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Dehydration of biomass to furfural catalyzed by reusable polymer bound sulfonic acid (PEG-OSO₃H) in ionic liquid[†]

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Polymer bound sulfonic acid (PEG-OSO₃H) is active for the dehydration of biomass to furfural. The furfural yield is improved when MnCl₂ is added to the reaction mixture. The catalyst was mild, non-volatile, and non-corrosive and can be recycled multiple times (>10) without an intermediate regeneration step and no significant leaching of $-OSO_3H$ groups is observed.

The conversion of biomass to liquid fuels has attracted renewed attention in recent years due to its environmental, economic, and strategic advantages.^{1–3} Furfural is a useful chemical and a potential building block for hydrocarbon fuels.^{4–6} It can be obtained by dehydrating pentoses derived from lignocellulosics (primarily xylose), using strong acid catalysts.⁷ Furfural has been hailed not only as a platform molecule for the production of the biofuel, such as 2-methylfuran, 2,5-dimethylfuran, 2-methyltetrahydrofuran, 5-methylfurfural (MF), and 5-(ethoxymethyl)furfural (EMF) which have been reported as promising biofuel components,^{8–10} but also for important molecules such as furfuryl alcohol, furan, and THF.¹¹

Furfural is the most common industrial chemical derived from lignocellulosic biomass, with an annual production volume of more than 200 000 tonnes.¹² The commercial utility of furfural was first discovered at the Quaker Oats Company in 1921.¹³ In this process, oat hulls are converted into furfural using concentrated sulfuric acid and high pressure steam to supply heat and strip out furfural. Following this, HCl and H_2SO_4 were used to produce furfural from the dehydration of xylose.⁷ However, the aqueous mineral acids are limited by the fact that they cause equipment corrosion and safety problems and require critical reaction conditions. FeCl₃·6H₂O was recently used successfully as a catalyst for xylose dehydration into furfural.¹⁴ As an isomer of xylose, the conversion of xylulose to furfural is more facile than the conversion of xylose to furfural.¹⁵ Furfural could be achieved by xylose-to-xylulose isomerization and xylulose dehydration in a one-pot fashion.¹⁶ Ebitani et al. have employed Amberlyst-15 as a Brønsted acid catalyst to obtain furfural from xylose, but the authors did not report on the use of xylan or biomass as starting materials.^{16a} Binder et al. used CrCl₃ conversion of xylose to furfural, and a yield of 56% was obtained at 100 °C for 4 h.^{16b} However, the furfural yield was only 25% from xylan, and 22% from corn stover even at the higher temperature of 140 °C and with HCl as a co-catalyst. Zhao et al. have shown that using CrCl₃ in ionic liquid leads to a furfural yield of 63% at 100 °C.17 Mosier et al. have used the high selectivity of maleic acid to convert biomass hemicellulose to furfural (29-61%).¹⁸ Yang et al. reported that AlCl₃·6H₂O could effectively produce furfural from biomass in AlCl₃·6H₂O-NaCl-H₂O/THF biphasic medium.¹⁹ Vlachos et al. have shown that Sn-beta is an effective catalyst for the isomerization of xylose into xylulose in an aqueous medium at temperatures as low as <100 °C.²⁰ Dumesic et al. demonstrated a biphasic system that can produce furfural and lead to a selectivity of 91% for dehydration of xylose.⁵ High yield of furfural (>90) was obtained from aqueous hemicellulose solutions in a biorefinery process composed of a biphasic dehydration, a liquid-liquid split, and subsequent three-stage distillations by Huber reported in 2011.²¹ Thus, an environmental friendly catalyst that can effectively convert pentoses and biomass to furfural is still needed.

In recent years, an abundant and cheap catalyst was widely used in many organic reactions. The utility of polymer-supported acid catalysts is well-recognized because of their ease of workup and separation of products and catalysts, from an economical point of view, and their application to industrial processes.²² We previously reported the preparation and utilization of polyethylene glycol (PEG)-bound sulfonic

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acid (PEG-OSO₃H)²³ in the Biginelli, Beckmann rearrangement and other multicomponent reactions.²⁴ We found that the PEG-OSO₃H is a mild, non-volatile and non-corrosive organic acid²⁵ and can efficiently convert pentoses to furfural in a one-pot fashion. Recently, ionic liquids as novel solvents to replace conventional organic reaction media had been widely applied to various organic reactions. So far, a number of available studies deal with producing furfural from xylose and xylan by solid catalysts in ionic liquid,²⁶ and the effect of ionic liquid on the catalytic activity of solid catalysts has been confirmed in this field.^{26,27}

Herein, our purpose is to develop an ecologically viable catalytic pathway for furfural production without the use of inorganic acids. Xylose, ribose, arabinose and biomass were converted to furfural with good to excellent conversions catalyzed by a co-catalyst system of PEG-OSO₃H (0.3 g, 0.1 mmol $-OSO_3H$) and MnCl₂ in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆).

Due to the ease in availability of xylose by dehydration of biomass, we initially investigated the reaction of xylose in [BMIM]PF₆ with PEG-OSO₃H as a catalyst at 120 °C (Scheme 1). The reaction was performed in the presence of 0.5 mmol xylose, 0.15 mmol manganese chloride (MnCl₂), 0.3 g PEG-OSO₃H (0.1 mmol -SO₃H), and 2 mL of various solvents (water, glycerol, PEG-400 and [BMIM]PF₆) (Fig. 1). In the presence of PEG-OSO₃H at 120 °C after 18 min, 99% of the starting xylose is converted. Furfural is produced via the dehydration of xylose at a yield of 75%, while the other 24% of reacted xylose is converted into unidentified degradation products, both soluble and insoluble. Among the tested solvents, *i.e.* water, glycerol or PEG-400, only [BMIM]PF₆ afforded the highest yield of 75% of furfural. In water, the desired product was not detected, while glycerol and PEG-400 exhibited a low effect, reaching furfural in lower yields.

One possible reason for this is that the IL may simultaneously play the role of an acid catalyst and a solvent; the ionic liquid could also stabilize the furfural product from the reaction mixture and could increase the reaction selectivity.^{26,28} Although some reasons were proposed for the inactivity of water, until now it is not clear.^{29–31} In glycerol and PEG-400, the reaction also gave lower yields, which may be due to the formation of an acetal of furfural with glycerol or PEG-400.³²

Further experiments demonstrate that co-catalysts play an important role in the complete conversion of xylose giving furfural, *i.e.* the yield of furfural dropped to 65% without MnCl₂ (Table 1, Entry 6). In addition, various co-catalysts were investigated (Fig. 2). The use of ZnCl₂, SnCl₂, and SnCl₄ resulted in moderate yields of the target product. MnCl₂ gave



Scheme 1 Conversion of xylose into furfural catalyzed by PEG-OSO₃H.



Fig. 1 Degradation of xylose at 120 °C catalyzed by PEG-OSO₃H in different solvents (■ [BMIM]PF₆, ◆ glycerol, ● PEG-400, ▲ water). Reaction conditions: xylose (0.5 mmol), PEG-OSO₃H (0.1 mmol), and MnCl₂ (0.15 mmol) in various solvents (2 mL) at 120 °C. ▼ Xylose recovery.

Table 1 Xylose conversion and furfural yield with $\mathsf{PEG}\text{-}\mathsf{OSO}_3\mathsf{H}$ as the catalyst $^{\alpha}$

Entry	PEG-OSO ₃ H (g)	Con. (%)	Yield (%)
1	0.4	>99	70
2	0.3	99	75
3	0.2	97	67
4	0.1	93	45
5	0.05	88	32
6 ^{<i>b</i>}	0.3	82	65

 a Reaction conditions: xylose (0.5 mmol) and MnCl₂ (0.15 mmol) in [BMIM]PF₆ (2 mL) at 120 °C for 18 min. Yields are based on HPLC analysis. b Without MnCl₂.

furfural in a high yield (75%). These results were similar with those of the previous studies.³³ Fe³⁺, Al³⁺, Cd²⁺ and Co²⁺ have less activity; however, Ni²⁺, Zn²⁺ and Cu²⁺ can inhibit the isomerization reaction. Therefore, they may be incapable of inducing the xylose-to-xylulose isomerization. The influence of the amount of MnCl₂ in the system on dehydration of xylose to furfural was investigated at 120 °C; the yield of furfural increased to a maximum of 75% with an increase in the amount of MnCl₂ from 0 to 0.03 g (0.15 mmol) and then slowly decreased to 66% with further increase in the amount of MnCl₂ from 0.03 to 0.1 g.

Continuing with PEG-OSO₃H as the catalyst and MnCl₂ as the co-catalyst in [BMIM]PF₆, we investigated the influence of different molar ratios and temperatures (Table 1). The best molar ratio of PEG-OSO₃H catalyst to xylose is 1:5, which gives the best conversion and yield (Entries 1–5). For example, when the catalyst amount is decreased to 0.05 g, xylose conversion and furfural yield were reduced to 88% and 32%, respectively (Entry 5). The temperature has a significant effect on the yield of furfural. At the temperature range of 80 to 140 °C, the maximum yield occurred at 120 °C. At lower temperatures (80 to 110 °C) and higher temperatures (130 to 140 °C), the yield of furfural was low. Thus, we decided to use 0.5 mmol xylose, 0.15 mmol MnCl₂, and PEG-OSO₃H



Fig. 2 The yield of furfural from xylose by various co-catalysts in [BMIM]PF₆ (■ reaction conditions: xylose (0.5 mmol), PEG-OSO₃H (0.1 mmol), and co-catalysts (0.15 mmol) in [BMIM]PF₆ (2 mL) at 120 °C for 18 min. ■ ^aReaction conditions: xylose (0.5 mmol) and MnCl₂ (0.15 mmol) in [BMIM]PF₆ (2 mL) at 120 °C for 18 min. ^bReaction conditions: xylose (0.5 mmol) and MnCl₂ (0.15 mmol) in [BMIM]PF₆ (2 mL) at 120 °C for 30 min. ^cReaction conditions: xylose (0.5 mmol) and MnCl₂ (0.15 mmol) in [BMIM]PF₆ (2 mL) at 120 °C for 18 min. ^dReaction conditions: xylose (0.5 mmol) and MnCl₂ (0.15 mmol) in [BMIM]PF₆ (2 mL) at 120 °C for 30 min. ^cReaction conditions: xylose (0.5 mmol) and MnCl₂ (0.15 mmol) in [BMIM]PF₆ (2 mL) at 140 °C for 30 min.).

(0.1 mmol) in 2 mL [BMIM]PF₆ at 120 °C for 18 min as the optimal reaction conditions for the preparation of furfural.

The recyclability is of great importance for applying a catalyst in industrial processes. The reusability of the catalyst PEG-OSO₃H was studied in this work and evaluated through ten repeated reactions (Fig. 3). After the reactions, the catalyst was extracted by dichloromethane. The white PEG-OSO3H catalyst can be obtained by adding cooled diethyl ether into the concentrated organic phase. The recovered catalyst can be used directly in the next run. The catalytic activity and repeatability of PEG-OSO₃H were tested in the reaction for xylose; the yields of furfural were 75%, 74%, 73%, 73%, 72%, 71%, 70%, 68%, 66% and 59%, respectively. After the cycle, the elemental analysis for the recycled PEG-OSO3H was performed. For the 7th experiment, the sulfur contents were measured by elemental analysis and found to be 3.0 mmol g^{-1} , which showed that S content was similar to that in the fresh polymer bound sulfonic acid (3.3 mmol g^{-1}). These results



Fig. 3 Reutilization study of PEG-OSO₃H for xylose converted into furfural in [BMIM]PF₆. Reaction conditions: molar ratio of xylose/PEG-OSO₃H/MnCl₂ (5:1:1.5) in [BMIM]PF₆ (2 mL) at 120 °C for 18 min.

indicated that the PEG-OSO₃H catalyst exhibited good activity for xylose conversion.

After reaction, the reaction system was extracted with diethyl ether (3 × 2 mL), removing the furfural, and the residue containing PEG-OSO₃H and MnCl₂ in [BMIM]PF₆ was reused for the next run. The reaction system was recycled and reused eight times in the process of furfural production (yield: 75%, 75%, 74%, 73%, 72%, 72%, 70%, and 68%, respectively) (Fig. 4). Elemental analysis of Mn was carried out using an atomic absorption (AA) spectrophotometer (Z-2000, Japan). About 0.1 mL of the sample was dissolved in 2 mL of distilled water in a PVC flask. It was then diluted to 100 mL, and the detection of Mn was found to be 4.05 g L⁻¹ (Fig. S4†), which is comparable to that of the fresh system (Mn, 4.13 g L⁻¹), suggesting that Mn leaching is very low in the ionic liquid medium.

To assess the validity of the PEG-OSO₃H, sulfuric acid $(H_2SO_4, 0.1 \text{ M})$ and PEG-OSO₃H (0.3 g, 0.1 mmol) were examined in a 2 mL [BMIM]PF₆ system (Table 2); better results were achieved with PEG-OSO₃H than with aqueous H_2SO_4 , under similar conditions. Furthermore, the amount of residual pentoses was analyzed with high performance liquid chromatography (HPLC) (Fig. S7†).

Subsequently, we applied the described reaction conditions to untreated lignocellulosics. The furfural yields were obtained from corn stover, corncob, pinewood, poplar, switchgrass and straw using PEG-OSO₃H (yield: 36, 35, 30,



Fig. 4 Recycling of the ionic liquid containing PEG-OSO₃H and MnCl₂. Reaction conditions: xylose (0.5 mmol), PEG-OSO₃H (0.1 mmol), and MnCl₂ (0.15 mmol) in [BMIM]PF₆ (2 mL) at 120 °C for 18 min.

Table 2 Pentose conversion and furfural yield catalyzed by sulfuric acid and the $\mathsf{PEG}\text{-}\mathsf{OSO}_3\mathsf{H}$ catalyst

	$H_2SO_4^{\ a}$		PEG-OSO ₃ H ^b	
Pentose	Con. (%)	Yield (%)	Con. (%)	Yield (%)
Xylose	96	64	99	75
Ribose	91	59	97	67
Arabinose	95	63	98	72

^{*a*} Reaction conditions: pentose (0.5 mmol), H_2SO_4 (0.1 M, 1 mL), and $MnCl_2$ (0.15 mmol) in [BMIM]PF₆ (2 mL) at 120 °C for 18 min. ^{*b*} Reaction conditions: pentose (0.5 mmol), PEG-OSO₃H (0.3 g, 0.1 mmol), and $MnCl_2$ (0.15 mmol) in [BMIM]PF₆ (2 mL) at 120 °C for 18 min. Yields are based on HPLC analysis. 24, 22, and 25%, respectively) as the catalyst in $[BMIM]PF_6$; the results are illustrated in Table 3. The yields of furfural were clearly dependent on the biomass feedstock. Similar observations were also reported in the literature. The research groups of Mazza,^{7c} Zhao¹⁷ and Mosier¹⁸ found disparate furfural yields using different biomass, suggesting that there is a noticeable difference in the behavior of the various biomass sources in furfural formation. The fact that yields of furfural obtained from raw materials were lower than those from pure pentoses under the typical reaction conditions could be attributed to the following possible reasons. First, a network of lignin-cellulose-xylan in lignocellulosic biomass made the hydrolysis of hemicellulose more difficult.³⁴ Second, the components of biomass are more complex, free fatty acids and phospholipids in the raw materials were impurities that can poison solid catalysts.35

On the basis of these observations, we propose that the reaction mechanism is similar with the earlier studies as shown in Scheme 2.³³ The xylose isomerization to xylulose requires hydrogen transfers from O2 to O1 and from C2 to C1. The H transfer from C2 to C1 is a hydride transfer, and it is activated by a proton abstraction from O2 to a solvation water molecule. This initial proton donation from O2 allows the formation of $Mn(\pi)$ chelate with the O2 and O1 oxygens of the saccharide molecule; the hydride transfer ensues and proton back-donation to the O1 oxygen completes the isomerization. In addition, Fig. S8† confirmed the existence of xylulose in the process of xylose dehydration.

Finally, kinetic modelling studies for the conversion of xylose were performed.^{33,36} These degradation products can

Table 3Furfural yields obtained from various sources of lignocellulosicbiomass a

Entry	Sample	Yield (%)
1	Corn stover	36
2	Corncob	35
3	Pinewood	30
4	Poplar	24
5	Switchgrass	22
6	Straw	25

^{*a*} Reaction conditions: biomass (0.3 g), PEG-OSO₃H (0.1 mmol), and $MnCl_2$ (0.15 mmol) in [BMIM]PF₆ (2 mL) at 120 °C for 18 min. Yield (wt/wt) for furfural based on 0.3 g biomass by HPLC analysis.



 $\label{eq:scheme 2} \begin{array}{l} \mbox{Possible reaction mechanism for xylose isomerization into xylulose using PEG-OSO_3H as a catalyst in [BMIM]PF_6. \end{array}$

be attributed to the following reactions: (a) xylose coupling with xylose-to-furfural intermediates, (b) furfural resinification (self-coupling), and (c) reaction between furfural and either xylose or xylose-to-furfural intermediates.³⁶ This set of xylose-derived reactions is shown in Scheme 3; the rate equations for xylose degradation and furfural formation can be described as the following:³⁷

(

$$\frac{d[X]}{dt} = -(k_1 + k_2[F] + k_3[X])[X][H^+]$$
(1)

$$\frac{\mathrm{d}[\mathrm{X}\mathrm{y}]}{\mathrm{d}t} = \left(k_1[\mathrm{X}] - k_4[\mathrm{X}\mathrm{y}]\right)[\mathrm{H}^+]$$
(2)

$$\frac{d[F]}{dt} = \left(k_4[Xy] - k_2[X][F] - k_5[F]^2\right)[H^+]$$
(3)

$$\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} = k_2[\mathrm{X}][\mathrm{F}][\mathrm{H}^+] \tag{4}$$

$$\frac{\mathrm{d}[\mathrm{Dp}]}{\mathrm{d}t} = k_3[\mathrm{X}]^2[\mathrm{H}^+] \tag{5}$$

$$\frac{\mathrm{d}[\mathrm{Rp}]}{\mathrm{d}t} = k_{\mathrm{s}}[\mathrm{F}]^{2}[\mathrm{H}^{+}] \tag{6}$$

where [X], [Xy], [F], [H], [Dp], and [Rp] are the xylose, xylulose, furfural, humins, degradation product, and resinification product concentrations, respectively. These equations can be simplified by considering experimental results. Xylose-to-xylulose isomerization was not observed in the present study during product analysis. Thus, the steady-state assumption can be invoked in the modeling of the intermediates such that $d[Xy]/dt = (k_1[X] - k_4[Xy])[H^+] \approx 0$, and hence $k_1[X] \approx k_4[Xy]$. Furthermore, we can assume that resinification does not occur to a significant extent based on the recent observation that furfural dissolved in ionic liquid is relatively stable in the presence of an acid catalyst and in the absence of xylose.³⁰ These assumptions lead to a modified differential equation representing change in furfural concentration with respect to time:



Scheme 3 The xylose dehydration/degradation scheme used in kinetic modelling.

Table 4 The reaction rate constants were determined by least squares minimization of residuals between predictions of kinetic models and the experimental data from Fig. 1^a

Entry	Rate constant		Unit
1	$k_1 = 3.10 \times 10^{-3}$	${}^{37}k_1 = 5.38 \times 10^{-4}$	$L \text{ mol}^{-1} \text{ s}^{-1}$
2	$k_2 = 3.67 \times 10^{-2}$	${}^{37}k_2 = 3.18 \times 10^{-3}$	$L^2 \text{ mol}^{-2} \text{ s}^{-1}$
3	$k_3 = 5.21 \times 10^{-2}$	${}^{37}k_3 = 4.40 \times 10^{-3}$	$L^2 \text{ mol}^{-2} \text{ s}^{-1}$

^{*a*} Reaction conditions: xylose (0.5 mmol), PEG-OSO₃H (0.1 mmol), and $MnCl_2$ (0.15 mmol) in 2 mL [BMIM]PF₆ at 120 °C for 18 min. ³⁷k (literature values).

$$\frac{\mathrm{d}[\mathrm{F}]}{\mathrm{d}t} = \left(k_1 - k_2[\mathrm{F}]\right)[\mathrm{X}][\mathrm{H}^+] \tag{7}$$

Values for k_1 , k_2 , and k_3 were determined by least squares minimization of the residuals between the predicted concentrations of X, H, Dp, and F, obtained by solving eqn (1), (4), (5), and (7) and the experimental data shown in Fig. 1. Finally, we obtained fit rate constants and listed them in Table 4. The lower value of k_1 in comparison with k_2 and k_3 is in agreement with that reported by Bell and Enslow³⁷ in that k_2 is also lower than k_3 in ionic liquid, $3.67 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ versus $5.21 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$. These rate constants reveal that degradation products are formed faster than humins.

Conclusions

The polymer bound sulfonic acid (PEG-OSO₃H) catalyst possesses interesting properties for converting pentoses to furfural in [BMIM]PF₆ at 120 °C. For xylose, the yield of furfural can mount to 75% under PEG-OSO₃H. It is confirmed that the key to successfully achieving the direct conversion of xylose to furfural is that a catalytic system should contain both Brønsted acid (polymer bound sulfonic acids) and Lewis acid (MnCl₂) and should combine the isomerization process with the dehydration step. Our chemical process uses simple, inexpensive, effective and reusable catalysts to transform biomass into furfural.

Experimental procedure

Xylose, ribose, and arabinose were purchased from J&K Scientific Ltd (Beijing, China). All chemicals were of analytical grade, and were used as received without further purification. Corn stover, corncob, pinewood, poplar, switchgrass and straw were obtained locally (Lanzhou, China). These materials were ground using a high-speed rotary cutting mill equipped with three blades, and then milled to pass 80 mesh, and dried at 80 °C to a constant weight. PEG-OSO₃H was prepared according to our previous procedures.²³

Analytical methods

All products were analyzed *via* HPLC using a Kromasil-C18-5 μ column at 30 °C, a P98-I pump, and a UV98-I detector at 254 nm. Acetonitrile and water (45:90) were used as the mobile phase at a flow rate of 0.6 mL min⁻¹. Furfural was quantified with calibration curves generated from commercially available standards. Following a typical experimental procedure reaction, the resulting mixture was diluted with a known mass of deionized water. The concentrations of products were calculated from HPLC-peak integrations and used to calculate molar yield.

Representative procedure for synthesis of furfural from xylose

A mixture of xylose (0.5 mmol), $MnCl_2$ (0.15 mmol) and PEG-OSO₃H (0.3 g, 0.1 mmol) in [BMIM]PF₆ (2 mL) was stirred at 120 °C for 18 min. After completion, monitored by TLC, the resulting mixture was cooled to room temperature. The mixture was extracted 3 times with 2 mL of diethyl ether absolute. The combined organic phase was dried over Na₂SO₄. After evaporating the solvent, a yellowish oily matter, furfural (73% isolated yield, 100% purity by HPLC), was obtained and dried under vacuum.

Representative procedure for synthesis of furfural from biomass

Biomass (0.3 g) was mixed with $[BMIM]PF_6$ (2 mL) and PEG-OSO₃H (0.3 g, 0.1 mmol), and the reaction mixture was stirred at 120 °C for 18 min.

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