly green systems.

1. Introduction

The increasing concern about the depletion of fossil fuels and the ever-increasing serious environmental problems have led to the exploitation of efficient conversion of renewable biomass into useful chemicals [1–3]. As a versatile biomass-derived platform compound for green biofuels and value-added chemicals, production of the 5-hydroxymethylfurfural (5-HMF) through dehydration of the fructose has attracted worldwide attention and it is a hot topic in green and sustainable chemistry nowadays [4–9].

As is known, dehydration of the fructose can be achieved under acidic condition. To date, the inorganic mineral acids (such as HCl, H_2SO_4 and H_3PO_4), organic acids (such as citric acid and levulinic acid), metal salts ($CrCl_2$ and $CrCl_3$) and metal oxides as Lewis acids have been widely investigated for dehydration of the fructose [10,11]. Nevertheless, relatively long reaction time and lower yield of 5-HMF are two drawbacks that restrict their further application. For example, Sievers et al. [12] investigated conversion of the fructose in [BMIM]Cl using H_2SO_4 as catalyst, and the 5-HMF can be obtained with the yield of 80% at 120 °C in 4 h. In contrast, polyoxometalates (POMs) have shown unmatched range of molecular structures, and they are strong Brønsted acids [13]. As such, it is reasonable to replace the above-mentioned inorganic, organic and Lewis acids by POMs. For example, the fructose can be selectively dehydrated into 5-HMF using $Ag_3PW_{12}O_{40}$ as catalyst with yield of 77.7% and selectivity of 93.8% in 60 min at 120 °C [14]. The Keggin cluster of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is able to catalyze conversion of the fructose to 5-HMF with yield of 74% and selectivity of 94.7% in 60 min at 115 °C [15]. These examples suggest that heteropolyanions (HPAs) are potentially promising candidates for the catalytic conversion of the fructose to 5-HMF.

Interestingly, ionic liquids (ILs) have been demonstrated to play significant roles for conversion of the fructose to 5-HMF as environmental-friendly green solvents [16–22]. For example, Zhao et al. reported that chromium (II) chlorides was able to catalyze conversion of the fructose to 5-HMF with the yield of 83% at 80 °C in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) in 3 h [23], in which solvation of the sugars occurs through the hydrogen bondings of chloride ions with the carbohydrate hydroxy groups. Inspired by the above results, in this work, we report the combination both ILs and HPAs for conversion of the fructose to 5-HMF. The results suggest that both $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ catalyze dehydration of the fructose into 5-HMF with 99% yield and selectivity using 1-butyl-3-methyl imidazolium chloride ([BMIM]Cl) as solvent in a very short time of 5 min at 80 °C (Scheme 1).

* Corresponding author. Tel.: +86 10 64431832; fax: +86 10 64431832.
E-mail addresses: songyufei@hotmail.com, songyf@mail.buct.edu.cn (Y.-F. Song).
[1] Tel.: +86 10 64431832; fax: +86 10 64431832.

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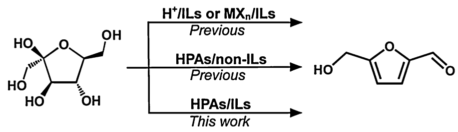

Scheme 1. Three different catalytic systems for dehydration of the fructose to 5-HMF [12,14,15,23].

2. Experimental

2.1. Chemical materials

Fructose (purity: 99%), 5-hydroxymethylfurfural, H_2SO_4, HCl, H_3PO_4, HNO_3, $NaVO_3$, $Na_2WO_4{\cdot}2H_2O$, $Na_2HPO_4{\cdot}2H_2O$, $Na_2MoO_4{\cdot}2H_2O$, $Na_2SiO_3{\cdot}9H_2O$, diethyl ether and the ionic liquids including [BMIM]Cl, $[BMIM]BF_4$, $[BMIM]PF_6$ (BMIM = 1-butyl-3-methylimidazolium) [OMIM]Cl, $[OMIM]BF_4$, $[OMIM]PF_6$ (OMIM = 1-methyl-3-octylimidazolium), 1-hydroxyethyl-3-methylimidazolium chloride ($[C_2OHMIM]Cl$) were purchased from Sigma–Aldrich and used directly without further purification. The HPAs including $H_3PW_{12}O_{40}$ [24], $H_4SiW_{12}O_{40}$ [25], $H_3PMo_{12}O_{40}$ [25], $H_4SiMo_{12}O_{40}$ [25], $H_4PMo_{11}VO_{40}$ [26], $H_5PMo_{10}V_2O_{40}$ [26], and $H_6PMo_9V_3O_{40}$ [26], were synthesized and characterized according to the reported procedures. The characterization data were summarized in the supporting information.

2.2. Analysis

FT-IR spectra were recorded on a Bruker Vector 22 infrared spectrometer by using KBr pellets. ^{13}C NMR spectra were recorded on a Bruker AV400 NMR spectrometer at 400 MHz, and the chemical shifts are given using TMS as internal reference. The content of 5-HMF was analyzed on an Agilent 1260 HPLC (UV wavelength: 284 nm; C18 column 5 μm; 250 mm × 4.6 mm), using 60% methanol in ultrapure water as mobile phase at a flow rate of 1 mL min^{-1}.

2.3. Dehydration of the fructose to 5-HMF

In a typical reaction, 0.5 g of fructose (2.78 mmol) was dissolved in 0.6 g of ILs firstly, and 0.1 mmol catalyst was added. The reaction mixture was stirred at 80 °C in oil bath. After reaction, each sample was diluted with 10 g of ultra-pure water before analysis.

For recycling of the ionic liquid and the catalyst, 3 mL of water and 8 mL of ethyl acetate were added to the above reaction mixture. Then, the organic phase was extracted out from the mixture. After extraction, the ionic liquid was heated at 60 °C for 24 h in a vacuum oven, and it can be used directly for the next run.

2.4. Yield and selectivity definitions

The fructose conversion (mol%), 5-HMF yield (mol%) and selectivity (mol%) were evaluated on a carbon basis as shown below:

Fructose conversion (mol%):

$$X = \left(1 - \frac{\text{Moles of fructose in product}}{\text{Starting amount of fructose}}\right) \times 100\%$$

5-HMF yield (mol%):

$$Y = \frac{\text{Moles of 5-HMF in product}}{\text{Starting amount of fructose}} \times 100\%$$

5-HMF selectivity (mol%):

$$S = \frac{\text{Yield of 5-HMF}}{\text{Fructose conversion}} \times 100\%$$

3. Results and discussion

3.1. Investigation of different catalysts for dehydration of the fructose

Firstly, two classical Keggin clusters of $H_3PW_{12}O_{40}$ (PW_{12}) and/or $H_4SiW_{12}O_{40}$ (SiW_{12}) have been applied as catalysts in the presence of [BMIM]Cl for the fructose dehydration. HPLC analysis shows that both the 5-HMF yield and selectivity reach as high as 99% in only 5 min. To have a better understanding of the efficiency of HPAs as catalysts, contrast experiments have been carried out using different non-HPAs catalysts in ionic liquids for the fructose dehydration to 5-HMF, and the results have been presented in Table 1. It can be seen that in the presence of [EMIM]Cl, $CrCl_2$ could catalyze conversion of the fructose to 5-HMF at 80 °C in 180 min with the yield of 83% (entry 5), whereas $CrCl_3$, $FeCl_3$, and $GeCl_4$ at 100 °C in the presence of ionic liquids exhibit the yield of 5-HMF ranging from 59% to 92.1% (entries 8–10). In the case of H_2SO_4, only 80% 5-HMF can be obtained at 120 °C in 240 min (entry 11). In contrast, the PW_{12} and/or SiW_{12} in the presence of [BMIM]Cl show shorter reaction times, relatively lower temperature and higher yield for dehydration of the fructose to 5-HMF (entries 1–2).

Further investigation has been carried out by using various HPAs such as $H_3PMo_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, $H_4PMo_{11}VO_{40}$, $H_5PMo_{10}V_2O_{40}$ and $H_6PMo_9V_3O_{40}$ as catalysts. As shown in Fig. 1, the highest yield of 99% with $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ as catalysts can be obtained under the experimental conditions. Furthermore, it should be noted that all the used HPAs exhibit better catalytic conversion results than that of H_2SO_4 and HCl.

The effect of the catalyst dosage on the fructose dehydration has been investigated. As shown in Fig. 2, almost no conversion can be found in the absence of catalyst. Even the reaction time is extended

Table 1
Effect of different catalysts on the fructose dehydration in ILs.

Entry	Solvent	Catalyst	*T* (°C)	*t* (min)	Conv. (%)	Yield (%)	Ref.
1[a]	[BMIM]Cl	$H_3PW_{12}O_{40}$	80	5	>99	99	This work
2[a]	[BMIM]Cl	$H_4SiW_{12}O_{40}$	80	5	>99	99	This work
3	Water-MIBK	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	115	60	78.1	74	[14]
4	Water-MIBK	$Ag_3PW_{12}O_{40}$	120	60	82.8	77.7	[15]
5	[EMIM]Cl	$CrCl_2$	80	180	92	83	[23]
6	DES	Citric acid	80	60	93.2	77.8	[27]
7	[BMIM]Cl	TfOH	100	60	96	88	[28]
8	[BMIM]Cl	$GeCl_4$	100	5	100	92.1	[29]
9	ChCl	$CrCl_3$	100	30	–	60	[30]
10	ChCl	$FeCl_3$	100	30	–	59	[30]
11	[BMIM]Cl	H_2SO_4	120	240	100	80	[12]
12	sec-Butanol	$[MIMPS]_3PW_{12}O_{40}$	120	120	99.7	99.1	[31]

[a] Reaction conditions: fructose (2.78 mmol), catalyst (0.1 mmol), [BMIM]Cl (1 g), 80 °C, 5 min. MIBK: methylisobutylketone; [EMIM]Cl: 1-ethyl-3-methylimidazolium chloride; ChCl: choline chloride; TfOH: trifluoromethanesulfonic acid; MIMPS: 1-(3-sulfonicacid)propyl-3-methyl imidazolium; DES: deep eutectic solvent.

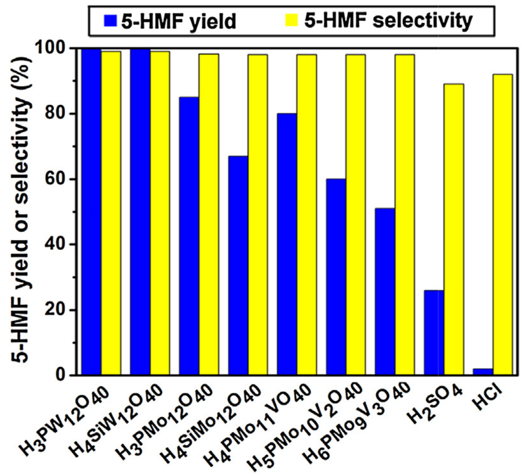

Fig. 1. Dehydration of the fructose to 5-HMF using different HPAs as catalysts. Reaction conditions: fructose (2.78 mmol, 0.5 g), [BMIM]Cl (0.6 g), catalyst (0.1 mmol), 80 °C, t = 5 min.

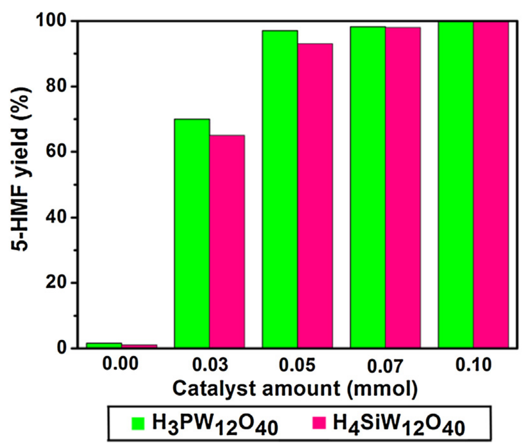

Fig. 2. Effect of the catalyst dosage on the 5-HMF yield (fructose 0.5 g, [BMIM]Cl 0.6 g, 80 °C, t = 5 min).

to 2 h, the 5-HMF yield is less than 5%. Further increase of the catalyst amounts, the 5-HMF yields increase accordingly. For example, the use of 0.03 mmol PW_{12} or SiW_{12} leads to the formation of 75% or 70% 5-HMF at 80 °C in 5 min in the presence of [BMIM]Cl, respectively, while 0.10 mmol of PW_{12} or SiW_{12} can promote complete conversion of the fructose to 5-HMF.

3.2. Effect of the reaction temperature and the time for dehydration of the fructose

The effect of the reaction temperature and time on the fructose conversion is shown in Table 2. It can be observed that the 5-HMF yield increases from 50% at 60 °C, 73% at 70 °C to 99% at 80 °C in 5 min, respectively. Extension of the reaction time from 5 to 10 min

Table 2
Effect of the reaction temperature and time on the fructose conversion to 5-HMF.

Entry	T (°C)	t (min)	Conv. (%)	Yield (%)	Selec. (%)
1	60	5	52	50	96
2	60	10	83	80	96
3	70	5	80	73	91
4	70	10	98	97	99
5	80	5	>99	99	99

Reaction conditions: fructose 0.5 g, $H_3PW_{12}O_{40}$ 0.3 g, [BMIM]Cl 0.6 g.

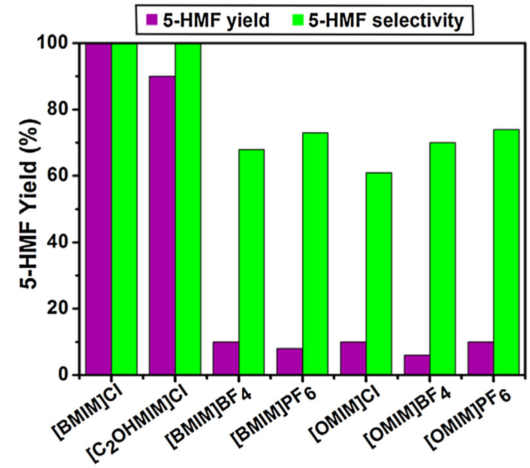

Fig. 3. Effects of different ILs on the catalytic conversion of the fructose to 5-HMF. Reaction conditions: fructose 0.5 g, $H_3PW_{12}O_{40}$ 0.3 g, ILs 0.6 g, 80 °C, 5 min.

helps the increase of the 5-HMF yield (entries 2 and 4). As such, the optimized condition for the fructose dehydration is 80 °C and 5 min.

3.3. Effect of the solvents on the 5-HMF yield

Previous studies have shown that the use of ILs as solvents can result in the lower reaction temperature and shorter reaction time compared with those conventional organic solvents [28–30]. Therefore, various ILs have been applied for the fructose dehydration at 80 °C. As shown in Fig. 3, under the same experimental conditions, the 100% 5-HMF yield can be achieved using [BMIM]Cl as solvent at 80 °C in 5 min, whereas the 90%, 10%, 8%, 12%, 6%, and 11% 5-HMF yields can be obtained using [C_2OHMIM]Cl, [BMIM]BF_4, [BMIM]PF_6, [OMIM]Cl, [OMIM]BF_4 and [OMIM]PF_6 as solvents, respectively. The results suggest that [BMIM]Cl generates a profound influence for the large enhancement of the fructose dehydration compared with other ionic liquids, which can be attributed to the solvation of the fructose through the hydrogen bondings between the chloride ions and the carbohydrate hydroxy groups [23].

Fig. 4 exhibits the effect of the [BMIM]Cl amount on the 5-HMF yield and selectivity. With the increase of the [BMIM]Cl amount from 0.0 g to 0.6 g, the 5-HMF yield can be improved from 0 to 99%,

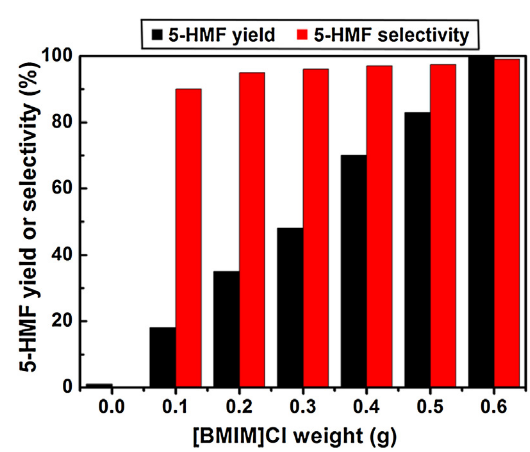

Fig. 4. Effect of the [BMIM]Cl amount on the 5-HMF yield and selectivity. Reaction conditions: fructose 0.5 g, $H_3PW_{12}O_{40}$ 0.3 g, T = 80 °C, t = 5 min.

Table 3
Effect of the fructose amounts on the 5-HMF yield and selectivity.

Entry	Fructose weight (g)	*t* (min)	Yield (%)	Selec. (%)
1	0.25	5	99	99
2	0.50	5	99	99
3	0.75	10	99	98
4	1.00	15	98	99
5	1.50	30	98	99
6	2.00	40	98	99

Reaction conditions: [BMIM]Cl 0.6 g, $H_3PW_{12}O_{40}$ 0.3 g, T = 80 °C.

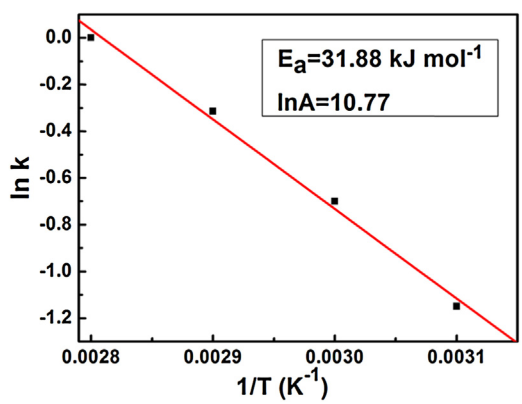

Fig. 5. The Arrhenius plot for the fructose conversion to 5-HMF. Reaction conditions: fructose 0.5 g, $H_3PW_{12}O_{40}$ 0.3 g, [BMIM]Cl 0.6 g, t = 5 min.

respectively. Further increase of the [BMIM]Cl amount from 0.6 g to 1.0 g, both the 5-HMF yield and selectivity remain 99%. As such, 0.6 g of [BMIM]Cl is used for the following experiments.

3.4. *Effects of the substrate amounts on the fructose conversion*

As shown in Table 3, with the increase of the substrate amounts from 0.25 g to 2.00 g, the time for achieving >98% yield and selectivity increases from 5 min to 40 min under the current experimental conditions.

3.5. *Reaction kinetics analysis*

In order to explain the high yield and selectivity of the fructose dehydration using [BMIM]Cl/HPAs system under mild condition, the Arrhenius plot for the fructose conversion to 5-HMF is accomplished by plotting $\ln(1-X)$ *vs.* reaction time (t) to obtain the rate constants at different temperatures (T). As shown in Fig. 5, kinetic analysis of dehydration of the fructose is a first-order process, which is in good agreement with previous reports [32]. The pre-exponential factor ln A from the intercept is 10.77. The activation energy calculated from the slope is 31.88 kJ mol^{-1}, which is much lower than those reported in the literature (~100 kJ mol^{-1}) [32–35]. This result again supports the advantages of the [BMIM]Cl/HPAs systems for dehydration of the fructose.

3.6. *Reaction mechanism*

To have a better understanding of the fructose dehydration, the ^{13}C NMR spectra have been utilized to follow this process. As shown in Fig. 6, at t = 0 min, the peaks between 60 and 110 ppm belong to the cyclic forms of fructose. With increase of the reaction time, the fructose signals start to decrease gradually, while the 5-HMF signals ranging from 110 to 200 ppm become stronger and stronger. In 5 min, the ^{13}C NMR spectrum shows the complete disappearance of the fructose signals, while only the 5-HMF and [BMIM]Cl signals can be observed. This result indicates that dehydration of the fructose is highly selective and efficient. Previous studies suggest that an intermediate may involve in dehydration of the fructose [36,37]. Since dehydration of the fructose is only in 5 min in this case, the lifetime of the intermediate may be very short [38].

3.7. *Recycling of the ionic liquid and the catalyst*

It is very important and essential to investigate the activity and stability of the solvent and the catalyst for dehydration of the fructose for practical application. Take the [BMIM]Cl/PW_{12} as an example, after reaction, the 5-HMF product is extracted by adding 3 mL of water and 8 mL of ethyl acetate into the reaction mixture [39]. Since the 5-HMF shows high solubility in ethyl acetate, it can be separated easily from the water phase to the ethyl acetate phase with approximate 96% separation efficiency. After extraction of the 5-HMF, the water phase is heated under vacuum at 60 °C for 24 h

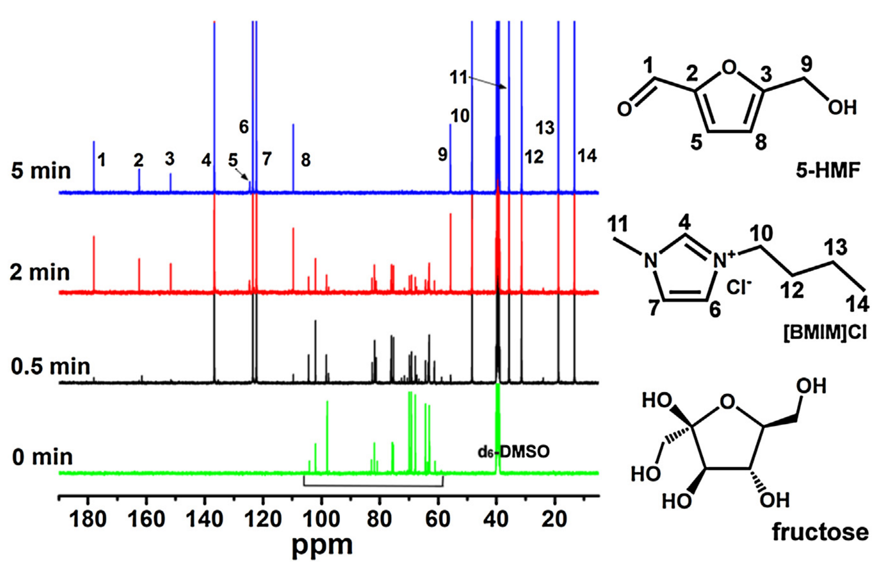

Fig. 6. The ^{13}C NMR spectra of dehydration of the fructose catalyzed by $H_3PW_{12}O_{40}$ in [BMIM]Cl at 80 °C.

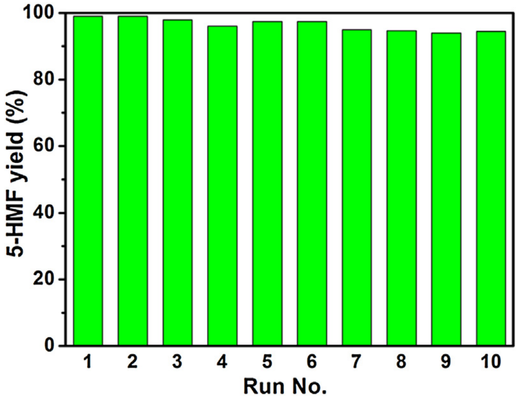

Fig. 7. Recycling of [BMIM][Cl] and $H_3PW_{12}O_{40}$ (fructose 0.5 g, $H_3PW_{12}O_{40}$ 0.3 g, [BMIM][Cl] 0.6 g, 80 °C, t = 5 min).

to remove water and small amount of residual ethyl acetate for recycling the ILs/HPAs system. The recycled [BMIM]Cl/PW_{12} can be applied for dehydration of the fructose for at least ten times with only slight decrease of reactivity (Fig. 7). It can be determined that the loss of PW_{12} is ~3.2% after 10 times of recycling and reusing of the catalyst, as indicated by inductive coupled plasma emission spectrometer measurement.

4. Conclusions

To summarize, application of the PW_{12} or SiW_{12} as catalyst and [BMIM]Cl as green solvent for the fructose dehydration suggests that both the 5-HMF yield and selectivity of 99% can be achieved under mild condition at T = 80 °C in 5 min. The activation energy of 31.88 kJ mol^{-1} by applying [BMIM]Cl/PW_{12} system for the fructose dehydration is much lower than those reported in the literature, which might be related to the hydrogen bondings between the chloride ions and the carbohydrate hydroxy groups on the fructose. Contrast experiments suggest that such efficient and selective catalytic results can be attributed to the synergetic effect of [BMIM]Cl, PW_{12} and the substrates. The [BMIM]Cl/PW_{12} system can be recycled and reused for at least ten times with only slight decrease of the reactivity. The reported [BMIM]Cl/PW_{12} and [BMIM]Cl/SiW_{12} are environment-benign and green systems for dehydration of the fructose.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.07.014.

References

[1] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411–2502.
[2] P. Gallezot, Chem. Soc. Rev. 41 (2012) 1538–1558.
[3] H. Kobayashi, A. Fukuoka, Green Chem. 15 (2013) 1740–1763.
[4] J.N. Chheda, Y. Roman-Leshkov, J.A. Dumesic, Green Chem. 9 (2007) 342–350.
[5] T.S. Hansen, J. Mielby, A. Riisager, Green Chem. 13 (2011) 109–114.
[6] S. Lima, P. Neves, M.M. Antunes, M. Pillinger, N. Ignatyev, A.A. Valente, Appl. Catal. A 363 (2009) 93–99.
[7] T. Okano, K. Qiao, Q. Bao, D. Tomida, H. Hagiwara, C. Yokoyama, Appl. Catal. A 451 (2013) 1–5.
[8] B. Saha, M.M. Abu-Omar, Green Chem. 16 (2014) 24–38.
[9] T. Wang, M.W. Nolte, B.H. Shanks, Green Chem. 16 (2014) 548–572.
[10] A.A. Rosatella, S.P. Simeonov, R.F.M. Frade, C.A.M. Afonso, Green Chem. 13 (2011) 754–793.
[11] R.-J. van Putten, J.C. van der Waal, E. de Jong, C.B. Rasrendra, H.J. Heeres, J.G. de Vries, Chem. Rev. 113 (2013) 1499–1597.
[12] C. Sievers, I. Musin, T. Marzialetti, M.B. Olarte, P.K. Agrawal, C.W. Jones, ChemSusChem 2 (2009) 665–671.
[13] W. Deng, Q. Zhang, Y. Wang, Dalton Trans. 41 (2012) 9817–9831.
[14] C. Fan, H. Guan, H. Zhang, J. Wang, S. Wang, X. Wang, Biomass Bioenergy 35 (2011) 2659–2665.
[15] Q. Zhao, L. Wang, S. Zhao, X. Wang, S. Wang, Fuel 90 (2011) 2289–2293.
[16] B.R. Caes, R.T. Raines, ChemSusChem 4 (2011) 353–356.
[17] J. He, Y. Zhang, E.Y. Chen, ChemSusChem 6 (2013) 61–64.
[18] Z. Huang, W. Pan, H. Zhou, F. Qin, H. Xu, W. Shen, ChemSusChem 6 (2013) 1063–1069.
[19] X. Qi, H. Guo, L. Li, R.L. Smith Jr., ChemSusChem 5 (2012) 2215–2220.
[20] M.E. Zakrzewska, E. Bogel-Łukasik, R. Bogel-Łukasik, Chem. Rev. 111 (2010) 397–417.
[21] C. Reichardt, Green Chem. 7 (2005) 339.
[22] Y. Roman-Leshkov, J.N. Chheda, J.A. Dumesic, Science 312 (2006) 1933–1937.
[23] H. Zhao, J.E. Holladay, H. Brown, Z.C. Zhang, Science 316 (2007) 1597–1600.
[24] R. Massart, R. Contant, J.M. Fruchart, J.P. Ciabrini, M. Fournier, Inorg. Chem. 16 (1977) 2916–2921.
[25] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, Inorg. Chem. 22 (1983) 207–216.
[26] G.A. Tsigdinos, C.J. Hallada, Inorg. Chem. 7 (1968) 437–441.
[27] S. Hu, Z. Zhang, Y. Zhou, B. Han, H. Fan, W. Li, J. Song, Y. Xie, Green Chem. 10 (2008) 1280.
[28] C. Shi, Y. Zhao, J. Xin, J. Wang, X. Lu, X. Zhang, S. Zhang, Chem.Commun. 48 (2012) 4103–4105.
[29] Z. Zhang, Q. Wang, H. Xie, W. Liu, Z.K. Zhao, ChemSusChem 4 (2011) 131–138.
[30] F. Ilgen, D. Ott, D. Kralisch, C. Reil, A. Palmberger, B. König, Green Chem. 11 (2009) 1948.
[31] Y. Qu, C. Huang, J. Zhang, B. Chen, Bioresour. Technol. 106 (2012) 170–172.
[32] M. Bicker, J. Hirth, H. Vogel, Green Chem. 5 (2003) 280–284.
[33] Y.-Y. Lee, K.C.W. Wu, Phys. Chem. Chem. Phys. 14 (2012) 13914.
[34] C. Moreau, R. Durand, S. Razigade, J. Duhamet, P. Faugeras, P. Rivalier, P. Ros, G. Avignon, Appl. Catal. A 145 (1996) 211–224.
[35] X. Qi, M. Watanabe, T.M. Aida, J.R.L. Smith, Green Chem. 10 (2008) 799.
[36] A.S. Amarasekara, L.D. Williams, C.C. Ebede, Carbohydr. Res. 343 (2008) 3021–3024.
[37] Y.-N. Li, J.-Q. Wang, L.-N. He, Z.-Z. Yang, A.-H. Liu, B. Yu, C.-R. Luan, Green Chem. 14 (2012) 2752–2758.
[38] C. Li, Z.K. Zhao, H. Cai, A. Wang, T. Zhang, Biomass Bioenergy 35 (2011) 2013–2017.
[39] X. Qi, M. Watanabe, T.M. Aida, J.R.L. Smith, Green Chem. 11 (2009) 1327–1331.