

Fructose Dehydration to 5-Hydroxymethylfurfural over Sulfated $\text{TiO}_2\text{-SiO}_2$, Ti-SBA-15, ZrO_2 , SiO_2 , and Activated Carbon Catalysts

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ABSTRACT: Different sulfated catalysts including $\text{SO}_4/\text{TiO}_2\text{-SiO}_2$, $\text{SO}_4/\text{Ti-SBA-15}$, SO_4/ZrO_2 , SO_4/AC , and SO_4/SiO_2 were tested in fructose dehydration to 5-hydroxymethylfurfural (HMF). Reactions were carried out in dimethyl sulfoxide (DMSO) at 110 °C. Characterization results indicated that no sulfur leaching was observed from SO_4/ZrO_2 , $\text{SO}_4/\text{TiO}_2\text{-SiO}_2$, and $\text{SO}_4/\text{Ti-SBA-15}$ catalysts in the reaction tests. The $\text{SO}_4/\text{TiO}_2\text{-SiO}_2$ catalyst had a high amount of strong acid sites and the highest amount of Bronsted sites. The highest selectivity to HMF at high conversion, that is, 89% selectivity at 77% fructose conversion was obtained over this catalyst. It preserved its activity after four times reuse.

■ INTRODUCTION

Diminishing fossil fuel reserves and CO_2 emission problems force people to find alternative and sustainable resources to produce valuable chemicals. Production of these chemicals from biomass is an environmentally friendly process compared to a petroleum based process. 5-Hydroxymethylfurfural (HMF) is one of the key intermediates in order to convert the biomass to valuable chemicals such as polymers, biofuels, and bulk chemicals.¹ The most effective way of producing HMF is by carbohydrate conversion, especially dehydration of fructose.

Fructose dehydration reaction occurs on the acid sites of the catalyst. Acid concentration, type of acid sites, and acid strength of the catalyst affect the product distribution significantly.^{2–4} It is reported that fructose conversion to intermediates takes place on the Lewis sites, whereas Bronsted sites are responsible for the HMF formation from these intermediates.⁵ Various acid catalysts including homogeneous (ionic liquids, mineral and organic acids) and heterogeneous types have been investigated. Because of the product contamination and recovery problems, heterogeneous catalysts are generally preferred. Wide ranges of heterogeneous catalysts (e.g., resins, metal sulfates, metal phosphates, heteropolyacids, zeolites, niobic acid based catalysts) have been tested.^{3,6–15} However, no satisfactory yields have been achieved yet. Some of the catalysts have low stabilities due to leaching and some of them are not selective and promote side product formation such as formic acid and levulinic acid. Therefore, there are still studies pursued to find a stable, active, selective, and cheap heterogeneous catalyst for fructose dehydration to HMF.

Sulfur ions and sulfate groups create Bronsted and strong acid sites when loaded on a support, such as iron oxide, alumina, titania, and zirconia. They were very active in fructose dehydration.^{7,17} However, they leached during the reaction in different solvents. Solvent type also affects HMF yield. Different types of solvents from environmentally benign alcohols and water to the high-boiling-point polar aprotic solvents (dimethyl sulfoxide (DMSO) and dimethylamide (DMA)) have been investigated. High yields of HMF have been achieved by using high-boiling-point solvents such as DMSO and DMA.⁹

Zirconia is known as a good support for sulfates.¹⁷ It strongly interacts with sulfur ions and creates strong acid sites. Thus, sulfated zirconia is known as a very acidic catalyst for many reactions. It has Bronsted sites which are effective for fructose dehydration. Also sulfated active carbon (AC) has been shown to have strong acidic sites.¹⁸ In addition, mixed oxides especially titania-silicates became important as acidic catalysts in recent years.^{19–21} They are prepared by several methods such as the sol–gel technique, precipitation, and impregnation where the most stable one is sol–gel. Sol–gel synthesized titania-silicates have a very stable structure, super acidic centers, and regular mesopores. However, they have only Lewis acid sites. Bronsted sites can be created by sulfation of these titania silicates. It was observed by many investigators that Ti in these mixed oxides prevented the leaching of sulfur even in alcohol or water.^{20,22}

In this study, various catalysts were prepared by sulfation of different supports. These catalysts were SO_4/ZrO_2 , SO_4/AC , SO_4/SiO_2 , $\text{SO}_4/\text{TiO}_2\text{-SiO}_2$, and $\text{SO}_4/\text{Ti-SBA-15}$. The effects of support type on fructose conversion and HMF selectivity were investigated. The catalysts were tested in DMSO solvent. Also, tests with homogeneous catalysts (HCl , H_3PO_4 , and H_2SO_4) were performed for comparison purposes.

■ EXPERIMENTAL STUDY

Catalyst Preparation. *Preparation of Sulfated Zirconia and Silica.* Zirconium oxychloride (Sigma-Aldrich, 99.5%) solution of 0.5 M was precipitated with 0.5 M NH_4OH (Riedel, 26%) at pH 9–10 to obtain $\text{ZrO}(\text{OH})_2$. The precipitate was washed with deionized water until the pH of the solution became 7. Then, it was dried for 24 h at 100 °C. The 1 g sample of $\text{ZrO}(\text{OH})_2$ obtained was added to 15 mL of 0.425 M chlorosulfonic acid (Sigma-Aldrich, 99%) in dichloromethane (Sigma-Aldrich, 99.5%) to prepare catalysts with a sulfur loading of 3.0 wt %. The solution was mixed for 5 min. After being washed with hot water (80 °C), it was dried at 120

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Table 1. Textural, Physicochemical, and Acidity Properties of Sulfated Catalysts

catalyst	BET surface area	pore diameter	total acidity	sulfur content of fresh catalyst		sulfur content of tested catalyst	
	m ² /g	Å	μmol NH ₃ /cat	wt %		wt %	
SO ₄ /AC	683	19 (H.K.)	813	2.75		2.27	
SO ₄ /SiO ₂	518	35 (BJH)	659	3.23		2.09	
SO ₄ /TiO ₂ -SiO ₂	321	51 (BJH)	967	6.92		6.97	
SO ₄ /Ti-SBA-15	636	60 (BJH)	1067	5.13		5.08	
SO ₄ /ZrO ₂	120	54 (BJH)	474	3.09		2.99	

°C in the oven for 24 h. The dried powder was then calcined at 450 °C for 6 h. The obtained catalyst was labeled as SO₄/ZrO₂.

SiO₂ (Sigma, 99.8%) was also sulfated following the same procedure using 0.5 M chlorosulfonic acid solution. This catalyst was labeled as SO₄/SiO₂.

Preparation of Sulfated Activated Carbon. AC (Sigma-Aldrich, 99.9%) weighing 0.1 g was added into 50 mL of 1 M H₂SO₄ (Sigma-Aldrich, 98%) solution. The mixture was transferred into an autoclave and then kept in an oven at 180 °C for 24 h. After the autoclave was cooled in an ice bath, the mixture was washed with hot distilled water at 80 °C and dried at 100 °C overnight. The obtained catalyst was labeled as SO₄/AC.

Preparation of Sulfated Titania Silicate. Titania silicate was prepared as follows. A solution of tetraethylorthosilicate (Aldrich, 98%) (7 mL), H₂O (40 mL), and ethanol (Sigma-Aldrich, ≥99.8%) (35 mL) was prepared. HCl (1 M, Sigma-Aldrich, 37%) was added dropwise until the solution pH reached 3. After stirring this solution for 2 h, 0.5 mL of titanium isopropoxide (Sigma-Aldrich, ≥97%) (TISOP) dissolved in 5 mL of ethanol was added. The solution temperature was kept at 20 °C during TISOP addition in order to prevent the precipitation of Ti particles. After that, the solution temperature was increased to 80 °C and stirred until a gel was formed. The formed gel was dried at 80 °C for 24 h. The powder obtained was ground and calcined at 550 °C for 6 h. The TiO₂-SiO₂ obtained was then sulfated by treatment with 5 mL of a 1 M (NH₄)₂SO₄ (Sigma-Aldrich, ≥99%) solution per gram of TiO₂-SiO₂ for 1 h. After sulfation, the powder was calcined at 450 °C for 6 h. This catalyst was labeled as SO₄/TiO₂-SiO₂.

Preparation of Sulfated Ti-SBA-15. Ti incorporated SBA-15 was prepared by dissolving 9 g of Pluoronic P-123 (Aldrich) in 220 mL of water and stirring the mixture for 2 h at 40 °C. Then, sequentially 4.54 g of HCl, 0.8 g of TISOP, and 20 g of TEOS were added to the solution. This solution was stirred for 24 h at 40 °C. The resulting gel was transferred to an autoclave and kept in an oven at 100 °C for 24 h. The final product was washed, centrifuged, dried at 100 °C for 24 h, and then calcined at 550 °C for 6 h. The Ti-SBA-15 prepared was sulfated using 5 mL of a 1 M (NH₄)₂SO₄ solution per gram of Ti-SBA-15. Sulfated powder was calcined at 450 °C for 6 h. The obtained catalyst was labeled as SO₄/Ti-SBA-15.

Characterization of Catalysts. *X-ray Diffraction.* The crystalline structures of the samples were determined by a Philips X'Pert diffractometer with Cu Kα radiation. The scattering angle 2θ was varied from 5° to 80°, with a step length of 0.02.

BET. Nitrogen physisorption studies were performed using Micromeritics ASAP 2010 model static volumetric adsorption instrument. The samples were dried in an oven at 100 °C overnight prior to degassing. Prior to adsorption experiments, the catalysts were outgassed at 300 °C for 24 h under 5 μmHg vacuum.

Temperature-Programmed Desorption. The acidity of the samples was determined by the temperature-programmed desorption of ammonia (NH₃-TPD) method using Micromeritics AutoChem II Chemisorption Analyzer instrument. The sample was heated to 500 °C by increasing the temperature at a rate of 5 °C/min and was kept at this temperature for 1 h under He gas flow of 70 mL/min. Then the sample was cooled under a He flow of 30 mL/min to 90 °C at a rate of 5 °C/min. This was followed by switching the flow to a NH₃-He gas mixture at the rate of 30 mL/min for 30 min. Physically adsorbed NH₃ was removed by degassing the sample at 90 °C under a He flow of 70 mL/min for 120 min and then at the rate of 30 mL/min for 150 min. NH₃ desorption of the sample was analyzed by heating the sample at the rate of 10 °C/min from 90 to 600 °C. The thermal conductivity detector signal was recorded during the NH₃-TPD.

Fourier Transform Infrared Spectroscopy (FTIR). The acidity measurements of the catalysts were also made by IR spectroscopy with a pyridine adsorption/desorption method. The samples were activated at 400 °C under vacuum (2 × 10⁻² mmHg) for 2 h. Adsorption of pyridine was carried out at 150 °C for 30 min. Before FTIR analysis the samples were kept at 150 °C vacuum (2 × 10⁻² mmHg) for 30 min in order to desorb the physisorbed pyridine. KBr pellets were prepared by pressing a mixture of 4.5 mg of catalyst sample and 150 mg KBr. IR characterizations were carried out between 400 and 4000 cm⁻¹ with Shimadzu FTIR-8201 model Fourier transform infrared spectrometer.

X-ray Fluorescence Spectroscopy (XRF). Elemental composition of the catalysts was determined by XRF before and after the reaction. The analysis was performed by the powder method with the use of a Spectro IQ II instrument and Cu Kα radiation.

Reaction Tests of Homogeneous Catalysts. Mineral acids, HCl (Sigma-Aldrich, 37%), H₃PO₄ (Sigma-Aldrich, 85%), and H₂SO₄ (Sigma-Aldrich, 98%) were also tested in fructose dehydration to investigate the role of sulfate and assess the activity of heterogeneous catalysts for comparison purposes. Tests were performed in the same reactor system as that for heterogeneous catalysts. After the reaction temperature was reached, 0.1 M homogeneous acid in DMSO was added to the reactor. The samples were taken and analyzed as for the heterogeneous catalysts.

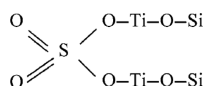
Reaction Tests of the Heterogeneous Catalysts Prepared. The activity tests were performed in a 200 mL stirred multiple reaction station at 110 °C. Initially, 0.5 g of catalyst was added into 40 mL of DMSO in the reactor. This mixture was stirred and heated to the desired reaction temperature. Then, 6 wt % of fructose dissolved in 10 mL of DMSO was added to the reactor. Samples were taken at every 30 min time intervals during 180 min of reaction time. Each sample was centrifuged and diluted 25 times with 5 mM H₂SO₄ solution. They were analyzed by a HPLC instrument equipped with a UV-vis and a

refractive index detector (RID) and a Bio-Rad Aminex HPX-87H column. The concentration of reactant and products was quantified by the external standard method. A control experiment showed that 5 mM H₂SO₄ solution used in the preparation of the reaction samples for analysis did not affect the concentration of the products and reactants.

For reusability tests, the used catalysts were separated from the reaction mixture, washed three times with deionized water and heat treated at 200 °C for 3 h. Catalysts were reused up to four times. A test without catalyst was also performed to examine the effect of DMSO in fructose dehydration.

RESULTS AND DISCUSSION

Characterization of the Catalysts. The XRD analysis showed that SO₄/ZrO₂ had only the tetragonal phase (results not given).²³ Textural properties of the sulfated ZrO₂, SiO₂, and AC, Ti-SBA-15 and TiO₂-SiO₂ catalysts are given in Table 1. All the catalysts had high surface areas except SO₄/ZrO₂. The AC-supported catalyst had the smallest pores among all the catalysts. Sulfated SiO₂, Ti-SBA-15, and TiO₂-SiO₂ had mesopore structures. SO₄/TiO₂-SiO₂ and SO₄/Ti-SBA-15 had the highest amount of sulfur content, around 6%. This was probably due to chelating bidentate bond formation which limited the decomposition of sulfur during calcination.¹⁹ These bonds form as follows:



The acidities of the catalysts determined by NH₃-TPD are given in Figure 1. Peaks at 130–250 °C were classified as weak

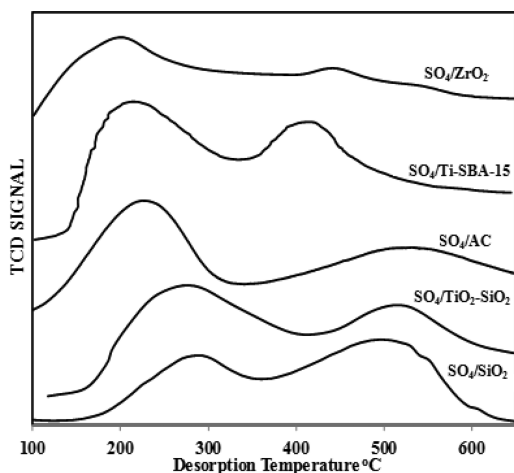


Figure 1. NH₃-TPD of sulfated ZrO₂, SiO₂, AC, Ti-SBA-15, TiO₂-SiO₂.

acid sites, peaks at 260–400 °C were medium acid sites, and those at 400–600 °C were classified as strong acid sites.²⁵ The strength of the acid sites of the catalysts were different. All the catalysts had weak acid sites. SO₄/TiO₂-SiO₂ and SO₄/SiO₂ catalyst had medium and strong acid sites centered at 300 and 520 °C, respectively. They had the highest amount of strong acid sites. This might be attributed to the good dispersion of the sulfur ions on the SiO₂ support and formation of strong chelating bonds in titania silicates. SO₄/Ti-SBA-15 had medium and strong acid sites (peak at 440 °C), the majority of which were the medium acid sites. SO₄/AC had strong acid sites

centered at 520 °C. From NH₃-TPD measurement of the catalysts, total acidities of the catalysts were determined as given in Table 1. Titanium containing catalysts had much higher acidities than other catalysts.

The pyridine adsorption spectra of the heterogeneous catalysts obtained by FTIR spectroscopy is given in Figure 2

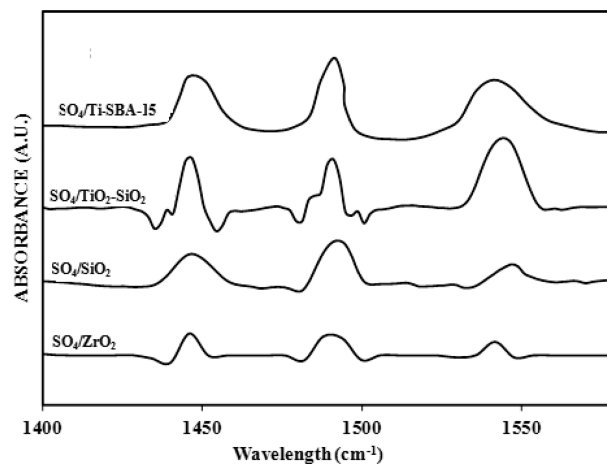


Figure 2. FTIR spectra of pyridine adsorption on sulfated ZrO₂, SiO₂, Ti-SBA-15, and TiO₂-SiO₂.

except for that of SO₄/AC. There is a broad band at 1548 cm⁻¹ which is assigned to Brønsted acid sites. The intense band at 1490 cm⁻¹ is assigned to Brønsted and Lewis acid sites. The band at 1455 cm⁻¹ is related to Lewis acidity. It was observed from each spectrum that all of the catalysts had Brønsted and Lewis acid sites. Sulfated titania silicates (SO₄/Ti-SBA-15 and SO₄/TiO₂-SiO₂) had a much higher amount of Brønsted and Lewis acid sites than other catalysts, with SO₄/TiO₂-SiO₂ having the largest amount of Brønsted sites.

Catalyst Testing. Fructose conversion and selectivity to HMF were defined as follows:

Fructose conversion:

$$X\% = \frac{\text{moles of fructose reacted}}{\text{moles of initial fructose}} \times 100$$

HMF selectivity (mol %):

$$S\% = \frac{\text{moles of HMF produced}}{\text{moles of fructose reacted}} \times 100$$

Fructose Conversion over Homogeneous Catalysts.

Fructose conversion was very rapid with the homogeneous catalysts (HCl, H₃PO₄, and H₂SO₄) (Figure 3). It reached 90% in less than 1 min, and complete conversion of fructose was achieved in 30 min. HMF, levulinic acid, formic acid, and glucose were formed as major products. Selectivities to HMF changed with the mineral acid used (Figure 4). It increased with reaction time and the highest selectivity (87%) was obtained when sulfuric acid was used.

Activities of Sulfated SiO₂, AC, TiO₂-SiO₂, and Ti-SBA-15 Catalysts in Fructose Dehydration. The product distribution obtained over the most selective catalyst SO₄/TiO₂-SiO₂ is given in Figure 5. Fructose was completely converted in 150 min and HMF was the main product. Glucose, levulinic, and formic acid were formed as side products. As the amount of HMF formed increased with reaction time, more HMF was rehydrated to levulinic acid

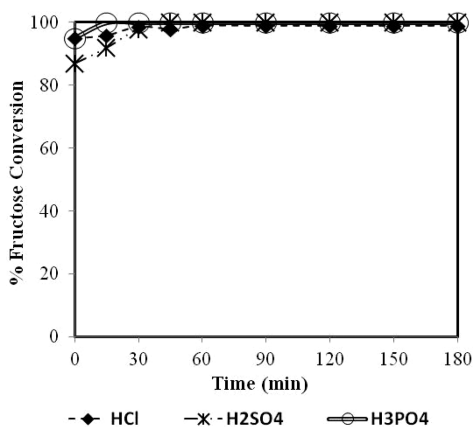


Figure 3. Fructose conversions over homogeneous catalysts, HCl, H₂SO₄, and H₃PO₄.

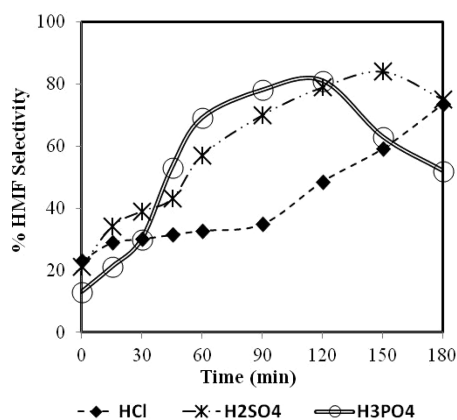


Figure 4. Selectivity to HMF over homogeneous catalysts, HCl, H₂SO₄, and H₃PO₄.

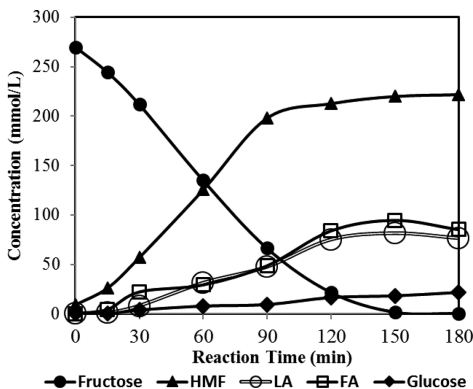


Figure 5. Product distribution over SO₄/TiO₂-SiO₂.

(LA), formic acid (FA), and glucose. These products formation were also observed with other catalysts.

Fructose conversions differed depending on the catalyst applied, see Figure 6. It was observed that all of the catalysts were active. The SO₄/ZrO₂ catalyst was found to be the most active catalyst; complete fructose conversion was achieved in 50 min. No leaching of sulfur was observed (Table 1) which was attributed to its tetragonal phase. This was also observed by Jiang et al.²⁸ SO₄/TiO₂-SiO₂ catalyst was also stable and converted fructose completely in 3 h reaction time. This could be attributed to the presence of more Lewis acid sites in SO₄/

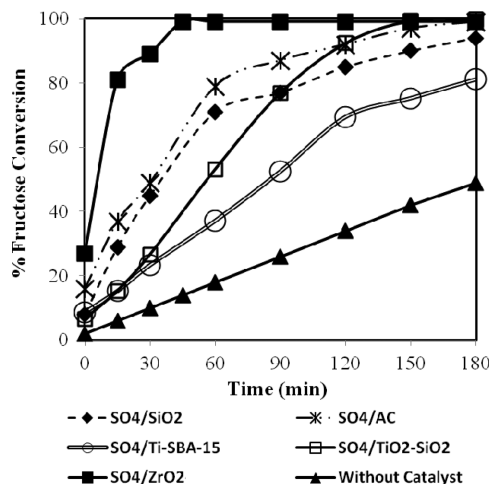


Figure 6. Fructose conversions without catalyst and over SO₄/ZrO₂, SO₄/SiO₂, SO₄/AC, SO₄/TiO₂-SiO₂, and SO₄/TiSBA-15.

TiO₂-SiO₂ which were reported to be responsible for the fructose conversion.⁵ SO₄/AC and SO₄/SiO₂ also showed high activity; however, they were not stable (Table 1).

The selectivities to HMF obtained over the catalysts are given in Figure 7. SO₄/TiO₂-SiO₂ provided the highest

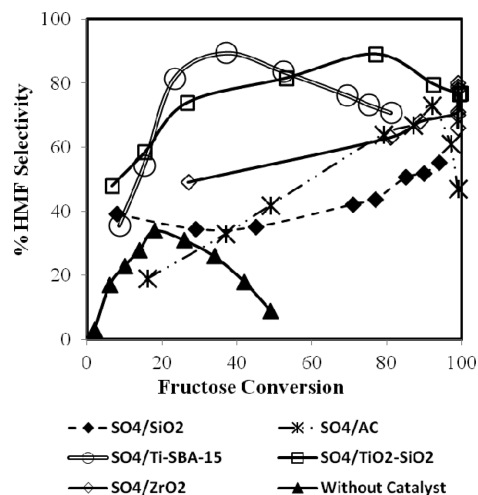


Figure 7. Selectivity to HMF without catalyst and over SO₄/SiO₂, SO₄/AC, SO₄/TiO₂-SiO₂, and SO₄/TiO₂-SiO₂.

selectivity (89%) at high conversion (77%). This selectivity was comparable with the selectivity obtained by H₂SO₄. SO₄/TiSBA-15 also provided high selectivity (77%) but at low conversion (37%). These catalysts had the highest amount of Brønsted acid sites among all the catalysts. Thus, high selectivity was related to the presence of chelating bonds (strong Brønsted sites) in these catalysts. These sites were probably responsible for the HMF formation from intermediates. The mesopores structure of SO₄/TiO₂-SiO₂ and SO₄/TiSBA-15 might also contribute to the selectivity achieved as the fructose molecule has a large size (0.87 nm).³ The rate of adsorption of intermediates and rate of product diffusion would be higher in mesopores which might lead to higher selectivities. Selectivity decreased over SO₄/TiSBA-15 when fructose conversion exceeded 40%. This might be due to the presence of more basic sites in SO₄/TiSBA-15, which might be

responsible for rehydration of HMF to levulinic and formic acids.^{26,27}

SO_4/ZrO_2 also provided high selectivity to HMF which was 81% at 100% fructose conversion. This high selectivity was attributed to the stable tetragonal phases and amount of Bronsted sites in this catalyst. The tetragonal phase has been reported to create Bronsted acid sites which improve selectivity to HMF.²³ However, the monoclinic phases were found to favor the side products formation.^{24,27} Selectivities obtained for SO_4/AC and SO_4/SiO_2 catalysts include the contribution from leached sulfur. Thus, the results cannot be related to their acidity only.

The effects of the nature of the acid sites on fructose conversion and HMF selectivity were investigated by Weingarten et al.⁵ and Ordonsky et al.² Weingarten et al.⁵ reported that fructose conversion to intermediates from fructofuranoses was carried out on the Lewis sites, whereas Bronsted sites were responsible for the HMF formation from these intermediates. These findings are in agreement with the results obtained in the present study. The formation of humins was related to the amount of Bronsted sites according to Ordonsky et al.² They are formed by an oligomerization reaction between intermediates and fructose or HMF. HMF oligomerization was inversely proportional with the amount of the Bronsted sites and strong acid sites. This also explained why in the current study the HMF selectivity increased with the amount of Bronsted sites.

Tests without catalysts showed that DMSO acted as catalyst (Figure 6). A fructose conversion of 40% and HMF selectivity of 38% (Figure 7) was observed. Amarasekara et al.²⁹ proposed that the dehydration of fructose to HMF is catalyzed by DMSO. They suggested the following mechanism for the role of DMSO. The dehydration occurred in three steps. In each step, covalent bonds were formed by electron sharing between DMSO and OH groups of furanoid fructose, then hydrogen bonded hydroxides (water) were separated from fructose. The presence of the furanoid forms of the fructose (α -furanoid or β -furanoid) in DMSO favored the HMF formation. Accordingly, Bicker et al.³⁰ stated that furanoid forms were much favored in organic solvents (acetone, DMSO). The highest concentration of furanoid forms were obtained in DMSO. However, they were the least favored in aqueous based solvents. In addition, Despax et al.¹⁶ in their study on HMF formation in various organic solvents under microwave conditions obtained high selectivity to HMF in DMSO. DMSO was reported to have a dual role: solvent and reaction mediator.

Reusability Tests of the Heterogeneous Catalysts. The catalysts reusability results up to four reuses are given in Figure 8. Only the activities of $\text{SO}_4/\text{Ti-SBA-15}$ and $\text{SO}_4/\text{TiO}_2\text{-SiO}_2$ catalysts did not change with reuse. These catalysts also did not show leaching of sulfur (Table 1). Therefore, $\text{SO}_4/\text{Ti-SBA-15}$ and $\text{SO}_4/\text{TiO}_2\text{-SiO}_2$ can be considered as highly stable catalysts.

CONCLUSIONS

All the catalysts were highly acidic and had different acidic properties. The presence of tetragonal phase prevented sulfur leaching from SO_4/ZrO_2 . Also no leaching was observed with Ti incorporating silicates (bidendate bond). High Bronsted acidity and amount of strong acid sites gave high selectivity to HMF. Only $\text{SO}_4/\text{TiO}_2\text{-SiO}_2$ preserved its activity after four reuses.

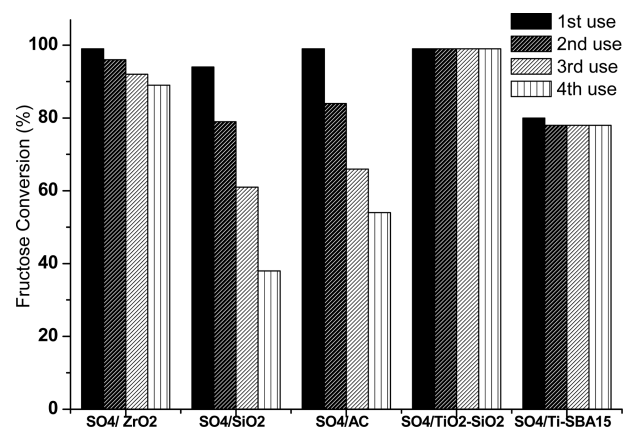


Figure 8. Reusability of the different sulfated catalysts in fructose dehydration.

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Notes

The authors declare no competing financial interest.

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