



Efficient catalytic system for the direct transformation of lignocellulosic biomass to furfural and 5-hydroxymethylfurfural



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HIGHLIGHTS

- An efficient strategy for the co-production of furfural and 5-HMF was proposed.
- SPTPA was used as catalyst to convert untreated corncob.
- Simultaneously encouraging yields of furfural (73.9%) and 5-HMF (32.3%) were achieved.

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ABSTRACT

A feasible approach was developed for the co-production of 5-hydroxymethylfurfural (5-HMF) and furfural from corncob via a new porous polytriphenylamine-SO₃H (SPTPA) solid acid catalyst in lactone solvents. XRD, SEM, XPS, N₂ adsorption-desorption, elemental analysis, TG-DTA, acid-base titration and FTIR spectroscopy techniques were used to characterize the catalyst. This study demonstrates and optimizes the catalytic performance of SPTPA and solvent selection. SPTPA was found to exhibit superior catalytic ability in γ -valerolactone (GVL). Under the optimum reaction conditions, simultaneously encouraging yields of furfural (73.9%) and 5-HMF (32.3%) were achieved at 448 K. The main advantages of this process include reasonable yields of both 5-HMF and furfural in the same reaction system, practical simplicity for the raw biomass utilization, and the use of a safe and environmentally benign solvent.

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1. Introduction

Non-feed lignocellulosic biomass is a greener and biorenewable resource to govern the bio-based economy by synthesizing valuable products (Teong et al., 2014). Among the special chemicals derived from lignocellulosic biomass, furfural and 5-hydroxymethylfurfural (5-HMF) are potential building block components to produce a variety of industrially important organic moieties (Mariscal et al., 2016; Mirzaei and Karimi, 2016). In a study supported by the U.S. Department of Energy, furfural and 5-HMF were both selected in the top 10 versatile platform chemicals that could be made from lignocelluloses (Agirrezabal-Telleria et al., 2014; Mamman et al., 2008).

Generally, furfural is produced from the hemicellulose fraction of lignocellulosic biomass, while 5-HMF is obtained by catalytic conversion of the cellulose fraction. Although furfural production has been industrialized since 1921, the current commercial tech-

nology for producing furfural relies on highly polluting and energy-intensive strategies with low yields (Peleteiro et al., 2016). Furthermore, the sole production of furfural from lignocellulosic biomass would be wasteful and uneconomic since hemicellulose only constitutes a portion of the total composition of lignocellulose (Dussan et al., 2013; Deng et al., 2016; Cui et al., 2016). Hence, the development of integrated conversion strategies to co-produce furfural and other value-added chemicals, such as 5-HMF, is important to improve process economics. (Alonso et al., 2013). However, robust crystalline cellulose is far less reactive than amorphous hemicellulose; thus, furfural formation occurs much sooner than 5-HMF production in conventional catalytic systems. Therefore, the development of a single catalytic system for the production of both furfural and 5-HMF from raw biomass is still challenging (Mazzotta et al., 2014).

To overcome these issues, alternative catalytic routes for the co-production of furfural and 5-HMF have been investigated (Agirrezabal-Telleria et al., 2014; Otomo et al., 2015). Lacerda et al. studied the production of 5-HMF and furfural from cellulose and lignocellulosic materials in a microwave oven, affording a

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maximum combined yield of furfural and 5-HMF of 53.24% (Lacerda et al., 2015). Seemala et al. investigated 5-HMF and furfural production from pinewood and eucalyptus sawdust in mono- and biphasic solvent systems by using levulinic acid as catalyst, but the molar yields were not satisfactory (below 10%) (Seemala et al., 2016). Cai et al. developed a particularly effective catalytic approach for direct biomass conversion by combining FeCl₃ with water/THF, achieving simultaneously high yields of furfural (95%) and 5-HMF (51%) (Cai et al., 2014). However, although the yields from this route are exciting, its large-scale application is still difficult due to the corrosion issues as well as the toxicity of the homogeneous systems.

Compared with homogeneous reaction systems, heterogeneous catalytic processes are more applicable to industrial production. Up to now, a vast range of solid acid catalysts have been developed for furan-based chemicals production reactions (Garciaolmo et al., 2016). Among these materials, the sulfonation of amorphous carbon or aromatic network materials to design heterogeneous acid catalysts with a high density of –SO₃H sites and high surface area has led to promising catalytic performance for the production of furanic compounds (Kaiprommarat et al., 2016; Yan et al., 2014; Zhang et al., 2016). In this study, sulfonated polytriphenylamine (SPTPA) was prepared by the oxidative self-polycondensation of triphenylamine followed by sulfonation of the resulting PTPA with chlorosulfonic acid to produce a polymeric aromatic structure embedded with active –SO₃H sites. The morphology and various properties of the prepared SPTPA were characterized, the catalytic activity and reusability of SPTPA in the co-synthesis of 5-HMF and furfural from corncob in lactone solvents were investigated in detail.

2. Materials and methods

2.1. Materials

Triphenylamine (TPA) and anhydrous FeCl₃ were purchased from Macklin. Chlorosulfonic acid was supplied by Xiya Chemical Co., Ltd. (Chengdu, China). γ -Valerolactone ($\geq 98\%$) was supplied by Sigma–Aldrich. Other reagents were supplied by Tianjin Kermel Chemical Co., Ltd. (Tianjin, China). All the commercial chemicals were used as received without further purification. Corncob was locally sourced material (Tianjin, North China) that was milled to pass 80 mesh and dried at 378 K to a constant weight before use. Chemical analysis results indicated that the hemicellulose, cellulose and lignin content in corncob was 36.9 wt%, 30.2 wt% and 32.9 wt%, respectively.

2.2. Synthesis of sulfonated porous polymer SPTPA

SPTPA was prepared by following the literature method (Iwan and Sek, 2011; Ni et al., 2015) with slight modifications. The preparation of SPTPA was carried out in a 150 mL glass reactor with a Teflon screw top. In a typical synthesis, triphenylamine monomer (982 mg, 4 mmol) was added to dichloroethane (60 mL) with vigorous magnetic stirring. After purging the system with nitrogen for air replacement, the anhydrous FeCl₃ (649 mg, 4 mmol) was added under a nitrogen atmosphere, the reactor was then sealed and the mixture was stirred for 18 h with constant heating at 353 K. A second portion of FeCl₃ (649 mg, 4 mmol) was subsequently added to the reaction mixture in the interval of 1 h, and the total amount of FeCl₃ used was two times that of TPA (molar ratio).

The reaction mixture was then poured into acetone to deposit the precipitate, which was then filtered and washed successively with DMF and methanol several times for purification. Finally,

the polymer product (PTPA) was dried under vacuum at 323 K overnight. Then, PTPA (600 mg) was added to DCM (60 mL) in an ice bath, and chlorosulfonic acid (6 mL) was added to the mixture over 20 min under continuous stirring, and the stirring was continued for 75 h at room temperature. Finally, the solid was filtered, substantially washed with methanol and distilled water, and dried to obtain sulfonated polymer SPTPA.

2.3. Characterization of the catalyst

The surface morphology and structure of SPTPA were observed by SEM (JSM-6510LV). The phase structure of the catalyst was determined by powder X-ray diffraction (XRD) spectroscopy (Ultima IV) using a Cu-K α radiation ($\lambda = 0.154$ nm), the data ranging from 10° to 90° were collected at a step size of 0.02°. The functional groups of the sample were detected by FT-IR spectroscopy (IR Prestige-21) using the standard KBr disc method with a 4 cm⁻¹ resolution in the range from 400 to 4000 cm⁻¹. N₂ adsorption–desorption isotherms of SPTPA was measured by surface analyzer (ASAP 2460 system from Micromeritics) at –196 °C. Before adsorption, the sample was degassed under vacuum at 120 °C for 10 h. The specific surface area was evaluated using the method of Brunauer–Emmett–Teller (BET), and the pore volume of the catalyst was calculated according to the method of Barrett–Joyner–Halenda (BJH). The thermogravimetric analysis of the as-synthesized sample was performed by thermal analyzer (TGA/SDTA851, Mettler–Toledo) under N₂ atmosphere with the temperature range from 40 to 800 °C at a heating rate of 10 °C min⁻¹. Sulfur (S) content of the catalyst was determined by Vario Micro cube elemental analyzer (Elementar, Germany). The total acid densities of SPTPA were measured by a well-established acid–base titration using 0.01 M NaOH aqueous solution as the titration base according to the literatures (Hu et al., 2015; Thombal and Jadhav, 2015). XPS analyses were carried out with a Kratos Axis Ultra X-ray photoelectron spectrometer using a monochromatic Al-K α X-ray source.

2.4. Procedure for the conversion of corncob into furfural and 5-HMF

In a typical reaction, corncob (25 mg), GVL (2 mL), and catalyst (6 mg) was added in a thick-walled glass reactor. The reaction mixture was then heated at a specified temperature for a given reaction time in a preheated oil bath. A magnetic stirrer was used for mixing during the reaction. After the desired reaction time had elapsed, the reactor was cooled in an ice bath. The reaction mixture was then diluted and filtered, and the filtered products were analyzed using HPLC.

2.5. Quantification procedure for products

The concentrations of furfural and 5-HMF were quantified using HPLC (Shimadzu LC-2010AHT) with an XDB-C18 column and a UV detector. A solution of acetonitrile/water (15/85, v/v) was used as the mobile phase at a flow rate of 1 mL/min, and the column temperature was maintained at 303 K. Product yields were calculated according to the following equations (Yields of 5-HMF and furfural from corncob were based on cellulose analysis of 30.2 wt%, xylan analysis of 31.7 wt%. When 25 mg corncob was tested, the original content of glucose unit and xylose unit present in corncob was 0.0466 mmol and 0.06 mmol respectively):

$$\text{furfural yield (mol\%)} = \frac{\text{moles of furfural produced}}{\text{moles of xylose unit in corncob}} \times 100$$

$$5\text{ - HMF yield (mol\%)} = \frac{\text{moles of 5 - HMF produced}}{\text{moles of glucose unit in corncob}} \times 100$$

3. Results and discussion

3.1. Characterization of the catalyst

The oxidative polymerization by FeCl_3 promoted the TPA molecules to undergo a polymerization reaction to produce PTPA polymer, and the subsequent sulfonation of the PTPA produced a porous polymer embedded with active $-\text{SO}_3\text{H}$ moieties. The acid strength of the solid acid catalyst is a vital factor closely related to the catalytic activity. The SPTPA obtained here had a total acid density of 1.8 mmol/g (Table S1), as estimated by acid–base titration. The morphology of the SPTPA was investigated by scanning electron microscopy (SEM) analysis (Fig. S1). It can be observed from the SEM images that the particulates obtained from the polymerization and sulfonation process possessed an irregular porous structure constructed of intertwined nanofibrils (100–200 nm) and hierarchical sheet flake-like structures. The BET surface area of the catalyst was found to be 344.3 m^2/g , and the pore volume was 0.134 cm^3/g (Table S1). The wide-angle powder X-ray diffraction patterns of SPTPA (Fig. S2) displayed a single broad diffraction peak between the 2θ values of 10–35°, which could be attributed to the (002) plane of amorphous carbon (Thombal and Jadhav, 2015).

Elemental analysis revealed the composition of S to be 5.04 wt%. The FTIR spectrum (Fig. S3) showed characteristic peaks at 1008 cm^{-1} , 1035 cm^{-1} , 1058 cm^{-1} , and 1384 cm^{-1} , which are ascribed to $\text{O}=\text{S}=\text{O}$ stretching vibrations in the $-\text{SO}_3\text{H}$ groups (Hu et al., 2015; Thombal and Jadhav, 2015; Zhao et al., 2015), and the peak at 1174 cm^{-1} is attributed to $-\text{SO}_3\text{H}$ stretching (Thombal and Jadhav, 2015). The peak at 1290 cm^{-1} can be assigned to the C–N stretching, and that at 817 cm^{-1} can be attributed to a C–H out-of-plane bending of the *para*-disubstituted benzene rings (Tanaka et al., 2001). XPS spectrum of SATPA exhibited a S2p peak (Fig. S4), which is assigned to $-\text{SO}_3\text{H}$ groups. These results indicate that the sulfonic acid groups have been successfully incorporated on the catalyst surface.

3.2. Production of furfural and 5-HMF from corncob catalyzed by SPTPA under different reaction temperatures and times

The effects of reaction temperature and time on the conversion of corncob to 5-HMF and furfural were examined and the results are given in Fig. 1. In the case of corncob transformation, the reaction temperature exhibited a marked effect on the reaction with

respect to the 5-HMF and furfural yields. The catalytic results reflected that 5-HMF and furfural yields increased with temperature in the selected temperature range, with values of close to 66% for furfural and 10% for 5-HMF achieved at 448 K, indicating that higher temperatures benefited the reaction process. Furthermore, the reaction time for achieving the 5-HMF peak value was longer than that for the furfural peak value at all the temperatures; the optimum furfural yield was achieved after 65 min, while the optimum 5-HMF yield was obtained after 85 min, mainly because hemicellulose is more acid-labile than crystalline cellulose. Upon further prolonging the reaction time beyond the peak value, both 5-HMF and furfural yields decreased, which may be ascribed to the notion that longer residence times gave rise to a series of side reactions.

3.3. Effect of catalyst dosage on the conversion of corncob into 5-HMF and furfural

The effect of the amount of SPTPA on the co-production of 5-HMF and furfural from corncob was investigated. As shown in Fig. 2, when 12 mg SPTPA catalyst was used, a furfural yield of 70% and 5-HMF yield of 28% could be obtained after a reaction time of 45 min, indicating the superior catalytic activity of the SPTPA catalyst. Moreover, reasonable furfural yields (70–73.9%) and 5-HMF yields (29.2–32.3%) could be obtained by increasing catalyst dosage from 18 mg to 30 mg in 30 min reaction time. Furfural formation from hemicellulose and 5-HMF formation from cellulose both consist of multiple successive steps, which mainly involve the hydrolysis of hemicellulose/cellulose to xylose/glucose followed by the isomerization and dehydration of the monosaccharide to furfural/5-HMF, and these steps can all be achieved by acid catalysts (Xu et al., 2015). Usually, a higher acid density affords better catalytic performances, thus the good catalytic activity of the SPTPA solid acid catalyst for the co-production of furfural and 5-HMF from corncob can be attributed to the $-\text{SO}_3\text{H}$ groups grafted on PTPA. As a strong protonic acid, SPTPA is capable of hydrolyzing the cellulose/hemicellulose into glucose/xylose by hydrolyzing the β -1,4-glycosidic bonds. In addition, the $-\text{SO}_3\text{H}$ groups also favor the isomerization and dehydration of the formed monosaccharide. Besides protonic acid catalysis, the $\text{S}=\text{O}$ structure in the $-\text{SO}_3\text{H}$ groups on SPTPA surfaces may act as a co-catalyst for the dehydration step (Amarasekara et al., 2008; Zhao et al., 2015),

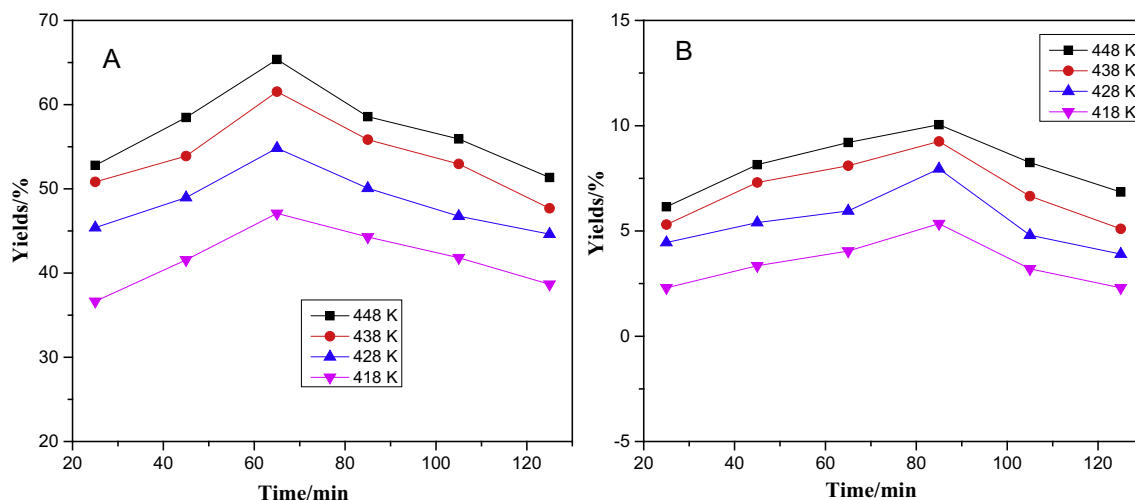


Fig. 1. Effect of temperature and time on 5-HMF and furfural production from corncob in GVL. Reaction conditions: 2 mL GVL, 25 mg corncob, 6 mg SPTPA. A: furfural yields; B: 5-HMF yields.

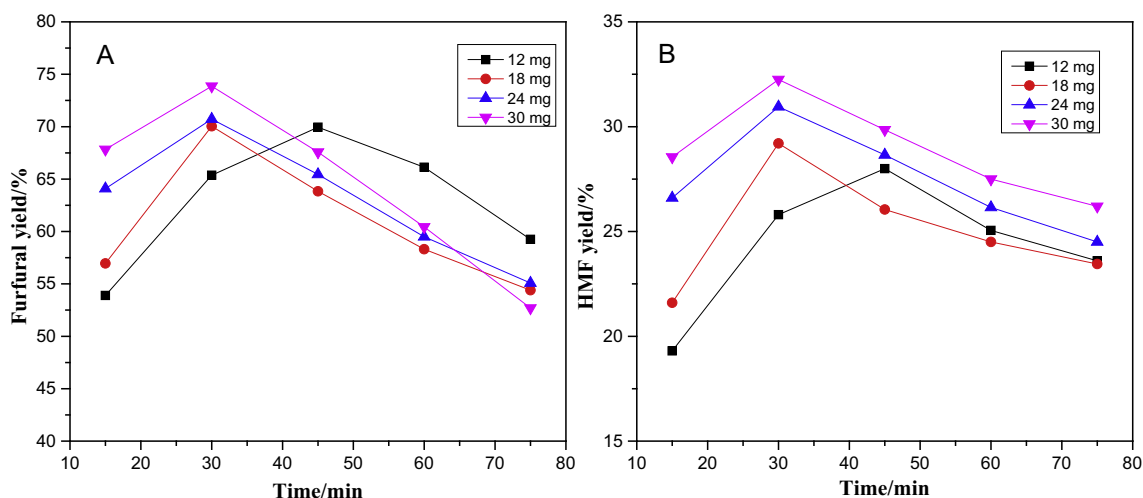


Fig. 2. Effect of catalyst dosage on corn cob conversion into 5-HMF and furfural. Reaction conditions: 2 mL GVL, 25 mg corn cob, 448 K. A: furfural yields; B: 5-HMF yields.

Table 1
Effect of feedstock loading on corn cob conversion into 5-HMF and furfural.^a

Entry	Feedstock loading (mg)	Furfural yield (%)	5-HMF yield (%)
1	40	62.4	27.1
2	50	57.6	14.8
3	60	50.8	11.4
4	70	29	8.5
5 ^b	70	22.7	6.8

^a Reaction conditions: 2 mL GVL, 12 mg SPTPA, 45 min, 448 K.

^b Reaction time: 60 min.

thus both protonic acid catalysis and S=O catalysis may synergistically facilitate these reactions.

Compared with 6 mg SPTPA dosage (Fig. 1, 448 K), the 5-HMF and furfural yields increased when the catalyst dosage was increased (Fig. 2), mainly because high acid density accelerated the reaction rate and improved the yields. However, the increases in both furfural and 5-HMF yields were limited when further increasing catalyst dosage from 18 mg to 30 mg. This result indicates that abundant catalytic sites in the reaction environment are needed to reach satisfactory yields of furanic compounds; nonetheless, excessive amounts of acid sites resulted in yield-loss reactions which decreased 5-HMF and furfural yields.

3.4. Effect of initial corn cob loading on furfural and 5-HMF yields

From an industrial viewpoint, in view of cost restrictions, a high substrate concentration is desirable. A series of experiments were conducted at different corn cob loadings at 448 K in GVL using SPTPA as catalyst, and the results are listed in Table 1. Notably, SPTPA still exhibited encouraging catalytic performance when 40 mg corn cob was tested, affording 62% furfural yield and 27% 5-HMF yield. Then the catalytic reactivity gradually decreased upon increasing the corn cob loading from 50 mg to 70 mg. When using 70 mg of corn cob, both furfural and 5-HMF yields decreased markedly, leading to a 29% furfural yield and 8.5% 5-HMF yield after 45 min reaction time. These results indicate that the yield-loss reactions are more likely to occur with increasing feedstock concentration. Previous studies have demonstrated that there are three main pathways for furfural yield-loss reactions (Antal et al., 1991; Du et al., 2010; Dias et al., 2006): 1. fragmentation of furfural; 2. resinification between furfural molecules; 3. condensation reactions between furfural and reactants (or intermediates). As for

5-HMF yield-loss reactions, two routes are considered to be dominant: 1. rehydration of 5-HMF to formic acid and levulinic acid; 2. condensation reactions between 5-HMF and other organic molecules in the reaction system to form humins and polymers (Atanda et al., 2015; Wang, 2015). From the view of furfural/5-HMF degradation mechanisms, a decrease of furfural/5-HMF yield with increasing corn cob concentration is associated with an increased probability of condensation reactions between furfural/5-HMF and other organic molecules. More reactants and intermediates exist in the reaction system when higher corn cob loadings are tested, and the formed 5-HMF and furfural are more tend to react with these molecules and then generate undesired by-products (Zhang et al., 2013). According to the literatures, the molecular structure and morphology of humins strongly depend on the reaction conditions (Zandvoort et al., 2013; Sevilla and Fuertes, 2009), and reactions such as aldol addition/condensation, etherification and nucleophilic attack are the main pathways for humins formation (Tsilomelekis et al., 2016).

3.5. Furfural and 5-HMF production in diverse solvents

Notably, the reaction solvent is also a critical factor determining the reaction environment in furfural and 5-HMF synthesis. Solvent not only mediates the dispersion and conversion of feedstock (Hu et al., 2012), but also affects product species and degradation (Cui et al., 2016), reaction network (Karinen et al., 2011) as well as activation energy (Mellmer et al., 2014). Besides, according to Hu et al., solvents not only physically dissolve but may also chemically interact with the feedstocks (Hu et al., 2014). For comparison, the production of furfural and 5-HMF from corn cob catalyzed by SPTPS in other green and sustainable lactone solvents was also examined, and the results were illustrated in Fig. 3. Considerable furfural yields were also obtained in γ -Butyrolactone (59.9%) and γ -Undecalactone (53%) under the same reaction conditions. Other solvents (γ -Octalactone, γ -Nonalactone, δ -Dodecalactone and γ -Dodecalactone) gave moderate furfural yields in the range of 33.6–48.5%. 5-HMF yields in these solvents were only 4.6–16.6%. It can be seen that γ -Valerolactone (GVL) and γ -Butyrolactone (GBL) exhibited higher solvent activity for furfural and 5-HMF formation from corn cob than the other five lactone solvents under the same experimental conditions. The results of solvent tests showed that hydrophilic lactone solvents were more suitable for furanic compounds production reactions compared with hydrophobic lactone solvents. What's more, the good solubility of corn cob in GVL

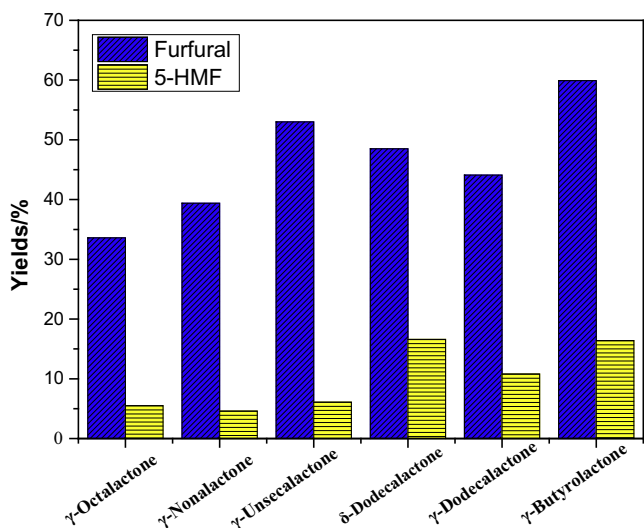


Fig. 3. 5-HMF and furfural yields from corn cob catalyzed by SPTPA in different lactone solvents. Reaction conditions: 2 mL solvent, 448 K, 25 mg corn cob as feedstock, 12 mg SPTPA, 45 min.

also facilitates these successive reactions (Zhang et al., 2014). The strong surface acidity of the prepared SPTPA along with the excellent solvent properties of GVL could be responsible for the enhanced performance in the co-production of furfural and 5-HMF from corn cob.

3.6. Catalyst recycles

The lifetime of the catalyst is of great importance for practical use, but the SPTPA could not be readily separated from the unreacted corn cob residues; thus, the cycle usage test of SPTPA was investigated by using the conversion of xylose and glucose mixtures as representative reactions, and the results are presented in Fig. 4. Run 0 represents the reaction catalyzed by fresh SPTPA, and Runs 1–4 are reuse tests. No insoluble compounds were formed and no humins deposited on the catalyst due to the excellent dissolving capacity of GVL (Gürbüz et al., 2013). After each reaction run, the catalyst was separated by centrifugalization and successively washed with acetone, ethanol, and water. Then, the

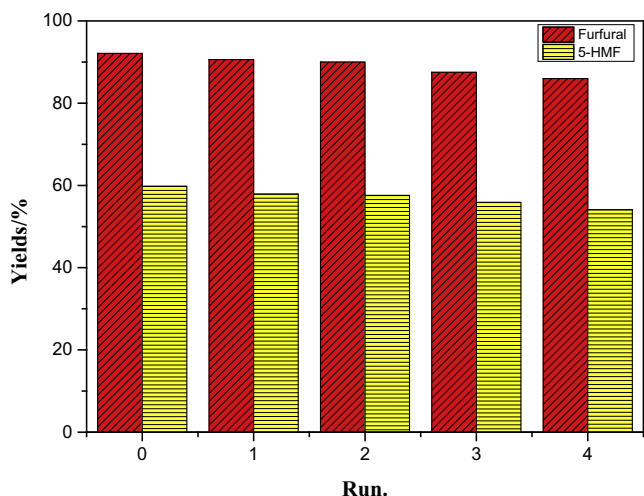


Fig. 4. 5-HMF and furfural yields from xylose and glucose catalyzed by SPTPA in cycle usage tests. Reaction conditions: 2 mL GVL, 448 K, 15 mg xylose and 15 mg glucose as feedstock, 12 mg SPTPA, 20 min.

SPTPA was dried under vacuum at 373 K for 2 h prior to reuse in the next run. As can be seen from Fig. 4, the furfural and 5-HMF yields decreased slightly from the first recycle run, which may be due to the slight decrease in $-\text{SO}_3\text{H}$ content during the reactions (Table S2). In order to investigate the thermal stability of SPTPA, TG-DTA analyses under N_2 flow have been carried out. As shown in Fig. S5, a first decrease in weight (13.5 %) up to 110 °C corresponds to the loss of physically adsorbed water molecules present on the catalyst surface. Furthermore, the minor weight loss up to 180 °C may be indicative of the loss of the strongly adsorbed water molecules having a noncovalent interaction with free sulfonic acid groups (Pramanik et al., 2012) and the small amount of destroyed surface sulfonic acid functional groups. The results of hot filtration experiments also revealed that the catalyst underwent partial leaching of $-\text{SO}_3\text{H}$, but the leaching of active $-\text{SO}_3\text{H}$ moieties was not significant under the typical reaction conditions (Table S3). A successful industrial catalyst is required not only to have high activity and selectivity, but also enough high reusability and stability. For the developed SPTPA catalyst, leaching out of $-\text{SO}_3\text{H}$ group in reaction solvent is to some extent responsible for the generation of toxic effluents and catalyst deactivation, more efforts are needed to enhance the feasibility of its industrial application. In addition, the furfural and 5-HMF obtained in the present reaction system were in a mixture solution. The next project will focus on improving catalyst durability and developing efficient product separation method.

4. Conclusions

The novel sulfonated porous polymer SPTPA having high acid strength was prepared and found to be a highly selective catalyst suitable for co-production of 5-HMF and furfural directly from raw corn cob in GVL. SPTPA converted corn cob efficiently and resulted in simultaneously good yields of furan-based compounds (36.6–73.9% furfural yields and 2.3–32.3% 5-HMF yields). Hydrophilic lactone solvents exhibited better performances for these reactions compared with hydrophobic lactone solvents. The developed process using SPTPA for furfural and 5-HMF production provides a promising strategy for the integrated utilization of hemicellulose and cellulose in crude biomass.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2016.11.097>.

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