

Catalysis of Glucose to 5-Hydroxymethylfurfural using Sn-Beta Zeolites and a Brønsted Acid in Biphasic Systems

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Selective and efficient dehydration of glucose to 5-hydroxymethylfurfural (HMF) has been a widely explored concept recently, especially from the perspective of employing environmentally benign heterogeneous catalysts. However, there has been a relative paucity of data regarding the application of Sn-Beta zeolites, a category of catalysts that are very innocuous, inexpensive, and effective, toward evaluating bio-based conversions. Sn-Beta was shown to possess good Lewis acidity for catalyzing glucose isomerization to fructose in aqueous media at low pH and accelerating dehydration of glucose to HMF in a biphasic system with high yields. Sn-Beta zeolite with NH₄F as the mineralizing agent (Sn-Beta-F) was a more effective catalyst for the selective dehydration of glucose to HMF. An optimal HMF yield of 53.0% was obtained over Sn-Beta-F zeolite in an acidic environment (pH 1) after 70 min at 190 °C. The reaction system was also effective for conversion of cellulose to HMF with a yield of 32.2% preliminarily.

Keywords: Glucose; 5-hydroxymethylfurfural; Biphasic system; Sn-based zeolite

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INTRODUCTION

Biomass has become an increasingly vital feedstock for the sustainable production of industrial materials and transportation fuels in addressing the long-term needs of society. Today, carbohydrates represent approximately 75% of the yearly output of the renewable feedstock available for materials manufacture (Schmidt and Dauenhauer 2007). One of the products of the dehydration of carbohydrates, HMF, has attracted significant attention because it can be potentially used as a platform chemical, a precursor for polymers, a fuel, or a solvent (Corma *et al.* 2007).

Several of the specific carbohydrates that have garnered particular research focus for HMF production are glucose and fructose (Eminov *et al.* 2014). Fructose has been demonstrated to provide high HMF yields using several homogeneous and heterogeneous catalyst systems (Vigier *et al.* 2012; Jadhav *et al.* 2013). However, it should be noted that fructose is far less abundant and more expensive than glucose. Therefore, the primary challenge is to find high-yield approaches for the conversion of glucose to HMF. This is not easy because glucose rings are too stable to be hydrolyzed under mild conditions. Nevertheless, glucose remains a preferred feedstock for the production of HMF because it is the most abundant and least expensive monosaccharide on the market as a viable raw material. Typically, the conversion of glucose proceeds *via* selective isomerization and

dehydration to HMF through either cyclic or acyclic avenues. Huang *et al.* (2010) attained 63% HMF yield by employing glucose isomerase in an HCl solution containing borate as the catalyst for isomerization and dehydration. Zhao *et al.* (2007) achieved an unprecedented HMF yield of nearly 70% from glucose in the ionic liquid 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), using CrCl₂ as the catalyst.

Interestingly, a biphasic reactor system (HCl solution and either a poly(1-vinyl-2-pyrrolidinone) or dimethyl sulfoxide organic solvent), in which the selective dehydration of fructose to HMF displays a high yield of roughly 72%, was studied by Román *et al.* (2009). It was concluded that the water-immiscible organic solvent has a positive effect on the dehydration of fructose because it suppresses undesired reactions.

Various heterogeneous catalytic systems have also been reported for HMF production. For example, an HMF yield of 23% was achieved over Zr-MCM-41 by Jiménez-Morales *et al.* (2014). Otomo *et al.* (2014) reported that beta zeolite prepared by calcination at 750 °C had 55% selectivity at 78% glucose conversion. Zeolite catalysts, a form of heterogeneous catalysts, offer several advantages over metalloenzymes and acids, including higher stability at higher temperatures, effortless separation of reaction product and catalyst, and strong acid sites (Lewis and Brønsted catalytic sites). Because of its unique performance, Sn-Beta has been applied for bio-catalysis for the past several years. Meanwhile, as a Lewis acid catalyst, Sn-Beta has large potential for application in the field of green catalytic chemistry. Moliner *et al.* (2010) investigated Sn-Beta for use in the isomerization of glucose to fructose or mannose at 110 to 140 °C *via* several cycles. In addition, reaction systems including Sn-Beta and various Brønsted acids have been studied to some extent. Nikolla *et al.* (2011) revealed that the combination of Sn-Beta zeolite with HCl resulted in a yield of 57% for the conversion of glucose to HMF in a biphasic system at 180 °C for 70 min. Despite the success of Nikolla *et al.*, the traditional Sn-Beta zeolite preparation process is quite complex, requiring a synthesis time of no less than 10 d. Thus, searching for more efficient green catalysts has become exceedingly imperative to attain a viable conversion platform.

The aim of the present work was to compare the catalytic behavior of two Sn-based zeolites in glucose conversion in a biphasic acidic environment. The catalysts systems examined were (a) Sn-Beta zeolite with NH₄F as the mineralizing agent (Sn-Beta-F), and (b) Sn-Beta-SAC, the zeolite described in part (a) but rapidly synthesized *via* steam-assisted conversion (SAC).

EXPERIMENTAL

Materials

D-(+)-glucose (99%), D-(-)-fructose (99%), sucrose, D-(+)-cellobiose (98%), cellulose, silicon dioxide nanoparticle (SiO₂, 99.8%), tetraethylammonium hydroxide solution (TEAOH, 25%), pyridine (99.9%), and methanol (HPLC grade) were purchased from Aladdin Industrial, Inc. (Shanghai, PR China). Tin tetrachloride (SnCl₄·5H₂O, 98%), ammonium fluoride (NH₄F), tetraethyl orthosilicate (TEOS), tetrahydrofuran (THF), 1-butanol, 2-butanol, dimethyl sulfoxide (DMSO), NaCl, methyl isobutyl ketone (MIBK), and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, PR China). Nitric acid (HNO₃, 65%) and sulfuric acid (H₂SO₄, 98%) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. An industrial Beta zeolite (Sinopec, Si/Al atomic ratio of 25) was used for all experiments. Ultrapure water (18 MΩ) was obtained

from an ELGA Micra water purification system (UK). All chemicals were used without further purification.

Synthesis of the Catalyst

Synthesis of Sn-Beta-F

The Sn-Beta-F zeolite was prepared following procedures previously described by Li *et al.* (2011), with slight modifications. An industrial Beta zeolite was de-aluminated by stirring it in HNO₃ solution at 80 °C for 8 h. The resulting powder was washed with deionized water and dried at 80 °C overnight. The powder was calcined at 500 °C overnight. For a typical SnCl₄ treatment, a fixed amount of TEOS was added to a TEOH solution while stirring at room temperature for 30 min. Next, a solution of SnCl₄ was slowly added while stirring in a water bath at 75 °C for 3 h. A fixed amount of NH₄F solution was gradually added with continuous stirring. The zeolite powder was added, and stirring was continued until a uniform, viscous gel with a molar composition of 1 SiO₂:0.00667 SnCl₄:0.6 TEOH: 0.54 NH₄F:7.5 H₂O was achieved. Finally, the mixed gel was loaded into a stainless steel, Teflon[®]-lined autoclave, followed by placement in a homogeneous reactor operating at 140 °C for 20 d. This was necessary because higher ratios of Si/Sn (lower Sn content) require shorter crystallization times. After the product crystallized, it was recovered by filtration, washed with distilled water, and dried at 100 °C overnight.

Synthesis of Sn-Beta-SAC

The Sn-Beta-SAC zeolite was rapidly synthesized *via* steam-assisted conversion (Kang *et al.* 2013). A wet gel was first prepared from silicon dioxide nanoparticles, SnCl₄·5H₂O, TEOH, and NH₄F. Following careful drying at 60 °C for 6 h, a dry gel with a composition of 1 SiO₂:0.27 (TEA)₂: 0.008 SnO₂:0.54 NH₄F:7.5 H₂O was obtained. Then, 2 g of dry stannosilicate gel was powdered and placed in a homemade autoclave that prevented condensation of water onto the dry gel during the steam-assisted conversion process. Approximately 1.5 mL of water was added to the autoclave while the steam was generated at 180 °C. Products were obtained following 6 h of treatment and were washed and dried at 110 °C for 8 h prior to air calcination at 550 °C for 6 h to remove the organic species.

Characterization

The powder catalysts were analyzed by X-ray diffraction (XRD) on a D8-ADVANCE diffractometer (Bruker AXS, Germany), using Cu-K α radiation from a Cu X-ray tube (40 kV, 40 mA). The data were collected from $2\theta = 10$ to 90° with a resolution step size of 0.02° and a scan step time of 5 s.

Scanning electron microscopy (SEM) of the catalysts was obtained using a Quanta 200 (FEI, America). Samples were dried at 120 °C for 1 h in air before analysis.

The textural properties were determined from nitrogen adsorption-desorption isotherms at -196 °C, obtained with a V-sorb 2800P apparatus/surface analyzer (Gold App Instruments, China) after degassing the samples at 350 °C overnight. The BET method was used to calculate the specific surface areas.

The Sn content was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) on an Optima 2000DV (PE, America) atomic emission spectrometer.

Analyses of the Lewis acidity and Brønsted acidity were carried out by pyridine probe FTIR spectroscopy (Shimadzu 8300 spectrometer, Japan). The samples were evacuated at 250 °C overnight and exposed to pyridine vapors at room temperature for 15 min. Next, the sample was put under vacuum and evacuated at 150 °C to remove the physisorbed pyridine. For quantitative calculations, the amounts of adsorbed pyridine were determined using the molar extinction coefficient (Maier *et al.* 2011).

Thermal programmed desorption of ammonia (NH₃-TPD) was used to obtain the total acidity and different types of acidity. Before ammonia adsorption at 50 °C, samples were heated from room temperature to 550 °C at a heating rate of 10 °C/min and maintained at 550 °C for 1 h. The NH₃-TPD was performed between 50 and 550 °C with a heating rate of 10 °C/min, and the ammonia desorbed was analyzed by an on-line chromatograph equipped with a TC detector.

Catalytic Reactions

Experiments were performed in 15-mL thick-walled glass reactors (Synthware) with Teflon[®] lids containing magnetic stirring rotors. Glucose, catalysts, and salts were dried at 60 °C under vacuum before use. In a typical experiment, 1 g of an aqueous solution containing 10 wt. % glucose, NaCl, and the corresponding catalysts (Glucose:tin molar ratio, 200), was adjusted to pH 1 using HCl. A set volume of organic solvents was added to the aqueous solution. The resulting mixture was stirred for 30 min and transferred to a glass reactor. This reactor was immersed in an oil bath at the desired temperature with stirring (600 rpm) for a defined time ranging from 30 to 150 min.

For the dehydration reactions, a two-phase reactor system was used. A sequence of organic solvents was introduced to promote the dehydration reaction by shifting the equilibrium toward HMF formation by immediately extracting the HMF by stirring. After the reaction, the products were quenched by immersing the reactor into a cooled water bath. The catalyst was removed from the reaction medium by filtration after the reaction time had elapsed. The catalyst was then washed with methanol and water to eliminate the adsorbed reaction products and used in the next catalytic cycle. All analyses and experiments were performed at least in duplicate.

Both the aqueous and the organic layers were analyzed by high-performance liquid chromatography (HPLC) using a Shimadzu LC-20A system equipped with a quaternary gradient pump (LC-20AT), column oven (CTO-20A), UV/Vis detector (SPD-20A), and a refractive index detector (RID-10A). The disappearance of carbohydrate was monitored using a refractive index detector, and HMF production was followed using a UV detector. Glucose disappearance was monitored with a Shodex Sugar SP0810 column using ultrapure water as the mobile phase at a flow rate of 0.6 mL/min at a column temperature of 65 °C. The concentration of HMF was quantified in the aqueous and organic phases with a Shim-pack VP-ODS reverse phase column using a 2:8 v/v methanol:water (pH = 2, H₂SO₄) gradient at a flow rate of 0.7 mL/min at a column temperature of 35 °C. The calculations were made as follows,

$$\text{Glucose conversion (\%)} = \frac{\text{Mole of glucose reacted}}{\text{Mole of starting glucose}} \times 100 \quad (1)$$

$$\text{HMF yield (\%)} = \frac{\text{Mole of HMF in products}}{\text{Mole of starting glucose}} \times 100 \quad (2)$$

HMF separation

After the degradation of glucose, the acid was neutralized to a pH of about 5 to 6 by using CaO. Then, the mixture was filtered to remove the insoluble products and solid catalysts. The filtrate was extracted four times with ethyl acetate. The organic layer was collected and dried with anhydrous sodium sulfate. Then the organic phase was distilled under reduced pressure at room temperature to obtain pure HMF as a main product.

When the produced yield of HMF was 53.0%, the isolated yield by this procedure was 36.8%, *i.e.* nearly 70% HMF could be recovered.

The ^1H NMR spectrum (DMSO) of separated products included the following peaks: 4.48 (s, 2H), 6.58–6.59 (d, 1H, $J = 4$), 7.47–7.48 (d, 1H, $J = 4$), 9.54 (s, 1H); whereas the ^{13}C NMR spectrum (DMSO) showed the following: 55.91, 109.58, 124.25, 151.72, 162.15, and 177.86.

RESULTS AND DISCUSSION

Structural Properties of the Catalysts

Powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and FTIR were used to characterize the catalysts. Figure 1 shows the XRD patterns of Si-Beta, Sn-Beta-F, and Sn-Beta-SAC. The Sn-Beta-F (Fig. 1b) and Sn-Beta-SAC samples (Fig. 1c) displayed well-defined reflections because of the beta polymorph A (BEA) topology (Maier *et al.* 2011).

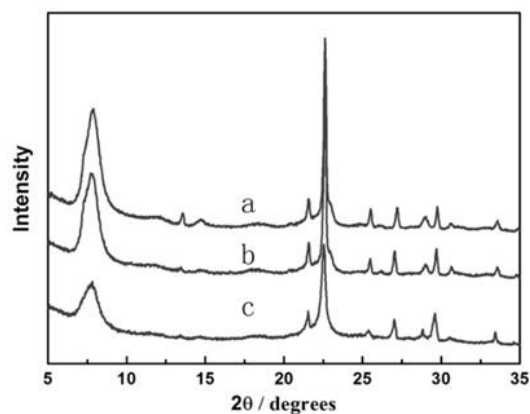


Fig. 1. Powder XRD patterns of the catalysts: (a) Si-Beta; (b) Sn-Beta-F, (c) Sn-Beta-SAC

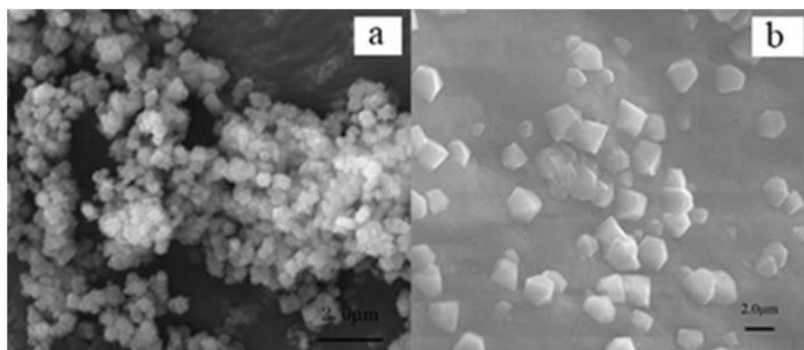


Fig. 2. SEM images of tin-containing catalysts: (a) Sn-Beta-F, (b) Sn-Beta-SAC

The patterns were comparable in diffraction intensity, indicating that no collapse of the crystalline structure had occurred during de-alumination or after SnCl₄ vapor treatment (Kang *et al.* 2013). As can be seen from Fig. 1b, Sn-Beta-F was pure, with good crystallinity. Compared to the Si-Beta zeolites, the Sn-Beta zeolites (Figs. 1b and 1c) also exhibited typical diffraction peaks that attributed to diffraction patterns of 330, 302, 304, and 306. Because the atomic radii of the hetero atoms were greater than the radius of Si or Al, the diffraction peaks shifted to lower angles (Mal *et al.* 1995). SEM also demonstrated the crystalline phase of the products, as shown in Figs. 2a and 2b, Sn-Beta crystals were very small, spherical particles (0.5 to 0.8 μm).

The acid site and the strength of the acid site are two main factors affecting the conversion of glucose to HMF. A suitable balance between the acid site density and the strength of the acid site is important for glucose conversion to HMF (Karinen *et al.* 2011). As can be seen in Table 1, all catalysts provided high HMF yields (greater than 30%) at 160 °C for 60 min. Furthermore, a greater HMF yield of 35% was obtained using Sn-Beta-F, which was better than that obtained with the Sn-Beta-SAC catalyst. This difference cannot be explained simply in terms of a higher number of active sites and more suitable strength of the acid site in the catalyst; rather, it indicates that the active sites in Sn-Beta-F were more suitable for activating the substrate. Sn-Beta-F contained pores (around 0.82 nm in diameter), which were of similar size to the glucose molecule (0.85 nm) (Li *et al.* 2001). However, the pores of Sn-Beta-SAC (around 0.68 nm in diameter) were relatively small, decreasing the chance of accommodating glucose molecules because of the active Sn-Beta center located within the pores. The effect of diffusion limitations should not be overlooked, although these likely have only a limited effect on this reaction because of the small size of the substrate. The mass pore size of the Sn-Beta-SAC is similar to the size of glucose. Part of the conversion of glucose to HMF may have taken place on the outer surface of the catalysts. However, Sn-Beta-SAC can still achieve a HMF yield of 30%. The total acidity of Sn-Beta-SAC is also similar to that of Sn-Beta-F. However, the number of Lewis sites is less than that of Sn-Beta-F. According to the previous report (Kang *et al.* 2013), some SnO₂ was formed during the Sn-Beta-SAC synthesis process. The Brønsted acid site contents were slightly more than that of Sn-Beta-F.

Table 1. Characterization of the Two Sn-based Catalysts

Catalyst	Sn Content ^b (mmol/g)	S ^c (m ² /g)	Pore Size ^c (nm)	Total Acidity ^d (mmol/g)	Medium and Strong Acidity ^d (mmol/g)	B/L ^e	HMF Yield (%)
Sn-Beta-F	0.178	620	0.82	0.94	0.69	0.15	35
Sn-Beta-SAC	0.211	480	0.68	0.86	0.65	0.09	30

^a Reaction conditions: 10 wt. % glucose solution, catalysts (glucose:tin molar ratio, 200), the aqueous phase (pH 1, HCl), $V_{org}/V_{aq} = 3$, 0.35 g of NaCl added to 1 g of water, 160 °C, 60 min.

^b Determined by ICP.

^c Surface areas and mass pore size were given by N₂ adsorption at -196 °C. The catalyst surface areas were measured by the BET method. The pore size is referred to the mass pore size.

^d The total acidities of catalysts were obtained by NH₃-TPD. The medium and strong acidity were measured from 200 °C < T < 550 °C.

^e The content ratios of Brønsted/Lewis acid sites were determined by FT-IR spectroscopy of adsorbed pyridine.

It is known that the active sites that promote glucose isomerization through a hydride transfer mechanism in Sn-Beta are incorporated into the framework. SnO₂ has less isomerization activity. Based on the above discussion, Sn-Beta-F was identified as the most suitable catalyst for further study.

Dehydration of Glucose

For further reaction study, Sn-Beta-F was combined with a Brønsted acid catalyst (HCl) in an aqueous system, and their catalytic activities toward glucose conversion to HMF using a single aqueous system and a biphasic reaction system were tested (Table 2, entries 1 and 2, respectively). The results clearly demonstrated that the use of a biphasic system resulted in higher glucose conversion and HMF yield at 160 °C for 60 min. The increased HMF yield obtained using the biphasic system is due to the presence of a water-immiscible organic phase that allows for the continuous extraction of HMF from the aqueous phase, demonstrating the benefit of avoiding the redegredation of HMF into undesired byproducts under aqueous acidic conditions. The addition of NaCl in the succeeding experiments improved glucose conversion (Marcotullio and De Jong 2010; Molina *et al.* 2012). The results (Table 2, entries 2 and 5) showed that without the addition of NaCl, a HMF yield of 16% was obtained at 160 °C after 60 min. Several researchers have suggested that the chloride ion changes the path of the products from a number of metal halides tested (Marcotullio and De Jong 2010). In addition, Table 2 (entries 3 to 5) shows that the combination of Sn-Beta-F with HCl brought about a higher HMF yield than a biphasic system with either Sn-Beta-F or HCl as the catalyst. This result could be because both Sn-Beta-F and HCl are consumed when converting glucose to HMF. Sn-Beta-F is essential for isomerization of glucose to fructose, whereas HCl is required for dehydration of fructose to HMF. Table 2, entries 6 and 7, show an interesting result that combination of Sn-Beta-F with HCl brought about a lower HMF yield than a biphasic system with HCl as the catalyst. This is because Sn-Beta-F could also isomerize fructose to glucose (Bermejo-Deval *et al.* 2012a).

Table 2. Glucose or Fructose Conversion to HMF under Various Reaction Conditions

Entry	Feed	Catalyst	Reaction System	Conversion (%)	HMF Yield (%)
1	Glucose	Sn-Beta-F, HCl	H ₂ O	29	3
2	Glucose	Sn-Beta-F, HCl	THF/H ₂ O	77	13
3	Glucose	Sn-Beta-F	THF/H ₂ O/NaCl	75	8
4	Glucose	HCl	THF/H ₂ O/NaCl	76	16
5	Glucose	Sn-Beta-F, HCl	THF/H ₂ O/NaCl	78	26
6	Fructose	HCl	THF/H ₂ O/NaCl	>99	76
7	Fructose	Sn-Beta-F, HCl	THF/H ₂ O/NaCl	>99	69

Reaction conditions: glucose: tin molar ratio of 200, $V_{org}/V_{aq} = 3$, aqueous phase pH of 1 (HCl). Entries 1 to 5: Feed was 10 wt. % glucose solutions; Entries 3 to 7: 0.35 g of salt was added to 1 g of water; Entries 6 to 7: Feed was 10 wt. % fructose solutions; Entries 1 to 7: 160 °C, 60 min.

Effect of volume ratio of THF to H₂O

The low selectivity of glucose conversion without the addition of an extracting solvent may be explained by formation of intermediate products or adsorption of HMF over the catalyst (Carniti *et al.* 2006). Ideally, separation of HMF from single organic solvent and THF-NaCl system would be less energy intensive. However, the solubility of

sugars in pure THF is exiguous; thus water is needed to allow this conversion at a practical scale. The HMF yield significantly increased with the volume ratio of THF to water increased to 3:1. On the other hand, adding more THF did not cause much increase in the HMF yield (Fig. 3). The result of high ratios of THF to water showed that the surfaces of catalyst were full of THF, and an increased amount of extracting solvent did not raise the HMF yield. These results can be attributed to condensation reactions between HMF and sugar. Ordonsky *et al.* (2012) also explained that an intensive interaction of the organic solvent with the catalyst was another major factor. In addition, using a large amount of organic solvent in the chemical process would increase production costs.

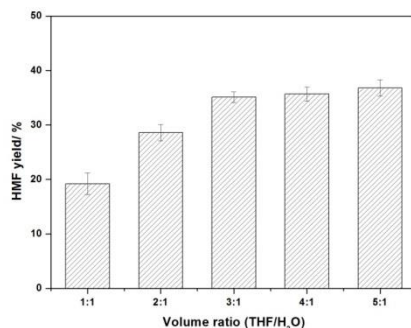


Fig. 3. Influence of volume ratios of THF to H₂O on HMF yield. Reaction conditions: Sn-Beta-F was added at a 1:200 Sn: glucose molar ratio to a 10wt% glucose solution, pH=1 in HCl, 0.35 g of NaCl was added in 1 g of water, 160 °C, 60 min

Effect of reaction temperature

Figure 4 shows that the reaction temperature had a pronounced effect on the dehydration of glucose into HMF. Experiments were performed at 160, 170, 180, 190, and 200 °C for 90 min. At the same reaction time, the yield of HMF first increased and then decreased as the reaction temperature was raised. When the reaction temperature was less than 170 °C, the HMF yield was below 40%. When the reaction temperature was 170 °C, the HMF yield increased to 40% over 90 min. At 180 °C, 82% of the glucose was converted and a 47% HMF yield was achieved after 90 min. In particular, at a reaction temperature of 190 °C after 90 min, glucose conversion and HMF yield reached to 90% and 50%, respectively.

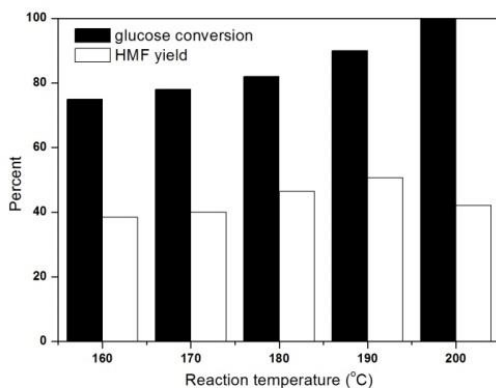


Fig. 4. Effect of reaction temperature on the conversion of glucose to HMF over Sn-Beta-F zeolite. Reaction conditions: glucose-to-tin molar ratio of 200, $V_{org}/V_{aq} = 3$, aqueous phase (pH 1, HCl). Feed was 10 wt. % glucose solution. 0.35 g of salt was added to 1 g of water, 90 min.

These results indicate that an increase in the reaction temperature not only increases the glucose conversion but also facilitates maximum HMF yield. However, when the reaction temperature was increased to 200 °C, the HMF yield dropped. It is well known that as the reaction temperature increased, the HMF yield decreases is due to the equilibrium shifts away from HMF formation and the low stability of HMF may suffer from condensation reactions (Ståhlberg *et al.* 2011), thus considerably reducing the HMF yield.

Effect of reaction time

Figure 5 shows that the reaction time had great effect on the dehydration of glucose into HMF. At 190 °C, the HMF yield first increased and then decreased as the reaction time increased. This result can be ascribed to the condensation of HMF into levulinic acid and formic acid, which were detected in minute amounts after HPLC analysis. The formation of levulinic acid was found to be a consequence of longer reaction times and strong acid sites (Bermejo-Deval *et al.* 2012b). The latter result signifies that as the reaction time increased, Sn-Beta zeolite and a Brønsted acid catalyst did not promote the desired transformation. After the reaction, the levulinic acid yield had slightly increased, suggesting that a Brønsted acid catalyst is able to rehydrate HMF. Further, dark, insoluble humins were formed during the reaction.

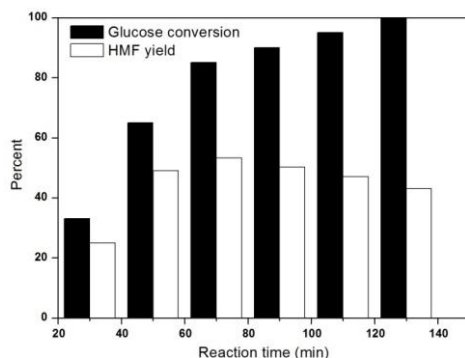


Fig. 5. Effect of reaction time on the conversion of glucose to HMF over Sn-Beta-F zeolite. Reaction conditions: glucose-to-tin molar ratio of 200, $V_{org}/V_{aq} = 3$, aqueous phase (pH 1, HCl). Feed was 10 wt. % glucose solution. 0.35 g of salt was added to 1 g of water, 190 °C.

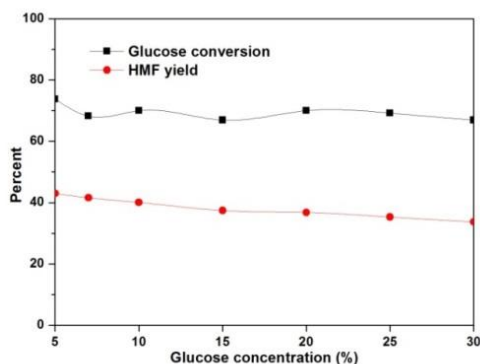


Fig. 6. Effect of glucose concentration on its conversion into HMF. Reaction conditions: different amount of glucose and Sn-Beta-F (Molar ratio of glucose-to-tin: 200) were added into solution. $V_{THF}/V_{H2O} = 3$ with the aqueous phase adjusted to pH 1.0 using HCl. Reaction temperature: 170 °C. Reaction time: 70 min.

Effect of glucose concentration

The effect of glucose concentration on the conversion of glucose into HMF is illustrated in Fig. 6. Glucose concentration had a slight influence on HMF yield. As shown in Fig. 6, when the glucose concentrations were 5, 7, and 10 wt.%, HMF yields were similar at a reaction temperature of 170 °C for 70 min. However, when the glucose concentration increased from 10 to 30 wt.%, HMF yields decreased slightly. The Sn-Beta-F/THF/H₂O catalytic system was most suitable for the conversion of high glucose concentrations into higher HMF yields. It follows that concentrated glucose conversion can be suitable for large-scale industrial production.

Catalyzed Conversion of Various Substrates into HMF with Sn-Beta-F

To further explore the extent of the range of possible substrates for this catalytic system, carbohydrates such as glucose, sucrose, cellobiose, and cellulose were further investigated. As shown in Fig. 7, a high yield of HMF, 53.0%, was obtained from glucose reacted at 190 °C for 70 min. When disaccharides such as sucrose and cellobiose were tested as the substrates, the HMF yields were 55.2% and 38.3%, respectively. Cellobiose exhibited lower HMF yields than sucrose because sucrose consists of glucose and fructose, whereas cellobiose has two glucose units. Cellulose is composed of repeating cellobiose units, which are glucose dimers joined by difficult-to-hydrolyze glycosidic linkages. Although, cellulose was more difficult to convert into HMF, The HMF yield of 32.2% in the present reaction system encouraged us to do further research work on cellulose and biomass as feedstock.

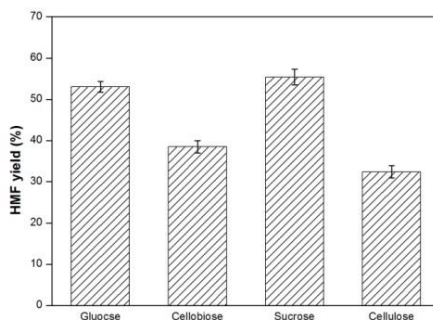


Fig. 7. Conversion of various carbohydrates into HMF in the presence of Sn-Beta-F. Reaction conditions were 190 °C for 70 min using a 10 wt. % carbohydrate solution (pH 1 in HCl) of various carbohydrates with a 1:200 Sn:glucose molar ratio. The ratio of THF volume to water volume was 3:1.

Catalyst Regeneration

Sn-Beta-F showed exceptionally robust isolation and recovery properties. With respect to catalyst life, minor deactivation occurred when the catalyst was recycled five times. To check whether the deactivation during the first recycling was due to leaching or the adsorption of product, the catalyst obtained after the initial recycling was filtered, washed with water and ethanol, and calcined in air at 550 °C for 6 h before being added to a new glucose solution. Table 3 shows that the reaction activities of these catalysts were maintained and that HMF yields of 51.9%, 51.0%, 49.8%, 49.0%, and 47.5% were obtained after each recycle utilization. These results showed that the catalyst possessed good thermal-stability. SEM and XRD were used to evaluate the morphology of the Sn-Beta-F catalyst after reactions in the presence of acid, salt, and organic solvent. XRD data

for the Sn-Beta-F catalyst after reaction in the presence of HCl and NaCl showed that no significant changes have occurred under same reaction conditions (Fig. 8a). Similar results were observed by using SEM (Fig. 8b). This further confirms the Sn-Beta-F catalyst had good recyclability.

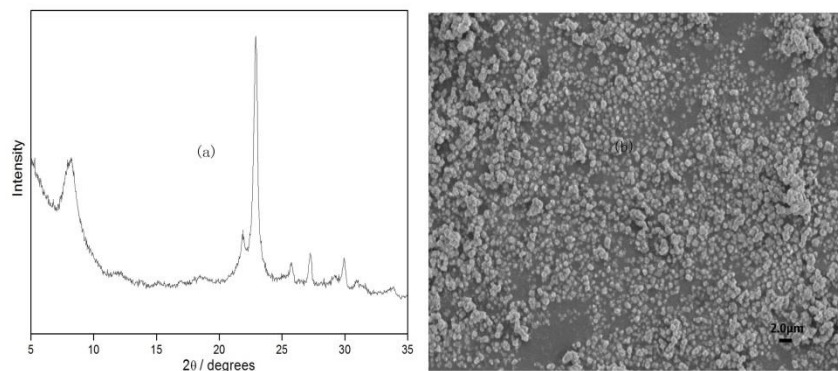


Fig. 8. Powder XRD pattern and SEM image of Sn-Beta-F catalyst reused after fifth recycle

Table 3. Reusability of Sn-Beta-F in the Dehydration Reaction of Glucose

Recycle Time	HMF Yield (%)
0	53.0
1	51.9
2	51.0
3	49.8
4	49.0
5	47.5

^a Reactions were performed at 190 °C for 70 min using a 10 wt.% glucose solution (pH of 1 in HCl) with a 1:200 Sn:glucose molar ratio. The ratio of THF volume-to-water volume was 3:1. Sn-Beta-F were calcined in air at 550 °C for 6 h for next recycle.

CONCLUSIONS

1. An optimal 5-hydroxymethylfurfural (HMF) yield of 53.0% can be obtained using Sn-Beta-F zeolite and a Brønsted acid catalyst after 70 min at 190 °C. Additional benefits of these catalysts include that they can be easily recovered by filtration, regenerated by calcination, and recycled multiple times with high yields.
2. Preliminarily, an HMF yield of 32.2% was achieved in conversion of cellulose, which indicates that further research work on cellulose and biomass as feedstock in this catalytic reaction system will be valuable.

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