PRODUCTION OF FURANS FROM PULP SHEET OVER SULFATED SOLID ACID CATALYSTS

Hongdan Zhang, Shubin Wu,* Jun Zhang, and Bo Li

Furans are high value-added biomass-derived chemicals that can be used to replace petrochemicals. In this study, sulfated solid acid catalysts were prepared by precipitation and impregnation and were used for the conversion of a cellulosic pulp sheet into furans. The physicochemical properties of the prepared sulfated solid acid with different calcination temperatures and different mol ratios of Ti-Al were characterized using XRD, elemental analysis, TG, and NH₃-TPD. Furthermore, the effects of various processing parameters such as temperature, time, and catalyst dosage on the reaction performance were studied. The combined yield of 5-hydroxymethyl-furfural and furfural reached 8.9% and 4.5% of pulp sheet mass with a 5% dosage of SO₄²⁻/TiO₂-Al₂O₃ catalyst at 220 °C for 30 min. The activity for recovered catalyst was also investigated in this study.

Keywords: Pulp sheet; Sulfated solid acid; 5-Hydroxymethylfurfural; Furfural

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INTRODUCTION

Nowadays, with the gradual depletion of fossil resources, abundant renewable biomass is regarded as a promising alternative to non-renewable natural resources for sustainable production of biofuels and biochemicals in the future (Huber et al. 2006; Christensen et al. 2008; Takagaki et al. 2008; Almeida et al. 2010). It is well known that furan compounds are valuable platform chemicals due to their extensive applications (Huber et al. 2005; Chheda et al. 2007). Presently, researchers are attempting to investigate various pathways for the production of 5-hydroxymethylfurfural (HMF) and furfural with different raw materials and efficient catalysts.

Typically, the materials for the production of HMF and furfural mainly are sugar-based (fructose, glucose, sucrose, and xylose) or carbohydrate-based (cellulose, xylan, and lignocellulosic) feedstocks. For glucose, an HMF yield of 22% was achieved in 10 min at 160 °C under microwave heating (Yang et al. 2012). The production of HMF and furfural with monosaccharides as reactants under biphasic reaction systems was studied, leading to selectivity of 89%, 91%, and 53% for the dehydration of fructose, xylose, and glucose, respectively (Chheda et al. 2007). Cassava waste with a sulfonated carbon-based catalyst at a temperature of 250 °C was investigated, reaching 10.8% HMF and 2.1% furfural (Daengprasert et al. 2011). The conversion of biomass resources to HMF and furfural can be accomplished in two main steps: (1) hydrolysis of biomass resources into xylose and glucose; (2) dehydration of the xylose into furfural and the glucose into HMF, including isomerization to fructose during the conversion of glucose to HMF. Both the
hydrolysis and dehydration reactions could be catalyzed by acid; as a result many acid catalysts have been used for the conversion of biomass resources into HMF and furfural.

In earlier studies, homogeneous acids such as H$_2$SO$_4$ and HCl were used for biomass conversion, and it is clear that the addition of these acid-catalysts can promote the dehydration reaction (Tuercke et al. 2009). With the development of green chemical processes, however, the utilization of heterogeneous catalysts, especially solid acid, is one of the effective approaches for both biomass conversion and maintaining green chemical processing conditions (Beach et al. 2009; Anastas and Eghbali 2010; Gupta et al. 2010). Solid acid catalyst has been widely reported to be easily separated and recovered from the process. Recently, a few studies have proposed the use of solid acid catalysts for the dehydration reaction. For instance, it was demonstrated that the production of HMF and furfural from monomeric sugars in the HCW process can be promoted by the use of TiO$_2$, ZrO$_2$, and mixed-oxide TiO$_2$–ZrO$_2$ catalysts under hot compressed water (HCW) conditions (Chareonlimkul et al. 2010). A series of Al–Zr mixed oxides with different molar ratios with glucose that were reacted in hot compressed water at 180 °C showed that the glucose conversion increased from 46.6 to 85% (Zeng et al. 2009).

Though there have been many studies on the production of HMF and furfural, few studies have focused on the use of a sulfated metal oxides solid catalyst, one kind of heterogeneous catalyst, for lignocellulosic biomass conversion. In this study, a SO$_4$$^{2-}$/TiO$_2$-Al$_2$O$_3$ catalyst prepared by precipitation and impregnation was employed for the production of HMF and furfural from a pulp sheet, which was selected due to its low price and broad source. For the SO$_4$$^{2-}$/TiO$_2$-Al$_2$O$_3$ catalyst, different mol ratios of Ti-Al and different calcination temperatures for the production of HMF and furfural were studied. The suitable temperature, reaction time, and the dosage of catalyst for the production of HMF, furfural, and sugar yield were also determined. Furthermore, the activity for recovered catalyst was also investigated in this study.

**EXPERIMENTAL**

**Materials**

The raw material (a pulp sheet made from a sulfate process of lobular acacia wood) used in this study was provided by a paper mill in Guangzhou, Guangdong, China. The dry pulp sheet was immersed in deionized water for 24 h, where it was stirred with a stirring rod to disperse the fiber bundles, then stored in a refrigerator until further use. The pulp sheet was composed of glucan 80.56% and xylan 17.63% (dry weight basis).

**Preparation of Catalysts**

SO$_4$$^{2-}$/TiO$_2$-Al$_2$O$_3$ catalysts were prepared by precipitation and impregnation. The main preparation process of the SO$_4$$^{2-}$/TiO$_2$ catalyst is presented below. TiCl$_4$ was dissolved in icy deionized water, and ammonia solution with 25% mass fraction was added to adjust the pH value of solution to between 9 and 10. The mixed solution was then aged for 24 h to form Ti(OH)$_4$. The obtained precipitate was thoroughly washed with deionized water until chloride was not detected by AgNO$_3$, and then the precipitate was dried at 110 °C for 24 h. The dried precipitate was ground to below 60 mesh.
followed by impregnation in a 0.5 mol/L H$_2$SO$_4$ solution and stirred at 500 rpm for 1 h. The obtained precipitated solid was filtered, subsequently dried at 110 °C for 12 h, and finally calcined at a specified temperature for 3 h to obtain SO$_4^{2-}$/TiO$_2$. For the preparation of the SO$_4^{2-}$/TiO$_2$-Al$_2$O$_3$ catalyst, the co-precipitates of Ti(OH)$_3$-Al(OH)$_3$ with different Ti to Al mol ratios were obtained by adding ammonia solution with 25% mass fraction to a mixed aqueous solution of TiCl$_4$ and Al$_2$(SO$_4$)$_3$ with stirring until the pH value was between 9 and 10. The subsequent procedures were the same as for the preparation of SO$_4^{2-}$/TiO$_2$.

**Characterization of Catalyst**

X-ray powder diffraction (XRD) was performed in a Bruker D8 Advance diffractometer with Cu Kα radiation. The operating voltage and current were 40 kV and 40 mA, respectively. The step length was 0.02 degrees with a scanning rate of 2°·min$^{-1}$. TG analysis was performed in a TG 209 F1 (made by NETZSCH) with N$_2$ used as the carrier gas, a temperature range of room temperature to 850 °C, and a temperature rise rate of 10 °C/min. The sulfur content of the catalyst was detected by an Elementar Vario EL according to the general method of element analysis (JY/T017-1996). The measurements of acidity of the samples were carried out in a Micromeritics AutochemII 2920 chemisorption analyzer following an NH$_3$ temperature-programmed desorption (TPD) method. The sample was heated up to 600 °C and kept for 30 min in a flow of He gas to remove adsorbed species on the surface. Then the sample was cooled down to 100 °C in He flow, followed by adsorption of NH$_3$ in 10% NH$_3$ gas flow for 1 h. After flushing with He for 1 h to remove physically adsorbed NH$_3$, the TPD data were measured from 100 °C to 600 °C with a ramp of 15 °C/min.

**Methods**

The conversion of the pulp sheet was carried out using an apparatus consisting of a 1L SS 316 stainless steel reactor, an electric heater, an agitator, and a temperature controller. The temperature and agitation speed during the hydrolysis was controlled and monitored by a modular controller (Cara et al. 2008). The amount of dry feedstock loaded was 18 g, and water was added at a solid/liquid ratio of 3/100 (w/v). Agitation was set at 500 rpm. Firstly, a comparison of catalyst activity of SO$_4^{2-}$/TiO$_2$-Al$_2$O$_3$ with different quantities of Al was made to determine the optimum addition of Al. Based on this approach, a suitable calcination temperature (400, 500, 600, and 700 °C) of SO$_4^{2-}$/TiO$_2$-Al$_2$O$_3$ was selected. Then the optimum conditions for pulp sheet conversion were pursued. The effects of reaction temperature (180, 200, 220, and 240 °C), reaction time (0, 15, 30, 45, and 60 min), and the dosage of catalyst (0, 5%, 10%, 20%, and 30%) were determined. Lastly, the activity for recovered SO$_4^{2-}$/TiO$_2$-Al$_2$O$_3$ catalyst was also studied. It should be noted that the reaction time of 0 min refers to the time at which the system reached the desired temperature after placing the reactor into the electric heater. When the hydrolysis was finished, the reactor was immediately removed from the heating jacket and then cooled with cooling water to stop the reaction. The residue was then separated by filtration. The liquid fraction was analyzed by high pressure liquid chromatography (HPLC) and ion chromatography (IC) to determine the concentration of HMF, furfural, glucose, xylose, and fructose.

Product Analysis

All liquid products from the hydrolysis tests were filtered using a 0.22 µm filter and then diluted appropriately with deionized water. The concentrations of glucose, xylose, and fructose were quantitatively analyzed at 30 °C by ion chromatography (Dionex ICS-3000) with a CarboPac™ PA1 column. The eluents were NaOH and CH₃COONa with a flow rate of 0.25 mL/min. The sample loop had a volume of 50 µL, and the column temperature was 30 °C. The quantification of HMF and furfural in the liquid product was analyzed at 30 °C using a high performance liquid chromatography (HPLC) system with a C18 column. Methanol and water (30/70 v/v) were used as the eluents at a flow rate of 1.0 mL/min. The concentrations of HMF and furfural in the liquid reaction product (20 µL of injection volume) were analyzed based on a photodiode array detector (DAD) at 284 nm and 277 nm, respectively.

The product yield on a dry weight basis (DWB) was calculated using the following equation:

\[ \text{Yield}_{\text{DWB}}(\%) = \left( \frac{\text{weight of product formed}}{\text{dry weight of substrate utilized}} \right) \times 100\% \quad (1) \]

RESULTS AND DISCUSSION

Catalyst Characterization

XRD test

Phase identification of the prepared catalysts was performed by XRD, as shown in Fig. 1a. For the SO₄²⁻/TiO₂ samples, several peaks appeared at 2θ = 25.4°, 38.0°, 48.1°, 55.0°, and 62.6°, which indicated the formation of an anatase phase. The catalyst SO₄²⁻/TiO₂-Al₂O₃ with a high concentration of TiO₂ (Ti/Al = 9/1 or 7/3) had similar peaks as pure SO₄²⁻/TiO₂, but the intensity of the related peaks decreased with decreasing titanium concentration; at the same time, the widths of the peaks increased.

Fig. 1. a. XRD patterns of SO₄²⁻/TiO₂-Al₂O₃ catalysts with different Ti / Al molar ratios, b. Effect of calcination temperature on the XRD patterns of SO₄²⁻/TiO₂-Al₂O₃ catalyst
The SO₄²⁻/TiO₂-Al₂O₃ catalysts with a Ti/Al mol ratio of 5/5 were amorphous as can be seen from the XRD patterns. This was probably due to the presence of Al₂O₃ in the samples, which could effectively suppress the growth of crystallites.

XRD studies of the SO₄²⁻/TiO₂-Al₂O₃ catalysts (9Ti/Al) with different calcination temperatures were undertaken. As the XRD lines in Fig. 1b showed, when the calcination temperature was 400 °C, the SO₄²⁻/TiO₂-Al₂O₃ catalyst was almost amorphous. When the calcination temperature reached 500 °C, the polymorphs of SO₄²⁻/TiO₂-Al₂O₃ formed with characteristic peaks appearing at 2θ values of 25.4°, 38.0°, 48.1°, 55.0°, and 62.6°. Then with the increase in calcination temperature, the polymorphs gradually became perfect. Calcination temperature therefore played an important part in the formation of the crystalline phase in the SO₄²⁻/TiO₂-Al₂O₃ catalyst. However, the results obtained in the catalytic experiment demonstrated that the furans product yields were not affected by the crystallinity of these catalysts.

Sulfur content test

The sulfur contents of catalysts prepared under different conditions were detected using an Elementar Vario EL. The results are shown in Table 1. A small amount of S was detected in all samples. The S mass fraction of the SO₄²⁻/TiO₂-Al₂O₃ catalysts at 500 °C calcination temperature was higher than that of the SO₄²⁻/TiO₂ catalyst. Especially when the Ti/Al mol ratio was 9/1, the S mass fraction reached 4.0%. This phenomenon could be explained by the addition of Al, which could stabilize the S mass of the catalyst. For the SO₄²⁻/TiO₂-Al₂O₃ catalyst (Ti/Al mol ratio of 9/1), when the calcination temperature was 400 °C, the S mass fraction reached 6.4%. With the increase in calcination temperature, the S mass fraction decreased gradually. When the calcination temperature reached 700 °C, the S mass fraction had decreased to 1.3%. It is concluded that the S mass fraction decreased because of its decomposition at higher calcination temperatures. The S content in catalyst was a reflection of the surface acidity of the catalyst (Samantaray and Parida 2001; Yadav and Nair 1999). The addition of Al could stabilize the S content in catalyst at high temperature, so the thermostability of catalyst SO₄²⁻/TiO₂ was increased with the addition of Al. It is important to note that the results obtained in the catalytic experiment demonstrated that the furans product yields were higher with catalyst SO₄²⁻/TiO₂-Al₂O₃ than the catalyst SO₄²⁻/TiO₂.
**TG analysis**

The TG analyses of the $\text{SO}_4^{2-}/\text{TiO}_2$ catalysts and $\text{SO}_4^{2-}/\text{TiO}_2$-$\text{Al}_2\text{O}_3$ (9Ti/Al) catalysts are shown in Fig. 2. Both of the lines showed lost weight under 250 °C due to the evaporation of physically adsorbed water; the weight loss between 500 and 850 °C was caused by the decomposition of $\text{SO}_4^{2-}$. Catalyst $\text{SO}_4^{2-}/\text{TiO}_2$ began to decompose at 539 °C, and then it stopped at 700 °C with a weight loss of 6.0%. Compared to catalyst $\text{SO}_4^{2-}/\text{TiO}_2$, catalyst $\text{SO}_4^{2-}/\text{TiO}_2$-$\text{Al}_2\text{O}_3$ decomposed from 553 °C to 850 °C, resulting in a weight loss of 7.5%. This phenomenon could be explained by the fact that with the addition of Al, the S of the catalyst became more stable at high temperature and the decomposition temperature was higher. From the weight loss of S, it could be concluded that the S mass fraction of catalyst $\text{SO}_4^{2-}/\text{TiO}_2$-$\text{Al}_2\text{O}_3$ was higher than that of catalyst $\text{SO}_4^{2-}/\text{TiO}_2$, which agreed with the sulfur content test mentioned above.

![TG analysis graph](image)

**Fig. 2.** TG analysis of the $\text{SO}_4^{2-}/\text{TiO}_2$ catalysts and $\text{SO}_4^{2-}/\text{TiO}_2$-$\text{Al}_2\text{O}_3$ catalysts

**NH$_3$-TPD measurement**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acid amount (mmol/g)</th>
<th>Peak temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 9Ti/Al, 500 °C</td>
<td>0.6</td>
<td>539,173</td>
</tr>
<tr>
<td>(b) $\text{SO}_4^{2-}/\text{TiO}_2$, 500 °C</td>
<td>0.4</td>
<td>527,262</td>
</tr>
<tr>
<td>(c) 9Ti/Al, 700 °C</td>
<td>0.3</td>
<td>207</td>
</tr>
</tbody>
</table>

![NH$_3$-TPD profiles graph](image)

**Fig. 3.** NH$_3$-TPD profiles and the corresponding results of acid amount for catalyst
The acidic properties and catalytic activity of sulphated oxides are dependent on sulfate groups and their intrinsic properties. The TPD profiles of desorbed ammonia (NH₃) on samples of catalyst and the corresponding results of acid amount as well as peak temperatures are listed in Fig. 3. As is well known, the desorption temperature indicated the acid strength of the catalyst; that is to say, the higher the temperature of desorption, the stronger the acid strength. The peak temperature of catalyst SO₄²⁻/TiO₂-Al₂O₃ was higher than catalyst SO₄²⁻/TiO₂. And it was also found that the acidity of catalyst SO₄²⁻/TiO₂-Al₂O₃ calcinated at 500 °C was more than catalyst SO₄²⁻/TiO₂. On this basis it can be concluded that acidic activity of catalyst SO₄²⁻/TiO₂-Al₂O₃ was more effective for the conversion of pulp sheet to furans, which was in agreement with further conversion results. When the catalyst was calcinated at 700 °C, the acid amount decreased to 0.3 mmol/g because of the loss of sulfur. As shown in the sulfur content test, the sulfur content of catalyst SO₄²⁻/TiO₂-Al₂O₃ (9Ti-Al) calcinated at 700 °C decreased from 6.4% (calcinated at 400 °C) to 1.3%, which verified the possible loss of the sulfur in the catalyst.

**Effect of Different Ti/Al Mol Ratio of SO₄²⁻/TiO₂-Al₂O₃ Catalyst**

This research was carried out to determine the activity of SO₄²⁻/TiO₂ and SO₄²⁻/TiO₂-Al₂O₃ catalysts with different mol ratios of Ti/Al. Firstly, the SO₄²⁻/TiO₂ catalyst and the 9/1, 7/3, and 5/5 Ti/Al mol ratios in the SO₄²⁻/TiO₂-Al₂O₃ catalysts were made and calcinated at 500 °C for 3h. The reactions were then carried out at 220 °C for 30 min with a 10% dosage of the catalyst. As clearly illustrated in Fig. 4, the yields of HMF and furfural increased with catalyst SO₄²⁻/TiO₂-Al₂O₃. That is to say that catalyst SO₄²⁻/TiO₂-Al₂O₃ was more effective than catalyst SO₄²⁻/TiO₂ during the conversion of the pulp sheet biomass.

![Fig. 4. Effect of SO₄²⁻/TiO₂-Al₂O₃ catalysts with different mol ratios of Ti/Al on 5-HMF yield and furfural yield](image-url)
With the addition of Al, the sulfur content improved (Guan et al. 2005). When the mole ratio of Ti/Al in the SO$_4^{2-}$/TiO$_2$-Al$_2$O$_3$ catalyst was 9/1, the product reached the highest with 9.0 % HMF yield and 4.0 % furfural yield. When the Al loading increased, the yield of furans decreased gradually. Therefore, the SO$_4^{2-}$/TiO$_2$-Al$_2$O$_3$ catalyst with a Ti/Al mol ratio of 9/1 was used for further study.

**Effect of Calcination Temperature of Catalyst SO$_4^{2-}$/TiO$_2$-Al$_2$O$_3$**

For solid acid catalysts, the raw material form, calcination time, calcination temperature, acid type, and acid density are all influencing factors on the catalysts’ performance. The most important factor, however, is calcination temperature, so its effect on the solid acid catalyst in the range of 400 °C to 700 °C was studied for the conversion of the pulp sheet with a 9/1 mol ratio of Ti/Al in the SO$_4^{2-}$/TiO$_2$-Al$_2$O$_3$ catalyst at 220 °C and 30 min. The results in Fig. 5 indicated that in the process with catalyst SO$_4^{2-}$/TiO$_2$-Al$_2$O$_3$ calcinated at 500 °C, the HMF and furalfur yields reached the highest values, and then they decreased gradually when the calcination temperature reached 600 °C and above. This phenomenon implies that at a certain calcination temperature, TiO$_2$-Al$_2$O$_3$ achieves a structure and composition favorable for the hydrolysis of biomass conversion, and the catalyst loses activity rapidly with further increase of the calcination temperature.

![Fig. 5. Effect of SO$_4^{2-}$/TiO$_2$- Al$_2$O$_3$ catalysts with different calcination temperatures on 5-HMF and furalfur yields](image)

**Determination of Suitable Conditions for Pulp Sheet Conversion**

**Effect of temperature**

The effect of reaction temperature was investigated in the range of 180 to 240 °C for the conversion of the pulp sheet in hot compressed water with a 9/1 mol ratio of Ti/Al in the SO$_4^{2-}$/TiO$_2$-Al$_2$O$_3$ catalyst (at 30 min and with a catalyst loading of 0.1 g/1.0 g material). As shown in Table 2, the main reaction products were HMF, furalfur, glucose, xylose, and a little fructose. When considering the sugar products (glucose, xylose, and fructose), the yield of glucose increased with the increasing temperature, reaching 9.5%
on DWB at 220 °C, while on the other hand, the xylose yield in the reaction product was found to decrease with increasing temperature; that is to say, more xylose was transformed to furfural. Fructose, the isomer of glucose, first reached the highest yield at 200 °C, and then it decreased with the increasing temperature due to its conversion to HMF at 220 °C. The total products also reached the highest yield of 22.9% on DWB at 220 °C, and then decreased with increasing temperature. All sugar products could not be observed at the reaction temperature of 240 °C. Figure 6 indicates that the conversion of material increased rapidly with increase in temperature. For HMF and furfural, the yields increased with the increasing reaction temperature from 180 to 220 °C, reaching the highest yields of 9.0% and 4.0% on DWB, respectively. When the reaction time reached 240 °C, the yield of levulinic acid was 5.4% on DWB. At higher temperature, however, the HMF and furfural yields decreased because of further decomposition to other byproducts such as LA, formic acid, gas products, or condensation products (Asghari and Yoshida 2006; Daengprasert et al. 2011).

Table 2. The Conversion and Yields of HMF, Furfural, and Sugars at Different Reaction Temperatures

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Conversion (%)</th>
<th>HMF</th>
<th>Furfural</th>
<th>Glucose</th>
<th>Xylose</th>
<th>Fructose</th>
<th>Total Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>20.6</td>
<td>0.6</td>
<td>2.0</td>
<td>3.0</td>
<td>2.1</td>
<td>0.4</td>
<td>8.2</td>
</tr>
<tr>
<td>200</td>
<td>40.7</td>
<td>2.2</td>
<td>1.8</td>
<td>6.7</td>
<td>0.4</td>
<td>0.9</td>
<td>12.1</td>
</tr>
<tr>
<td>220</td>
<td>82.3</td>
<td>9.0</td>
<td>4.0</td>
<td>9.5</td>
<td>0.1</td>
<td>0.2</td>
<td>22.9</td>
</tr>
<tr>
<td>240</td>
<td>83.7</td>
<td>0.1</td>
<td>2.7</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>2.8</td>
</tr>
</tbody>
</table>

nd: not detected; Conversion(%) = (dry weight of substrate utilized – dry weight of residue) / ( dry weight of substrate utilized)*100 (%)

Fig. 6. Effect of temperature on conversion, HMF, and furfural yield at 30 min, with the dose of 10% SO₄²⁻ / TiO₂-Al₂O₃ catalyst
**Effect of Reaction Time**

The effect of reaction time between 0 and 60 min on the production yields was determined for the reaction with 0.1 g catalyst/1.0 g material at 220 °C. The results shown in Table 3 indicate that the glucose yield reached the highest level of 10.1% on DWB and then decreased with time. Further increase in reaction time brought about a slight decrease in the xylene and fructose yields. Figure 7 shows the conversion of the pulp sheet and the yields of HMF and furfural at different reaction times at 220 °C. It can be seen that the conversion of material could amount to 82.3% only after 30 min of reacting, indicating that the catalyst is highly active for the dehydration of the pulp sheet. A gradual increase was observed between 0 and 30 min for HMF yield obtained from the pulp sheet. After 30 min, the HMF obtained from the pulp sheet reached its highest yield of 9.0% on DWB.

**Table 3. The Conversion and Yields of HMF, Furfural, and Sugars at Different Reaction Temperatures**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Conversion (%)</th>
<th>Yield of Product (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HMF</td>
<td>Furfural</td>
</tr>
<tr>
<td>0</td>
<td>49.2</td>
<td>6.0</td>
</tr>
<tr>
<td>15</td>
<td>59.2</td>
<td>7.4</td>
</tr>
<tr>
<td>30</td>
<td>82.3</td>
<td>9.0</td>
</tr>
<tr>
<td>45</td>
<td>81.0</td>
<td>3.2</td>
</tr>
<tr>
<td>60</td>
<td>79.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

**Fig. 7.** Effect of reaction time on conversion and HMF and furfural yields at a temperature of 220 °C with a 10% dosage of SO₄²⁻/TiO₂-Al₂O₃ catalyst.
The furfural reached its highest yield of 4.4% on DWB at 0 min and remained around 4.0% between 15 min and 30 min of reaction time, then decreased gradually at 45 min and beyond, possibly due to the decomposition of HMF and furfural to other products (Watanabe et al. 2005). Of the reaction times studied, 30 min was found to be the optimal time for the formation of HMF and furfural; a further increase in reaction time to 45 min and above resulted in a decrease in the furans and sugars yields obtained from the pulp sheet.

**Effect of dose of SO$_4^2$-TiO$_2$-Al$_2$O$_3$ solid catalyst.**

The suitable quantity of SO$_4^2$-TiO$_2$-Al$_2$O$_3$ catalyst was determined from the yield of HMF, furfural, and sugar products, in which the reaction of the pulp (at 3 wt% of material) was carried out at 220 °C for 30 min with various catalyst amounts (no catalyst, 5%, 10%, 20%, and 30% of material). The influence of the catalyst dose is shown in Table 4 and Fig. 8. The data show that changes in the dose of the catalysts strongly affected the furans and sugars yields obtained from the pulp. Without the catalyst, the HMF and furfural yields were only 4.4% and 3.8% on DWB, respectively. When the quantity of catalyst was 5%, the HMF and furfural yields increased from 4.4% to 8.9% and from 3.8% to 4.5% on DWB, respectively. Thus, for the process with a catalyst, the production yields were considerably higher than those obtained without the catalyst. When the dose of catalyst was increased from 5% to 10%, the conversion of the pulp increased from 70.7% to 82.3%, but the yields of furfural, glucose, xylose, and fructose decreased. That is to say, the selectivity of the HMF, furfural, and sugar products are higher with a 5% than with a 10% dose of catalyst. For HMF, though, the yield (8.9% on DWB) with 5% dose was a little lower than the yield (9.0% on DWB) with a dose of 10%; the furfural and sugar products achieved the highest yields with a dosage of 5%. The product yields then decreased with an increase in the mass of the catalyst. A further increase in the dosage of the catalyst up to 30% of material showed no positive effect. Above all, a catalyst dosage of 5% was chosen as the most suitable condition.

| Catalyst (%) | Conversion (%) | HMF (%) | Furfural (%) | Glucose (%) | Xylose (%) | Fructose (%) | Total Yield (%) |
|--------------|---------------|---------|--------------|-------------|------------|-------------|----------------
| 0            | 37.0          | 4.4     | 3.8          | 8.0         | 0.9        | 0.4         | 17.5           |
| 5            | 70.7          | 8.9     | 4.5          | 12.6        | 0.3        | 0.3         | 26.6           |
| 10           | 82.3          | 9.0     | 4.0          | 9.5         | 0.2        | 0.2         | 22.9           |
| 20           | 83.4          | 1.1     | 2.8          | 0.5         | nd         | nd          | 4.5            |
| 30           | 80.1          | 0.2     | 2.3          | nd          | nd         | nd          | 2.6            |

**The Activity of Recovered Catalyst**

Recyclability and stability are advantages of solid catalysts, and many particular processes rely on catalysts based on them. After the first reaction was finished, the SO$_4^2$-TiO$_2$-Al$_2$O$_3$ catalyst was separated from other residue and then calcinated at 500 °C for 3h to regenerate the activity (Sun et al. 2010). Then it was reused in the next experiments under the same reaction conditions.

The results in Table 5 show the four times repeated reactions of $SO_4^{2-}/TiO_2-Al_2O_3$ catalyst. It indicated that the secondary use of catalyst decreased more than half of the HMF yield, from 8.9% to 3.9% on DWB, then decreased gradually for the next cycles. For furfural, the yield decreased slowly with each cycle. Some explanations for the decrease of product yield was that the sulfur in the catalyst was lost gradually by solvation or the acid sites became covered by products during the hydrolysis reaction (Peng et al. 2011). Catalytic activity can be restored to a certain extent by calcination. Accordingly, how to improve the long-term stability and high activity of the solid acid catalyst need future exploration.

### Table 5. The Activity for Recovered Catalyst

<table>
<thead>
<tr>
<th>Number of Use</th>
<th>Yield of Product (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HMF</td>
</tr>
<tr>
<td>1</td>
<td>8.9</td>
</tr>
<tr>
<td>2</td>
<td>3.9</td>
</tr>
<tr>
<td>3</td>
<td>3.4</td>
</tr>
<tr>
<td>4</td>
<td>2.9</td>
</tr>
</tbody>
</table>

### CONCLUSIONS

1. $SO_4^{2-}/TiO_2-Al_2O_3$ catalysts were prepared by precipitation and impregnation with different Ti/Al mol ratios. The products were characterized and applied to catalyze pulp sheet hydrolysis and dehydration.
2. SO$_4^2-/TiO_2-Al_2O_3$ catalysts with a 9/1 mol ratio of Ti/Al with different calcination temperatures were characterized and applied to catalyze pulp sheet hydrolysis and dehydration.

3. Characterization and activities of the SO$_4^2-/TiO_2-Al_2O_3$ catalyst with a 9/1 mol ratio of Ti/Al at a 500 °C calcination temperature were examined. The SO$_4^2-/TiO_2-Al_2O_3$ catalyst was determined as a feasible alternative for pulp sheet biomass conversion to HMF and furfural.

4. The total yield of the product reached 26.59% on DWB and the yields of HMF and furfural were 8.9% and 4.5% on DWB, respectively, at 220 °C for 30 min with a 5% dosage of catalyst.

5. Studies on recovered catalyst indicated that the catalytic activity of SO$_4^2-/TiO_2-Al_2O_3$ catalysts still needed to be enhanced.

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