

Dehydration of Sugar Mixture to HMF and Furfural over $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ Catalyst

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A series of sulfated zirconia-titanium dioxide ($\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$) catalysts with different Zr-Ti molar ratios were prepared by a precipitation and impregnation method and characterized by ammonia adsorption/temperature programmed desorption ($\text{NH}_3\text{-TPD}$), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) techniques. The catalysts were used in the catalytic conversion of a sugar mixture (glucose and xylose) to 5-hydroxymethylfurfural and furfural in a water/n-butanol reaction system. An optimized yield of 26.0 mol% for 5-hydroxymethylfurfural and 47.5 mol% for furfural was obtained within 2 h at 170 °C over the $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ catalyst with a Zr-Al molar ratio of 7:3. Catalysts with higher acidity and moderate basicity were more favorable for the formation of the target product.

Keywords: Glucose; Xylose; HMF; Furfural; Solid acid

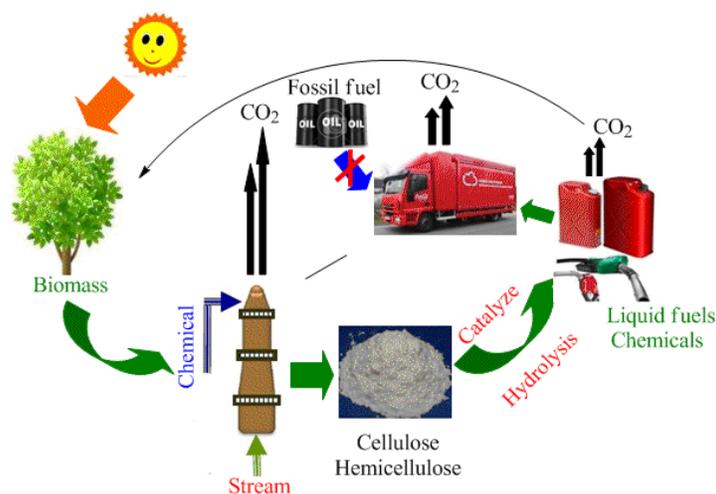
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INTRODUCTION

The production of fuels and chemicals from renewable biomass has become a hot topic as a promising means of dealing with the growing shortage of fossil resources, environmental pollution, and a possible crisis in energy supply (Scheme 1). Furfural compounds, including 5-hydroxymethylfurfural (HMF) and furfural, are universal and key renewable platform chemicals from biomass-based carbohydrate chemistry. HMF, furfural, and their derivatives are known to have many applications as strategic chemicals, such as furan derivatives (Zhang *et al.* 2012) γ -valerolactone (Yan *et al.* 2009), 2,5-furandicarboxylic acid (Davis *et al.* 2012), and levulinic acid (Peng *et al.* 2011), through specific catalytic transformation. These chemicals have been shown to be value-added chemicals and high-quality fuels that can substitute corresponding chemicals from fossil resources (Reman-Leshkov *et al.* 2007).

Several researchers have reported the production of HMF from hexose (glucose or fructose) and furfural from xylose. For instance, Roman-Leshkov *et al.* (2006, 2007) and Chheda *et al.* (2007) used hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) as homogenous catalysts to dehydrate saccharides, with a moderate HMF yield of 40% to 80% obtained under certain reaction conditions. However, these processes have some disadvantages, such as significant energy input, high cost owing to the troublesome

separation processes, expensive solvents, and material corrosion. Therefore, the development of environmentally benign catalysts with high activity is critical.



Scheme 1. Concept of a bio-refinery

In recent decades, solid acid catalysts have attracted considerable interest due to their strong acidity and catalytic activity; they can also serve as an environmentally benign alternative for easy catalyst separation and regeneration with relatively low process costs (Busca 2007; Chareonlimkun *et al.* 2010). Among the various solid acid catalysts available, sulfated metal oxides are enormously popular with researchers due to their strong acidity and excellent thermal stability. For example, Yan *et al.* (2009) reported that sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) and sulfated zirconia-aluminum oxide ($\text{SO}_4^{2-}/\text{ZrO}_2\text{-Al}_2\text{O}_3$) can be used as optimal performance catalysts for the dehydration of glucose to HMF. Kim and Lee (2001) and Dias *et al.* (2007) reported that xylose can be converted into furfural with high efficiency when $\text{SO}_4^{2-}/\text{ZrO}_2$ and sulfated titanium dioxide ($\text{SO}_4^{2-}/\text{TiO}_2$) are used as catalysts.

Previous research by the authors also indicated that $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ (SZT) can be used as a perfect catalyst for the dehydration of xylose to furfural (Zhang *et al.* 2011). Nevertheless, these reports are all based on a single sugar such as fructose, glucose, or xylose as raw material, and little research has involved the dehydration of a sugar mixture to a furfural compound. However, it is known that glucose and xylose are monomer units of lignocellulose, so this may be a potential field for dehydration research of sugar mixtures, which will contribute to the furfural compound research directly derived from lignocellulose.

In the present work, a series of $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ catalysts with different Zr-Ti molar ratios were prepared by a precipitation and impregnation method for the production of HMF and furfural from sugar mixtures (glucose and xylose) in a water/n-butanol reaction system. The physicochemical properties of the representative and thermally regenerated catalysts have been characterized by a variety of techniques.

EXPERIMENTAL

Materials

Glucose, xylose, HMF, and furfural with a purity of over 98% were obtained from Aladdin Reagent (Shanghai, China) and used as standard samples. Analytical grade HMF was purchased from Shandong Tengzhou Wutong Aromatizer Company (Shandong, China). Other reagents and chemicals of analytical grade were purchased from Sinopharm Chemical Reagent Company (Shanghai, China) and used without further purification or treatment. Deionized water was used for all experiments.

Methods

Catalyst preparation

All solid acid catalysts were prepared according to the procedures reported in our previous research (Zhang *et al.* 2011, 2012). Briefly, co-precipitates of $Zr(OH)_4$ - $Ti(OH)_4$ with various Zr/Ti mole ratios were obtained by adding concentrated ammonium hydroxide (NH_4OH) to a mixed aqueous solution of zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) and titanium tetrachloride ($TiCl_4$) with stirring until the pH value reached between 9 and 10 with aging for 24 h. The precipitate was washed thoroughly with de-ionized water until the chloride ion in the filtrate could not be identified and dried at 110 °C for 24 h. The dried precipitate was powdered below 60 mesh, then impregnated with a solution/solid ratio of 15 mL/g in 0.5 M H_2SO_4 and stirred at 500 rpm for 1 h. The resulting precipitated solid was then filtered using a filter paper with 45 μm aperture, subsequently dried at 110 °C for 12 h, and calcined at 750 °C for 5 h. Thus, a series of SO_4^{2-}/ZrO_2 - TiO_2 catalysts was obtained with various Zr-Ti molar ratios.

Catalyst characterization

The acid amounts corresponding to the amounts of absorbed NH_3 were estimated by temperature-programmed desorption of ammonia (NH_3 -TPD) on a Micromeritics Autochem II 2920 instrument (Micromeritics, USA). For NH_3 -TPD measurements, a thermal conductivity detector was used for continuous monitoring of the desorbed ammonia, and the areas under the peaks were integrated to estimate the amount of acid in the catalysts. Approximately 0.2 g of sample was heated at a rate of 15 °C/min to 500 °C and maintained for 0.5 h in a flow of He gas (20 mL/min) to remove adsorbed species on the surface. The sample was cooled down to 100 °C in a flow of He gas, followed by the adsorption of NH_3 in a 10% NH_3 gas flow (balance He, 20 mL/min) for 1 h. After flushing with He (20 mL/min) for 1 h to remove the physically adsorbed NH_3 , the TPD data was recorded from 100 to 600 °C with a ramp of 15 °C/min.

X-ray diffraction (XRD) patterns were used for the crystal structure determination of the solid catalysts, and recorded on a BRUKER D8 Advance X-ray diffractometer (Bruker AXS, GER), operating at 40 kV and 40 mA and using nickel-filtered Cu $K\alpha$ radiation. Data was collected from 2θ between 20 ° and 80 ° with a step of 0.02 ° at a scanning speed of 3 °/min. The phases were identified using the power diffraction file (PDF) database (<http://www.icdd.com>).

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Ultra system employing an Al $K\alpha$ radiation source (Kratos, UK) to obtain

information regarding chemical environment and elemental concentrations present in the solid catalysts. Samples were outgassed in a vacuum (5 Pa) oven overnight before XPS measurements. The binding energies for each spectrum were calibrated with a C 1s spectrum of 284.6 eV. Survey spectra for each sample over a binding energy range of 0 to 1100 eV were recorded at a pass energy of 160 eV and a resolution of 1 eV per step. High-resolution spectra of S 2p, O 1s, and Zr 3d were recorded at a pass energy of 40 eV and a resolution of 0.1 eV per step for quantitative measurements of binding energy and atomic concentration.

Activity tests and analytical procedures

The dehydration of sugar mixtures and catalyst recovery were carried out according to the procedures reported in our previous research (Zhang *et al.* 2012). For a typical experiment, 3.0 g of glucose, 3.0 g of xylose, 50 mL of n-butanol, 50 mL of water, and a given weight amount of solid acid catalyst were mixed to form a suspension and were poured into the reactor. The reactor was then heated to the desired temperature by external heating and shaken at 300 rpm. After running the reaction for a desired duration, the reactor was taken from the stove and quenched in an ice cool water bath to terminate the reaction. After each dehydration run, the aqueous and organic phases were filtered using a microstrainer with an aperture of 0.22 μm (Shanghai Xingya purification materials company, China). The residual glucose and xylose were determined by DIONEX ICS-3000 ion chromatography (Thermo Fisher, USA) equipped with a CarboPac PA1 (2 mm \times 250 mm) analytical column and an electrochemical detector. A solution of sodium hydroxide (100 mmol) was used as the eluent with a volumetric flow rate of 0.3 mL/min at 30 $^{\circ}\text{C}$. The content of HMF and furfural was analyzed with an Agilent 1100 high-performance liquid chromatograph (HPLC) (Agilent, USA) and quantified with calibration curves generated from commercially available standards. The HPLC was equipped with a pump and an Agilent Hypersil ODS column coupled to a Gilson 118 UV/Vis detector (280 nm). The mobile phase consisted of 40% methanol in water (flow rate 1.0 cm³/min), and the column temperature was maintained at 30 $^{\circ}\text{C}$.

RESULTS AND DISCUSSION

NH₃-TPD Measurement

The TPD profiles of desorbed ammonia on SO₄²⁻/ZrO₂-TiO₂ catalysts with different Zr/Ti molar ratios are displayed in Fig. 1. The desorption temperature indicates the acid strength of the catalyst; *i.e.*, the higher the temperature of desorption, the stronger the acid strength. The acid amounts corresponding to the amounts of absorbed NH₃ are estimated by integrating the areas under the peaks (Peng *et al.* 2011). The profiles of all the catalysts displayed very broad desorption peaks. Thus, the acid sites were heterogeneous. The SO₄²⁻/ZrO₂-TiO₂ catalysts showed two distinct peaks appearing from 150 to 300 $^{\circ}\text{C}$ and 300 to 600 $^{\circ}\text{C}$, which are attributed to weak and strong acid sites, respectively. It can be deduced from Fig. 1 that the Zr-Ti molar ratio had an obvious effect on the NH₃-TPD of SO₄²⁻/ZrO₂-TiO₂ catalysts, as the weak and strong acid sites appeared at 167 and 304 $^{\circ}\text{C}$, respectively, for the catalyst composed of TiO₂. However,

the two acid sites appeared at 240 and 526 °C, respectively, when the Zr-Ti molar ratio changed to 3:7. As the Zr-Ti molar ratio was further increased, the desorption temperature of NH₃ decreased slightly and the weak and strong acid sites appeared at 234 and 501 °C, respectively, for the SO₄²⁻/ZrO₂-TiO₂ catalyst with the Zr-Ti molar ratio of 1:1 and at 230 and 500 °C, respectively, for the SO₄²⁻/ZrO₂-TiO₂ catalyst with the Zr-Ti molar ratio of 7:3. Moreover, the two acid sites further decreased to 201 and 408 °C, respectively, when the catalyst was composed only of ZrO₂. Accordingly, the total amount of acid sites for SO₄²⁻/ZrO₂-TiO₂ catalysts had an obvious effect, and the results are presented in Table 1. It can be concluded that the total amount of acid sites was relatively low for the SO₄²⁻/ZrO₂-TiO₂ catalyst consisting of only one kind of active ingredient. For instance, the total amount of acid sites for the SO₄²⁻/ZrO₂-TiO₂ catalyst composed of only TiO₂ or ZrO₂ was 0.07 mmol/g and 0.20 mmol/g, respectively, and these values were less than with the catalyst composed of both ZrO₂ and TiO₂. Previous research by the authors has revealed that the increase in acid strength was caused by the formation of Zr-O-Ti, generating additional acidic active sites (Zhang *et al.* 2011). Moreover, the molar ratio of Zr/Ti will affect the formation of Zr-O-Ti and thus influence the acid strength of the catalyst correspondingly. It can be deduced that the acid strength decreased gradually, and with increasing Zr-Ti, the amount of zirconium further increased.

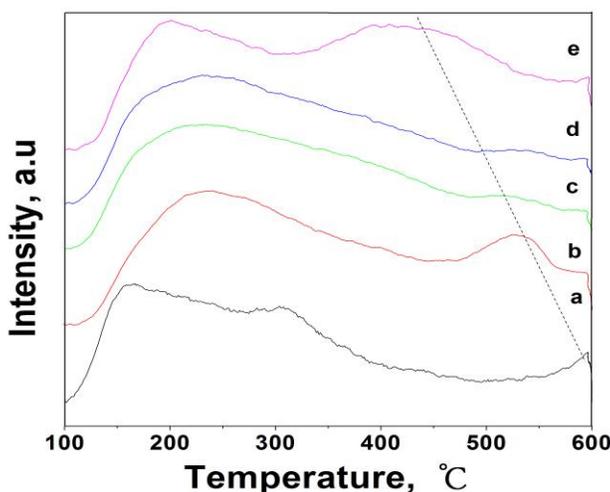


Fig. 1. Effect of Zr-Ti molar ratio on the NH₃-TPD of SZT catalysts: (a) 100% Ti, (b) 3:7, (c) 1:1, (d) 7:3, and (e) 100% Zr

Table 1. Results of NH₃-TPD for Different Catalysts

Zr-Ti molar ratio	Peak temperature (°C)	Total NH ₃ desorbed (mmol/g)
100% Ti	167, 304	0.07
3:7	240, 526	0.25
1:1	234, 501	0.23
7:3	230, 500	0.21
100% Zr	201, 408	0.20
1 st reuse	226	0.12
2 st reuse	218	0.11

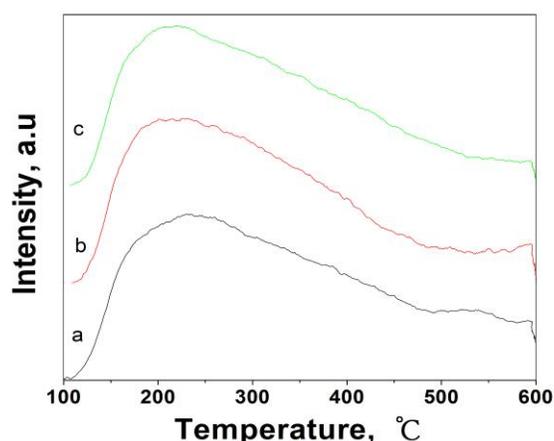


Fig. 2. Effect of catalyst recovered on NH_3 -TPD of $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ catalysts with Zr-Ti molar ratio 7:3 (a, b, c: fresh, 1st reuse, and 2st reuse catalyst, respectively)

The effect of the catalyst recovered on the NH_3 -TPD was also studied, and the results are shown in Fig. 2 and Table 1. It can be concluded that the desorption temperature of NH_3 was slightly decreased as the catalyst recovery number was increased, and a weak peak appeared at 230, 226, and 218 °C for the fresh, 1st reuse, and 2st reuse of the catalyst, respectively. At the same time, the total amount of acid sites decreased from 0.21 mmol/g for fresh catalyst to 0.12 mmol/g and 0.11 mmol/g, respectively, for 1st reuse and 2st reuse of the catalyst. This demonstrated that the acid strength of the $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ catalyst with the Zr-Ti molar ratio of 7:3 decreased gradually as the number of reuses increased. However, the effect of these changes in acid strength on the production of furfurals was found to be negligible, according to the dehydration results displayed in Table 3.

XRD

Figure 3 presents the XRD patterns of the $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ catalyst with the Zr-Ti molar ratio of 7:3, with a, b, and c representing fresh, 1st reuse, and 2st reuse catalyst, respectively. It can be deduced that the formation of brookite TiO_2 and monoclinic ZrO_2 occurred in the fresh catalyst. Furthermore, the formation of crystalline ZrTiO_4 compounds can be clearly noted in the case of the fresh catalyst, consistent with the reported literature (Reddy *et al.* 2002). Although ZrTiO_4 was found to be thermally stable in the absence of any additive atoms due to a different preparation method and precursor compounds used for the preparation of the binary oxide support, it could be decomposed to tetragonal and monoclinic ZrO_2 and (brookite or rutile) TiO_2 at a higher calcination temperature (Reddy and Chowdhury 1998). The XRD patterns of the catalyst remained constant with an increase in the reuse cycle number, and the ZrTiO_4 compound, brookite TiO_2 , and $\text{Zr}(\text{SO}_4)_2$ crystalline phases can be clearly noted at the 2θ of 30°, 25°, and 63° respectively, and the formation of monoclinic ZrO_2 can be observed at the 2θ of 34°, 37°, 51°, 52°, 58°, and 62°. Moreover, it can be deduced from Fig. 3 that the absorption peak intensity in the corresponding position of the catalyst was degraded by a small amount with an increase of the catalyst reuse cycle number. These results indicate that the crystal components undergo a slight loss during the recovery of the catalyst.

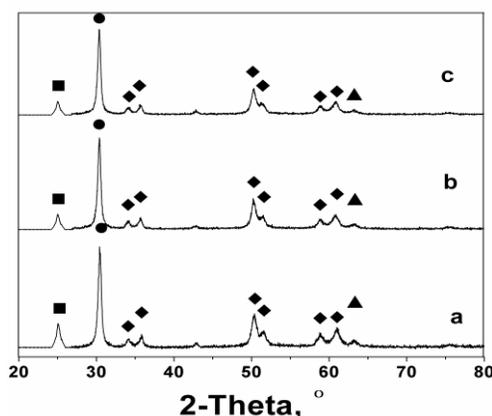


Fig. 3. Effect of recovered catalyst on XRD patterns of $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ catalyst with Zr-Ti molar ratio 7:3. ●ZrTiO₄; ■brookite TiO₂; ▲Zr(SO₄)₂; ◆ monoclinic ZrO₂ (a, b, and c: fresh, 1st reuse, and 2nd reuse catalyst, respectively)

XPS Analysis

XPS analysis was used to obtain information regarding chemical environment and elemental concentrations present in the fresh and regenerated $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ catalysts with the Zr-Ti molar ratio of 7:3. Table 2 summarizes the experimental elemental compositions as confirmed by the XPS spectra analysis. High-resolution scans of the XPS spectra of O 1s, Ti 2p, and Zr 3d with a different intensity scale as ordinate are presented in Fig. 4. Zr, Ti, and O were the predominant species, and the corresponding binding energy and intensity were found to be nearly the same for the fresh and regenerated SZT-4 catalyst, suggesting their chemical environments were unchanged during the reaction. The binding energy (BE) of the Zr 3d photoelectron peaks was observed at 181.3 to 181.7 eV of Zr 3d_{5/2} line and 183.5 to 184.0 eV of Zr 3d_{3/2} line for the fresh catalyst and the regenerated catalyst after the first and second run. Furthermore, the BE of Ti 2p photoelectron peaks was discovered at 457.8 to 458.1 eV of Ti 2p_{3/2} line and 463.6 to 463.9 eV of Ti 2p_{1/2} line (Table 2). However, the BE of the Zr 3d line and Ti 2p line in pure ZrO₂ and TiO₂ sample was observed at 182.3 eV and 458.5 eV, respectively. The shift in the BE of the Zr 3d and Ti 2p line for the catalyst was probably caused by the formation of ZrTiO₄ compounds in the catalyst (Benjaram *et al.* 2001; Reddy *et al.* 2002). A moderate decrease in zirconium content, from 37.4% in the fresh catalyst to 33.8% in the regenerated catalyst after the second run, demonstrating that part of zirconium was lost during the regeneration process. However, the titanium content increased from 11.1% in the fresh catalyst to 17.2% and 18.0% in the regenerated catalyst after the first and second run, respectively, indicating that titanium was relatively stable in the catalyst and the loss of titanium was less than other components during the recycling process. The O 1s photoelectron spectrum was more complicated, due to the overlapping contribution of oxygen from zirconia and titanium (Khawaja *et al.* 1993). Therefore, the O 1s photoelectron spectrum can be separated into three bonding peaks, with the binding energy of O-Zr, O-Ti, and Zr-O-Ti observed at 531.1 to 531.4 eV, 528.9 to 529.0 eV, and 529.7 to 529.9 eV, respectively (Zhu and Liu 2004). The decrease of the O-Zr and O-Ti peak area with the catalyst recycling process also indicates that part of the

zirconium and titanium was lost during the regeneration process. Fortunately, there was not any substantial change in the product yield when the catalyst was reused multiple times after calcination.

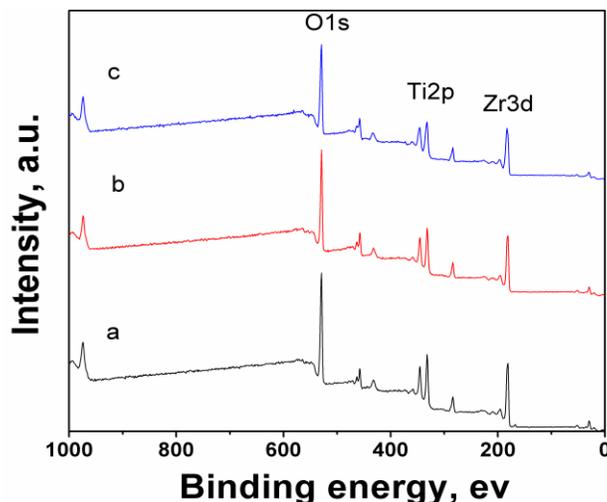


Fig. 4. XPS spectra of O 1s, Ti 2p, and Zr 3d of fresh and regenerated $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ catalysts with Zr-Ti molar ratio 7:3. (a, b, and c: fresh, 1st reuse, and 2nd reuse catalyst, respectively)

Table 2. Experimental Elemental Composition by XPS Analysis for Fresh and Regenerated Catalyst with Zr/Ti Molar Ratio 7:3

Catalyst	Elemental	BE (eV)	Peak area	Content (%)
Fresh	O 1s	531.3	15066.3	51.6
		529.8	17674.4	
	Ti 2p	529.0	14914.3	11.1
		458.0	6313.0	
		463.8	3932.1	
		181.4	17244.9	
Zr 3d	183.7	17313.0	37.4	
1 st reuse	O 1s	531.1	13340.7	49.7
		529.7	15958.4	
	Ti 2p	528.9	12992.8	17.2
		457.8	8426.8	
		463.6	5678.0	
		181.3	14784.3	
Zr 3d	183.5	13638.0	34.7	
2 th reuse	O 1s	531.4	10338.9	46.6
		529.9	18896.5	
	Ti 2p	529.0	12777.3	18.0
		458.1	9960.1	
		463.9	6824.4	
		181.7	15374.3	
Zr 3d	184.0	16169.5	33.8	

Catalytic Activity and Catalyst Stability

It has been reported that HMF, levulinic acid (LA), and formic acid (FA) were generated during the dehydration of glucose catalyzed by $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ (Zhang *et al.* 2012). However, a double reaction system composed of n-butanol and water was constructed in this paper, and the generated HMF will be extracted from the aqueous phase. This will hinder the further degradation of HMF; therefore, LA and FA could not be found in our experiments. And our previous work has shown that the Zr-Ti molar ratio of the $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ catalyst has an obvious effect on the dehydration of a sugar mixture, and the catalyst with the Zr-Ti molar ratio of 7:3 was the most effective catalyst (Table 3) (Zhang *et al.*, 2011). A yield of 26.0 mol% for HMF and 47.5 mol% for furfural can be obtained within 2 h at 170 °C. The catalyst recovery experiments further clarified that the thermally regenerated catalyst maintained better catalysis active and that the yield of HMF and furfural changed little for the 1st reuse and 2st reuse catalyst.

Table 3. Catalytic Activity and Catalyst Stability of Effect of $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ with Zr-Ti Molar Ratio 7:3*

Catalyst	Conversion (%)		Yield (%)	
	Glucose	Xylose	HMF	Furfural
Fresh	96.5	98.3	26.0	47.5
1 st reuse	97.3	95.7	24.5	44.3
2 st reuse	96.9	97.5	25.4	46.8

* Reaction conditions: reaction temperature 170 °C, reaction time 2 h, substrate concentration 6 wt%, catalyst dose 50 wt%, agitation speed 300 rpm)

CONCLUSIONS

The present study described a catalytic process and its evaluation relative to the feasibility of converting the sugar mixtures to furfural compounds, using $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ as a catalyst. It was found that a yield of 26.0 mol% for HMF and 47.5 mol% for furfural can be obtained with a Zr-Ti molar ratio of 7:3. Although the $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ catalyst used here tends to give low product yield, heterogeneous catalysts show unparalleled advantages in comparison to the traditional homogenous acids in terms of recycling and equipment corrosion. Consequently, future studies will focus on developing new and environmentally benign catalysts with higher activity for the formation of furfural compounds derived from sugar mixtures.

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