High Yield Production and Purification of 5-Hydroxymethylfurfural

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Conversion of carbohydrates to 5-hydroxymethylfurfural (HMF) will provide a new step toward achieving renewable biomass-based chemicals and fuels platform. Recently, the excellent yield of HMF (91.0%) in dimethyl sulfoxide (DMSO) catalyzed by sulfonated carbon was demonstrated, but the separation of HMF from the reaction mixture remains challenging because of the high boiling point of DMSO. As a solution, herein, low boiling point solvent tetrahydrofuran (THF) mixed with DMSO was used for the fructose dehydration and high yield of HMF (98.0%) was still obtained. Besides, the stability of the sulfonated carbonaceous catalyst was also confirmed. More importantly, HMF from the reaction solution was successfully separated by using simple extraction method, and high purity of HMF (ca. 96.4%) was obtained. Compared with pure DMSO solvent, the combination of low boiling point THF with DMSO not only gives higher yield of HMF, but also improves the separation efficiency and reduces environmental risk. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 2558–2566, 2013

Keywords: fructose dehydration, hydroxymethylfurfural, extraction, sulfonated carbon

Introduction

Biomass is an abundant and only sustainable carbon resource, and carbohydrates derived from biomass are the key biomass components and important potential sources of chemical intermediates to produce many high value products.[1–4] Among them, 5-hydroxymethylfurfural (HMF) is an important compound that is obtainable directly from the acid-catalyzed dehydration of carbohydrates, and it could be potentially used as a platform compound for further processing into high quality fuels and commercially valuable chemicals.[5–8] Therefore, the development of simple and effective routes to transform biomass into HMF would be of great significance.

The most conventional methods for the preparation of HMF were the acid-catalyzed dehydration of fructose or fructose-precursors.[1,5,7,9–21] These methods have been widely investigated and many types of acid catalysts have been explored, such as mineral acid (such as HCl, H_2SO_4),[3,5,11,22] organic acids (such as oxalic acid, citric acid, maleic acid, formic acid),[22,23] transition metal ions,[24,25] H-moredenites/zeolites,[26] solid metal phosphates,[13,16] and strong acid cation exchanged resins.[17–19] As we know, homogenous acids are inexpensive and act as high activity for the acid-catalyzed dehydration reactions, but they have the drawbacks in terms of separation and recycling in addition to the equipment corrosion. Solid acid catalysts, such as H-form zeolites and metal phosphates can be easily separated and recycled, but still suffer from low fructose conversions (about 30–60%).[24–26] Strong cation exchanged resin could be a candidate as a green catalyst for HMF production. Shimizu et al.[14] reported that 100% HMF yield can be obtained in dimethyl sulfoxide (DMSO) with an improved removal of generated water catalyzed by Amberlyst-15. But, unfortunately, these acidic resins have low-thermal stability due to their organic frameworks and were normally used below 130°C, thus partially limited their applications. Besides, the separation of HMF from DMSO solution is also a big problem.[27]

Recently, a novel carbon-based solid acid catalyst with high acid density was prepared via a facile and low-danger approach in our group, and it has also been proved to be highly effective in the dehydration of fructose into HMF in DMSO solvent.[28,29] However, HMF and DMSO have very high boiling points (114–116°C at 1.33 mbar and 189°C at 1 atm, respectively), consequently, it is much difficult to directly evaporate HMF or distill DMSO from the reaction solution to obtain pure HMF. Moreover, the distillation of solvent (DMSO) will not only need significant energy input, but also result in a highly concentrated HMF, which is unstable at high temperatures due to the formation of undesired byproducts, such as humins and other soluble polymers.[3,21] Dumesic and coworkers[3] pointed out that at 343 K and 1.3 mbar, evaporating DMSO from 10 wt % HMF solution will lead to a 30% loss of HMF. Qi et al.[19] reported that the combination of low boiling point acetone with DMSO not only gave highly selective HMF formation, but also improve the separation efficiency, but how to effectively separate HMF from the reaction solution was not mentioned. In addition, some other reaction systems also have been studied,

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such as subcritical or supercritical solvents,[22,30–32] ionic liquids,[10,12,15,17] or aqueous systems.[5,9,16] However, all these processes have some disadvantages, such as significant energy input for subcritical or supercritical solvents, high cost of expensive ionic liquids, and much more complicated side reactions in aqueous processes, all of which have limited their applications on practical scale.

Tetrahydrofuran (THF) has a relatively low boiling point (339 K) and low heat of vaporization (30.26 KJ·mol^{-1} at 339 K). In THF, fructose is much favorable to be converted to the furaniod form, which is much more easier to generate HMF.[21,33] Moreover, its miscibility with water can take the generated water away from the reaction system, thus prevents the side reactions due to the presence of water molecules.[20,34] As a result, the separation of THF from reaction system to get pure HMF would be less energy intensive.[33] Unfortunately, the solubility of fructose in pure THF is negligible, and thus, either water or another solvent is needed to allow conversion at practical scale. According to our previous study, fructose has a good solubility in DMSO, and a high HMF yield of up to 91.2% can be obtained in pure DMSO solvent. Although DMSO has a good miscibility with THF, the partition coefficient in the aqueous phase or organic phase was much more different: DMSO is apt to move into the aqueous phase and THF is preferable to stay in the organic phase. Besides, HMF is favor to divert to the organic phase from the aqueous phase as well. As a result, the extraction method would be a good choice to separate the reaction solution to obtain HMF. Thus, the objective of this work was to study the dehydration of fructose to HMF in THF/DMSO mixtures using the sulfonated carbonaceous catalyst. In addition, the separation of HMF from the reaction solution by extraction with adding diethyl ether (DEE) as an extracting phase and the analysis of the extracted HMF were also demonstrated in this work.

Experimental

Materials

Fructose (99.8%), glucose (99.8%), *p*-toluene sulfuric acid (99.5%, TsOH), sodium sulfate (99.5%), DMSO (99.5%), and THF (99.5%) were purchased from Shanghai chemicals company. 5-hydroxymethylfurfural was purchased from Alfa Aesar company. All reagents were commercial products of the highest purity available (>98%) and used as received without further purification.

Catalyst preparation

The method for the preparation of sulfonated carbonaceous catalyst was similar to our previous report[28,29] just with a slight modification. In a typical synthesis, 4 g of glucose, 6 g of TsOH, and a certain amount of sodium sulfate were mixed, ground, and placed in 100 mL Teflon-lined stainless steel autoclave. Subsequently, the autoclave was put into an oven of 180°C and aged for one day. Then, the resulting dark powder was collected from the autoclave and placed in the oven of 180°C for another day to remove the small organic compounds adsorbed on the surface of the material. After ground, washed with hot water until sulfate ions were no longer detected and dried at 100°C overnight, the catalyst was obtained and denoted as GTS.

Catalyst characterization

Brunauer–Emmett–Teller (BET) Characterization. The nitrogen adsorption experiment was measured at 77 K with a NOVA 4200e sorption analyzer. Before the measurements, the samples were outgassed at 200°C for 8 h. The Brunauer–Emmett–Teller (BET) method was used to calculate the apparent surface areas.

Acidity Titration Characterization. The titration method of the surface functional groups over GTS catalyst was similar to our previous report.[29] First, for the measurement of the $-SO_3H$ group, the GTS catalyst (0.25 g) was added to a sodium chloride aqueous solution (0.05 M, 30 mL). Then, the mixture was stirred for 60 min at room temperature under ultrasonic vibration. After centrifugal separation, the supernatant solution was titrated by a sodium hydroxide (0.05 M) aqueous solution using phenolphthalein as an indicative and the SO_3H group was calculated as C_1 mmol·g^{-1}. Second, for the measurement of $-SO_3H$ plus $-COOH$ groups, the GTS catalyst (0.25 g) was added to a sodium bicarbonate aqueous solution (0.05 M, 30 mL). After the vibration and separation treatment, the supernatant solution was titrated by a hydrochloric acid (0.05 M) aqueous with an indicative of phenolphthalein and the content of this two groups was calculated as C_2 mmol·g^{-1}. So the content of $-COOH$ groups was (C_2-C_1) mmol·g^{-1}. Finally, to determine the total content of functional groups ($-SO_3H$, $-COOH$, and $-OH$ groups), the GTS catalyst (0.25 g) was added to a sodium hydroxide aqueous (0.05 M, 30 mL). Via the vibration and separation treatment, the supernatant solution was titrated by a hydrochloric acid (0.05 M) with phenolphthalein as an indicative, and the total content of functional groups was C_0 mmol·g^{-1}. Hence, the content of $-OH$ groups was (C_0-C_2) mmol·g^{-1}.

NH_3-TPD Characterization. The temperature-programmed desorption of ammonia (NH_3-TPD) was performed on an apparatus PX200 (Tianjin Golden Eagle Technology Limited Corporation). The sample (50 mg) charged into the quartz reactor, and the temperature was increased from room temperature to 120°C over 1 h at a rate of 10°C min^{-1} under a flow of N_2 (40 mL min^{-1}), and then the temperature was decreased to 90°C. NH_3 was pulsed into the reactor at 90°C under a flow of N_2 (40 mL min^{-1}) until the acid sites were saturated with NH_3. The adsorbed NH_3 was removed by a flow of N_2 (40 mL min^{-1}). When the baseline was stable, the temperature was increased from 90 to 500°C at a rate of 10°C min^{-1}. A blank measurement was also conducted without adsorption of ammonia, and after deducted the blank measurement, the NH_3-TPD curve of GTS was obtained.

Typical workup procedure

The experimental procedure is similar to that used in related works.[14–16] Briefly, a solution of fructose in THF/DMSO (total volume = 10 mL) and a given amount of the sulfonated carbonaceous catalyst (GTS) were loaded into a Teflon-lined stainless steel autoclave and the autoclave was placed into an oil-bath container with magnetic stirring for reaction. N_2 gas was used for purging air outside the reactor and keeping a certain pressure to prevent boiling. When the reactor was raised to the desired temperature, zero time was recorded. Then, the reactor was held at this temperature for a given period of time. After the desired reaction time passed, the reactor was cooled down by loading cooling water. After each reaction, the catalyst was collected with filtration and the filtrate was taken for analysis. The collected GTS catalyst was washed with water and ethanol, and the dried for the next usage.

Products analysis

The analysis of the reaction products was carried out by means of a HPLC apparatus (Agilent 1200 Series) equipped with an XDB-C18 column (4.5 μm, 250 mm, Eclipse USA) operated at 35°C based on the external standard, and the identities of the compounds were authenticated by comparing their retention times with those of pure compounds. An auto-sampler (Agilent G1329A) was used to enhance the reproducibility. HMF was quantified with an ultraviolet detector (Agilent G1314B) at 282 nm. The eluent with flow rate of 0.6 mL min^{-1} was a mixture of methanol to water with volumetric ratio of 20:80. The fructose concentration was analyzed with a refractive index detector (Agilent G1362A). The eluent was pure water with a flow rate of 1.0 mL min^{-1}.

HMF was the main product of the dehydration reaction of fructose regardless of the experimental conditions. The by-products were furfural, levulinic acid, 2,5-diformylfuran, and 5-methylfurfural detected by GC-MS, the concentrations of these by-products were too low to be quantified in the HPLC analysis. In addition, when the reactions were carried out at higher temperature for long reaction time, there were also some polymer products, such as humins, which were not characterized in this work as well. In addition, the MS analysis of the separated HMF was conducted on Agilent Mass spectrometer with Triple-Axis Detector and ^{1}H NMR spectra were recorded by using a Bruker AVANCE III spectrometer (600 MHz) with $CDCl_3$ as the solvent.

Fructose conversion (C, mol %) and HMF yield (Y, mol %) are defined as follows:

$$C(\text{mol }\%)=\text{Mole of fructose reacted}/\text{mole of starting fructose,} \quad (1)$$

$$Y(\text{mol }\%)=\text{Mole of HMF produced}/\text{mole of starting fructose} \quad (2)$$

The weight ratio of substrate to sulfonated carbonaceous catalyst was defined as R:

$$R=\text{Weight of fructose}/\text{weight of sulfonated carbonaceous catalyst} \quad (3)$$

Results and Discussions

Characterization of GTS catalyst

BET Analysis. Like our previous report, glucose was used as the carbon precursor, and TsOH was used as the sulfonation agent. Fortunately, with the addition of sodium sulfate in the formation stage of GTS, the resultant carbonaceous material had a high surface area of 188.9 $m^2\ g^{-1}$, which was much higher than that of the sulfonated carbonaceous material (<2 $m^2\ g^{-1}$).[28,35,36] This may be because that the inorganic salt (sodium sulfate) added in the synthesis process (especially in the carbonization step) was acted as porogen (crystal nucleus in this anhydrous environment) and resulted in the dramatic increase in surface area.

Acidity Titration Analysis. With acidity titration measurement, the concentration of $—SO_3H$ (C_1), $—SO_3H$ plus $—COOH$ (C_2), total functional groups (C_0, $—SO_3H$ and $—COOH$ and $—OH$) were 0.7, 1.3, and 2.5 mmol g^{-1}, respectively. So, the acid density of $—SO_3H$, $—COOH$, and $—OH$ groups was 0.7, 0.6, and 1.2 mmol g^{-1}, respectively.

NH_3-TPD Analysis. The acid strength was determined by the programmed desorption of chemisorbed ammonia (NH_3-TPD), and after deducted the blank measurement, the NH_3-TPD curve of the GTS was shown in Figure 1, it can be seen that there are abundant weak to moderate acid sites, in which ammonia was desorbed at 100–450°C. The NH_3-TPD results were also in accordance with the results of neutralization titration.

Determination of suitable conditions for fructose conversion

Influence of the Reaction Media Composition. First, we have investigated the dehydration of fructose in water in the presence of the carbonaceous catalyst (GTS). The results showed that the GTS catalyst exhibited low activity in water, with the 68.9% fructose conversion, 15.8% HMF yield and 22.9% HMF selectivity at 160°C for 60 min ($R=2$). This is because water is not favorable for the dehydration reaction and can promote the rehydration of HMF to by-products, such as levulinic acid. However, it should be noted that the 15.8% yield of HMF was still higher than that using the previous catalyst (8%, Glu—TsOH) in water,[29] indicating that the modification with sodium sulfate may enhance the hydrophobicity of the catalyst and partly improve the activities reacted in water. In addition, the yield of HMF was also below 10% with Amberlyst-15 as a catalyst in water. As a result, to enhance the HMF yield and depress the formation of by-products in water, changing the reaction solvent was considered.

In the previous work, we have demonstrated that DMSO was an effective solvent that can depress side-reactions in the fructose dehydration because the furanoid form was preferred in DMSO,[3,11,29] which is easy to dehydrate to HMF,[37,38] but its high boiling point limits its application. Conversely, THF is easily separated from the reaction solution and fructose has been shown to rearrange to the furanoid form in the THF solvent.[21,33] Therefore, solvent composition was changed with THF to replace some part of the DMSO to study the dehydration of fructose in THF/DMSO using GTS as catalyst and the experimental results were shown in Figure 2. It can be seen that THF/DMSO mixtures can effectively suppress the formation of by-products and increase the selectivity to HMF, which indicated that THF/DMSO mixtures are highly preferable to pure DMSO for the dehydration of fructose to HMF. Moreover, as the percentage of THF in the solution increased, HMF yield, the conversion

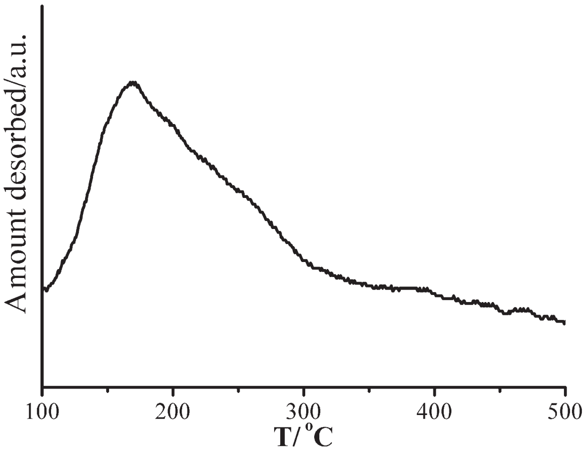


Figure 1. The NH_3-TPD curve for the sulfonated carbonaceous material.

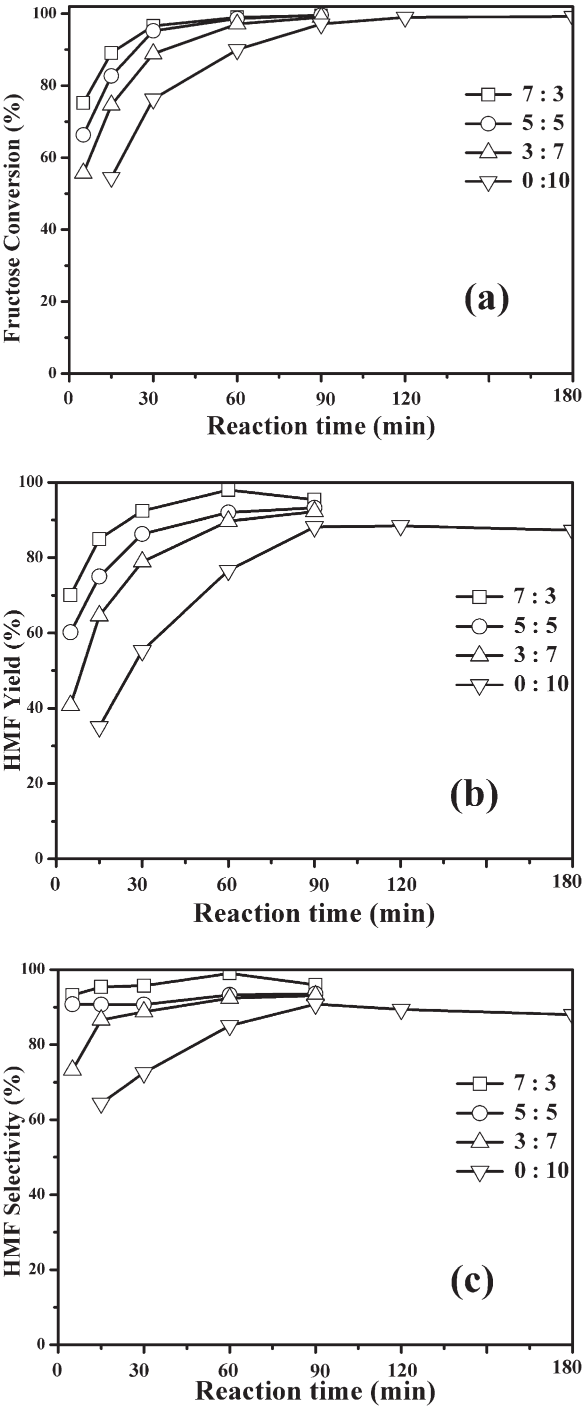


Figure 2. Influence of the reaction solvent composition on fructose conversion (a), HMF yield (b), and HMF selectivity (c).

***Reaction conditions*: 10 mL of reaction solution, 5 wt % fructose, $R=2$, 160°C.**

rate and HMF selectivity increased, and the HMF yield reached 98.0% with 99.0% HMF selectivity and 99.0% fructose conversion in the 70:30 (v/v) THF/DMSO mixture for a reaction time of 60 min at 160°C, higher than the HMF yield of 89.8% obtained in the 70:30 (w/w) acetone/DMSO mixture.[19] But with the prolonging of the reaction time, the yield and selectivity of HMF decreased due to the polymerization of HMF from the dark color of the reaction solution. In addition, if we further increase the percentage of THF, the solubility of fructose decreases rapidly, and fructose almost cannot be dissolved in pure THF solution. Therefore, a THF-DMSO mixture of 70:30 (v/v) was used as reaction media hereafter.

Influence of the Reaction Temperature with Reaction Time. The influence of reaction temperature on the fructose dehydration to HMF catalyzed by GTS was studied, and the experiments were conducted at 80, 100, 130, and 160°C. Figure 3 shows the influence of the temperature with respect

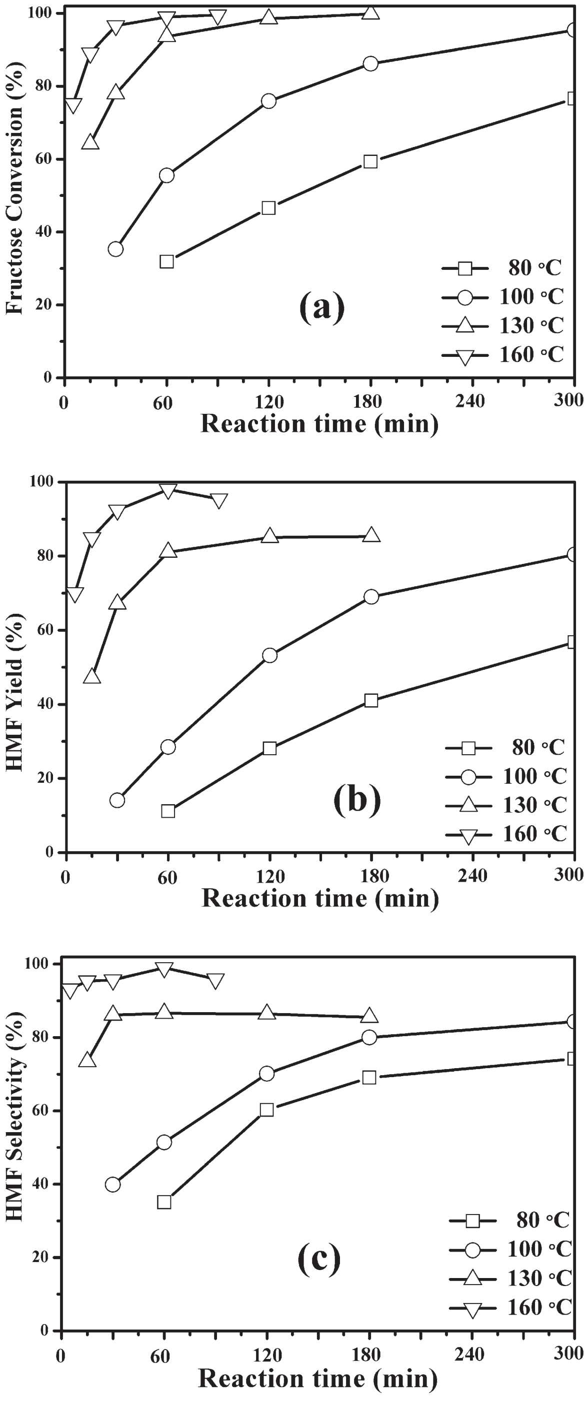


Figure 3. Influence of the reaction temperature on fructose conversion (a), HMF yield (b), and HMF selectivity (c).

***Reaction conditions*: 10 mL of reaction solution, THF/DMSO=70:30 v/v, 5 wt % fructose, $R=2$.**

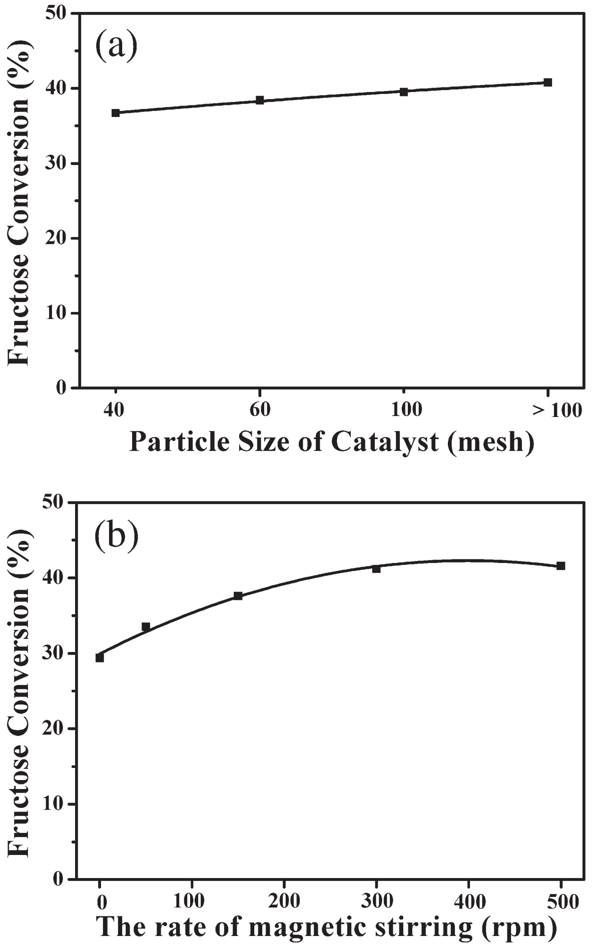


Figure 4. Influence of the particle size of catalyst (a) and the rate of magnetic stirring (b) on fructose conversion.

***Reaction conditions*: 10 mL of reaction solution, THF/DMSO=70:30 v/v, 5 wt % fructose, *R*=2, 80°C.**

to the fructose conversion, the HMF yield and the HMF selectivity. We can see that reaction temperature had a great influence on the fructose conversion, the HMF yield and the HMF selectivity. When the reaction was carried out at 80°C, the fructose conversion was only 76.6% for 300 min reaction time, but when the temperature was increased to 100°C, the fructose conversion, HMF yield, and HMF selectivity increased to 95.4, 80.4, and 84.3%, respectively, for 300 min reaction time. Conversion of fructose, yield, and selectivity of HMF reached 98.5, 85.1, and 86.4%, respectively, for 120 min reaction time at 130°C. When the temperature was increased to 160°C, the highest fructose conversion, HMF yield and selectivity were reached, which were 99.0, 98.0, and 99.0%, respectively, for 60 min reaction time. Further increasing the reaction temperature, HMF decomposition to levulinic acid, self-polymerization, or cross-polymerization would take place gradually.[14,29] Thus, a reaction temperature of 160°C was chosen as the best temperature hereafter.

Reaction Kinetics Analysis. According to the reports, the dehydration of fructose to HMF has been generally assumed to be a pseudo-first-order reaction. Generally, with increasing the surface area of the catalyst, the numbers of the accessible active sites would increase and the reaction rate could be accelerated, but it would has no or less influence on the activation energy. However, the mass-transfer limitation (MTL) often affects the determination of reaction activation energy, especially in heterogeneous reaction system. To make clear the kinetics of the dehydration reaction and accurately calculate the activation energy, the elimination of MTL is necessary. Actually, the influence of the internal and external diffusions can be eliminated by decreasing the particle size of catalyst and increasing the rate of magnetic stirring. Therefore, the influences of the internal and external diffusions in the fructose dehydration into HMF catalyzed by GTS were investigated by changing the particle size of the catalyst and altering the rate of magnetic stirring, respectively. The results are shown in Figure 4. It can be seen that changing the particle size of the catalyst from 40 to 100 mesh, fructose conversion increases a little bit, which means that the internal diffusion can be easily eliminated by grounded the catalyst into small particles (>60 mesh). But the rate of magnetic stirring, the external diffusion, played an important role in fructose conversion. When the reaction was conducted without stirring, fructose could not touch the surface of catalyst very well and made the fructose conversion lower. Increasing the rate of stirring, the fructose conversion increased as well. But further increase the stirring rate (>300 rpm), the fructose conversion almost did not change, meaning that the external diffusion could be eliminated at this stirring rate. Hence, with proper catalyst size and stirring rate, the MTL effect can be eliminated in the measurement of reaction activation energy.

If the fructose dehydration reaction is considered to follow the first-order kinetics, a plot of $-\ln(1-\text{Conversion}_{\text{fructose}})$ as a function of time will be linear, with a slope equal to the reaction rate constant k, as proposed by Kuster.[27] With the elimination of MTL, Figure 5a shows the plots of $-\ln(1-\text{Conversion}_{\text{fructose}})$ vs. reaction time at different reaction temperatures (ranging from 30 to 80°C) over GTS catalyst and obtained straight lines, validating the first-order reaction model. The slopes of the lines provided the rate constants (k) at different temperatures and were used to determine the activation energy (E_a) using the Arrhenius equation. The activation energy was 50.3 $\text{kJ}\cdot\text{mol}^{-1}$ as shown in Figure 5b, with the corresponding pre-exponential factor of 5.8×10^6. Bicker et al.[32] reported an activation energy of 99 $\text{kJ}\cdot\text{mol}^{-1}$ of fructose dehydration in sub and supercritical acetone with 3 $\text{mol}\cdot\text{L}^{-1}$ H_2SO_4 as catalyst. Qi et al.[18,19] obtained activation energies of 103.4 and 60.4 $\text{kJ}\cdot\text{mol}^{-1}$ in acetone–water (70:30, w/w) and acetone/DMSO (70:30, w/w) catalyzed by ion-exchanged resin, respectively. We can see that this activation energy of 50.3 $\text{kJ}\cdot\text{mol}^{-1}$ catalyzed by GTS was lower than that obtained with H_2SO_4 or ion-exchanged resin as catalyst, indicating that the GTS catalyst is much more active and greatly reduces the energy barrier, and then further lowers the reaction activation energy.

Influence of the GTS Catalyst Dosage. The effect of GTS catalyst dosage on fructose dehydration to HMF in THF/DMSO (70:30 v/v) was investigated. In the absence of GTS catalyst, at a reaction temperature of 160°C, the conversion of fructose was only 8.6% and the yield of HMF was 7.1% at a reaction time of 60 min. Conversely, when the GTS catalyst was added into the reaction with *R*-values of 1.0, 2.0, and 4.0, as shown in Table 1, the fructose conversion, the HMF yield, and HMF selectivity increased remarkably at the same reaction temperature and time. When *R*-value was 2.0, fructose conversion, HMF yield, and

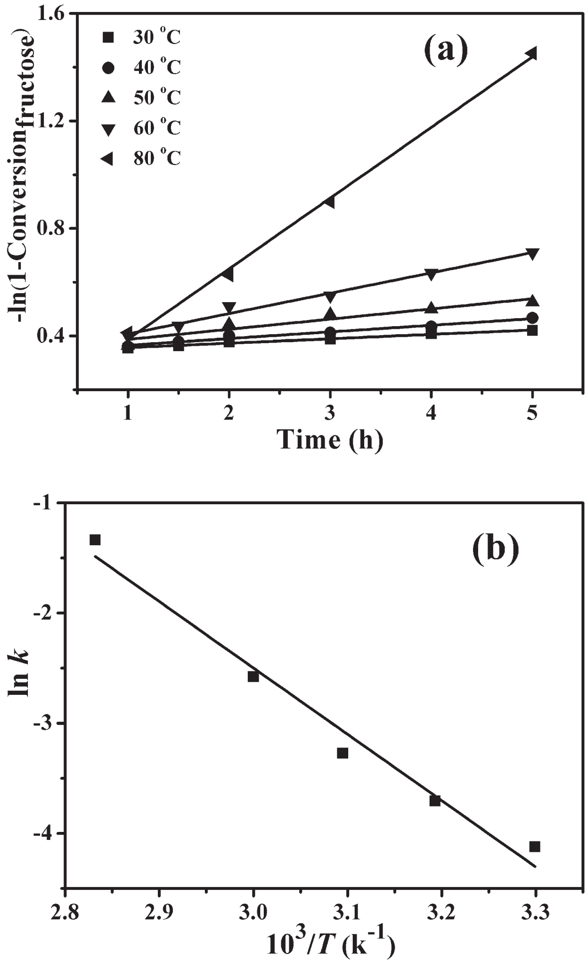


Figure 5. Determination of the activation energy from Arrhenius equation for fructose dehydration.

(a) Plots of $-\ln(1-\text{Conversion}_{\text{fructose}})$ vs. time at different reaction temperatures. (b) Arrhenius plot of ln *k* vs. $10^3/T$ for the dehydration of fructose. *Reaction conditions*: 10 mL of reaction solution, THF/DMSO=70:30 v/v, 5 wt % fructose, *R*=2.

selectivity were 99.0, 98.0, and 99.0%, respectively, at 160°C for 60 min. But when *R*-value was lowered to 1.0, that is, the concentration of GTS catalyst increased, the fructose conversion was a little higher than that of *R*-value of 2.0, whereas the yield of HMF decreased. It was because that lower *R*-value would offer much more active sites and increase the conversion of fructose, but it also favored the decomposition and polymerization reactions. However, when the GTS catalyst was used with *R*-value of 4.0, it indicated that there were not enough active sites for the dehydration reaction. As a result, the fructose conversion and HMF yield were low. Therefore, an *R*-value of 2.0 was chosen as an appropriate catalyst concentration in subsequent experiments if not otherwise indicated.

Table 1. Influence of the Weight Ratio of Fructose to Catalyst (R[a]) on the Fructose Conversion, HMF Yield,[b] and HMF Selectivity

R (w/w)	Reaction Time (min)	Fructose Conversion (%)	HMF Yield (%)	HMF Selectivity (%)
1.0	5	80.2	60.1	74.9
	10	89.5	76.0	84.9
	30	98.2	89.7	91.3
	60	99.3	97.2	97.9
2.0	5	75.2	70.1	93.2
	15	89.1	85.0	95.4
	30	96.6	92.4	95.6
	60	99.0	98.0	99.0
4.0	5	63.4	36.3	57.3
	30	88.2	80.7	91.5
	60	93.4	90.7	97.1
	120	95.2	89.2	93.7

[a] *R*=weight of fructose/weight of sulfonated carbonaceous catalyst (g/g).
[b] *Reaction conditions*: 10 mL of reaction solution, THF/DMSO=70:30 v/v, 5 wt % fructose, 160°C.

Influence of the Initial Fructose Concentration. A high substrate concentration is usually preferred to improve the efficiency of the process and make the process much more constructive and economical. So different initial concentrations of fructose for 5, 10, and 20 wt % were studied and the results were shown in Table 2. It can be seen that the fructose conversion, HMF yield, and selectivity were partly affected by the initial concentration of fructose. The highest HMF yield was 98.0% with 99.0% fructose conversion and 99.0% HMF selectivity at 5 wt % of initial fructose concentration for 160°C with a reaction time of 60 min in THF/DMSO (70:30 v/v) mixture catalyzed by GTS catalyst. In addition, when the fructose concentration was increased to 20 wt %, the yield of HMF was still high (53.2%), indicating the high efficiency of GTS catalyst. The partial loss of HMF at high fructose concentration was due to the increasing collision probability of fructose and generated HMF, leading to self- or cross-polymerization and forming humins.[18,19,27]

GTS catalyst recycles

The stability of the catalyst is of great importance for practical usage, so the cycle usage test of GTS was conducted. The results showed that the catalytic activity and selectivity of the catalyst for the dehydration of fructose to HMF had a nearly constant activity after being reused five times in THF/DMSO (70:30 v/v) mixture at 160°C for 60 min in each case. The fructose conversion, HMF yield, and selectivity remained at about 99, 98, and 99%, respectively, for all runs, indicating an excellent stability of our catalyst.

Separation of HMF by DEE extraction and analysis

Separation and purification of HMF from the reaction solution is another challenge that has to be solved and the

Table 2. Influence of Different Initial Fructose Concentration on Activity in THF/DMSO Medium (70:30 v/v) Catalyzed by GTS Catalyst[a]

Fructose Concentration	*R* (w/w)	Reaction Time (min)	Conversion (%)	HMF Yield (%)	HMF Selectivity (%)
5 wt %	2.0	5	75.2	70.1	93.2
		15	89.1	85.0	95.4
		30	96.6	92.4	95.7
		60	99.0	98.0	99.0
10 wt %	2.0	5	69.9	49.9	71.4
		15	85.7	68.9	80.4
		30	93.9	75.3	80.2
		60	96.1	75.3	78.4
20 wt %	2.0	5	79.2	23.8	30.1
		15	89.5	41.0	45.8
		30	93.6	48.9	52.2
		60	96.4	53.2	55.2

[a] *Reaction conditions*: 10 mL of reaction solution, 160°C.

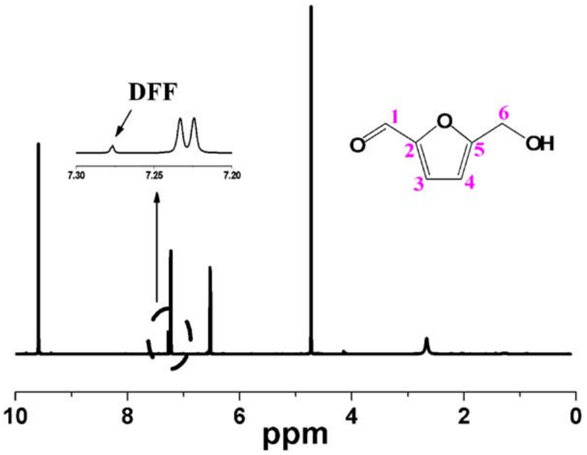


Figure 6. ^{1}H-NMR spectra of HMF isolated from the reaction mixture (600 MHz, $CDCl_3$ as solvent).

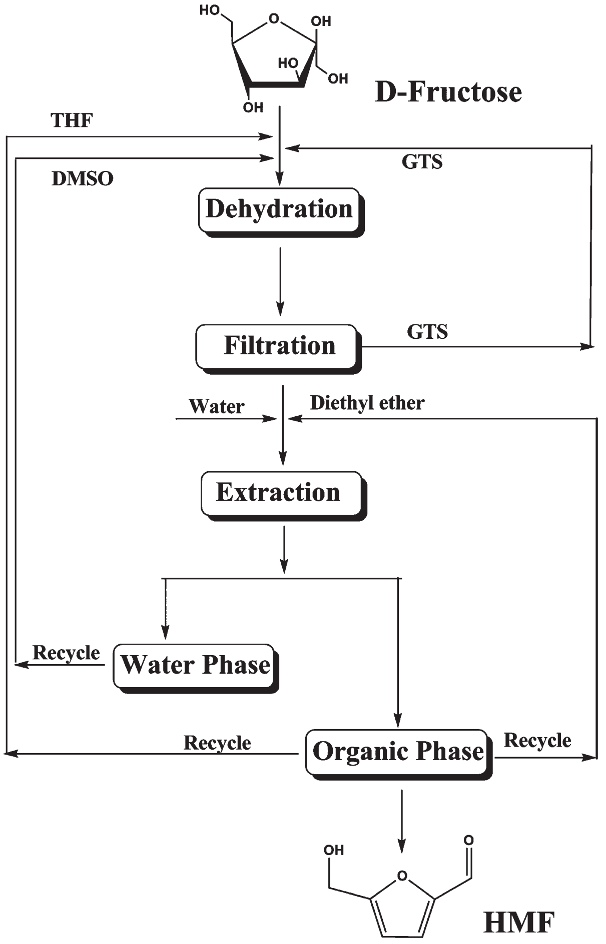
[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

recycling of the solvent should also be considered to reduce the production cost. As introduced above, extraction is widely applied in the separation and purification of HMF[3,20,34] because the solubility of HMF in several organic solvents is high. In our experiments, we found that after adding 10 mL of water saturated with sodium chloride into the filtrate of 5 wt % fructose, the mixture separated into two phases: the upper organic layer, containing THF, HMF, and very little amount of DMSO; and the lower aqueous phase with HMF and DMSO in it detected by GC-MS. Moreover, the concentration of HMF in organic layer was 3.9 times higher than that in aqueous phase analyzed via HPLC, which meant that THF not only lower down the boiling point of the solvent, but also enable to partition HMF form aqueous phase into the organic layer, but similar results could not be obtained in the acetone/DMSO reaction system. In addition, we can see that the THF partition coefficient for extraction of HMF was low and there was still a certain amount of HMF lingered in the aqueous phase. To extract the HMF in aqueous phase into organic phase, another extraction solvent, DEE (10 ml × 3) with a high partition coefficient, was added to the mixture to increase the gap of polarity between the aqueous and organic phase and force the HMF in the aqueous phase moving into the organic phase, while DMSO and other by-products can still stay in the aqueous phase. Through this process, ca. 94.5% (mass ratio) of HMF partitioned into the upper organic layer, resulting in 1.16 wt % HMF in the organic layer analyzed via HPLC, and no chlorinated organic compounds were detected within the detection limitation. Finally, the THF and DEE in the upper organic layer were removed by distillation at 323 K, and the residue in the bottle was pure HMF, with the isolated yield of HMF about 46.9%. In addition, for the filtrates of 10 and 20 wt % fructose, the mass ratios of HMF in the organic layer were 1.87 and 2.95 wt %, with the isolated yield of HMF about 48.6 and 50.1%, respectively.

With the purpose to confirm the structure of the extracted product, MS analysis was performed. From the MS spectra, the m/z peaks at 29, 39, 41, 69, 97, 109, and 126 were appeared, all of which were corresponding to the structure of HMF. To analyze the purity of the HMF separated from the reaction system, ^{1}H NMR analysis was carried out (Figure 6). ^{1}H NMR for HMF (600 MHz, $CDCl_3$): δ 9.59 (s, 1H, CHO), δ 7.22 (d, 1H, furan ring C-3 proton), δ 6.52 (d, 1H, furan ring C-4 proton), δ 4.73 (s, 2H, CH_2). But a new peak at about 7.28 ppm appeared, which was attributed to some impurities. When compared with the ^{1}H NMR of pure 2,5-diformylfuran (DFF), we can see that the main impurity in the extracted HMF was DFF, which was also favor to be extracted in the organic layer. From the peak areas of 7.28 ppm and 7.22 ppm in the ^{1}H NMR spectra, which corresponded to the C-3 hydrogen of each furan ring, the content of DFF in HMF was estimated to be ca. 3.6%. Although a very small amount of DFF existed in the extracted HMF, the separation of HMF from the reaction system by extraction with THF and DEE is feasible because HMF was soluble in THF and DEE phase, whereas DMSO and other by-products were not soluble in it.

Conceptual process and recycling

At first sight, the process of mixing two kind of organic solvent together to obtain high HMF yield and the addition of DEE to extract HMF from the reaction system might be seen to be counterproductive. However, we can see that the separation and recycling can be done with simple methods, as illustrated in Scheme 1. It shows the whole process to obtain HMF, including the dehydration, filtration separation, and extraction. First, the sulfonated carbonaceous material



Scheme 1. Proposed processes for conversion of fructose to HMF with recycling of sulfonated carbonaceous catalyst (GTS) and various organic solvents.

(GTS) used as catalyst in the dehydration reaction has already been investigated for its recyclability above. As a result, after reaction, GTS was easily separated from the reaction mixture and reused in the new reaction system. Water and DEE were added into the filtrate, and then the mixture began to separate into two layers, the upper organic phase and the lower water phase. Because the boiling points were much different from each other, HMF, THF, and DEE can be easily separated from the organic phase by distillation, and DMSO can be separated from the water phase by distillation as well. Thus, the separated THF and DMSO can be reused in the dehydration system and DEE can be reused in the extraction system. In short, in the proposed process, the GTS catalyst, the reaction solvent (THF and DMSO), and the extraction solvent (DEE) are internally recycled and represent an efficient method for producing HMF from fructose.

Conclusions

Solid acid catalyst of sulfonated carbonaceous material (GTS) was prepared easily and environment friendly with high surface area, and used in the acid-catalyzed dehydration of fructose to HMF in THF/DMSO mixed solvents. In a 70:30 (v/v) THF/DMSO mixture, a high fructose conversion of 99.0% with HMF yield of 98.0% were obtained at 433 K for 60 min reaction time. This GTS catalyst was very stable and maintained the same yield of HMF even reused for five times. With the addition of DEE and H_2O into the reaction system to extract HMF from the solution, high purity of HMF was obtained. Furthermore, THF, DMSO, and DEE can be recycled and reused. Therefore, fructose can be converted to HMF in high yield at mild conditions in THF/DMSO mixtures in the presence of a novel carbonaceous catalyst and high purity of HMF was easily obtained through extraction method. So with all of these advantages, it is indicated that this catalyst and this process has great potential in industry applications.

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