Biomass

Bifunctional Polyacrylonitrile Fiber-Mediated Conversion of Sucrose to 5-Hydroxymethylfurfural in Mixed-Aqueous Systems

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Abstract: A highly efficient catalytic system composed of a bifunctional polyacrylonitrile fiber (PANF-PA[BnBr]) and a metal chloride was employed to produce 5-hydroxymethylfurfural (HMF) from sucrose in mixed-aqueous systems. The promoter of PANF-PA[BnBr] incorporates protonic acid groups that promote the hydrolysis of the glycosidic bond to convert sucrose into glucose and fructose, and then catalyzes fructose dehydration to HMF, while the ammonium moiety may promote synergetically with the metal chloride the isomerization of glucose to fructose and transfer HMF

Introduction

In recent years, with growing concerns about diminishing fossil fuel reserves, global warming and environmental pollution, the development of alternative sources for energy and chemicals has attracted much attention of research-

ers worldwide.^[1,2] In this respect, renewable biomass is abundant and carbon-neutral, thus constituting a promising alternative for the sustainable supply of liquid fuels and valuable intermediates.^[3,4] Particularly, carbohydrates comprise the main class of biomass compounds, and finding feasible ways to convert them into useful chemicals, such as 5-hydroxymethylfurfural (HMF), 2,5-furandicarboxylic acid and others, has become increasingly important.^[5,6] HMF, which is

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obtained by acid-catalyzed dehydration of carbohydrates (e.g., fructose, glucose, and sucrose, Scheme 1), is a particularly valuable and versatile intermediate in biofuel chemistry and the pharmaceutical industry.^[7,8] Recently, great efforts have been devoted towards converting carbohydrates into HMF; however,

from the aqueous to the organic phase. The detailed charac-

terization by elemental analysis, FTIR spectroscopy, and SEM

confirmed the rangeability of the fiber promoter during the

modification and utilization processes. Excellent results in

terms of high yield (72.8%) of HMF, superior recyclability

(6 cycles) of the process, and effective scale-up and simple

separation procedures of the catalytic system were obtained.

Moreover, the prominent features (high strength, good flexi-

bility, etc.) of the fibers are very attractive for fix-bed reactor.



Scheme 1. The dehydration of sucrose to HMF.

1

to the best of our knowledge, low yields are normally obtained, strongly hampering its industrial application.^[9] Fructose has been shown to be the preferred feedstock for a higher yield,^[10] while it is clear that generation of ample amounts of HMF will require more inexpensive and abundantly available raw materials, such as glucose and sucrose. Especially sucrose, a disaccharide consisting of glucose and fructose units, is a key low-molecular-weight carbohydrate resource derived from cane or beet, and widely present in the plant kingdom. Besides, the dehydration of glucose has been extensively investigated. Accordingly, the development of highly efficient and environmentally acceptable approaches for the production of HMF from low-cost sucrose would be of great value and significance.

The production of HMF from sucrose has been investigated in practice, and generally conversion of sucrose to HMF involves two steps, that is, sucrose first rapidly hydrolyzes to the

These are not the final page numbers! 77





monosaccharides glucose and fructose, which is followed by their dehydration to give HMF.[11] Currently, the majority of the evaluated catalysts were mineral and organic acids,^[12-14] solid acids,^[15,16] and metallic compounds^[17,18] in multiple reaction media, including water, organic solvents, ionic liquids, and mixed-aqueous systems.^[19] However, in these reports, the yields of HMF are relatively low, and the apparent reason is that only the fructose moiety from sucrose was efficiently transformed into HMF, which left most of glucose molecules unconverted.^[20] For instance, Chheda and co-workers studied the conversion of sucrose into HMF using HCl as the catalyst in a biphasic reactor system (an aqueous phase modified with DMSO and an organic extracting phase consisting of a 7:3 (w/ w) methyl isobutyl ketone (MIBK)/2-butanol mixture), and only a 50% yield of HMF was achieved.^[12] It is worth mentioning that the conversion of glucose into HMF further needs an isomerization process to fructose; however, many acid catalysts are unfavorable for this transformation. Recently, catalytic systems consisting of metallic halides and ionic liquids were used for the conversion of sucrose into HMF, and good results were obtained. Hu et al.^[21] reported that sucrose could be converted into HMF in good yield (65%) by using $SnCl_4$ in 1-ethyl-3methyl imidazolium tetrafluoroborate ([BMIM]BF₄) medium. Later, Qi et al.^[22] studied the production of HMF from sucrose in 1-butyl-3-methyl imidazolium chloride ([BMIM]Cl) with CrCl₃ as the catalyst, and a 76% yield of HMF was obtained by microwave irradiation. The above two methods for the conversion of sucrose into HMF appear to be promising; however, they depend on the use of expensive ionic liquids as solvents. Improvements have been made in recent years by applying different solvent types and extraction methods, and by applying bifunctional catalytic systems. In fact, the large-scale, costeffective transformation of carbohydrates to HMF will require the development of new, functional-group-tolerant catalysts compatible with continuous processing. Among those, the application of a fixed-bed reactor in biphasic systems might be a good choice.

In our previous work, a highly efficient and selective process for the production of HMF from sucrose has been achieved in the presence of metal chlorides and ammonium halides in N,Ndimethylacetamide (DMAc) solvent. NH₄Br was verified to be an effective promoter for this transformation, and a possible mechanism for this catalytic process has been proposed.^[23] In addition, we have firstly exploited polypropylene fiber as a new support for a class of reusable fiber-supported ionic liquids (FSILs), and the FSILs were used to catalyze the dehydration of fructose to HMF in DMSO and a mixed-aqueous system.^[24] Moreover, we also adequately demonstrated the easily synthesized polyacrylonitrile fiber-supported poly(ammonium methanesulfonate)s as active and recyclable heterogeneous Brønsted acid catalysts for different types of reactions including the conversion of fructose into HMF.^[25] Following our pioneering studies on fiber catalysts and carbohydrate dehydration, especially our excellent results obtained in aqueous systems, and given their several advantages such as low cost, high strength, light density, larger coverage area as well as potential performance for a fixed-bed reactor of fiber, we investigated the use of fibers in further work on biomass conversion. Herein, we report a new efficient catalytic system composed of a bifunctional polyacrylonitrile fiber (PANF) promoter and a metal chloride that was employed to form HMF from sucrose in mixed-aqueous systems under mild conditions.

Results and Discussion

The preparation of the fiber promoters

Based on our previous work,^[25] we started this study to synthesize the designed fiber promoters. The functional PANFs were prepared according to a simple two-step strategy as shown in



2

Scheme 2. Preparation of the fiber promoters.

Chem. Asian J. **2015**, 00, 0–0

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Scheme 2. The first step is an amination procedure, and the extent of immobilization was measured by weight gain (weight gain = $[(W_2 - W_1)/W_1] \times 100\%$, where W_1 and W_2 are the weight of the fiber sample before and after amination, respectively). Under the screened conditions of amination with polyethylene polyamine in water, a weight gain of 35% polyethylene polyamine-functionalized PANF (PANF-PA) was acquired. The next step is salt formation with haloid acids in water and benzyl halides in acetonitrile, respectively. Finally, four types of functional PANFs were obtained. PANF-supported poly(benzylammonium bromide)s (PANF-PA[BnBr]) was selected as a model in view of its performance, and the final ammonium moiety loading was 2.56 mmol g^{-1} by weight.

The characterization of fiber promoters

To avoid any errors during the preparation process and investigate the rangeability of the fiber promoters before and after the conversion of sucrose into HMF, we performed a detailed characterization of fiber samples at different stages. The original PANF, PANF-PA, PANF-PA[BnBr], the promoter recovered after the first cycle in the dehydration of sucrose (PANF-PA[BnBr]-1), and the promoter recovered after the 6th cycle (PANF-PA[BnBr]-6) were all characterized by means of elemental analysis (EA), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM).

Elemental analyses (EA). EA data of PANF, PANF-PA, PANF-PA[BnBr], PANF-PA[BnBr]-1, and PANF-PA[BnBr]-6 are listed in Table 1. Compared to the original PANF, the C and N contents of PANF-PA were decreased and the H content was increased, as expected (Table 1, entries 1 and 2). After the formation of salt, the amounts of C, H, and N of PANF-PA[BnBr] all decrease

Table 1. Elemental analysis of PANF, PANF-PA, PANF-PA[BnBr], PAN PA[BnBr]-1, and PANF-PA[BnBr]-6. PA						
Entry	Fiber sample	C [%]	H [%]	N [%]		
1	PANF	65.55	5.669	23.54		
2	PANF-PA	55.51	7.503	20.52		
3	PANF-PA[BnBr]	54.00	6.054	14.64		
4	PANF-PA[BnBr]-1	57.64	6.327	13.36		
5	PANF-PA[BnBr]-6	57.86	6.215	13.03		

because benzyl bromide has no N and less H and C than PANF-PA. After the PANF-PA[BnBr] was used as the promoter in the dehydration of sucrose for one and six times (Table 1, entries 4 and 5), the C content was increased, especially for the first cycle (PANF-PA[BnBr]-1), while the H and N contents of PANF-PA[BnBr]-1 and PANF-PA[BnBr]-6 varied slightly. These results are perhaps due to the combined effect of the absorption of insoluble substances (such as humins, see SEM images and color change in the Supporting Information)^[26] and damages to the fiber sample (the hydrolysis of cyano or amide groups with acid on the fiber is cannot be completely avoided). Although the absorption amount increases with the number of cycles, the hydrolysis shows the same changing trend, which led to the final results of elemental analyses data.

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Figure 1. FTIR spectra of (a) PANF, (b) PANF-PA, (c) PANF-PA[BnBr], (d) PANF-PA[BnBr]-1, and (e) PANF-PA[BnBr]-6.

Fourier transform infrared spectroscopy (FTIR). Samples of PANF, PANF-PA, PANF-PA[BnBr], PANF-PA[BnBr]-1, and PANF-PA[BnBr]-6 were pulverized by cutting and then prepared into KBr pellets, and their FTIR spectra are shown in Figure 1. Comparing the FTIR spectra of PANF-PA (Figure 1b) and PANF (Figure 1 a), the most striking change is in the high wavenumber: the broad absorption bands around 3250 cm⁻¹ can be characterized as the N-H stretching vibration; besides, the strong absorption band at 1650 cm^{-1} is assigned to the amide I bands. After salt formation, the PANF-PA[BnBr] (Figure 1c) displays two new absorption bands at 745 and 702 cm⁻¹, which belong to the vibrational modes of the benzene ring and provide evidence that PANF-PA[BnBr] has been successfully prepared. Moreover, the specific absorption peaks of PANF-PA[BnBr]-1 (Figure 1 d) and PANF-PA[BnBr]-6 (Figure 1 e) are quite similar to that of PANF-PA[BnBr], which indicates that PANF-PA[BnBr] is very stable and can be reused several times.

Scanning electron microscopy (SEM). Figure 2 presents the SEM images of PANF, PANF-PA, PANF-PA[BnBr], PANF-PA[BnBr]-1, and PANF-PA[BnBr]-6. After amination, the diameter of



Figure 2. SEM images of (a) PANF, (b) PANF-PA, (c) PANF-PA[BnBr], (d) PANF-PA[BnBr]-1, and (e) PANF-PA[BnBr]-6.

Chem. Asian J. 2015, 00, 0-0

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PANF-PA body extended obviously, and the surface of the PANF-PA was thickly dotted with scarring (Figure 2b). With each sequential modification or utilization, the surface of the fiber samples became increasingly coarser, especially PANF-PA[BnBr]-1 (Figure 2 d) and PANF-PA[BnBr]-6 (Figure 2 e), which provided further evidence that some of the insoluble humins were adsorbed to the surface of the fiber promoter. However, the overall integrity of the fiber was untouched. This means that PANF possesses good properties for PANF-PA[BnBr] as a promoter in the conversion of sucrose into HMF.

Application of the fiber promoters for the conversion of sucrose into HMF

Screening the fiber promoters for the dehydration of sucrose to HMF. Water is the most clean and abundant solvent for organic reactions, and sucrose is particularly soluble in water, so the investigation of water as a co-solvent for the production of HMF from sucrose is worthwhile.^[27,28] Metal chlorides such as $CrCl_{3^{}}{}^{[22,29]}$ $SnCl_{4^{}}{}^{[21]}$ $AlCl_{3^{}}{}^{[30]}$ and $FeCl_{3}{}^{[31]}$ are commonly used for glucose isomerization to fructose and have been verified to be efficient for the dehydration of sugars. Based on our previous work^[23] and with the object of converting sucrose into HMF in mixed-aqueous systems, we first screened a series of metal chlorides for this transformation in a mixed water/DMAc solvent (DMAc has been verified to be the most efficient solvent for sucrose dehydration^[23, 29]). As can be seen from Table 2 (entries 1-6), at 10 mol % (based on the substrate), CrCl₃·6H₂O, SnCl₄·5H₂O (abbreviated as SnCl₄ in the following), SnCl₂·2H₂O, and AlCl₃·6H₂O were all active. In particular, SnCl₄ was the most efficient and was selected as the catalyst for further study. Although CrCl₃·6H₂O has been verified to be the most efficient catalyst in a previous work,^[23] addition of

Entry	Cat.	Catalyst loading [mol %]	Promoter	Promoter loading [mol%]	Yield [%] ^[b]
1	CrCl ₃ ⋅6H ₂ O	10	-	-	19.9
2	SnCl₄·5 H₂O	10	-	-	30.2
3	SnCl ₂ ·2H ₂ O	10	-	-	12.5
4	CuCl ₂ ·2H ₂ O	10	-	-	traces
5	FeCl ₃ ·6H ₂ O	10	-	-	traces
6	AlCl ₃ ⋅6 H ₂ O	10	-	-	14.7
7	SnCl₄·5 H₂O	10	PANF-PA[HCI]	10	46.9
8	SnCl₄·5 H₂O	10	PANF-PA[HBr]	10	54.1
9	SnCl₄·5 H₂O	10	PANF-PA[BnCl]	10	48.3
10	SnCl₄·5 H₂O	10	PANF-PA[BnBr]	10	55.6
11	SnCl₄·5 H₂O	0	PANF-PA[BnBr]	10	36.6
12	SnCl₄·5 H₂O	5	PANF-PA[BnBr]	10	44.5
13	SnCl₄·5 H₂O	15	PANF-PA[BnBr]	10	58.7
14	SnCl₄·5 H₂O	20	PANF-PA[BnBr]	10	58.9
15	SnCl₄·5 H₂O	15	PANF-PA[BnBr]	5	46.4
16	SnCl₄·5 H₂O	15	PANF-PA[BnBr]	15	60.7
17	SnCl₄·5 H₂O	15	PANF-PA[BnBr]	20	62.1
18	SnCl₄·5 H₂O	15	PANF-PA[BnBr]	25	61.4

90 °C for 2 h. [b] Yield determined by HPLC.

water to the system may impede the coordination ability of chromium with glucose, which would then reduce the formation of HMF from a glucose unit. Sucrose is a disaccharide consisting of glucose and fructose linked by a glycosidic bond, and the glycosidic bond can be easily hydrolyzed by an acid catalyst. Besides, porous coordination polymers with acid groups showed high conversion of glucose into fructose.[32] Thus, acidic functional fibers were added into the system to test the effect for the dehydration of sucrose. Polyacrylonitrile fiber-supported poly(ammonium hydrochloride)s (PANF-PA[HCI], Table 2, entry 7) and poly(ammonium hydrobromide)s (PANF-PA[HBr], Table 2, entry 8) were used first. The results show that both fiber promoters were active for this conversion, and the yields increased to 46.9% and 54.1%, respectively. Based on these results, the use of another two functional PANF-supported poly(benzylammonium chloride)s fibers. (PANF-PA[BnCl], Table 2, entry 9) and PANF-PA[BnBr] (Table 2, entry 10) was examined. Gratifyingly, the yields of HMF increased to 48.3% and 55.6%, respectively. Moreover, it is worth noting that the functional fibers with the bromide ions were more effective than those with the chloride ions. As discussed in our previous work,^[23] bromide, which offers the optimal balance between coordination ability and nucleophilicity, is more effective as an ionic additive than chloride for the isomerization of glucose to fructose. These results are in agreement with the halide effect reported by Binder.^[29] As PANF-PA[BnBr] afforded the best result it was used for further optimization. Next, the influence of the catalyst dosage (Table 2 entries 11-14) and promoter loading (Table 2 entries 15-18) were examined concisely. It was found that 15 mol% of SnCl₄ with 20 mol% promoter loading gave the best result, affording HMF in a yield of 62.1% (Table 2 entry 17).

HMF can be isolated by extraction with various organic sol-

vents, such as methyl isobutyl ketone (MIBK),^[2,33] 2butanol,^[12] ethyl acetate,^[34] diethyl ether,^[10,35] and toluene.^[36] Here we chose a multiphase system including an aqueous phase modified with DMAc and organic solvents to further verify the promoting activity of PANF-PA[BnBr] (Table 3). Based on our previous work^[24], MIBK was first selected as the extractant for this attempt (Table 3, entry 1). Using a mixture of MIBK/water/DMAc (2:3:5, v/v/v), the yield of HMF increased to 68.2%. Encouraged by this good result, we examined other organic solvents in further tests. Extractants such as esters or toluene were not very efficient for this dehydration (Table 3, entries 2-4), while alcohols also had a positive effect on this transformation (Table 2, entries 5-7). Finally, the mixedaqueous system composed of MIBK/water/DMAc was selected to be further tested (Table 3, entries 8-16). After further optimization of the composition of solvent and the reaction time, the results show that the MIBK/water/DMAc mixture at the ratio of 3:2:5 (v/v/ v) at a reaction time of 2.5 h gave the highest yield of 72.8% (Table 3, entry 15). Moreover, the promoter PANF-PA[HBr] was also investigated under the optimized conditions; however, no higher yield of HMF

Chem. Asian J. 2015, 00, 0-0

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4

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a mixed-aqueous system using functional fibers as the promoter. ^[a]						
Entry	Mixed solvent	Composition (v/v)	<i>t</i> [h]	Yield [%] ^[b]		
1	MIBK/water/DMAc	2:3:5	2	68.2		
2 ^[c]	Ethyl acetate/water/DMAc	2:3:5	2	45.6		
3	Butyl acetate/water/DMAc	2:3:5	2	62.4		
4	Toluene/water/DMAc	2:3:5	2	62.9		
5	1-Butanol/water/DMAc	2:3:5	2	63.2		
6	2-Butanol/water/DMAc	2:3:5	2	65.5		
7	MIBK/2-butanol/water/DMAc	1:1:3:5	2	67.6		
8	MIBK/water/DMAc	2:4:4	2	49.4		
9	MIBK/water/DMAc	2:1:7	2	67.1		
10	MIBK/water/DMAc	3:2:5	2	69.6		
11	MIBK/water/DMAc	3:1:6	2	69.5		
12	MIBK/water/DMAc	4:1:5	2	68.9		
13	MIBK/water/DMAc	4:2:4	2	67.7		
14	MIBK/water/DMAc	3:2:5	1.5	64.9		
15	MIBK/water/DMAc	3:2:5	2.5	72.8		
16	MIBK/water/DMAc	3:2:5	3	70.3		
17	MIBK/water/DMAc	3:2:5	2.5	70.5 ^[d]		

PANF-PA[BnBr] with 10 mL of solvent at 90° C at the indicated time. [b] Yield determined by HPLC. [c] At 80° C. [d] Promoted by PANF-PA[HBr].

was obtained (Table 3, entry 17). Taken together, the results suggest that both PANF-PA[BnBr] and SnCl₄ play a role in this reaction, and they may have a synergistic effect on the formation of HMF. The promoter PANF-PA[BnBr] incorporates protonic acid groups that are very active for the hydrolysis of glycosidic bond to convert sucrose into glucose and fructose, and then catalyze fructose dehydration to HMF; in the meantime, the ammonium moiety may have a synergetic effect with SnCl₄ to promote the isomerization of glucose to fructose (the possible mechanism was discussed in our previous work^[23]) and transfer HMF from the aqueous to the organic phase.

The production of HMF from different sugars promoted by PANF-PA[BnBr]. In order to further reveal the merits of the fiber promoter, the conversions of fructose, glucose, inulin, starch, and cellulose were investigated in the screened mixedaqueous system, and the results are summarized in Table 4. It was found that the system is efficient for the dehydration of fructose to HMF, affording HMF in 71.6% and 80.9% yield at a reaction time of 2.5 h and 1.0 h, respectively (Table 4, en-

Table 4. The dehydration of different sugars in the mixed-aqueous system. ^[a]					
Entry	Sugar	<i>t</i> [h]	Yield [%] ^[b]		
1	Fructose	2.5	71.6		
2	Fructose	1.0	80.9		
3	Glucose	2.5	50.1		
4	Inulin	2.5	69.7		
5	Starch	2.5	14.5		
6	Starch	6	26.4		
7	Cellulose	2.5	1.9		
8	Cellulose	8	4.6		
[a] Reaction conditions: Substrate (0.5 g), 15 mol% SnCl ₄ and 20 mol% PANF-PA[BnBr] with 10 mL of solvent (BIMK/water/DMAc, 3:2:5, v/v/v) at 90° C at the indicated time. [b] Yield determined by HPLC					

Chem. Asian J. 2015, 00, 0 – 0 v

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tries 1 and 2). Moreover, glucose was also efficiently dehydrated to give HMF in 50.1% yield (Table 4, entry 3). Furthermore, the conversions of inulin, starch and cellulose were studied. The HMF yields from inulin and starch could reach up to 69.7% and 26.4%, respectively, under the corresponding conditions (Table 4, entries 4 and 6). However, when cellulose was used as the substrate in the dehydration, only 1.9% yield of HMF was obtained after 2.5 h (Table 4, entry 7), and when the reaction time was prolonged to 6 h, the HMF yield was increased to 4.6% (Table 4, entry 8). These results indicated that the bifunctional fiber-mediated system can promote the conversion of a range of carbohydrates and furthermore provided a new direction for further studies.

The recyclability of the bifunctional fiber-mediated conversion of sucrose into HMF in mixed-aqueous systems. To evaluate the reusability of the fiber promoter and the recyclability of the process, PANF-PA[BnBr] was reused in the mixedaqueous system. After completion of each cycle, PANF-PA[BnBr] was simply taken out with common tweezers and washed with MIBK. The remaining liquid was separated and extracted three times with the above MIBK, and then the recycled fiber promoter and the aqueous phase (without additional SnCl₄) were used directly for the next cycle without any further treatment. The results show that the reaction proceeded smoothly without any extension of reaction time or marked loss in the yield (72.7–69.0%, Figure 3). Moreover, the weight



Figure 3. Recyclability of the fiber promoter for the conversion of sucrose into HMF in the mixed-aqueous system.

of PANF-PA[BnBr] was almost unchanged after 6 cycles (from 0.1145 to 0.1139 g), which is consistent with the EA data (Table 1, entries 3 and 5), further demonstrating the high stability of the fiber promoter under the vigorous operating conditions in the mixed-aqueous system.

Scale-up procedure for the conversion of sucrose into HMF. Finally, to illustrate the utility of the fiber promoter-mediated system, a large-scale experiment for the production of HMF from sucrose was also conducted. The process was scaled up to gram scale, and HMF was obtained simply by distillation. It is worth noting that the reaction proceeded smoothly without any extension of reaction time to afford HMF in an isolated yield of 61%. From the above results and the prominent simple separation operation of the mixed-aqueous system, it is obvious that the fiber promoter-mediated system is very attractive for application in the chemical industry.

Comparison of the dehydration of sucrose in different catalytic systems

According to the results above and compared with different catalytic systems under the optimized experimental conditions (Table 5), it is worth mentioning that the performance of a system depends both on the type of catalyst and solvent.

chemical industry for the production of HMF. Further studies on the dehydration of different sugars such as starch and cellulose using the fiber promoter in mixed-aqueous systems are ongoing.

Experimental Section

Commercially available polyacrylonitrile fiber (PANF, the number average molecular weight of the spinning solution is 53000 to 106000, 93.0% acrylonitrile, 6.5% methyl acrylate and 0.4–0.5% sodium styrene sulfonate) with a length of 10 cm and a diameter

Table 5. Comparison of the dehydration of sucrose to HMF using different catalytic systems.						
Entry	Catalytic system ^[a]	Catalyst dosage ^[b]	T [°C]	t	HMF yield $[\%]^{[c]}$	Ref.
1	HCl, pH 1 (MIBK/2-BuOH/water/DMSO)	-	170	5 min	50	[12]
2	CrCl ₂ (choline chloride ^[d])	10 mol%	100	1 h	62	[13]
3	Hydrotalcite/Amberlyst 15 (DMF)	200 wt %	120	3 h	54	[15]
4	H-form Zeolite (water/MIBK)	29 wt %	165	1 h	28	[17]
5	GeCl₄ ([BMIm]Cl)	10 mol%	120	0.5 h	55	[18]
6	SnCl ₄ ([EMIm]BF ₄)	10 mol%	100	3 h	65	[21]
7	CrCl ₃ ([BMIm]Cl)	20 mol%	100	5 min ^[e]	76	[22]
8	Al-TUD-1/(toluene/water)	200 wt %	170	6 h	17	[36]
9	SnCl ₄ /PANF-PA[BnBr] (MIBK/water/DMAc)	15 mol%	90	2.5 h	72.8	This work
[a] Solvents are listed in parenthesis. [b] Catalyst/substrate. [c] Yields under optimized experimental conditions.						

[d] Melt. [e] Under microwave irradiation.

However, the fiber promoter-mediated system still has some advantages with regard to reaction conditions, yield of HMF, and excellent reusability and recyclability of the catalyst lacking in most previous reports. Moreover, the commercially availability of the fibers (PANF), easy process for fiber promoter preparation, the efficient scaled-up procedure, as well as simple post-processing make the fiber promoter-mediated system a highly attractive alternative to current methodologies. Furthermore, the good flexibility and high mechanical strength of the fiber are very attractive for fixed-bed reactors in continuous processing.

Conclusions

In summary, a series of functional PANFs have been synthesized and successfully used as promoter for the conversion of sucrose into HMF in mixed-aqueous systems. The detailed characterization of functional PANFs by elemental analysis, IR spectroscopy, and SEM confirmed that ammonium moieties were immobilized to the surface layer of PANF and were recycled with excellent stability. Such fiber promoters were used for the first time in the dehydration of sucrose to HMF and displayed high activity and reusability. The yield of HMF reached up to 72.8% in a mixed-aqueous system, and the fiber promoter and the aqueous phase (containing the catalyst SnCl₄) could be recycled for at least six times. In addition, the dual role of the fiber promoter for this transformation with high activity in a mixed-aqueous system is revealed. The prominent features of PANF and the remarkable performance of the fiber promoters are very attractive for their use in a fix-bed reactor in the

of $30\pm0.5\;\mu\text{m}$ (from the Fushun Petrochemical Corporation of China) was used. All the sugars, polyethylene polyamine, HCI (37.5%, aq), HBr (68.8%, aq), benzyl chloride, benzyl bromide and the other reagents used were of analytical grade and employed without further purification. Water was deionized. A standard sample of HMF was obtained from J&K Co. Ltd.

The elemental analyses (EA) were performed on a Vario micro cube analyzer (Elementar). Fourier transform infrared (FTIR) spectra were obtained with an AVATAR 360 FTIR spectrometer (Thermo Nicolet), KBr

disc. A scanning electron microscope (Hitachi, model S-4800) was used to characterize the surface of the fibers. The quantitative analyses of the product were performed on a Waters 1525 HPLC system equipped with both UV and refractive index detectors.

Preparation of fiber promoters

Step 1. Dried PANF (3.00 g), polyethylene polyamine (30 g) and deionized water (30 mL) were introduced into a three-necked flask connected with a condenser. The mixture was refluxed (105 °C) with stirring for 24 h. The fiber was filtered off and washed repeatedly with water (60–70 °C) until the pH of the filtrate was 7, and then the fiber sample was dried overnight at 60 °C under vacuum to give PANF-PA (4.05 g, with a weight gain of 35 %).

Step 2. A typical procedure for the preparation of fiber promoter is as follows: Benzyl bromide (10 g) was dissolved in acetonitrile (80 mL), and then the dried PANF-PA (3.00 g) was introduced into the solution. The mixture was stirred under reflux for 24 h. Finally, the sample was filtered off, rinsed with acetonitrile (20 mL), and then dried overnight at 60 °C under vacuum to give PANF-PA[BnBr] (5.34 g, 2.56 mmol g⁻¹ ammonium moiety loading by weight).

General procedure for the conversion of sucrose into HMF

All the dehydration experiments were performed in a 50 mL flask equipped with magnetic stirring and a condenser. A typical procedure for the dehydration of sucrose is as follows: Sucrose (0.5 g, 1.46 mmol), SnCl₄ (15% mol, 0.0768 g) PANF-PA[BnBr] (20% mol, 0.1141 g) and 10 mL of mixed-aqueous solvent (MIBK/water/DMAc, 3:2:5, v/v/v) were added into the flask. The mixture was stirred and preheated to 90 °C and then maintained at 90 °C for 2.5 h. After completion of the reaction, PANF-PA[BnBr] was taken out with common tweezers and rinsed with MIBK (15 mL), which was combined with the reaction mixture. The mixture was then decanted

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6





into a volumetric flask (500 mL) and ethanol was used as the diluent. The mixture was then analyzed by using a Waters 1525 HPLC system equipped with UV and refractive index detectors. For the recycling process, after completion of each cycle, PANF-PA[BnBr] was simply taken out with common tweezers and rinsed with MIBK (15 mL). The remaining liquid was separated and extracted three times with the above MIBK. The MIBK phase was combined and diluted for analysis, and the recycled fiber promoter and the aqueous phase (without additional $SnCl_4$) were used directly for the next cycle.

Typical separation procedure for HMF (10× scale-up)

Sucrose (5 g, 14.61 mmol), $SnCl_4$ (15% mol, 0.7680 g) PANF-PA[BnBr] (20% mol, 1.141 g) and 100 mL of mixed-aqueous solvent (MIBK/water/DMAc, 3:2:5, v/v/v) were added into a 250 mL flask. The mixture was stirred, preheated to 90°C and then maintained at 90°C for 2.5 h. After completion of the reaction, PANF-PA[BnBr] was taken out with common tweezers and rinsed with MIBK (30 mL). The remaining liquid was separated and extracted three times with the above MIBK. The MIBK phase was combined, dried with anhydrous sodium sulfate, and then the MIBK phase was distilled under reduced pressure (1 mm Hg, 55°C) to obtain pure HMF (isolated yield 60.9%, the purity was 97% by HPLC analysis).

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Bifunctional Polyacrylonitrile Fiber-Mediated Conversion of Sucrose to 5-Hydroxymethylfurfural in Mixed-Aqueous Systems



High in fiber: A highly efficient bifunctional polyacrylonitrile fiber-mediated system for the production of 5-hydroxymethylfurfural (HMF) from sucrose in a mixed-aqueous solvent is presented. Excellent results were obtained in terms of high yield of HMF, superior recyclability of the process, and effective scale-up and operation procedure of the catalytic system. Moreover, the prominent features of the fiber are very attractive for fixed-bed reactors.

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