Research Article

Catalytic Conversion of 5-Hydroxymethylfurfural and Fructose to 5-Ethoxymethylfurfural over Sulfonated Biochar Catalysts

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Abstract

5-Hydroxymethylfurfural (HMF) is a key platform compound that can be produced by the dehydration of typical carbohydrates like glucose and fructose. Among the derivatives of HMF, 5-ethoxymethylfurfural (EMF) is the etherification product of HMF with ethanol. Owing to some advantages (*i.e.*, high energy density), EMF has been regarded as a potential liquid fuel. Therefore, catalytic conversion of HMF and fructose to EMF is of significance, especially using heterogeneous catalysts. In this paper, we demonstrated the preparation of biomass-based catalysts for the synthesis of EMF from HMF and fructose. Some sulfonated biochar catalysts were prepared by the carbonization of biomass-based precursors at high temperature in N_2, followed by the subsequent sulfonation process employing concentered H_2SO_4 as sulfonation reagent. The obtained catalysts were characterized by scanning electron microscope (SEM), Fourier transform infrared spectrometer (FT-IR), X-ray diffraction (XRD), and element analysis. The catalytic conversion of HMF to EMF was carried out in ethanol, providing a 78% yield with complete conversion at 120 °C. The catalytic activity of the used catalyst showed slight decrease for the etherification of HMF. Moreover, the catalysts were effective for the direct conversion of fructose towards EMF in 64.9% yield.

1. Introduction

Due to the fast consumption of non-renewable fossil resources, human beings are facing serious issues, such as greenhouse effect, atmospheric contamination, and resource shortage. Renewable and abundant biomass contains organic carbon, thereby being deemed as the sole candidate to replace fossil resource. To develop methods for effective utilization of renewable biomass resources is a promising strategy to overcome these problems, which attracted increasing attention last decade. Hexose (*i.e.*, glucose and fructose) is a typical type of carbohydrate. The dehydration of hexose catalyzed by acid catalysts produces HMF [1]. As one of the most important bio-based platform compound, HMF can be further converted into a number of value-added chemicals and biofuels [2,3]. Among the downstream products of HMF, EMF can be prepared by the etherification with ethanol [4–6]. The energy density of EMF is 30.3 MJ/L, which is higher than ethanol (23.5 MJ/L) and comparable to diesel (33.6 MJ/L) and gasoline (31.2 J/L) [7]. Moreover, the use of EMF produces less gas pollutant according to engine test results [8]. Therefore, EMF is regarded as one of promising biofuels.

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Acid-catalyzed etherification of HMF with ethanol has been widely investigated. And satisfactory yields of EMF have been obtained [9]. Nevertheless, the high price and poor stability of HMF limit its practical application. The direct conversion of carbohydrates like fructose to EMF without separation of HMF intermediate is a more promising strategy, because it is less energy-intensive. Some typical homogeneous acidic catalysts, such as H_2SO_4, HCl, $H_3PW_{12}O_{40}$, and $AlCl_3$, have been used for the conversion of fructose to EMF in ethanol, providing 40-76% yield [10–13]. Compared to homogeneous acids, the use of heterogeneous catalysts is highly desirable due to the advantages like good recyclability and reusability. So far, some solid acid catalysts, such as supported heteropolyacids [14,15], sulfonated resins [11], sulfonated silica [16], carbonaceous solid acids [17,18] and acidic molecular sieves [19], have been reported for the one-pot synthesis of EMF from fructose. Among these examples, the use of biomass-derived sulfonated biochar catalysts is of significance, where biomass is used as both precursor for the preparation of catalyst and substrate for the synthesis of value-added biofuels. Cellulose, glucose, lignin, and raw biomass have been employed for preparing sulfonated carbon materials, and the resulting catalysts showed good catalytic activity [17,20–24]. For example, Chen *et al.* [24] reported the preparation of a magnetic cellulose-derived carbonaceous solid acid catalyst (MCC-SO₃H) by impregnation, carbonization and sulfonation. The MCC-SO₃H catalyst could catalyze the conversion of fructose to EMF, offering a 63.2% EMF yield and 24.5% yield of EL at 120 °C for 16 h.

In addition to lignocellulose that has been extensively studied, chitin is another abundant bioresource. Owing to its bio-fixed nitrogen, chitin has been regarded as a good candidate to prepare nitrogen-containing chemicals and materials [25,26]. Previous studies revealed that acidity strength had profound effect on acid-catalyzed conversions in biorefinery. For instance, Dai *et al.* [27,28] prepared a series of nitrogen-containing sulfonated organic polymer catalyst for the conversion of fructose to HMF or EMF. It was found that the nitrogen-containing species as basic sites could suppress the acidity of the solid acid catalyst, which inhibited some undesirable side-reactions, for example, the rehydration of HMF/EMF to levulinic acid / ethyl levulinate (EL). Compared to unrenewable and toxic organonitrogen precursors (*i.e.*, aniline) [27,28], chitin biomass containing nitrogen seems a better choice to prepare sul-

fonated catalyst for the synthesis of EMF from HMF and fructose.

Inspired by above interesting findings, we demonstrated the use of chitin to prepare nitrogen-containing carbon (NC), and the sulfonation of NC generates sulfonated biochar catalysts (SBC). The morphology and structure of SBC were characterized by means of SEM, elemental analysis, FT-IR, and X-ray diffraction (XRD). The catalytic performance of SBC for the conversion of HMF and fructose to EMF was investigated in detail.

2. Materials and Methods

2.1 Materials

HMF (99%), ethanol (AR) and dimethylsulfoxide (DMSO, AR) were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). D-(-)-Fructose (99%), chitin (60 mesh), α-cellulose (particle size: 35-70 μm), and EL (99%) were purchased from Titan Scientific Co., Ltd. (Shanghai, China). EMF (97%) was purchased from Sigma-Aldrich. Naphthalene (>98%) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Sulfuric acid was purchased from Chron Chemicals Co., Ltd. (Sichuan, China). All chemicals were directly used without further purification.

2.2 Catalyst Preparation

Chitin-derived nitrogen-containing carbon was prepared by pyrolysis of chitin in N_2. Typically, chitin (3 g) was loaded into a quartz tube, then the quartz tube with chitin was transferred into a tubular furnace in N_2 flow. The furnace was heated at a rate of 10 °C/min from room temperature to the desired temperature. And this temperature was held for 2 h before cooling down. The obtained powder was termed as NC-X, where X represents the carbonization temperature. Cellulose-derived biochar was produced by similar methods.

Sulfonated biochar catalysts (SBC) were prepared via post-treatment of biochar by H_2SO_4. Typically, 0.6 g NC-X and 8 mL H_2SO_4 were loaded into a round-bottom flask, followed by the reflux in oil bath with stirring at 120 °C for 4 h. After cooling down, the mixture was added into a large amount water. The obtained solid products were filtered off, washed with water several times, dried at 80 °C for at least 4 h, and ground to powder. The as-prepared SBC-X-Y-Z catalysts were named according to the sulfonation temperature and time, where Y and Z represent sulfonation temperature and time, respectively.

2.3 Catalyst Characterization

The content of C, H, N and S was analyzed by a Thermo Finnigan (FLASH, 1112 SERIES) instrument. The SEM images were collected on a low vacuum SEM (FEI Inspect F) instrument. The FT-IR spectra of the catalysts were collected employing a Nicolet Nexus 6700 spectrometer, where a spectral resolution is 4 cm⁻¹. The XRD data were collected by X-ray diffractometer (XRD-6100) from Shimadzu Company of Japan. The acidity strength was assessed by temperature-programmed desorption of ammonia (NH$_3$-TPD, Belcat II).

2.4 Catalytic Reaction

In a typical procedure, 0.3 mmol of substrate (HMF or fructose), 20 mg of catalyst and 3 mL of solvent (ethanol or ethanol-DMSO cosolvent) were loaded into a 35 mL thick-walled glass tube. Then the reactor was heated in a pre-heated oil bath at target temperature (110–150 °C) for the desired reaction time (0.5–12 h). After the mixture was cooled to room temperature, the solid catalysts were separated by filtration. The recovered catalysts were washed with water several times, and dried at 80 °C for recycling experiment. And the resulting liquid was analyzed by GC and HPLC.

2.5 Product Analysis

The yield of EL was analyzed by GC (7820A) with a Kromat PC-INNOWAX column (30 m × 0.25 mm), a hydrogen flame-ionization detector (FID) under the following conditions: injector temperature (250 °C), FID temperature (270 °C), naphthalene as internal standard, and N$_2$ as the carrier gas. The oven temperature of GC was programmed as follows: the column was held initially at 50 °C for 0.5 min, then increased to 200 °C at 20 °C/min and held for 4 min. The conversions of substrates and yields of other products were analyzed by HPLC (Agilent) based on external standard curves established with authentic samples. The HPLC was equipped with an Aminex column (HPX-87H column, Bio-Rad) (50 °C), a refractive index detector (35 °C) and a PDA detector. An aqueous solution of H$_2$SO$_4$ (0.5 mM) at a flow rate of 0.6 mL min⁻¹ was used as the mobile phase. The conversions and yields were calculated based on external standard curves as follows.

$$Conversion = \frac{\left(n_{f0} - n_{fi}\right)}{n_{f0}} \times 100\% \qquad (1)$$

$$Yield = \left(\frac{n_p}{n_{f0}}\right) \times 100\% \qquad (2)$$

where, n_{f0} stands for moles of the initial reactant, n_{fi} stands for moles of the final reactant, and n_p stands for moles of product.
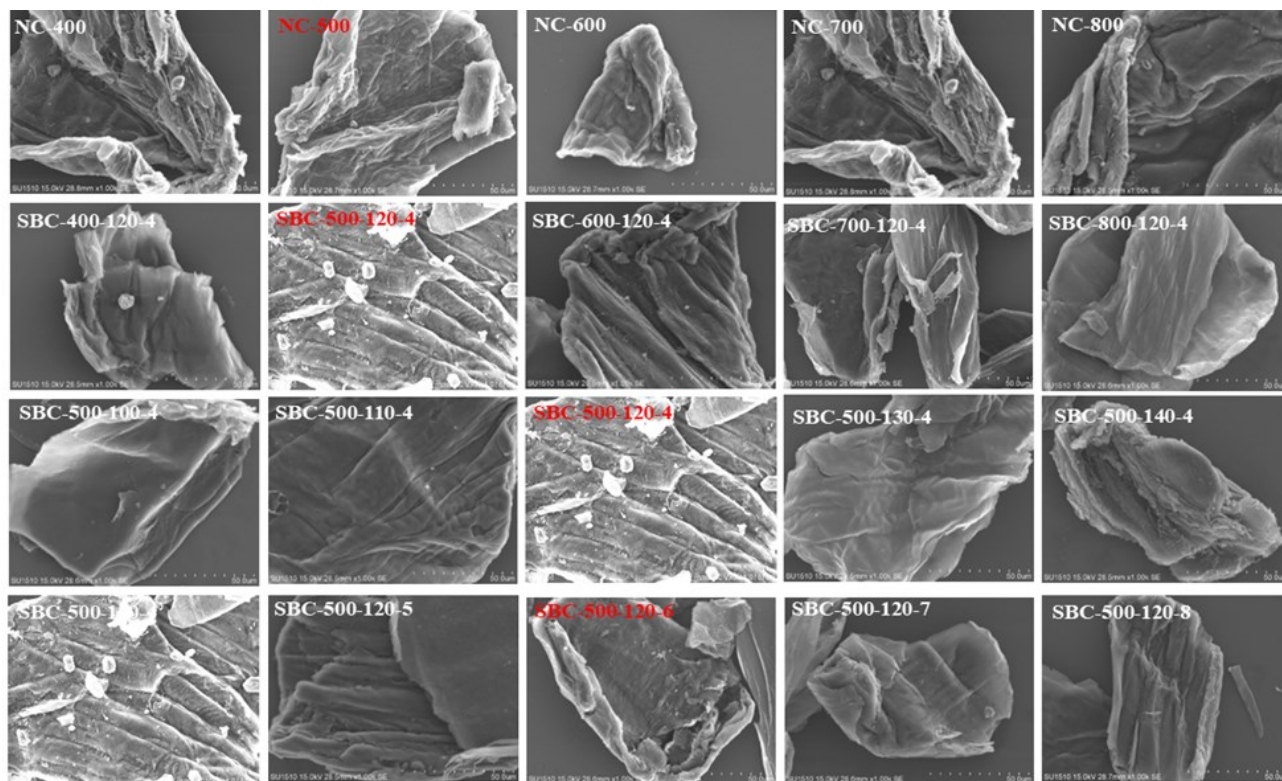

Figure 1. The SEM images of NC-X and SBC-X-Y-Z catalysts.

3. Results and Discussion

3.1 Characterization of NC and SBC

NC-X was prepared by the carbonization of chitin in N_2 at high temperature. And the subsequent sulfonation of NC-X generates SBC-X-Y-Z. As shown in Figure 1, the SEM images of NC-X and SBC-X-Y-Z catalysts all showed a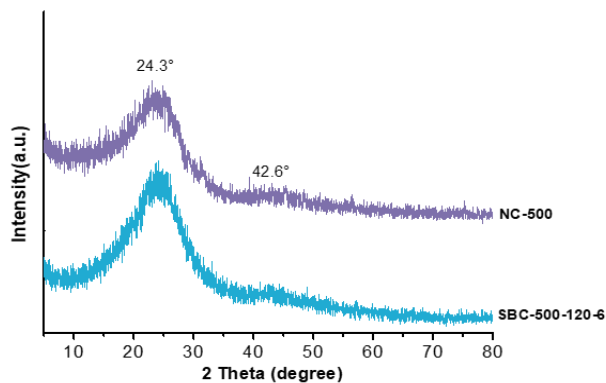 rough and loose surface. Figure 2 has shown the XRD patterns of NC-500 and SBC-500-120-6. The peaks at $2\theta = 24.3°$ and $42.6°$ were attributed to the diffraction of (002) and (100) planes, respectively, which indicated the existence of interlayer structure and graphite phase in NC-500 and SBC-500-120-6 [21,29]. The FT-IR spectra of chitin and NC-X were shown in Figure 3(a). For chitin, the peaks at 3105, 1659, 1558 and 1076 cm^{-1} were assigned to the stretching vibrations of N−H, C=O, C−N, and C−O, respectively [29]. These characteristic peaks disappeared after carbonization, suggesting that the structure of chitin was destroyed during carbonization. The FT-IR spectra of SBC-X-120-4, SBC-500-Y-4 and SBC-500-120-Z were shown in Figure 3(b)-(d). After sulfonation, some characteristic peaks concerning sulfonic acid group appeared in the spectra. Three peaks at 1183, 1039 and 698 cm^{-1} were assigned to the O=S=O, SO$_3^-$ and C−S stretching vibrations [30,31], suggesting the successful introduction of acidic group on NC. Consistent with FT-IR spectra, the elemental anal-

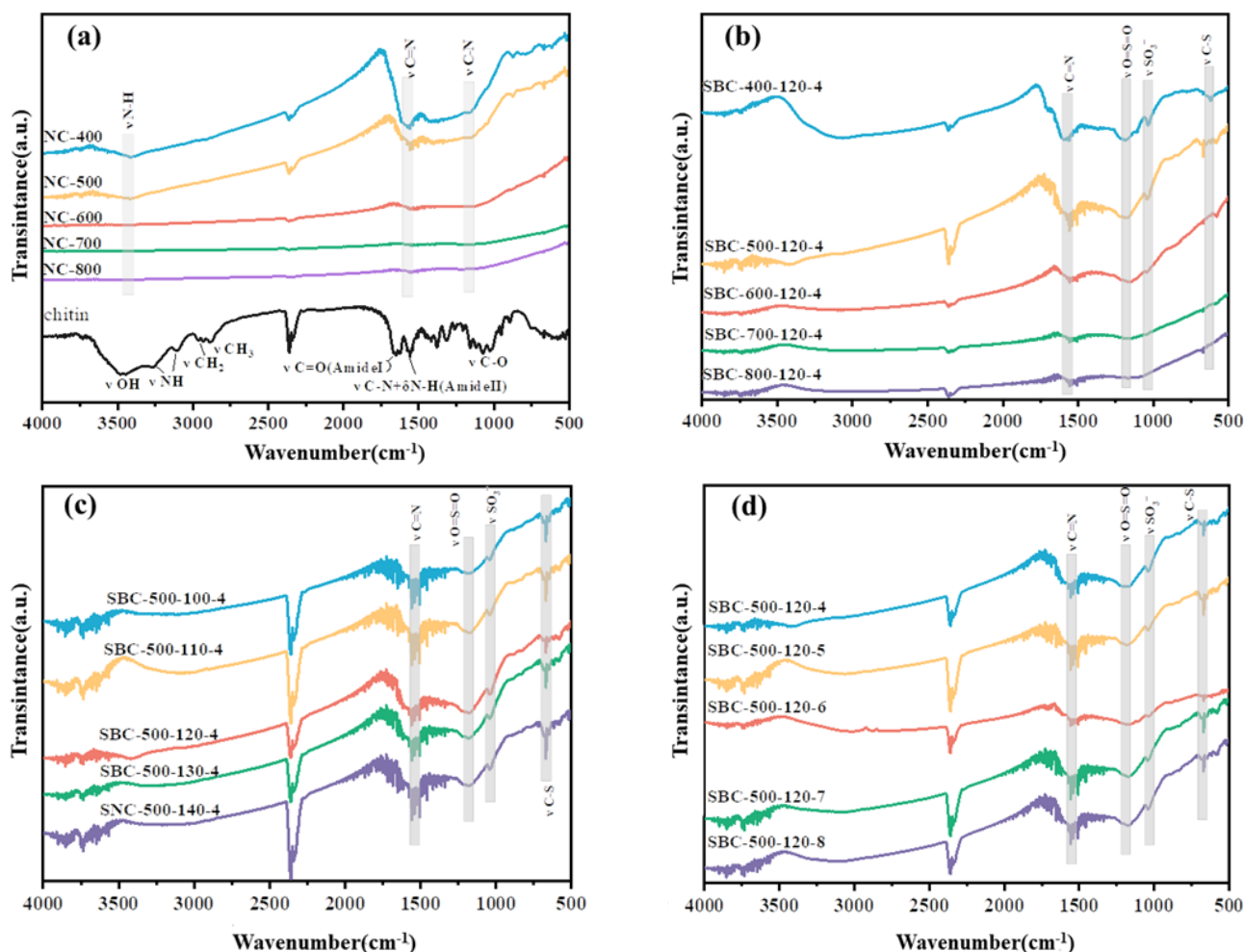Figure 2. The XRD spectra of NC-500 and SBC-500-120-6.

Figure 3. The FT-IR spectra of (a) chitin and NC-X; (b) SBC-X-120-4; (c) SBC-500-Y-4; (d) SBC-500-120-Z catalysts.

ysis results confirmed the existence of approximately 3wt% S in SBC-500-120-6 catalyst, as shown in Table 1, which supported the successful introduction of sulfonic acid groups. The acidity strength was investigated by NH₃-TPD, as shown in Figure 4. Compared to that of SBC (cellulose)-500-120-6 (283 °C), the NH₃-TPD profile of SBC (chitin)-500-120-6 displayed a lower desorption temperature (279 °C). We speculated that the nitrogen-containing basic species might inhibit the acid strength of solid acid catalysts.

3.2 Catalytic Activity

The catalytic activity for the etherification of HMF to EMF in ethanol was comparatively studied at 120 °C for 4 h, and the results were shown in Table 2 (entry 1-6). When no catalyst was used, HMF conversion and EMF yield were 5.9% and 0.6%, respectively, suggesting that non-catalytic process is not effective for the pro-
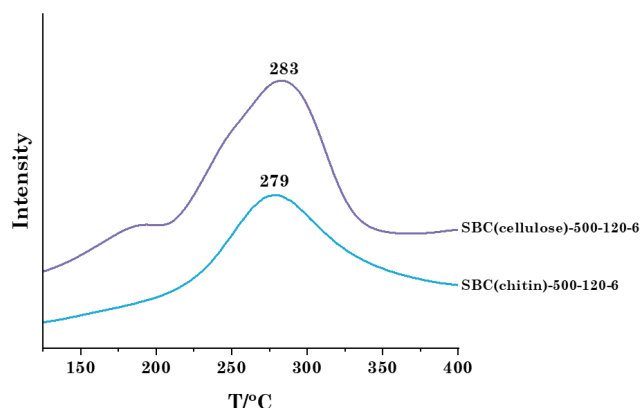

Figure 4. NH₃-TPD profiles of SBC (cellulose)-500-120-6 and SBC (chitin)-500-120-6.

duction of EMF from HMF. The use of SBC-X-120-4 catalysts obviously increased the conversion of HMF and promoted the formation of EMF. With the increase of carbonization temperature from 400 °C to 500 °C, the HMF conversion increased from 80.6% to 90.5%, while the EMF yield increased from 62.1% to 75.5%. When the carbonization was carried out at 600 or 700 °C, no significant changes in HMF conversion and EMF yield were observed. The further increase of carbonization temperature to 800 °C led to slight decrease of HMF conversion and EMF yield. Interestingly, the EMF selectivity was always ca. 77% using SBC-X-120-4 catalysts under investigated conditions. In addition to EMF, EL was detected as the minor product. The rehydration of EMF generates EL and formic acid. Despite the energy density of EL (24.6 MJ/L) is slightly lower than that of EMF (30.3 MJ/L), EL is also regarded as a potential biofuel [32]. Therefore, the formation of EL as a by-product for the conversion of HMF to liquid fuels is acceptable. As we can see from Table 2, the total yield of EMF and EL over SBC-500-120-4 reached to 93%, which was close to the HMF conversion, indicating that HMF was selectively transformed into liquid fuel candidates in ethanol.

The effects of sulfonation temperature and time on the catalytic activity were studied. And the catalytic activity results were shown in Table 3. When the sulfonation was performed at 100–140 °C, the HMF conversions were above 90% with 74.0-78.1% EMF yields, while the selectivity was ca. 80% in all cases. When the sulfonation temperature was fixed at 120 °C, the increase of sulfonation time from 4 h to 7 h had minor effect on HMF conversion and EMF

Table 1. Elementary analysis results of NC-500 and SBC-500-120-6 catalyst.

Entry	Catalysts	Mass fraction/%			
		N	C	H	S
1	NC-500	8.10	77.84	2.89	0
2	SBC-500-120-6	7.21	68.56	2.97	2.96

Table 2. Catalytic conversion of HMF to EMF over SBC-X-120-4 catalysts.

Entry	Catalysts	Conversion (%)	Yields of products (%)		
			EMF	EL	EMF+EL
1	none	5.9	0.6	0.8	1.4
2	SBC-400-120-4	80.6	62.1	8.9	71
3	SBC-500-120-4	95.9	75.5	17.5	93
4	SBC-600-120-4	97.0	76.0	15.6	91.6
5	SBC-700-120-4	94.8	73.5	10.1	83.6
6	SBC-800-120-4	88.2	67.4	12.7	80.1

Reaction conditions: 0.3 mmol of HMF, 3 mL of ethanol, 20 mg of catalysts, 120 °C, 4 h.

yield. When the sulfonation was carried out for 6 h, EMF selectivity increased to 80.6%. And the SBC-500-120-6 catalyst was used for further study. Interestingly, cellulose-derived catalyst provided higher HMF conversion but poorer EMF yield than SBC-X-Y-Z (Table 3, entry 11). As discussed early, the interaction between nitrogen-containing species and sulfonic acid group might suppressed the acidity strength of SBC catalysts, which inhibited some undesirable side-reactions [27].

After the optimization of preparation parameters, the effect of reaction conditions on HMF conversion was investigated. The reaction temperature influences not only reaction rate but also product selectivity. As shown in Figure 5(a), with the temperature increasing from 110 °C to 120 °C, HMF conversion increased from 74.6% to 94.8% significantly, while the EMF yield increased from 55% to 78%. Meanwhile, the EMF selectivity increased from 73% to 80.6%. Nearly complete conversion of HMF was obtained after the reaction at above 130 °C. The higher temperature significantly promoted the formation of EL, resulting in the decrease of EMF yield. For example, EMF yield decreased to 51.1% at 150 °C. Based on above results, 120 °C was an appropriate
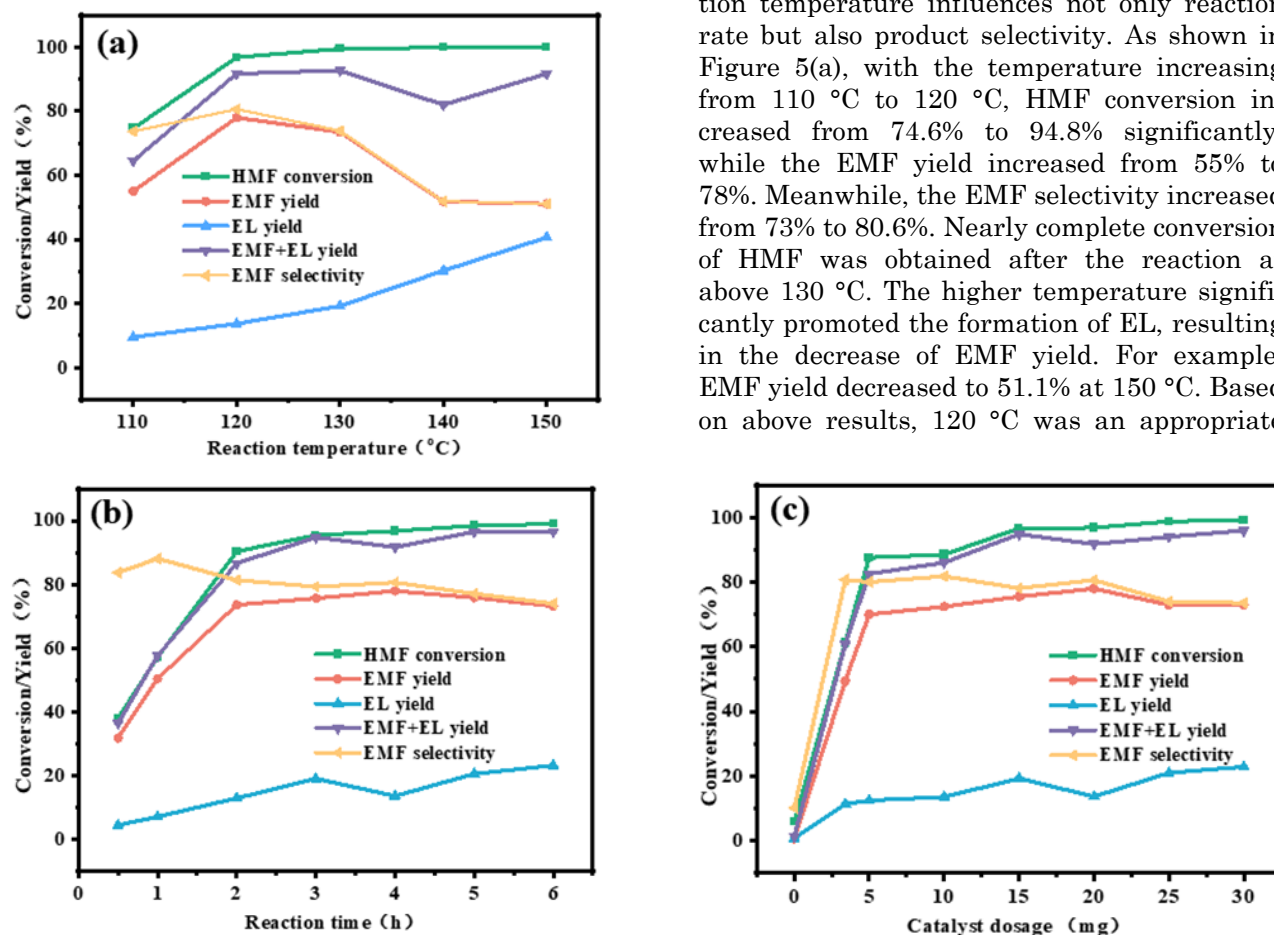

Figure 5. The effect of (a) reaction temperature, (b) time, (c) catalyst dosage on HMF conversion. Reaction conditions: 0.3 mmol of HMF, 3 mL of ethanol. (a) 20 mg of catalysts, 4 h; (b) 120 °C, 20 mg of catalysts; (c) 120 °C, 4 h.

Table 3. Catalytic conversion of HMF to EMF over SBC-500-X-Y catalysts.

Entry	Catalysts	Conversion (%)	Yields of products (%)		
			EMF	EL	EMF+EL
1	SBC-500-100-4	93.8	74.6	9.9	84.5
2	SBC-500-110-4	98.2	78.1	15.3	93.4
3	SBC-500-120-4	95.9	75.5	17.5	93
4	SBC-500-130-4	92.1	74.0	12.8	86.8
5	SBC-500-140-4	96.7	76.8	14.3	91.1
6	SBC-500-120-4	95.9	75.5	17.5	93
7	SBC-500-120-5	97.7	78.6	14.1	92.7
8	SBC-500-120-6	96.8	78.0	13.7	91.7
9	SBC-500-120-7	98.2	76.7	16.3	93
10	SBC-500-120-8	98.3	72.3	13.7	86
11	SBC-500-120-6[a]	99.9	58.0	15.3	73.3

Reaction conditions: 0.3 mmol of HMF, 3 mL of ethanol, 20 mg of catalysts, 120 °C, 4 h. [a] cellulose as catalyst precursor.

temperature for EMF generation with the formation of EL being inhibited. As the reaction time prolonged, HMF conversion monotonically increased. Meanwhile, the increase of EL yield and the decrease of EMF yield indicated the conversion of EMF to EL at the later stage. A highest 78.0% yield of EMF was afforded after 4 h's reaction, and 13.7% yield of EL was obtained, as shown in Figure 5(b). The effect of catalyst amount was displayed in Figure 5(c). Overall, the larger amount of catalyst accelerated the formation of EMF due to more active sites, but excess catalyst led to undesirable side-reactions. Typically, EMF yield increased remarkably with the increase of catalyst dosage. When 20 mg of SBC-500-120-6 was used, a 78.0% yield of EMF was obtained.
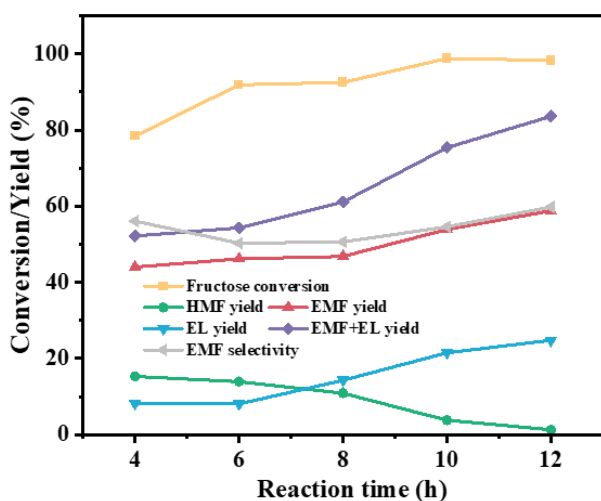

Figure 6. The effect of reaction time on one-pot conversion of fructose to EMF in ethanol. Reaction conditions: 0.3 mmol of fructose, 3 mL of ethanol, 20 mg of catalysts, 120 °C.
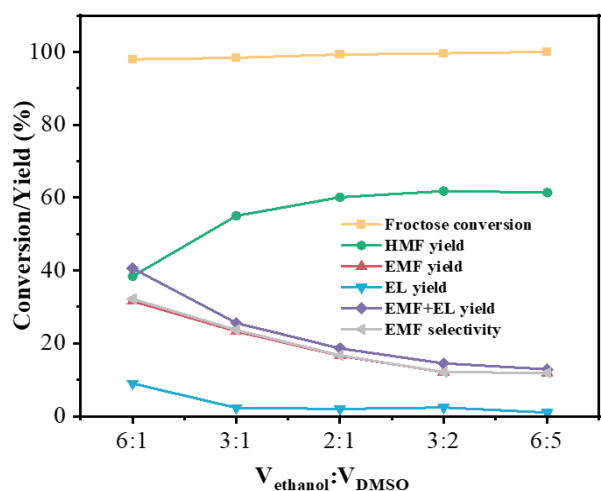

Figure 7. The effect of DMSO on one-pot conversion of fructose. Reaction conditions: 0.3 mmol of fructose, 3 mL of solvent, 20 mg of catalysts, 120 °C, 4 h.

Compared to the etherification of pure HMF, the direct conversion of fructose is a more promising strategy. The one-pot conversion of fructose to EMF was investigated initially in ethanol at 120 °C, and the results were displayed in Figure 6. After reaction for 4 h, 78.4% of fructose was converted, providing EMF, HMF, and EL in 44%, 15.3%, and 8.2% yields, respectively. The increase of reaction time from 4 h to 12 h led to gradual increase of fructose conversion and EMF yield, while the HMF yield decreased to 1.3%. Meanwhile, the increase of EL yield was observed. After 12 h's reaction, EMF yield and EL yield increased to 58.8% and 24.8%, respectively. In order to improve EMF yield, DMSO was added. DMSO could catalyze the dehydration of fructose to HMF and inhibit some undesirable side-reaction of HMF [33,34]. As shown in Figure 7, the addition of DMSO significantly promoted the conversion of fructose. When the volume ratio of ethanol/DMSO was 6/1, EMF yield and HMF yield were 31.6% and 38.4%, respectively. The further increase of volume ratio of ethanol/DMSO led to the increase of HMF yield while EMF yield showed a reverse trend. There are two possible reasons. First, DMSO might prevent the further conversion of HMF to other compounds. Second, the decrease of ethanol content suppressed the etherification of HMF. After one-pot conversion of fructose for 12 h, the full conversion of fructose with 64.9% yield of EMF. The activity of as-prepared chitin-derived solid acid for the conversion of fructose to EMF in this work was comparable to that of some typical solid acid catalysts, such as sulfonated polymeric materials and sulfated car-
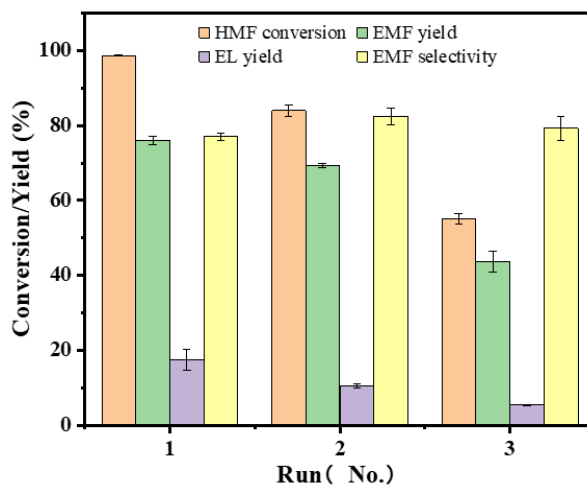

Figure 8. Recycle experiments for the catalyst SBC-500-120-6. Reaction conditions: 0.3 mmol of HMF, 3 mL of ethanol, 20 mg of catalysts, 120 °C, 4 h.

bonaceous solid acid catalysts (Table S1). And the possible reaction mechanism of EMF synthesis from fructose is shown in Figure S1.

Finally, the stability and reusability of the SBC-500-120-6 catalyst were evaluated, and the results were shown in Figure 8. The catalytic activity of used catalyst exhibited decreasing trend. For the third catalytic run, the HMF conversion, EMF yield and EL yield declined to 56.3%, 46.5% and 5.6%, respectively. Notably, the selectivity of EMF was still ca. 80%. According to previous reports [35], strong adsorption of organic compounds on the catalyst surface and poisoning of acid sites by the water (a etherification product) might be responsible for the partial deactivation.

4. Conclusion

In this work, we prepared novel sulfonated biochar catalysts employing chitin as carbon sources. The carbonization of chitin provided nitrogen-containing biochars, and the further sulfonation by H_2SO_4 generated solid acid catalysts. The as-prepared catalyst (SBC-500-120-6) could catalyze the conversion of HMF to EMF in ethanol in 78% yield, and the total yield of biofuels (EMF and EL) reached to 91.3%. After three catalytic runs, the selectivity of EMF was still ca. 80%, despite the decreasing conversion of HMF was obtained. SBC-500-120-6 also could catalyze one-pot conversion of fructose to EMF. Compared to the use of ethanol, the addition of DMSO with appropriate amount enhanced EMF yield. A 64.9% yield of EMF was obtained in ethanol/DMSO (V/V, 6/1) at 120 °C for 12 h. This work highlights the application of novel sulfonated biochar catalysts for the production of liquid biofuel from biomass-derived platform compound and fructose.

Acknowledgments

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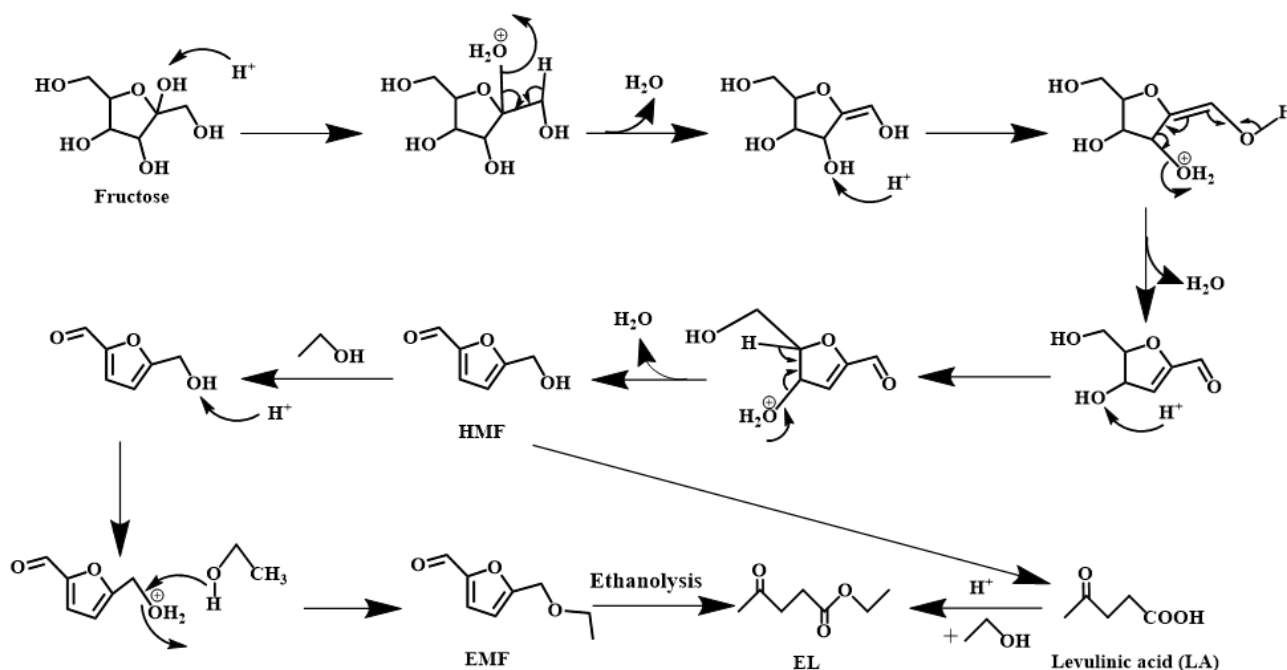
Appendices / Supplementary Materials

Figure S1. The reaction pathway for the synthesis of EMF from fructose [S1].

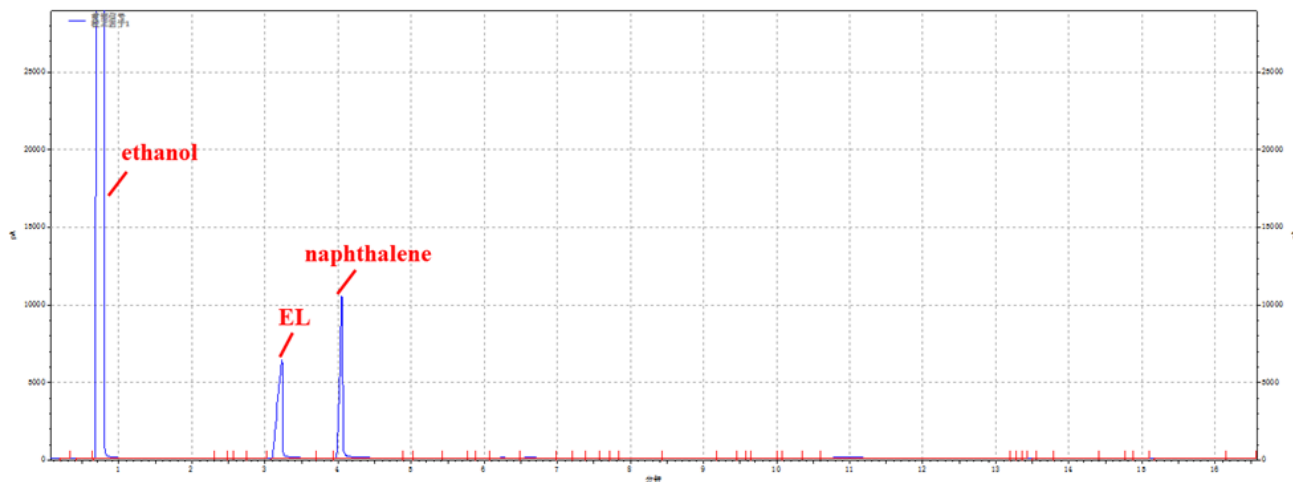# Appendices / Supplementary Materials (Continued)

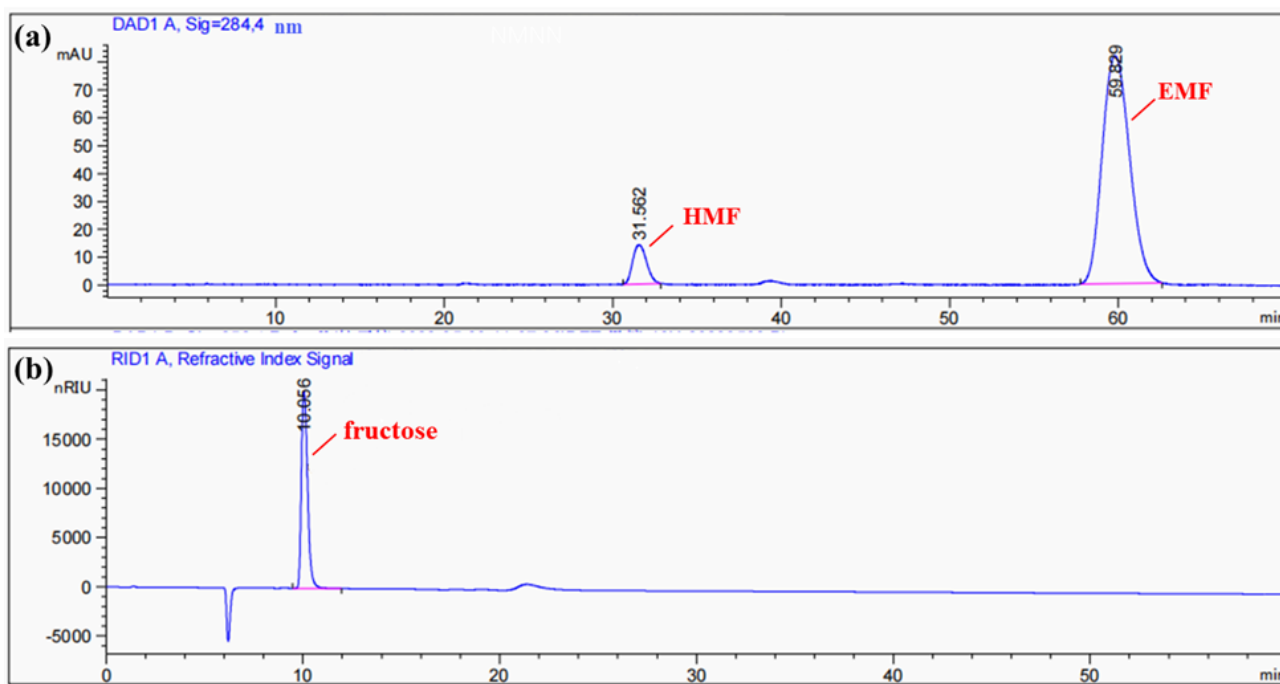Figure S2. The GC spectra of EL and naphthalene.

Figure S3. The HPLC spectra of (a) HMF, EMF and (b) fructose.

Appendices / Supplementary Materials (Continued)

Table S1 Some typical sulfonated solid acid catalysts for the EMF synthesis from fructose.

Entry	Catalysts	T (°C)	t (h)	Conv.(%)	Yields of products (%)			Ref.
					HMF	EMF	EL	
1	SBC-500-120-6	120	12	100	7.5	64.9	20.1	This work
2	MCC-SO$_3$H	120	16	99.7	4.1	63.2	24.5	[S2]
3	D0.5-SPC-0.25–9/3	140	18	100	0.8	68.8	5.3	[S3]
4	MIL-101-SO$_3$H	130	15	-	-	45	-	[S4]
5	OMC-SO$_3$H	140	24	100	1.2	55.7	-	[S5]
6	Silica-SO$_3$H	100	24	-	11.2	63.1	-	[S6]
7	Fe$_3$O$_4$@C–SO$_3$H	140	24	100	3	68	19	[S7]

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