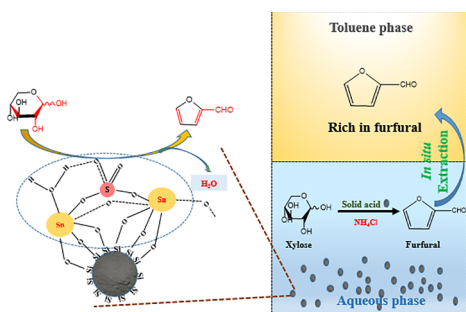# Composite coal fly ash solid acid catalyst in synergy with chloride for biphasic preparation of furfural from corn stover hydrolysate

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GRAPHICAL ABSTRACT

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ABSTRACT

A solid acid catalyst $SO_4^{2-}/SnO_2-Al_2O_3$-CFA was synthesized based on industrial waste coal fly ash (CFA) as carrier and applied in the conversion of oxalic acid pretreated corn stover hydrolysate to produce furfural. Physical properties of the solid acid catalyst were characterized by SEM, FTIR, XRD, BET, EDAX, and NH_3-TPD. Highly wrinkled structure of $SO_4^{2-}/SnO_2-Al_2O_3$-CFA could provide more specific surface area for the covalent linkage between SiO_2 and SnO_2. Factors influencing the efficacy of $SO_4^{2-}/SnO_2-Al_2O_3$-CFA were systematically explored. The highest furfural yield of 84.7% was reached in NH_4Cl-toluene biphasic system at 180 °C for 30 min. The recyclability of $SO_4^{2-}/SnO_2-Al_2O_3$-CFA and toluene could be achieved for five batches with stable performance in transformation of xylose-rich corn stover hydrolysate. This study provided a novel solid acid catalyst with promising potential in the synthesis of furfural from corn stover.

1. Introduction

The depletion of fossil fuels and the deterioration of environmental pollution have stimulated the development of sustainable and environmentally friendly processes for producing fuels and chemical feedstocks from renewable resources (Lozano and Lozano, 2018). Lignocellulosic biomass, mainly consisted of cellulose, hemicellulose and lignin, is abundant, inexpensive and renewable, and could be facilely converted into value-added chemicals and biofuels after pretreatment with physical and chemical methods (Xu et al., 2016; Di et al., 2018; Hassan et al., 2018). Furfural can be produced from hemicellulose fraction of lignocellulosic biomass by acid-catalyzed reaction, and is widely used as a key intermediate in organic synthesis with a broad range of industrial applications (Luo et al., 2019; Zhang et al., 2017; Delbecq et al., 2018).

Generally, the production of furfural can be divided into one-step and two-step processes. In one step conversion, lignocellulosic biomass is converted into xylose and then dehydrated into furfural in the same

reactor. This process is technically simple and easy to operate, whereas also has disadvantages such as low furfural yield, serious pollution and waste of raw materials. With the development of biomass chemical utilization, researchers have focused on comprehensive utilization of raw materials and environmental protection. In the two-step process, lignocellulosic biomass is hydrolyzed to xylose hydrolysate and then dehydrated to form furfural in two different reactors. The two-step method has obvious superiority, including higher furfural yield, limited side reactions and utilization of solid residue (mainly cellulose and lignin) (Mesa et al., 2014). Currently, various strategies have been attempted to improve the furfural yield by designing new catalysts and optimizing catalytic systems (Qing et al., 2017; Wang et al., 2019).

Currently, furfural is commercially produced from biomass-derived pentose cyclodehydration by using mineral acid as catalyst and steam as stripping agent to avoid further degradation. (Agirrezabal-Telleria et al., 2011). However, there are many disadvantages such as relatively low furfural yield (around 45–55%), high energy consumption, unsatisfactory catalyst recovery, equipment corrosion and waste disposal etc. In contrast to homogenous catalytic processes, heterogeneous solid acids display higher feasibility in furfural production, which has drawn an increasing attention (Agirrezabal-Telleria et al., 2014). Various types of solid acid catalysts have been synthesized, such as SO_4^{2-}/SnO_2-ATP (He et al., 2017), zeolites (Rao et al., 2019), heteropolyacid (Guo et al., 2018), ion-exchange resins (Ramirez et al., 2017), sulfonic acid-functionalized MCM materials (Kaiprommarat et al., 2016), metal salts and oxide (Yemis and Mazza, 2019; Li et al., 2018a,b), and sulfonated biochar materials (Deng et al., 2016). They have been applied in the dehydration of xylose into furfural with relatively higher furfural yield and easier recyclability than homogeneous catalysis.

Coal fly ash (CFA) is available as industrial waste from coal combustion in power plants. Generally, burning two tons of coal produces one ton CFA. In 2016, 565 million tons CFA was produced in China, ranking the highest in the world (Li et al., 2018a,b; Wang et al., 2016). The disposal of CFA is however challenging. Only a small portion of CFA could be reused in the manufacture of cement and concrete (Yao et al., 2014). Traditionally, most CFA were deposited directly in land, whereas it is toxic to human health and environment safe (Gollakota et al., 2019). The utilization of CFA for value-added application could turn the trash into treasure, and mitigate environmental issues. Thus, development of new utilization of CFA is of special interest. Recently, CFA has been reported as a heterogeneous catalyst to produce chemicals and medical intermediates (Volli and Purkait, 2015; Chandane et al., 2017). Stable property of CFA rendered its utilization as an efficient catalyst carrier in photoreaction (Zhang et al., 2013), fenton process (Zhang et al., 2012), knovenagel condensations (Dhokte et al., 2011), and esterification (Mazumder et al., 2015). CFA is an aluminosilicate mixture of amorphous and crystalline phases with oxides of Si, Al, Ca, Fe, Mg. To enhance the Brønsted acidity, CFA can be chemically activated with H_2SO_4, and the activated CFA could be used in the synthesis of dimethyl ether, acetylsalicylic acid (aspirin) and methyl salicylate (oil of wintergreen) (Zeng et al., 2014; Khatri and Rani, 2008). Moreover, CFA can also be used as a solid support for cerium triflate in the synthesis of 3,4-dimethoxy acetophenone (antineoplastic) (Khatri et al., 2010). To the best of our knowledge, CFA based solid acid catalyst has not been used in the selective conversion of xylose-rich hydrolysate into furfural.

The reaction system has a great influence on the production of furfural. Water is a good solvent, but the high polarity of water makes furfural less soluble and forms undesired side reaction (Zhang et al., 2016). Therefore, various reaction medias such as ionic liquids (e.g., [BMIM]Cl, [EMIM]Cl, [OMIM]Cl), dimethyl sulfoxide (DMSO), 2-butanol, toluene, γ-valerolactone (GVL), methyl isobutyl ketone (MIBK) were utilized to enhance furfural production in monophasic or biphasic reaction systems (Jiang et al., 2018). Combining biphasic systems (water-organic solvent) with some metal chlorides (e.g., NaCl, FeCl₃, AlCl₃, CrCl₃, ZnCl₂, etc.) as Lewis acids was reported as an efficient

resolution for xylose dehydration (Zhou and Zhang, 2016). In biphasic systems, the produced furfural could accumulate in the organic phase, which inhibits the by-products formation in water phase.

In this study, a novel sustainable solid acid catalyst, SO_4^{2-}/SnO_2-Al_2O_3-CFA, was synthesized with CFA as carrier and loaded with SnO_2-Al_2O_3 as active components. The physical properties of the solid acid catalyst was characterized by brunauer emmett teller (BET), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), energy dispersive analysis by X-ray (EDAX), NH_3 temperature programmed desorption (NH_3-TPD). Factors influencing the catalytic efficiency of the solid acid catalyst, including catalyst loading, organic solvent, chloride salt, reaction temperature and reaction time, were systematically optimized to achieve high furfural yield. The reusability of the solid acid catalyst and toluene was also evaluated for enhanced application potential.

2. Materials and methods

2.1. Materials

Corn stovers (CS) obtained from local farms in Wuxi (Jiangsu, China) were washed with double-distilled water and dried at 80 °C to constant weight, and then milled and passed through 60–80 mesh for future use. Chemical compositions of CS were determined by the National Renewable Energy Laboratory (NREL) analytic methods (Sluiter, 2005), which were 32.7% of cellulose, 20.9% of hemicellulose, 25.4% of lignin, and 8.6% of ash. Coal fly ash (CFA, 5000 mesh) was purchased from Henan Borun Casting Material Co., Ltd. (Henan, China). D-(+)-Xylose, $SnCl_4$·$5H_2O$, $Al(NO_3)_3$·$9H_2O$, toluene, methyl isobutyl ketone (MIBK), γ-valerolactone (GVL), dimethyl carbonate (DMC), cyclopentyl methyl ether (CPME), $CrCl_3$·$6H_2O$, $AlCl_3$·$6H_2O$, $FeCl_3$, $ZnCl_2$, $MnCl_2$·$4H_2O$, $NiCl_2$·$6H_2O$, $MgCl_2$·$6H_2O$, $CuCl_2$·$2H_2O$, $CaCl_2$·$2H_2O$, $BaCl_2$·$2H_2O$, $CoCl_2$·$6H_2O$, NaCl, LiCl, KCl, NH_4Cl, furfural, oxalic acid, ammonia and sulfuric acid were of chemical grade and purchased from Sinopharm Group Chemical Reagent Co., Ltd.

2.2. Preparation of SO_4^{2-}/SnO_2-Al_2O_3-CFA solid acid catalyst

Since NaOH is a chemical activator of CFA and can increase the hydration activity of CFA (Aughenbaugh et al., 2015). CFA was pretreated with base before co-condensation in order to improve the activity of solid acid catalyst and eliminate the impurities. Fifty grams of CFA was mixed and stirred in 500 mL NaOH solution (2.5 M) for 3 h, and the mixture was filtered to obtain activated CFA which was then desiccated at 110 °C for 12 h.

In 5% solution of crystallized $SnCl_4$, the required amount of Al $(NO_3)_3$·$9H_2O$ corresponding to Sn/Al molar ratios of 4:1–15:1 and 10–80 wt% activated-CFA were added. After vigorous agitation under room temperature and atmospheric pressure, a homogeneous turbid liquid was formed. Then the liquid was adjusted to pH 8.0–9.0 using 25% concentrated ammonium hydroxide, and aged at 4 °C overnight to form the colloidal solution of $Sn(OH)_4$-$Al(OH)_3$-CFA. The resultant solution was washed with double-distilled water until none residual chloride ion was detected by 0.1 M $AgNO_3$. Afterwards, the solution was dried at 80 °C for 12 h. Finally, the produced hydroxide was grinded to a powder, and impregnated in 0.5 M H_2SO_4 at a proportion of 15 mL·g⁻¹ for 3 h, Then the solid residue was filtrated and dried to constant weight and calcined at 550 °C for 4 h to obtain SO_4^{2-}/SnO_2-Al_2O_3-CFA as solid acid catalyst. Other solid acids, including SO_4^{2-}/CFA, SO_4^{2-}/SnO_2, SO_4^{2-}/SnO_2-Al_2O_3 and SO_4^{2-}/SnO_2-Al_2O_3-CFA were prepared accordingly.

2.3. SO_4^{2-}/SnO_2-Al_2O_3-CFA catalyzed conversion of xylose-rich CS hydrolysate into furfural

Oxalic acid pretreatment of lignocellulosic biomass is an effective

method for highly selective saccharification of hemicellulose without significant degradation of cellulose (Lu and Mosier, 2007). In this work, xylose-rich hydrolysate from CS was prepared as follows: In a 200 mL Teflon-lined autoclave reactor (Zhengzhou Huate Instrument Equipment co., Ltd, China), 0.56 g oxalic acid, 10 g CS, and 100 mL deionized water were added and thoroughly mixed together. Then the reaction mixture was maintained at 140 °C in an oven for 1 h, followed by quick cooling to lower than 50 °C in an iced-water bath. The xylose-rich hydrolysate was obtained by vacuum filtration, and the xylose concentration was determined as $20 \, g \cdot L^{-1}$, which can be used for further experiments.

Xylose-rich hydrolysate (50 mL) was mixed with different amounts of SO_4^{2-}/SnO_2-Al_2O_3-CFA solid acid catalyst, different kinds and quantities of chloride salts and organic solvents in a stainless steel autoclave reactor. Then the reactor was rapidly heated to desired reaction temperature by an electric heating jacket and hold for a given reaction durations. After the reaction, the reactor was rapidly cooled down to below 50 °C in an iced-water bath. The products and remaining reactants in both aqueous and organic phases were analyzed to evaluate the catalytic activity and efficiency. Three parallel experiments were carried out, and the values were expressed as the means ± standard deviations.

2.4. Analytical methods

The concentrations of glucose, xylose and arabinose were quantified by High Performance Liquid Chromatography (HPLC, 1260 Infinity, Agilent Technologies Ltd., USA) employing external standard method, equipped with a Hi-Plex column (Agilent, 300 × 7.7 mm) and a differential refractive index detector. The temperature of column oven was maintained at 65 °C and 5 mM sulfuric acid was used as the mobile phase at a flow rate of $0.6 \, mL \cdot min^{-1}$. For furfural, reverse HPLC was used with a Diamonsil C18 column (Dikma, 250 × 4.6 mm) and mobile phase of methanol/distilled water (1/4, v/v) at a flow rate of $0.6 \, mL \cdot min^{-1}$, column temperature of 30 °C, and detection wavelength of 280 nm.

The furfural yield, xylose conversion, and furfural selectivity from xylose were calculated according to the following equations:

$$\text{Furfural yield} = \frac{\text{Furfural produced (g)}}{\text{Initial xylose in hydrolysate (g)}} \times \frac{150}{96} \times 100\%$$

$$\text{Furfural selectivity} = \frac{\text{Furfural produced (g)}}{\text{Xylose reacted (g)}} \times \frac{150}{96} \times 100\%$$

$$\text{Xylose conversion} = \frac{\text{Xylose reacted (g)}}{\text{Initial xylose in hydrolysate (g)}} \times 100\%$$

2.5. Characterization of solid acid catalyst

Scanning electron microscopy (SEM, JSM-6360LA, JEOL, Japan) was used to record the changes of the surficial morphological features of fresh CFA and SO_4^{2-}/SnO_2-Al_2O_3-CFA. Fourier transform infrared (FTIR) spectroscopy was employed to obtain infrared spectra (PROTÉGÉ 460, Nicolet, USA) from 4000 to $500 \, cm^{-1}$. The samples were prepared by mixing the products with KBr and pressing into a compact pellet. Particle phases were characterized using X-ray diffraction (XRD, Rigaku D/max-2500 diffractometer) with Cu Kα radiation (Rigaku Ltd, Japan) over the range of $2\theta = 5°$–$80°$. The porosity and specific surface areas of the yielded hollow spheres was determined by adsorption–desorption of ultrapure N_2 on a micromeritics instrument corporation system via Brunauer–Emmett–Teller (BET) method surface area. Energy dispersive analysis by X-ray (EDAX, Falion 60 s, EDAX Ltd, USA) was used to determine the elemental composition of the solid acid catalysts·NH_3-TPD was performed to determine the acid strength of the prepared catalyst by chemisorption analyzer

(ChemiSorb 2720, Micromeritics, USA). Approximately 100 mg of catalyst was pretreated in helium at 550 °C for 60 min. After NH_3 adsorption at 100 °C for 30 min, the catalyst was treated by helium purgation to remove excess ammonia until baseline stabilized. Then the samples were heated to 800 °C at a rate of $10 \, °C \cdot min^{-1}$ for NH_3 desorption. All gas flows were $25 \, mL \cdot min^{-1}$.

3. Results and discussion

3.1. Preparation of solid acid catalyst

Sulfated tin oxide could be used as solid acid catalyst with good performance in the dehydration of xylose to furfural (Suzuki et al., 2011). Using Al_2O_3-doped sulfated Tin oxide (SnO_2-Al_2O_3), increased furfural yield was resulted, largely due to the stabilized surface of sulfate oxides complex and increased catalytically effective acid sites on the catalysts (Hua et al., 2000; Laugel et al., 2012). As a novel heterogeneous catalyst carrier, CFA is mainly composed of silica glass spheres, and its hollow structure can effectively disperse and fix the active components to improve catalytic activity. Here, SnO_2-Al_2O_3 was synthesized and then loaded on the surface of CFA to generate higher Lewis acids groups for xylose dehydration. Different chemical compositions of catalysts could affect the furfural production from xylose-rich CS hydrolysate. In a 200-mL Teflon-lined autoclave reactor (Zhengzhou Huate Instrument Equipment co., Ltd, China), 100 mL xylose-rich CS hydrolysate ($20 \, g \cdot L^{-1}$), 3.7 g catalyst (3.5 wt%) were thoroughly mixed together. Then the reaction mixture was maintained at 180 °C for 30 min. The furfural yield of fresh CFA, SO_4^{2-}/CFA, SO_4^{2-}/SnO_2, SO_4^{2-}/SnO_2-Al_2O_3, SO_4^{2-}/SnO_2-CFA and SO_4^{2-}/SnO_2-Al_2O_3-CFA were compared and determined. The newly developed solid acid catalyst, SO_4^{2-}/SnO_2-Al_2O_3-CFA, displayed the highest furfural yield of 20.5%, much higher than 3.8% of fresh CFA, 12.5% of SO_4^{2-}/CFA and 13% of SO_4^{2-}/SnO_2-CFA. As a result, SO_4^{2-}/SnO_2-Al_2O_3-CFA solid acid is regarded as an innocuous, inexpensive, and effective catalyst in biomass utilization.

Effect of the molar ratio of SnO_2 to Al_2O_3 ($Ratio_{S/A}$) on the activity of solid acid catalyst was investigated (Table 1). Along with the increased $Ratio_{S/A}$ from 4:1 to 15:1, the furfural yield was quickly increased from 12.4% to 20.5% and slightly decreased to 18.8%. The optimal $Ratio_{S/A}$ was 9:1, at which the highest furfural yield of 20.5% was achieved. Due to the high loading of SiO_2 on surface, CFA provided supports as carrier for the derivation of SnO_2 to Al_2O_3. Influence of CFA amount ranging from 10% to 80% on the activity of solid acid catalyst was also examined (Table 1). With the increase of CFA, the furfural yield was increased at first and then decreased, with the highest furfural yield of 20.6% at 40% CFA. The increase of CFA from 10% to 40% provided increased carrier supports for loading of SnO_2 to Al_2O_3. While further increase of CFA from 40% to 80% resulted in decreased furfural

Table 1
Effects of SO_4^{2-}/SnO_2-Al_2O_3-CFA catalyst components on furfural yield.

n(Sn):n(Al)[a]	Furfural yield/%	Activated-CFA/wt%[b]	Furfural yield/%
4:1	12.4 ± 0.46	10	15.3 ± 0.38
6:1	15.7 ± 0.53	20	15.9 ± 0.59
9:1	20.5 ± 0.64	30	17.2 ± 0.75
12:1	19.4 ± 0.37	40	20.6 ± 0.67
15:1	18.8 ± 0.48	50	18.4 ± 0.52
		60	17.8 ± 0.87
		70	17.2 ± 0.43
		80	16.2 ± 0.31

[a] Reaction conditions: xylose-rich CS hydrolysate $20 \, g \cdot L^{-1}$, 3.5 wt% catalyst (40 wt% activated-CFA, n(Sn)/n(Al) = 4:1–15:1) in a 100 mL reaction system at 180 °C for 30 min.

[b] Reaction conditions: xylose-rich CS hydrolysate $20 \, g \cdot L^{-1}$, 3.5 wt% catalyst (n(Sn)/n(Al) = 9:1, 10–80 wt% activated-CFA) in a 100 mL reaction system at 180 °C for 30 min.

yield, indicating excessive CFA prevented the access of active sites to the reactant and led to inefficient diffusion of the furfural out of the catalyst pore or active sites (Chatteriee et al., 2019). As a result, the 40% CFA was regarded as the optimal amount.

3.2. Characterization of solid acid catalyst $SO_4^{2-}/SnO_2-Al_2O_3$-CFA

Considering the significant effect of the newly synthesized solid acid catalyst $SO_4^{2-}/SnO_2-Al_2O_3$-CFA, the physical properties including surface structure, characteristic peaks of chemical groups, pore properties, elemental composition and acid strength were characterized by SEM, FTIR, XRD, BET, EDAX, and NH_3-TPD analysis. As illustrate in the SEM images (E-Supplementary data), CFA was composed of a variety of spherical particles, mainly of amorphous glassy bodies, which rendering the CFA with high capability in adsorption of ions. The surface of fresh CFA was smooth, while the smooth surface was destroyed in $SO_4^{2-}/SnO_2-Al_2O_3$-CFA, resulting in varied particle size distribution. This wrinkled structure of $SO_4^{2-}/SnO_2-Al_2O_3$-CFA could provide higher specific surface area for the covalent linkage between SiO_2 and SnO_2.

FTIR analysis of fresh and derivatized CFA was also conducted (E-Supplementary data). Significant difference was detected at wavenumber range of 500–900 cm^{-1}. The adsorption peak became flat and wide, which reflected the smaller size of $SO_4^{2-}/SnO_2-Al_2O_3$-CFA caused by the inhibition of flocculating Al_2O_3 on the growth of sample particles. The wavenumbers of 1637 and 3423 cm^{-1} represented the adsorbing water peak of –OH and stretching vibration peak of Al-OH, respectively. The characteristic peak of S=O caused by the interaction between SO_4^{2-} and SnO_2 located near 1400 cm^{-1}. The adsorption peaks of SnO_2 were observed at wavenumber of 665 and 595 cm^{-1}. There was a strong adsorption peak near 1100 cm^{-1} related to stretching vibration of Si-O bond in CFA.

According to XRD spectrum of fresh CFA (E-Supplementary data), a single and broad diffraction peak at 18.5°–38.5° was monitored, which were mainly attributed to more vitreous bodies, silicon oxide, and silica-alumina structures in CFA. These structural characteristics render CFA with higher hydrophilicity, surface activity, and adsorption properties. In $SO_4^{2-}/SnO_2-Al_2O_3$-CFA, several peaks shifted toward higher diffraction angles. The amorphous structure could induce structural defects and misalignment of the catalyst, and therefore lead to more active sites. Significant diffraction peaks were detected at the diffraction angles of 26.5°, 33.8°, 51.7° and 64.7°, which belongs to the tetrahedral of SnO_2. Since fresh CFA does not contain SnO_2, it is the diffraction peak of quartz (26.6°) instead of SnO_2 (26.5°), and the two peaks are close to each other. Doping a small amount of Al_2O_3, as reported, can inhibit the crystallization of SnO_2 and the growth of tetrahedral SnO_2 grains, and thus further enhance the catalytic activity (Laugel et al., 2012).

The difference in surface area of fresh CFA and $SO_4^{2-}/SnO_2-Al_2O_3$-CFA was determined employing BET analysis. Average surface area, pore volume and pore size were calculated accordingly and listed in Table 2. In comparison with the statistical data of fresh CFA, larger surface area of 27.141 m^2·g^{-1}, higher pore volume of 0.021 cm^3·g^{-1} and bigger pore size of 3.093 nm were found in $SO_4^{2-}/SnO_2-Al_2O_3$-CFA. In the synthetic process of solid acid catalyst, CFA was sequentially treated with alkaline (NaOH) and acid (H_2SO_4), releasing some

metal ions and other compounds, which could lead to disordered structure and increased surface roughness. More mesoporous characteristics of $SO_4^{2-}/SnO_2-Al_2O_3$-CFA might be favorable for the catalytic activity through prompting the diffusion of xylose into the catalytic sites in the solid acid catalyst.

The EDAX spectrum result of fresh CFA in the E-Supplementary data showed a high percentage of O, Si, Al with traces of Na, Mg, K, Ca, Ti, Fe. Since CFA samples are amorphous aluminosilicate particles consisting mainly of SiO_2 and Al_2O_3, the most abundant element is Si, which occupied 28.98 wt% of the mass and 22.71 at% of the total atoms. Besides, CFA contains certain amount of Na_2O, MgO, K_2O, CaO, TiO_2, and Fe_2O_3. Compared with CFA, significantly higher contents of 4.72 at% Sn, 16.25 at% Al, and 1.02 at% S were determined in $SO_4^{2-}/SnO_2-Al_2O_3$-CFA, indicating Sn, Al, and S were introduced into the CFA successfully.

NH_3-TPD was performed to evaluate the acidic strength of $SO_4^{2-}/SnO_2-Al_2O_3$-CFA (E-Supplementary data). Normally, the higher desorption temperature of NH_3 corresponds to the stronger acid center. The adsorption peaks of acid centers can be divided into weak, medium and strong according to NH_3 desorption temperatures of 25–200 °C, 200–400 °C, and 400–800 °C, respectively. Result showed that $SO_4^{2-}/SnO_2-Al_2O_3$-CFA had a weak acid center (< 200 °C) and a strong acid center (> 400 °C) at 180 °C and 700 °C, respectively.

3.3. Effect of catalyst loading on furfural yield

To develop an economic process, effect of the amount of $SO_4^{2-}/SnO_2-Al_2O_3$-CFA on the conversion of xylose-rich CS hydrolysate into furfural were examined, aiming at decreasing the loading of solid acid catalyst. Different amount of $SO_4^{2-}/SnO_2-Al_2O_3$-CFA ranging from 0.25% to 8.0% (w/w) was added into the reaction mixture and the furfural yield was determined. Clearly, supplementation of higher acid afforded higher furfural yield and better catalytic performance with addition of 0.25% to 2.0% solid acid catalyst. However, excessive solid acid catalyst of 3.5–8.0% provided sufficient acid amount and active sites for the undesired side reactions of furfural, which promoted the production of byproducts (such as humins). As a result, the furfural yield dropped accordingly, which was in coincidence with other reports (Xu et al., 2015, Zhang et al., 2016, Wang et al., 2019). The highest furfural yield of 22.8% was obtained with addition of 2.0% $SO_4^{2-}/SnO_2-Al_2O_3$-CFA.

3.4. Effect of organic solvents on furfural yield

It is known that furfural could react with xylose and also be spontaneously hydrolyzed in acidic environment. The low solubility of furfural in aqueous reaction is another limitation. Biphasic system consisted of organic solvent and water is a prospective approach for increased furfural productivity since the produced furfural could be extracted to the organic phase, which could prevent the adverse side-reaction and spontaneous hydrolysis (Jia et al., 2014). Five different organic solvents, including toluene, methyl isobutyl ketone (MIBK), γ-valerolactone (GVL), dimethyl carbonate (DMC), cyclopentyl methyl ether (CPME), were introduced in the $SO_4^{2-}/SnO_2-Al_2O_3$-CFA catalyzed conversion of xylose-rich CS hydrolysate (water-organic solvent, 1:1, v:v). The results showed that no inhibition was observed in all the organic solvents tested. Furfural yields in DMC and GVL were 29.2% and 27.2% respectively, slightly higher than 25.1% of the aqueous system. Maybe the esters could be hydrolyzed under acidic conditions, which was not conducive to furfural production. Remarkable effect was observed in the biphasic systems with MIBK, toluene and CPME as organic phase. Especially, the furfural yield in toluene system is 64.7%, 2.5-fold of the aqueous system. Therefore, toluene was regarded as the most suitable organic solvent for the production of furfural catalyzed by $SO_4^{2-}/SnO_2-Al_2O_3$-CFA.

Furthermore, the volume of organic solvent played important role in

Table 2
Characterization of Fresh CFA and $SO_4^{2-}/SnO_2-Al_2O_3$-CFA.

Catalyst	BET surface area [m^2·g^{-1}]	Pore volume [cm^3·g^{-1}]	Pore size [nm]
Fresh CFA	1.447	0.001	1.869
$SO_4^{2-}/SnO_2-Al_2O_3$-CFA	27.141**	0.021**	3.093**

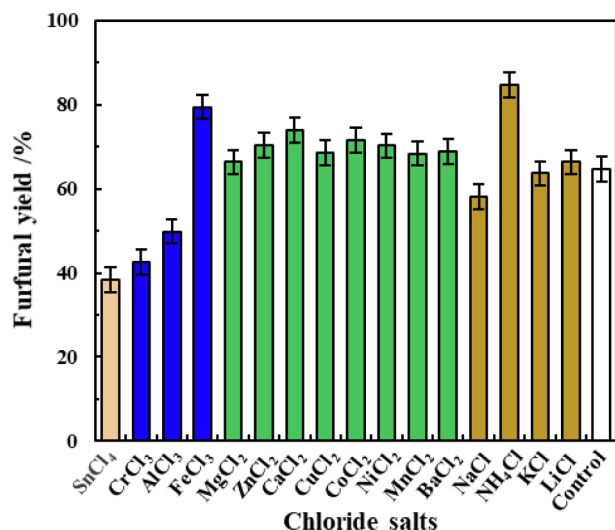Note: *T*-test was conducted and *P* value < 0.01 was denoted as "**".

Fig. 1. Effect of various chloride salts on furfural yield. Reaction conditions: xylose-rich CS hydrolysate 20 g·L^{-1}, 2 wt% SO_4^{2-}/SnO_2-Al_2O_3-CFA catalyst, toluene to water phase volume ratio of 1:1 and different chloride salts (100 mM) in 100 mL reaction system at 180 °C for 30 min.

the distribution of furfural. Various volume ratios of organic phase to aqueous phase ranging from 9:1 to 1:9 were evaluated. To achieve homogenous disperse of organic solvents, thermal uniformity and extraction efficiency, stirring speed of 800 rpm was adopted. The furfural yield increased gradually with the increasing of toluene. When the ratio of toluene to water was 1:9, the furfural yield was 52.4%, while the yield was 70.9% at the ratio of 9:1. Increased toluene led to more furfural dissolved in organic phase, and thus elevated the furfural yield. However, no significant improvement was monitored at ratios from 1:1 (64.6%) to 9:1 (70.9%). As a result, considering a lower environmental issue caused by toluene, the ratio of 1:1 was adopted in further study.

3.5. Effect of chloride salts on furfural production as reaction assistants

It has been reported that the addition of chloride could promote the production of furfural from xylose (Enslow and Bell, 2015). Sixteen chloride salts including $SnCl_4$, $FeCl_3$, $CrCl_3$, $AlCl_3$, $ZnCl_2$, $CuCl_2$, $CoCl_2$, $NiCl_2$, $MnCl_2$, $MgCl_2$, $CaCl_2$, $BaCl_2$, KCl, NaCl, LiCl and NH_4Cl were evaluated in the conversion of xylose-rich CS hydrolysate. Only $FeCl_3$ and NH_4Cl exhibited significant positive effect with furfural yield of 79.4% and 84.7% respectively, much higher than 64.6% of the control (Fig. 1). Chloride salts can not only increase the thermodynamic activity of furfural in water, but also lead to salting-out of furfural in the biphasic system, therefore, resulting in enhanced furfural selectivity and yield (Sun et al., 2018). Considering the positive effect of NH_4Cl, different concentrations of NH_4Cl (0, 20, 50, 100, 200, 300, 500 mM)

were also investigated. The results showed that 100 mM NH_4Cl was the optimal amount for the activity of SO_4^{2-}/SnO_2-Al_2O_3-CFA. In comparison with the control (absence of NH_4Cl), the furfural yield was 20% higher with the addition of 100 mM NH_4Cl. Cation ion NH_4^+ has the similar properties as alkali metal ions. Meanwhile, NH_4Cl was an acidic salt consisted of strong acid and weak base. Consequently, NH_4Cl could synergistically catalyzed with solid acid catalyst, which was beneficial for furfural production. It has been reported that ammonium salts could activate and modify CFA at high temperatures (Li et al., 2006).

3.6. Effect of reaction conditions on production of furfural

Reaction conditions for the conversion of xylose-rich CS hydrolysate catalyzed by SO_4^{2-}/SnO_2-Al_2O_3-CFA were explored. Different temperatures ranging from 150 to 190 °C and incubation time from 5 to 180 min on the furfural yield, furfural selectivity and xylose conversion were determined and illustrated in Fig. 2. Conversion of xylose quickly reached over 90% in all tested temperatures. At 150 °C for 90 min, the conversion of xylose was 90.4%, whereas conversion of 91.3% was obtained at 190 °C for 10 min, indicating higher temperature was favorable for the conversion of xylose (Fig. 2A). Since xylose might be converted into byproducts such as acetic acid, formic acid and levulinic acid (Qing et al., 2017), the effects of temperature and incubation time on the furfural yield and selectivity were also investigated. As shown in Fig. 2B, the furfural yields increased in the beginning and then decreased. Take 180 °C for example, the furfural yield increased quickly from 42.4% (10 min) to 84.7% (30 min), followed by decreased to 71.1% (60 min). The highest furfural yield was obtained at 180 °C for 30 min. Similar tendency was observed for the furfural selectivity (Fig. 2C), indicating a well consistency between xylose conversion and furfural production. The highest furfural selectivity was 85.2% obtained at 180 °C for 30 min. Although higher temperature was favorable for the conversion xylose, the furfural yield and selectivity slightly increased in the initial 10 min and kept decreasing along with the elongation of incubation time. Higher temperature can lead to the decomposition of furfural itself and the production of insoluble black solids, which could precipitate on the outer surface of the solid catalyst and prevent the dehydration reaction between catalyst and xylose (Jia et al., 2019). Therefore, the optimal temperature and incubation time were 180 °C and 30 min.

3.7. Reusability of solid acid catalyst and toluene

Regeneration and reusability of catalysts and organic solvents are important for the potential application of furfural production process (Bruce et al., 2016). To investigate the reusability of SO_4^{2-}/SnO_2-Al_2O_3-CFA and toluene, both solid acid catalyst and toluene were recovered and reused for five sequential fed batches under above optimal conditions. After each batch, the catalyst was filtered and washed with ethanol and deionized water to remove the residual furfural and humins
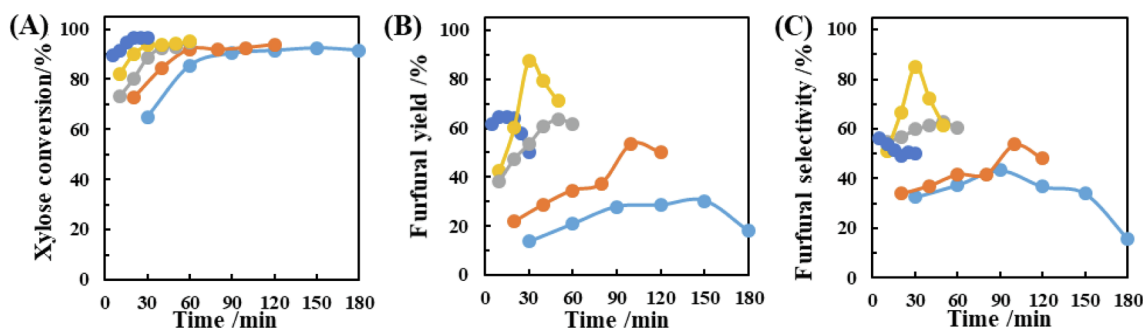

Fig. 2. Effects of temperature and incubation time on SO_4^{2-}/SnO_2-Al_2O_3-CFA catalyzed conversion of xylose to furfural. (A) xylose conversion, (B) furfural yield, (C) furfural selectivity. Symbols: (●) 150 °C, (●) 160 °C, (●) 170 °C, (●) 180 °C, (●) 190 °C. Reaction condition: xylose-rich CS hydrolysate 20 g·L^{-1}, 2 wt% SO_4^{2-}/SnO_2-Al_2O_3-CFA catalyst and toluene to water phase volume ratio of 1:1 with an addition of 100 mM NH_4Cl in a 100 mL reaction system.

Fig. 3. Reuse of SO_4^{2-}/SnO_2-Al_2O_3-CFA. (▢) furfural yield, (▢) furfural selectivity, (▢) xylose conversion. Reaction condition: xylose-rich CS hydrolysate 20 g·L^{-1}, 2 wt% SO_4^{2-}/SnO_2-Al_2O_3-CFA catalyst and toluene to water phase volume ratio of 1:1 with an addition of 100 mM NH_4Cl in a 100 mL reaction system at 180 °C for 30 min.
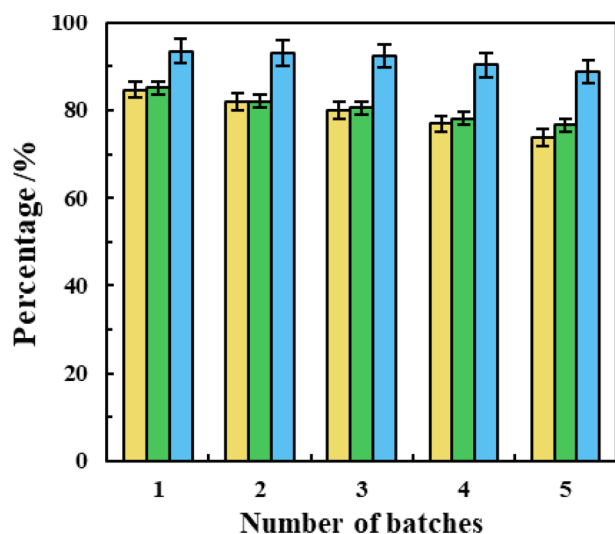
from the surface, followed by drying at 110 °C. Then, the recovered catalyst was impregnated in 0.5 M H_2SO_4 for 3 h before calcining. Toluene was recovered by phase separation and vacuum distillation. According to Fig. 3, in the first batch, the furfural yield, furfural selectivity and xylose conversion were 84.7%, 85.1% and 93.5% respectively, while 73.9%, 76.7% and 88.8% was attained in the fifth batch. There was a slightly decrease in the catalytic efficiency of the recycled SO_4^{2-}/SnO_2-Al_2O_3-CFA. Toluene could also be recycled for 5 times without any effect on furfural yield, which reduced costs and environmental hazardness. The newly developed furfural synthesis process demonstrated promising applicability with reusability potential.

4. Conclusion

A novel solid acid catalyst SO_4^{2-}/SnO_2-Al_2O_3-CFA was developed employing solid waste as carriers, which exhibited excellent catalytic activity and reusability for furfural production from xylose-rich CS hydrolysate. A remarkable synergic effect was found in NH_4Cl-solution/ toluene system, with the highest furfural yield of 84.7% and a xylose conversion rate of 93.5%. The solid acid catalyst could be recycled for five batches without significant decrease in furfural yield. This study provided a sustainable way for resource utilization of CFA as a cheap, facile, and efficient solid acid catalyst with promising application in the conversion of corn stover hydrolysate into furfural.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2019.122065.

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