Catalytic Conversion of Biomass-derived Carbohydrates into 5-Hydroxymethylfurfural using a Strong Solid Acid Catalyst in Aqueous γ-Valerolactone

Wenzhi Li,[a,]* Zhiping Xu,[b] Tingwei Zhang,[a] Guojun Li,[b] Hasan Jameel,[c]
Hou-min Chang,[c] and Longlong Ma [d]

Selective conversion of biomass-derived carbohydrates into 5-hydroxymethylfurfural (HMF) is of great significance for biomass conversion. In this study, a novel solid Brønsted acid was prepared simply by the copolymerization of paraformaldehyde and *p*-toluenesulfonic acid and then used to catalyze the conversion of various carbohydrates into HMF in γ-valerolactone-water (GVL/H_2O) reaction medium for the first time. The catalyst exhibited strong acidity, good water resistance, and high thermal stability. The present work focuses on the effects of various reaction parameters, including reaction temperature, time, water concentration, solvent, fructose level, and catalyst loading, on fructose dehydration. The catalyst exhibited excellent catalytic performance for HMF production from fructose in GVL and furnished a high HMF yield of 78.1% at 130 °C in 30 min. The recycling experiments suggested that the solid acid catalyst could be recycled at least seven times without a noticeable decrease in the catalytic activity. In addition, an attempt to study the one-step conversion of sucrose, glucose, and cellulose into HMF and furfural was performed using the same catalytic system.

Keywords: Fructose; 5-Hydroxymethylfurfural; Dehydration; γ-Valerolactone; PTSA-POM catalyst

*Contact information: a: Department of Thermal Science and Energy Engineering, University of Science and Technology of China, Hefei 230026, PR China; b: Department of Chemistry, University of Science and Technology of China, Hefei 230026, PR China; c: Department of Forest Biomaterials, North Carolina State University, Raleigh, NC 27695-8005, USA; d: CAS Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China; * Corresponding author: liwenzhi@ustc.edu.cn*

INTRODUCTION

Currently, the world is entering into an era of diminishing fossil fuel resources. The emergences of environmental pollution issues and energy crises have attracted more and more attention in recent years. Lignocellulosic biomass, the most abundant non-edible resource in nature, is a promising renewable alternative to petroleum-based resources for the future. In recent years, extensive research has been carried out for converting lignocellulosic biomass into transportation fuels and value-added chemicals (Climent *et al.* 2014; Isikgor and Becer 2015). In this process of biomass conversion, 5-hydroxymethylfurfural (HMF) plays a crucial role and can serve as a precursor for the synthesis of liquid alkanes and other biomass-derived chemicals.

HMF is one of the “Top 10 + 4” important platform compound from bio-based carbohydrates (van Putten *et al.* 2013). It can be used to produce many important chemicals, such as 2,5-diformylfuran (Zhang *et al.* 2014b), 2,5-furandicarboxylic acid (Wang *et al.* 2015), 1,6-hexanediol (Tuteja *et al.* 2014), levulinic acid, and γ-valerolactone (Heeres *et* *al.* 2009). HMF has built a bridge between raw biomass materials and liquid fuels or chemicals, and it has a large market potential with a promising future. Hence, highly efficient production of HMF has attracted much attention from researchers.

HMF is produced from the acid-catalyzed dehydration of hexose sugars. Presently, there are two main effective methods to produce HMF: one is to use glucose or glucose-based polysaccharides (such as cellulose) as feedstocks, and the other one is the use of fructose as a substrate. Glucose and cellulose are the most abundant and cheapest carbohydrates in nature; therefore, efficient transformation of cellulose and glucose into HMF is of high current interest (Shi *et al.* 2013; Guo *et al.* 2016; Yuan *et al.* 2016). Unfortunately, common Brønsted acids fail as effective catalysts with low HMF yield. It is widely acknowledged that, before dehydration, glucose first undergoes isomerization to fructose by Lewis acids such as metal chlorides (Zhao *et al.* 2007), Sn-Beta (Román-Leshkov *et al.* 2010; Yang *et al.* 2015a), Sn-MCM-41 (Xu *et al.* 2014), or enzymes (Huang *et al.* 2014). Although metal chlorides (such as $CrCl_3$, $AlCl_3$, $SnCl_4$) are favored for this reaction, they are poisonous, corrosive, hazardous to human health, and also impractical to recycle. Sn-Beta is difficult to prepare and enzymes are costly. Another method to increase the HMF yield from glucose and cellulose is the use of ionic liquids such as [BMIM]Cl (Dutta *et al.* 2012) and [EMIM]Cl (Zhao *et al.* 2007) as solvents. However, ionic liquids are also expensive and not suitable for industrial applications (Shi *et al.* 2013).

Compared with the complicated dehydration process for glucose and cellulose, fructose is dehydrated to form HMF under mild conditions without using toxic metal chlorides and costly ionic liquids because of its fructofuranosic structure (Wang *et al.* 2014). Moreover, fructose is also cheap and is readily available. Based on these facts, the production of HMF from fructose has been extensively studied. Traditional mineral acids such as H_2SO_4 and H_3PO_4 are efficient for fructose dehydration (Qi *et al.* 2014; Liu *et al.* 2014). However, they are highly corrosive and difficult to recycle, so they cannot meet the principles of green chemistry. Also, the HMF formed is highly unstable in these strongly acidic reaction media. Recently, many novel heterogeneous acids have been used to catalyze the dehydration reaction. Jain *et al.* (2015) revealed that mesoporous zirconium phosphate exhibited excellent activity for HMF formation in H_2O-diglyme medium, and 80% HMF yield was achieved. Xu *et al.* (2015a) also used the same catalyst in DMSO for HMF production with 79.6% HMF selectivity. Other catalysts such as $FePO_4$ (Yang *et al.* 2015b), Nb_2O_5 (Wang *et al.* 2013), graphite derivatives (Nie *et al.* 2014), and sulfonic acid-functionalized metal-organic frameworks MOF-SO_3H (Chen *et al.* 2014) have also been developed to produce HMF. In addition, a variety of biomass-derived carbonaceous solid acid materials have been demonstrated to be efficient for HMF production from fructose. For instance, Qi *et al.* (2015) prepared a carbonaceous microspheric material by hydrothermal carbonization of glucose without sulfonation, which gave a high HMF yield of 88.1% at 100 °C. Liu *et al.* (2013) reported that using cellulose sulfuric acid as catalyst, 93.6% HMF yield was obtained in DMSO at 100 °C in 45 min. Shen *et al.* (2016) prepared a novel sulfonated bamboo-derived carbon (SBC) and discovered that the catalytic performance in the dehydration of fructose to HMF was excellent, and HMF yield reached 92.1% in THF/DMSO reaction medium. Hu *et al.* (2015) described a magnetic lignin-derived carbonaceous solid catalyst for HMF production in DMSO, and as high as 81.1% HMF yield was achieved at 130 °C in 40 min.

Most carbon-based solid catalysts require high-temperature carbonization and sulfonation with a large amount of concentrated sulfuric acid or fuming sulfuric acid, which makes the synthetic processes hard and complicated. These methods of HMF preparation are mostly carried out in DMSO, which is slightly toxic and odorous. Recently, Dumesic and Horváth's groups developed a green reaction system for biomass conversion that uses γ-valerolactone (GVL) as a solvent (Alonso *et al.* 2013; Qi *et al.* 2014). The solvent GVL, as a new generation of green sustainable solvent, has advantages compared with other common solvents. It can be obtained from lignocellulosic biomass, and it is nontoxic, secure, and eco-friendly. GVL offers a promising reaction medium for the efficient and selective conversion of renewable biomass feedstocks. Herein, GVL is selected as a reaction solvent for carbohydrate transformation into HMF.

Recently, we have prepared a strong solid acid catalyst, *via* copolymerization of *p*-toluenesulfonic acid (PTSA) and paraformaldehyde (POM), denoted PTSA-POM. According to a previously reported preparation method (Liang *et al.* 2008; Fan *et al.* 2010), the catalyst cannot be used in an aqueous solution. When the untreated catalyst was used in aqueous solutions, the weight loss was very serious and the filtrate color was black because of the dissolution of PTSA-POM. However, after high-temperature calcining treatment, the catalyst showed improved water resistance and higher thermal stability (250 °C). The catalyst has been successfully applied in conversion of xylose, xylan, and even raw corn stalk to furfural (Xu *et al.* 2015b). Additionally, the catalyst has many other advantages, such as ease of preparation, low cost, and high activity, and it possesses strong acidity (2.4 $\text{mmol}\cdot\text{g}^{-1}\ \text{H}^{+}$).

In this paper, to further extend the catalytic application of PTSA-POM for biomass conversion, the catalyst was selected for the production of HMF from fructose in GVL-H_2O reaction medium. Based on this study, the effects of various experimental parameters, including temperature, reaction time, water concentration, various solvents, fructose levels, and PTSA-POM loading, as well as catalyst recycling, on fructose dehydration were systematically investigated. Furthermore, one-step conversion of sucrose, glucose, and cellulose to HMF was also examined using the efficient catalytic system.

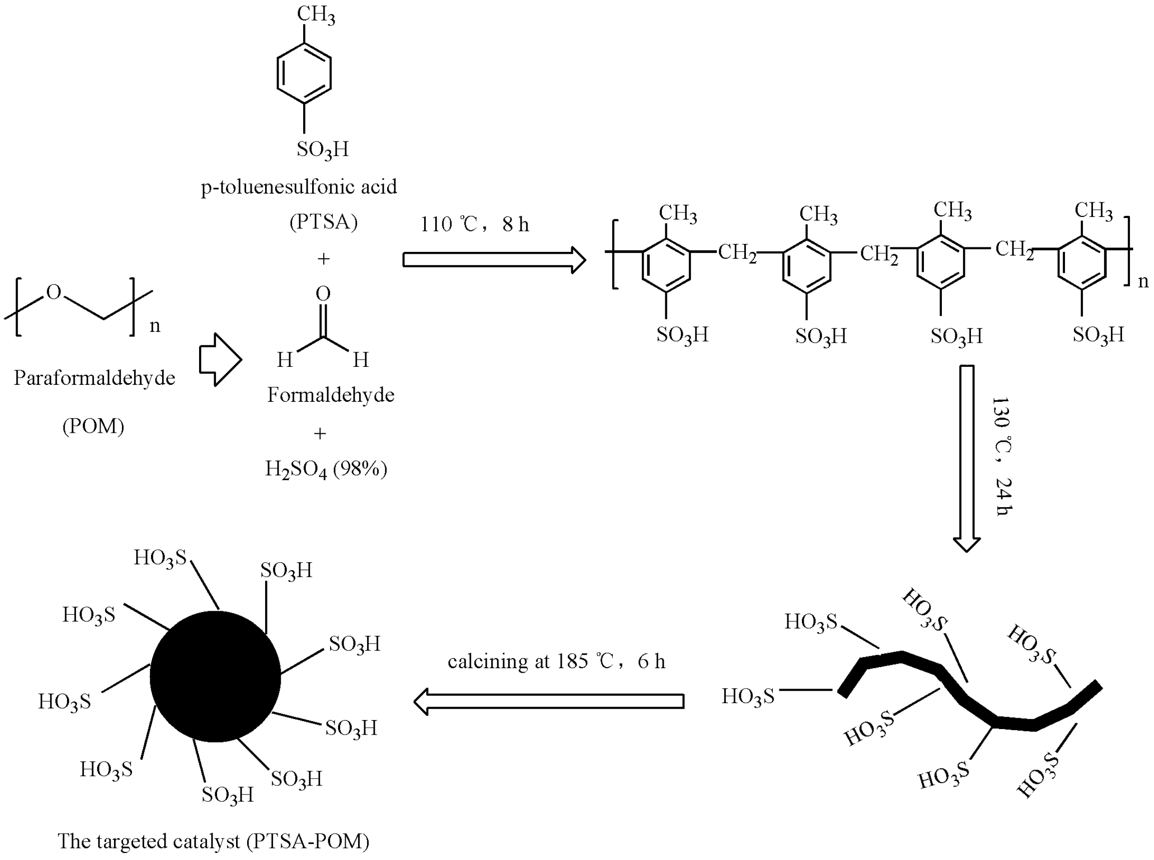
EXPERIMENTAL

Materials

D-fructose (99%), sucrose (AR), D-(+)-glucose (GC, ≥ 99.5%), microcrystalline cellulose (average particle size 25 μm), *p*-toluenesulfonic acid monohydrate (PTSA•H_2O ≥ 98.5%), paraformaldehyde (POM, AR), γ-valerolactone (GVL, 98%), furfural (99%), and 5-hydroxymethylfurfural (HMF, 98%) were purchased from Aladdin Industrial Inc. (Shanghai, China). Sulfuric acid (H_2SO_4, 96% to 98%, AR), 1,4-dioxane (AR), tetrahydrofuran (THF, AR), dimethyl sulfoxide (DMSO, AR), and NaCl (AR) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals in this work are commercially available and were used without further purification.

Catalyst Synthesis

The solid acid PTSA-POM was prepared following the literature procedure (Liang *et al.* 2008; Fan *et al.* 2010) with a slight modification. Typically, a mixture of PTSA•H_2O (10.00 g) and H_2SO_4 (98%, 0.2 mL) was heated at 110 °C in a three-necked round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. When PTSA•H_2O was completely melted, 4.00 g of POM was added immediately. The reaction mixture was heated to 110 °C for 8 h, and to 130 °C for 24 h to form a black solid. The black solid was filtered and washed repeatedly with deionized water until the filtrate reached pH 7. The resulting sample was dried at 120 °C for 12 h and further ground into powder. After that, the black powder was calcined at 185 °C for 6 h in a muffle furnace to get the desired catalyst, as shown in Scheme 1.



Scheme 1. The synthetic route for the solid catalyst PTSA-POM

Carbohydrate Conversion into HMF

The catalytic decomposition of carbohydrates into HMF was performed in a high-pressure stainless steel reactor (25 mL) equipped with an electric heating jacket and a magnetic stirrer. In a typical experiment, approximately 0.40 g of carbohydrate feed, 0.20 g of PTSA-POM catalyst, 15.0 mL of GVL, and 1.5 mL of deionized water were loaded into the reactor. The sealed autoclave was then heated to the desired temperature for 30 min at a stirring speed of 500 rpm. When the reaction ended, the reactor was quickly removed from the electric heating jacket and placed into tap water to quench the reaction. Samples were diluted by distilled water and filtered with a 0.45-μm syringe filter prior to HPLC analysis.

HPLC Analysis

The yields of HMF and furfural were quantified by HPLC analysis (Waters, 515 pump, USA) using a Symmetry®-C18 column (5 μm, 4.6×150 mm, Waters, USA) and a UV/Vis detector (Waters 2489, USA) set at 280 nm. The temperature of the column oven was maintained at 30 °C. Methanol-distilled water mixture (2:3, v/v) was used as the mobile phase at a flow rate of 0.4 mL/min. Fructose was determined by means of XBridge™ amide column (3.5 μm, 4.6×150 mm, Waters, USA) and a refractive index detector. Column oven and detector temperature was maintained at 45 °C. The mobile phase used was acetonitrile-distilled water mixture (3:2, v/v) with a flow rate of 0.4 mL/min. Authentic samples of fructose, HMF, and furfural were used as standards, and their calibration curves were used for quantification.

Fructose conversion (mol %), HMF and furfural yield (mol %), and HMF selectivity (%) were defined as follows:

$$\text{Fructose conversion (mol \%)} = \frac{\text{moles of reacted fructose}}{\text{moles of starting fructose}} \times 100\% \tag{1}$$

$$\text{HMF yield (mol \%)} = \frac{\text{moles of HMF produced}}{\text{moles of starting carbohydrate}} \times 100\% \tag{2}$$

$$\text{HMF selectivity (\%)} = \frac{\text{HMF yield}}{\text{fructose conversion}} \times 100\% \tag{3}$$

$$\text{Furfural yield (mol \%)} = \frac{\text{moles of furfural produced}}{\text{moles of starting carbohydrate}} \times 100\% \tag{4}$$

RESULTS AND DISCUSSION

Production of HMF from Fructose

The conversion of fructose into HMF catalyzed by PTSA-POM was investigated by performing experiments in GVL (containing 10 wt.% water) at various temperatures and reaction times (Fig. 1).

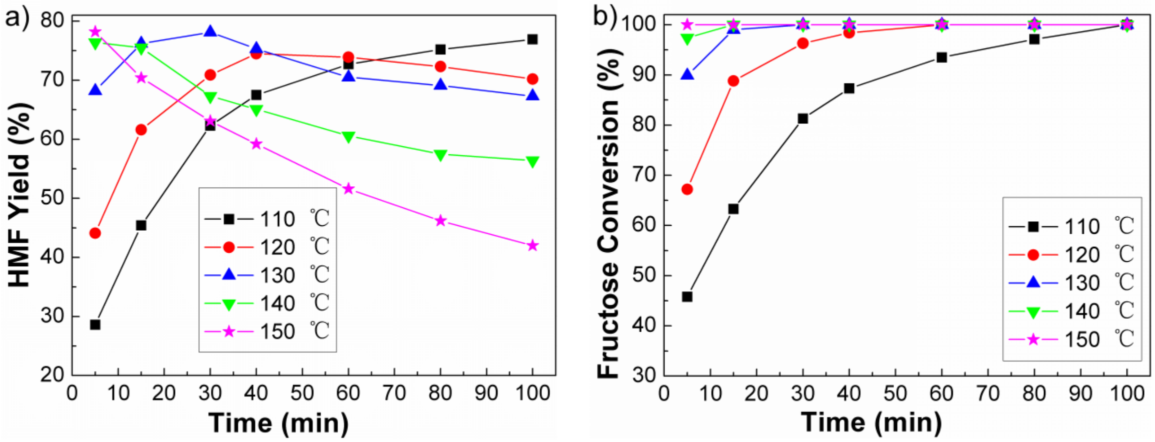


Fig. 1. Effect of reaction temperature on fructose conversion into HMF in GVL catalyzed by PTSA-POM: a) HMF yield; b) fructose conversion. Reaction conditions: fructose 0.40 g, PTSA-POM 0.20 g, GVL 15.0 mL, H_2O 1.5 mL, 500 rpm, and 30 min heating-up time was required to achieve the desired temperature.

The formations of HMF and side products are highly dependent on the reaction temperature and time. Compared with the initial stage of HMF yield and fructose conversion at various temperatures, it seems that higher temperatures favored the fructose dehydration reaction. For instance, when the reaction was carried out at 110 °C, a 28.6% HMF yield with 45.8% fructose conversion was obtained in 5 min, and the HMF yield increased to 68.2% (89.9%

conversion) at the same time by increasing temperature to 130 °C. With a further increase of the reaction temperature to 150 °C, a high HMF yield of 78.2% was achieved, with complete fructose conversion. At low temperature (110 °C), the yield of HMF gradually increased when the reaction time was extended from 5 min to 100 min. At 120 and 130 °C, the HMF yield first increased over time, and then decreased. At higher temperatures (140 and 150 °C), the HMF yield reached a maximum value quickly within a short time and then decreased rapidly. This indicated that high temperature not only was beneficial for the desired transformation of fructose to HMF, but also accelerated undesired side reactions. Obviously, HMF was unstable in the GVL/H_2O mixture at high temperature. The disappearance of HMF at higher temperature can be attributed to the formation of humins by HMF degradation reactions (*i.e.*, fragmentation, resinification, and condensation reactions), which are unavoidable in HMF production.

Considering the properties of biomass resources, water is inevitable and essential in the biomass conversion process. Gürbüz *et al.* (2013) investigated the effect of water concentration on the conversion of xylose into furfural in GVL-H_2O with H-mordenite and found that the presence of water had negative effects on furfural production. Water not only decreased the rate of furfural production, but also accelerated furfural degradation reactions. Hence, the present work also studied the fructose dehydration to HMF over PTSA-POM in GVL with various concentrations of water (5 to 30 wt%) (Fig. 2). It should be noted that all of the water weight ratios were based on GVL. Figure 2 shows the presence of water considerably affected fructose dehydration reaction rate.

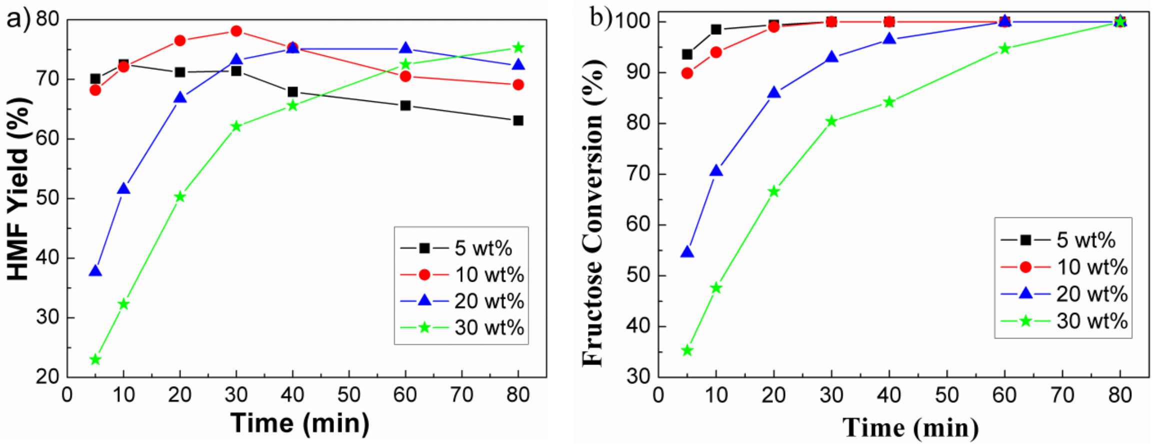


Fig. 2. Effect of water concentration on fructose conversion into HMF in GVL catalyzed by PTSA-POM: a) HMF yield; b) fructose conversion. Reaction conditions: fructose 0.40 g, PTSA-POM 0.20 g, GVL 15.0 mL, 130 °C (30 min heating-up time), and 500 rpm. Note: Water weight ratios are based on GVL.

With higher water concentrations, lower HMF formation rates were observed. It is interesting to note that high water concentration decreased the rates of HMF degradation reactions, leading to a prominent increase in HMF stability in the reaction medium, which is contrary to previous results concerning furfural production. Zhang *et al.* (2014a) found a similar phenomenon in the process of xylose dehydration to furfural. For instance, when the reaction was conducted with 5 wt% water, an HMF yield of 72.5% was obtained in 10 min, and the HMF yield decreased rapidly to 63% by prolonging the reaction time to 80 min. When water concentration increased to 30 wt%, the HMF yield increased from 23.0% (5 min) to 75.3% (80 min). HMF suffered a severe side reaction with reduced water content.

In other words, adding a proper amount of water could contribute to HMF stability (preventing the occurrence of side reaction to produce undesired humins) in this reaction system, although the reaction rate of HMF formation declined. However, this kind of abnormal phenomenon is not well understood at present. It is extremely interesting and deserves further investigation in the future.

The effect of solvent is important for biomass conversion. Thus, the conversion of fructose to HMF was studied in solvents including H_2O, THF, dioxane, DMSO, and GVL using the novel catalyst PTSA-POM at 130 °C. As shown in Fig. 3, DMSO proved to be the best solvent for HMF production and gave the highest HMF yield of 90.6% in 40 min. With a further increase in the reaction time to 80 min, the HMF yield loss was negligible. This indicated that HMF is stable in DMSO, which can suppress side reactions. This result was consistent with previous studies (Liu *et al.* 2013). The solvents THF and dioxane also were efficient solvents and had almost the same effect on the dehydration of fructose to HMF (the two curves were difficult to separate from each other). The highest HMF yields of 81.9% in THF and 81.7% in dioxane were obtained. Although DMSO, dioxane, and THF were better solvents for HMF production, they cannot be applied for industrial-scale production. This is because THF and dioxane will bring about safety issues because of the formation of peroxides (Qi *et al.* 2014), and DMSO is slightly toxic and odorous. GVL, as a green renewable solvent, also displayed outstanding behavior, producing HMF with 78.1% yield. Thus, GVL can be regarded as a promising alternative solvent for biomass conversion. Moreover, water as a green and ideal solvent was investigated for HMF production. However, the fructose dehydration rate was very low compared with other organic solvents, and low HMF yield (21.1%) with low fructose conversion (32.2%) was obtained after 80 min.

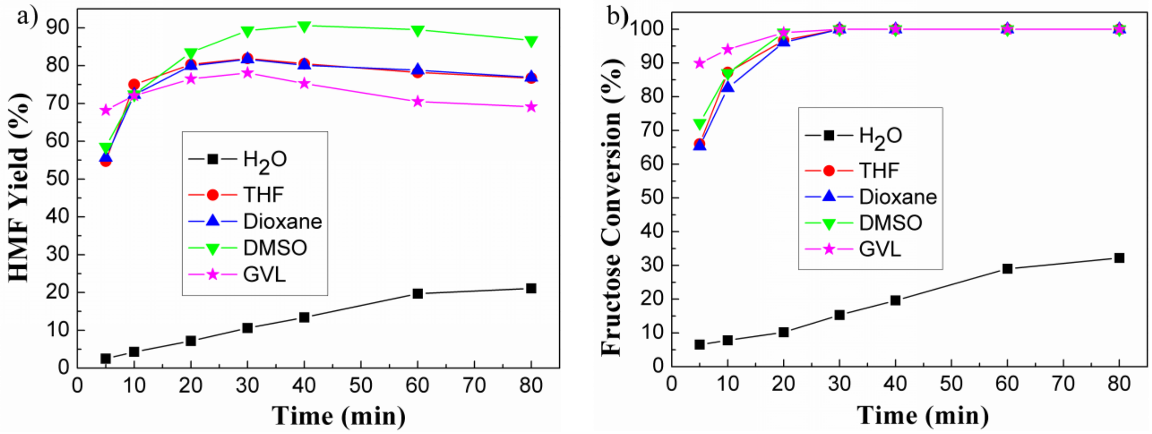


Fig. 3. Effect of diverse solvents on fructose conversion into HMF catalyzed by PTSA-POM: a) HMF yield; b) fructose conversion. Reaction conditions: fructose 0.40 g, PTSA-POM 0.20 g, organic solvents 15.0 mL, H_2O 1.5 mL, 130 °C (30 min heating-up time), 500 rpm. Note: when pure water was used as a solvent, H_2O = 16.5 mL.

From an application point of view, if a catalytic system possesses the ability to process feedstock at high concentrations, the process will be more profitable for industrial production. Hence, the influence of starting fructose loading on the dehydration of fructose to HMF catalyzed by PTSA-POM in GVL/10 wt% H_2O was investigated, and the results are shown in Table 1. According to the experimental details described herein, the initial loading amount of fructose had a substantial impact on HMF production. HMF yield and selectivity increased with increasing starting fructose amount at the initial stage of the reaction. When 0.40 g fructose in 16.5 mL of GVL/H_2O was used, the highest HMF yield and selectivity were obtained, with complete fructose conversion. After that, HMF yield, selectivity, and fructose conversion decreased slightly with increasing fructose loading. A high concentration of HMF generated with increased initial fructose loading led to an increase in undesired side reactions, such as self-polymerization of HMF or cross-polymerization between HMF and fructose (Hu *et al.* 2015; Qi *et al.* 2015), resulting in a poor HMF yield.

Table 1. Effect of Fructose Concentration on the Conversion of Fructose into 5-HMF in GVL Catalyzed by PTSA-POM

Entry	Fructose Loading (g)	HMF Yield (%)	Fructose Conversion (%)	HMF Selectivity (%)
1	0.15	72.4	100	72.4
2	0.30	74.5	100	74.5
3	0.40	78.1	100	78.1
4	0.45	77.5	100	77.5
5	0.60	76.5	99.5	76.9
6	0.90	73.4	99.3	73.9
7	1.20	69.1	98.4	70.2
8	1.50	68.8	97.8	70.3
9	1.80	66.5	96.5	68.9
Reaction conditions: 0.20g PTSA-POM, 15.0 mL GVL, 1.5 mL H_2O, 130 °C (30 min heating-up time), 30 min, 500 rpm.				

Table 2. Effect of Catalyst Loading on the Conversion of Fructose into HMF

Entry	Catalyst loading (wt.%)	HMF Yield (%)	Fructose Conversion (%)	HMF Selectivity (%)
1	5	50.2	69.0	72.8
2	10	62.2	84.5	73.6
3	20	72.9	96.3	75.7
4	30	75.4	98.2	76.8
5	40	77.8	99.2	78.4
6	50	78.1	100	78.1
7	60	76.8	100	76.8
8	80	73.0	100	73.0
9	100	72.6	100	72.6
Reaction conditions: 0.40 g fructose, 15.0 mL GVL, 1.5 mL H_2O, 130 °C (30 min heating-up time), 30 min, 500 rpm. Note: catalyst loading is relative to fructose.				

The effect of the catalyst dosage (based on the weight of fructose) on the dehydration of fructose to HMF is shown in Table 2. HMF yield, selectivity, and fructose conversion first rapidly increased with increasing PTSA-POM dosage. After arriving at the peak values, the HMF yield and selectivity decreased gradually. For example, when only 5 wt% (0.02 g) PTSA-POM was added, 50.2% HMF with 69.0% fructose conversion yield was achieved, which suggested that the prepared catalyst PTSA-POM can catalyze the reaction effectively. When the added catalyst loading was below 50 wt% (0.20 g), PTSA-POM dosage had a positive effect on HMF yield. A total of 40 to 50 wt% catalyst loading was considered the optimum addition of PTSA-POM, and this condition was selected in the present work. The addition of more than 50 wt% of the catalyst resulted in a decline in the HMF yield for fructose dehydration reaction. This suggests that excessive PTSA-POM accelerated undesired HMF side reactions such as decomposition, condensation, and polymerization (Hu *et al.* 2015).

Recyclability Study of PTSA-POM

The reusability of solid acid catalyst is of prime importance in industrial production, so the activity and stability of PTSA-POM for the conversion of fructose to HMF in GVL/10 wt.% H_2O reaction system at 130 °C was tested. To alleviate the effect of the inevitable weight loss caused by multiple recycling operations, 0.30 g of catalyst (60 wt%) was used in these recycling experiments. After the dehydration reaction, the catalyst was collected by suction filtration, repeatedly washed with distilled water, dried at 105 °C until the catalyst weight remained unchanged, and then used for the next reaction. As depicted in Fig. 4, HMF yield was always maintained above 70%. The first time PTSA-POM was used, the HMF yield reached 75.3%. After the seventh cycle, the yield was 70.3%, a decrease of only 5.0%. These results suggested that PTSA-POM showed a good catalytic stability and reusability for fructose dehydration to HMF in GVL-H_2O, although HMF yield and fructose conversion had a minor reduction trend with successive catalytic cycles, which might be ascribed to a slight leaching of SO_3H groups and an unavoidable weight loss of PTSA-POM. In summary, there was no obvious decrease in catalytic activity after seven successive reaction runs for the catalyst.

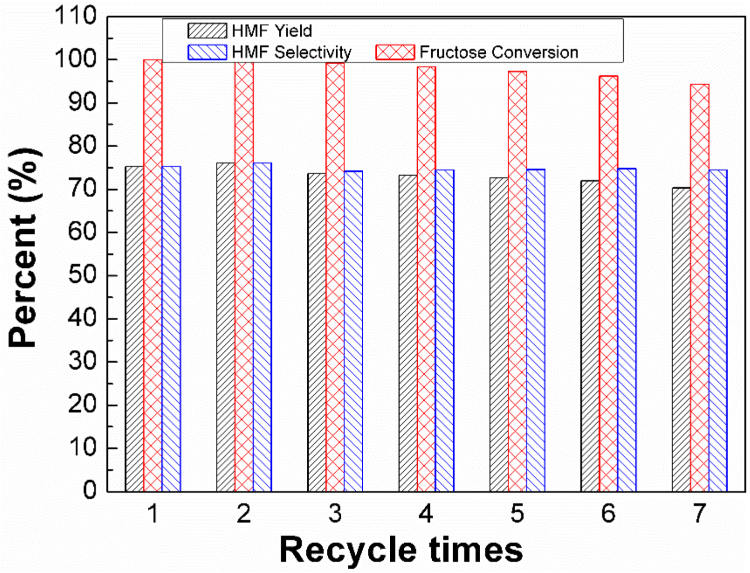


Fig. 4. Recycling study of PTSA-POM in the dehydration of D-fructose to HMF in GVL. Reaction conditions: fructose 0.50 g, PTSA-POM 0.30 g, GVL 15.0 mL, H_2O 1.5 mL, 130 °C (30 min heating-up time), 30 min, 500 rpm.

Dehydration of Sucrose, Glucose, and Cellulose to HMF

The conversion of sucrose to HMF in GVL/10 wt% H_2O reaction system over PTSA-POM was also investigated (Fig. 5). Sucrose is a non-reducing disaccharide composed of an α-D-glucopyranose and a β-D-fructofuranose linked together by a 1-2 glycosidic bond. Therefore, HMF production from sucrose cannot be readily compared with that from fructose. When the reaction was conducted at 130 °C from 5 to 80 min, HMF yields always remained above 37%, equal to one-half of those from fructose (*ca.* 76%). This indicated that only fructose units were dehydrated and that glucose units in sucrose were still stable under the reaction conditions. Further increasing the reaction temperatures or prolonging the reaction time brought about serious side reactions for HMF. For instance, when the temperature increased to 160 °C, HMF yield was only 24.1% after 80 min, a decrease of 15.1% (the highest yield, 39.2%, was obtained at 130 °C after 20 min).

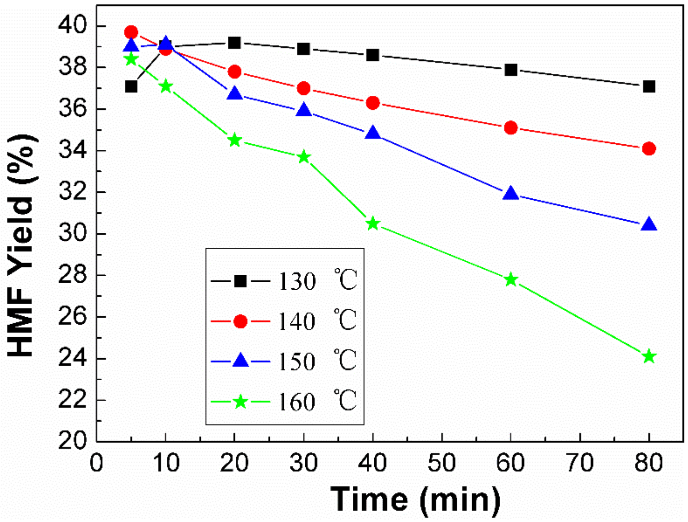


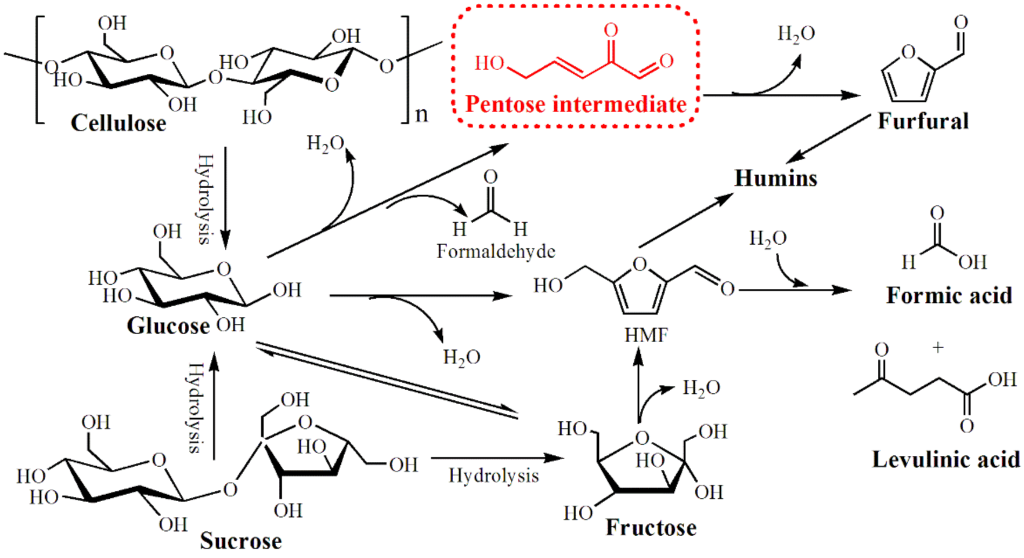
Fig. 5. Effect of reaction temperature on sucrose conversion into HMF in GVL catalyzed by PTSA-POM. Reaction conditions: 0.20 g PTSA-POM, 0.40 g sucrose, 15.0 mL GVL, 1.5 mL H_2O, 30 min heating-up time, 500 rpm.

According to the work described above and as per other relevant literature, fructose is an optimal feedstock for HMF production with high yield in various catalytic systems. However, it should be noted that fructose is less abundant than glucose and cellulose in nature. Glucose and cellulose (a linear macromolecule consisting of anhydroglucose units) are the most abundant and cheapest available monosaccharide and polysaccharide, respectively. Direct conversion of glucose and cellulose to HMF is extremely vital for biomass resources conversion. Therefore, we explored the one-step conversion of glucose and cellulose into HMF using the abovementioned catalytic system, and the results are summarized in Table 3.

HMF yields from glucose and cellulose increased with increasing temperature or extended reaction time. Unfortunately, under these reaction conditions, HMF yields were below 15%, far lower than those obtained from fructose and sucrose. A higher reaction temperature and a longer reaction time did not noticeably improve the HMF yields. The different dehydration behaviors between glucose and fructose can be ascribed to their different structures. Glucose has a pyranosyl structure, which is much more stable than the furanosyl structure of fructose in the reaction medium (Hu *et al.* 2015). Glucose must first be isomerized to fructose before transformation to HMF by Lewis acids such as metal chlorides or Sn-Beta. However, PTSA-POM is a type of Brønsted acid, failing to isomerize glucose to fructose. Thus, designing a bifunctional solid catalyst bearing Lewis and Brønsted acid sites for the conversion of glucose and cellulose into HMF is indispensable in future studies.

Table 3. Conversion of Glucose and Cellulose into HMF using PTSA-POM

Feed	Temp (°C)	Time (min)	Yield (%)	
			HMF	Furfural
glucose	160	5	7.0	3.8
		10	9.7	6.8
		20	10.0	10.5
		30	13.2	14.0
		40	13.9	16.0
	170	10	9.5	10.3
		20	13.2	15.6
		30	14.6	18.7
	180	10	11.6	14.5
		20	14.1	19.8
		30	14.2	22.3
cellulose	170	20	5.9	6.9
		30	7.4	9.3
		40	8.9	11.9
	180	10	5.8	6.6
		20	9.4	12.4
		30	11.1	16.1
		40	11.7	21.3
	190	10	8.9	11.8
		20	12.1	19.1
		30	12.3	22.3
Reaction conditions: 0.20 g PTSA-POM, 0.40 g glucose or cellulose, 15.0 mL GVL, 1.5 mL H_2O, 30 min heating-up time, 500 rpm				



Scheme 2. Reaction route for HMF and furfural production from various carbohydrates

Interestingly, in the HMF production process, some furfural was also detected in this reaction system, and furfural yields increased with an increase in temperature. A furfural yield of 22.3% from glucose was obtained at 180 °C for 30 min, which was even higher than the HMF yield (14.2%). The same furfural yield was also achieved from cellulose under more severe conditions (190 °C for 30 min). Gürbüz *et al.* (2013) and Zhang *et al.* (2014a) also found this phenomenon when using H-mordenite and $FeCl_3{\cdot}6H_2O$ as catalysts for furfural production in GVL, respectively. According to previous reports, this may occur because glucose can transform to a pentose by tautomerization and a subsequent retro-aldol reaction in the presence of an acid catalyst in GVL (Aida *et al.* 2007; Jin and Enomoto 2011). The pentose intermediate is then dehydrated to form furfural (Scheme 2).

CONCLUSIONS

1. A novel solid acid catalyst, PTSA-POM, was prepared by the copolymerization of PTSA and POM. The catalyst showed good water resistance, high thermal stability (250 °C), strong acidity (2.4 mmol/g H^+), excellent reusability, and ease of preparation.
2. The prepared PTSA-POM was effective for the conversion of fructose and sucrose into HMF in GVL, and high HMF yields of 78.1% and 39.2% were obtained at 130 °C, respectively.
3. Catalyst recycling experiments demonstrated that PTSA-POM can be reused at least for seven cycles with only a slightly reduced activity toward fructose conversion into HMF. This may provide an efficient and eco-friendly route for HMF production.
4. The catalytic system was also used to explore the one-step conversion of glucose and cellulose into HMF. However, HMF yields were below 15%. Hence, it is necessary to design an effective heterogeneous catalyst with Lewis and Brønsted acid sites for transforming biomass carbohydrates into fine chemicals in the future.

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