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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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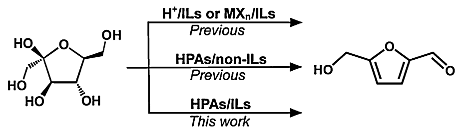

Scheme 1. Three different catalytic systems for dehydration of the fructose to 5-HMF [12,14,15,23].

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.