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Magnetically-Recoverable Carbonaceous Material: An Efficient Catalyst for the Synthesis of 5-Hydroxymethylfurfural and 5-Ethoxymethylfurfural from Carbohydrates[1]

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Abstract—A novel, magnetically recoverable carbonaceous solid acid Fe_3O_4@C-SO_3H catalyst for the conversion of carbohydrates to 5-ethoxymethylfurfural (EMF) was developed. The effect of the DMSO fraction in the ethanol–DMSO binary solvent on the distribution of the reaction products was investigated. The catalyst showed an excellent activity in the synthesis of EMF from fructose and 5-hydroxymethylfurfural (HMF). 5-Ethoxymethylfurfural was also obtained with a high yield of 64.2% in an ethanol–DMSO solvent system via one-step conversion of fructose. After reaction, the catalyst could be recovered by exposure of the reaction mixture to external magnetic field and reused several times without a loss of catalytic activity.

Keywords: fructose, 5-ethoxymethylfurfural (EMF), 5-hydroxymethylfurfural (HMF), DMSO

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Over the last decades, fossil fuels gave us a wide variety of fuels and chemicals. With the growing demand for fuels and chemicals, petroleum production will be not enough to keep pace with the market demand in the future. Therefore, much effort has been devoted to the production of chemicals and fuels from renewable biomass. Biomass is an abundant renewable resource considered as the most proper substitute for the synthesis of alternative fuels [1, 2]. It is a challenge to convert biomass-derived carbohydrates to platform chemicals, such as 5-hydroxymethylfurfural (HMF) and its derivatives, by economic and efficient processes. 5-Hydroxymethylfurfural (HMF) is considered a versatile intermediate in biorefinery processes [3, 4], which can be converted into biofuels (2,5-dimethylfuran) [5], monomers for high-value polymers(furan-2,5-dicarboxylic acid [6] and 2,5-bis(hydroxymethyl)furan) [7], as well as valuable intermediates for fine chemistry. In the past decades, much effort has been devoted to transform hexoses, such as glucose and fructose, and even cellulose and lignocelluloses into HMF [8, 9].

The etherification product of HMF, 5-ethoxymethylfurfural (EMF), unlike HMF, has been scarcely explored. At the same time, it is considered to hold promise as a liquid biofuel or fuel additive [10]. 5-Ethoxymethylfurfural is a high-boiling liquid (bp 235°C). It has a high energy density of 8.7 kW h L^{-1}, which is close to the respective value for standard gasoline (8.8 kW h L^{-1}) and significantly higher compared to ethanol (6.1 kW h L^{-1}) [11]. In recent years, several efficient methods for the synthesis of EMF from HMF or 5-chloromethylfurfural (CMF) have been developed [12–14]. One attractive synthetic approach to EMF involves the reactions of HMF and CMF environment due to their carbon frameworks, and carbon-based solid acid catalysts exhibit super efficiency in biodiesel production and other esterification reactions [26–29]. Unfortunately, the tedious recovery procedure of carbon-based solid acid catalysts via filtration or centrifugation and the attendant loss of the material, prevent their wide application in industrial process.

Over the past years, magnetically loaded materials have gained special attention as a kind of catalyst support, due to their numerous advantages such as good stability, facile separation by magnetic forces [30], ease of selective functional modifications, and soft operation conditions. The fact that magnetic nanoparticles (MNPs) can be easily separated under magnetic field prevents inevitable loss of the catalyst

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[1] The text was submitted by the authors in English.

in the separation process, suggesting strong potential for applications. Wheat straw, as an agricultural byproduct with sufficient supply and low cost, is an excellent source for developing solid acid catalyst of high quality. In the present work we used a wheat straw biomass as the raw material to prepare a magnetically-recoverable carbonaceous solid acid catalyst bearing -COOH, -SO_3H, and -OH groups [31], and tested it in the synthesis of EMF from fructose. The carbonaceous solid acid catalyst could be easily separated by exposure to external magnetic field, and the separated catalyst retained its catalytic activity and could be reused. The new catalytic system has shown a relatively high catalytic activity for in the synthesis of EMF from a renewable biomass resource.

EXPERIMENTAL

Materials. $Fe(NO_3)_3 \cdot 9H_2O$, mercaptoacetic acid, hydrogen peroxide (30 wt %), ammonia water (25 mol %), ethanol, DMSO, fructose, and *p*-toluenesulfonic acid were used as received from Sinopharm Chemical Reagent (Shanghai, China). Wheat straw (Henan, North China) was milled and dried at 80 ℃ for 3 days before use

Preparation of the magnetically-recoverable carbonaceous solid acid catalyst. **Synthesis of the carbonaceous material from wheat straw**. Dried wheat straw was heated to 450°C at a rate of 200°C h^{-1}, and keeping it at the maximum temperature for 10 h. The heating tube furnace was purged with an N_2 flow during the temperature rise and carbonization process until the carbonaceous material was cooled to room temperature after carbonization.

Synthesis of magnetically-recoverable carbonaceous material. The carbonaceous material (2 g) was dispersed in a $Fe(NO_3)_3 \cdot 9H_2O$ aqueous solution (40 mL). Ammonia water solution (25 mol %) was then added until pH 10, and the mixture was vigorously mechanically stirred at room temperature for 24 h. The resulting black solid was heated at 400°C for 10 h in an N_2 atmosphere.

Synthesis of magnetically-recoverable carbonaceous material functionalized with sulfonic acid groups. The synthesized magnetically-recoverable carbonaceous material (1 g) and 0.04 g *p*-toluenesulfonic acid were dispersed into 20 mL water. Mercaptoacetic acid (20 mL) was added to the mixture with vigorous mechanical stirring for 24 h and then ammonia water (10 mol %) was added with stirring until the pH of the mixture reached 7. The precipitate that formed was dried at 60°C overnight and then heated at 400°C for 10 h in an N_2 atmosphere. Water (20 mL) was poured over the resulting solid material, and 20 mL of hydrogen peroxide (30 wt %) was added with vigorous stirring for 10 h. The solid was then collected by a permanent magnet, repeatedly washed with distilled water, and dried at 80°C overnight.

Catalyst characterization. The FTIR spectra of the catalyst were recorded on an ABB Bomem FTLA2000 -104 spectrophotometer in the 4000–500 cm^{-1} range. Field emission scanning electron microscopy (SEM) was performed on a HITACHI S-4800 instrument. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100 instrument operated at 200 kV. X-ray diffraction (XRD) analysis was carried out on a Bruker AXS D8 Advance diffractometer using a Ni-filtered CuK_α (λ = 0.15406 nm) radiation source (2θ = 20°–70°). SQUID analysis was carried out on a Quantum Design PPMS-9 device. The BET surface areas were measured on a Micromeritics ASAP 2020 analyzer at 77 K. The sulfur content was determined with a PerkinElmer 2400 Series II CHNS/O organic elemental analyzer. The content of H^+ in Fe_3O_4@C-SO_3H was determined by titration of the solution after 24-h stirring of Fe_3O_4@C-SO_3H in a 0.1 M NaCl solution with a standard NaOH solution.

Synthesis of EMF. **Synthesis of EMF from HMF**. 5-Hydroxymethylfurfural (126 mg, 1 mmol), Fe_3O_4@C-SO_3H (45 mg) and ethanol (5 mL) were charged in a 10 mL stainless steel vessel with a Teflon lining. The reactor was placed into an oil bath kept at 100°C, and the reaction mixture was magnetically stirred at 600 rpm. Time zero was taken, when the reactor was immersed into the oil bath. Reaction progress was followed by HPLC analysis of the samples withdrawn from the reaction mixture at preset interval and diluted with deionized water.

Synthesis of EMF from fructose was performed in the same reactor. Fructose (180 mg, 1 mmol) was added to 5 mL of a vigorously stirred solvent (1.5 mL DMSO plus 3.5 mL ethanol) until a clear solution formed, after which Fe_3O_4@C-SO_3H (45 mg) was added. Further steps were carried out as described above.

HPLC analysis of the reaction mixtures was performed on an Agilent Alliance 1100 Series System with UV and refractive index detectors and a Shodex SURGER SP0810 (300 × 8.0 mm) column at 25°C; the mobile phase was ultrapure water at the flow rate of

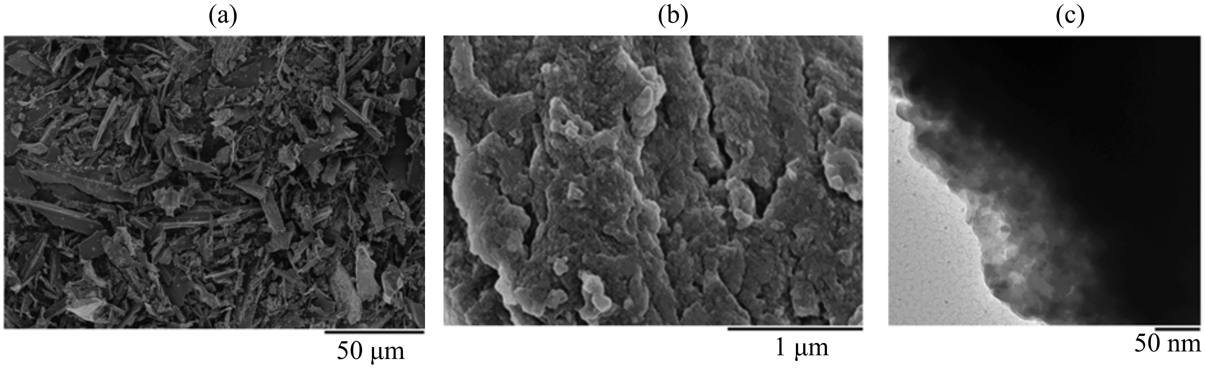

Fig. 1. (a) SEM image of the carbonaceous material from high-temperature calcination of wheat straw, (b) SEM image of the carbonaceous material functionalized with sulfonic acid groups; and (c) TEM image of the magnetically-recoverable carbonaceous material functionalized with sulfonic acid groups.

0.7 mL/min. The yields of HMF and EMF were calculated from multipoint calibration curves.

Recycling of the catalyst. For catalyst recycling experiments we used both the etherification of HMF to EMF and the synthesis of EMF from fructose. All runs were performed under the above-described conditions. After reaction, the Fe_3O_4@C-SO_3H catalyst was recovered from the reaction mixture by a permanent magnet, washed three times with water and ethanol to remove the adsorbed product, dried at 60°C in a vacuum oven overnight, and reused in a subsequent reaction.

RESULTS AND DISCUSSION

The magnetically recoverable carbonaceous solid acid catalyst was characterized by FTIR spectroscopy, field emission scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis, superconducting quantum interference device (SQUID) techniques, and BET specific surface measurements.

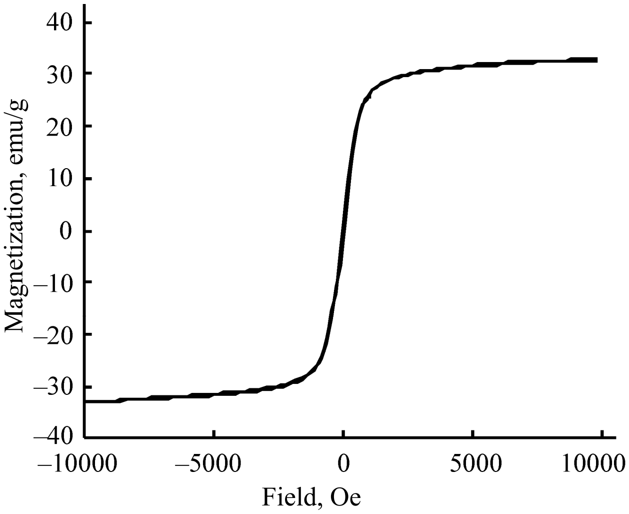

Fig. 2. Magnetization curve for the magnetically-recoverable carbonaceous material functionalized with sulfonic acid groups at room temperature.

The SEM image of the carbonaceous material obtained after high-temperature calcination of wheat straw is shown in Fig. 1a. As seen from the figure, this mesoporous materials is slightly bubbly in nature. The SEM image of the carbonaceous material functionalized with sulfonic acid groups (Fig. 1b) reveals some morphological changes are observed. The TEM micrograph of the Fe_3O_4@C-SO_3H catalyst (Fig. 1c) confirms that the Fe_3O_4 nanoparticles have successfully embedded in the synthesized carbonaceous material.

The magnetic properties of the Fe_3O_4@C-SO_3H catalyst were characterized by SQUID analysis (Fig. 2). The saturation magnetization of Fe_3O_4@C-SO_3H was 32.8 emu/g at 25°C, which implied sufficient separation of the catalyst under external magnetic field. On the other hand, the permanent magnetization and magnetic coercive force were all zero, showing that the catalyst is superparamagnetic and its particles do not aggregate with each other in the absence of external magnetic field [32].

The XRD pattern of Fe_3O_4 nanoparticles and Fe_3O_4@C-SO_3H catalyst are presented in Fig. 3. The diffraction peaks at $2\theta = 30.1°$, 35.5°, 43.1°, 57.0°, and 62.5° responded to (220), (311), (400), (511) and (440) planes of the face-centered cubic Fe_3O_4 lattice. The absence of any obvious difference between the two samples provides evidence that the Fe_3O_4 nanoparticles have been embedded into the particles [33, 34].

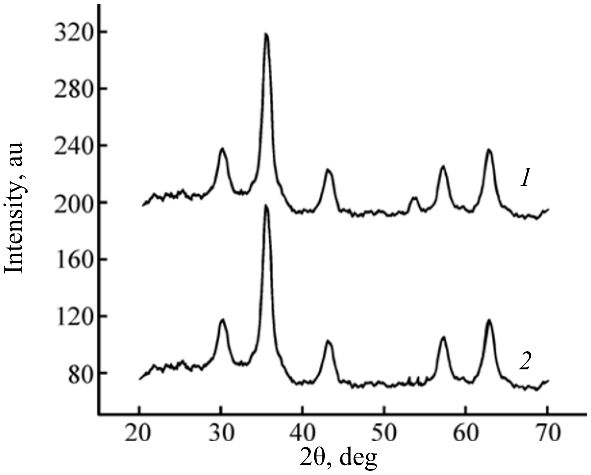

Fig. 3. XRD patterns of the (*1*) Fe_3O_4 microspheres and (*2*) Fe_3O_4@C composite.

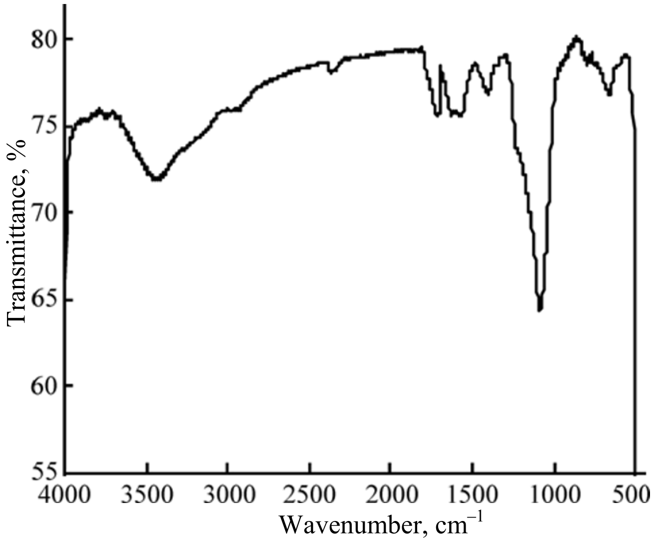

Fig. 4. FTIR spectrum of the Fe_3O_4@C-SO_3H catalyst.

The FT-IR spectrum of the prepared Fe_3O_4@C-SO_3H is shown in Fig. 4. The absorption band near 610 cm^{-1} is assigned Fe–O vibration [35, 36]. The band at 3378 cm^{-1} is assigned to OH stretching vibration [37], and those at 1708 and 1620 cm^{-1}, to COO- and C=C stretching vibrations [38, 39]. The observation of bands at 1045 cm^{-1} (SO_3^- stretching) and 1368 cm^{-1} (O=S=O stretching in SO_3H) indicates that the synthesized catalyst contains –SO_3H functionalities [40].

The sulfur content in the catalyst was estimated at 1.40 mmol/g, and the H^+ content at 1.44 mmol/g. The BET surface area, average pore diameter, and pore volume were estimated at 86.8 m^2/g, 8.3 nm, and 0.14 m^3/g, respectively.

We also studied the effect of the DMSO fraction in the DMSO–ethanol binary solvent in the one-step catalytic conversion of fructose on the distribution of the reaction products HMF and EMF and the conversion of fructose (Fig. 5) [41]. As seen from the figure, the DMSO content does not obviously affect the conversion of fructose but obviously affects the product distribution. In straight ethanol (DMSO fraction 0%), the major product was EMF (yield 31.8%), whereas the yield of HMF was much lower. As the fraction of DMSO in the binary solvent was increased to 20%, the yield of EMF improved from 31.8 to 64.2%, and the yield of HMF slowly increased. Moreover, as seen in Fig. 5, when the DMSO fraction was lower than 20%, the rate of fructose dehydration was lower than the rate of HMF etherification. It might be due to the fact that ethanol is the major component of the solvent system. When the content of DMSO is more than 20%, the yield of HMF increases rapidly, and the yield of EMF sharply decreases. Therefore, the optimal volume fraction of DMSO is 20%.

The catalytic activity of our prepared catalyst was evaluated in the etherification of HMF. We use various catalysts to evaluate the advantages of Fe_3O_4@C-SO_3H, and the results are summarized in Table 1. In the presence of the homogeneous acids H_2SO_4 and $H_3PW_{12}O_{40}$ (Table 1, entries 1 and 2), the yields of EMF were 79.8% and 80.3% and the HMF conversions were 100 and 91.0%, respectively. However, H_2SO_4 and $H_3PW_{12}O_{40}$ are difficult to recycle, because they are readily soluble in the ethanol; this circumstance entails a high production cost. Therefore, in terms of green chemistry, preference should be given to heterogeneous catalytic systems.

Table 1. Synthesis of EMF from HMF, catalyzed by various catalysts[a]

Entry no.	Catalyst	HMF conversion, %	EMF yield, %
1	H_2SO_4	100.0	79.8
2	$H_3PW_{12}O_{40}$	91.0	80.3
3	HY-zeolite	10.0	8.5
4	NKG-9 resin	100.0	82.8
5	Fe_3O_4@C	1.7	0.3
6	Fe_3O_4@C-SO_3H	97.0	85.6

[a] Reaction conditions: HMF 126 mg; ethanol 5 mL; catalyst 30 mg; temperature 100°C; time 10 h.

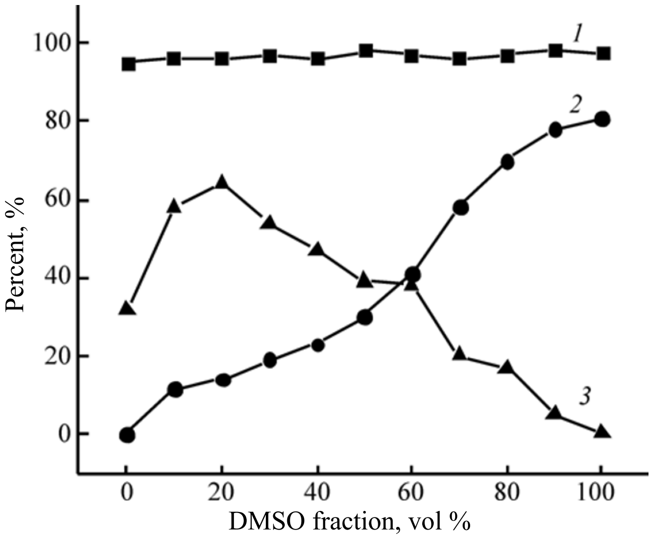

Fig. 5. Effect of the fraction of DMSO in the ethanol–DMSO binary solvent content on the synthesis of EMF from fructose: (*1*) fructose conversion, (*2*) HMF yield, and (*3*) EMF yield. Reaction conditions: solvent 5.0 mL; fructose, 1 mmol; Fe_3O_4@C-SO_3H 30 mg; temperature 100°C; time 10 h.

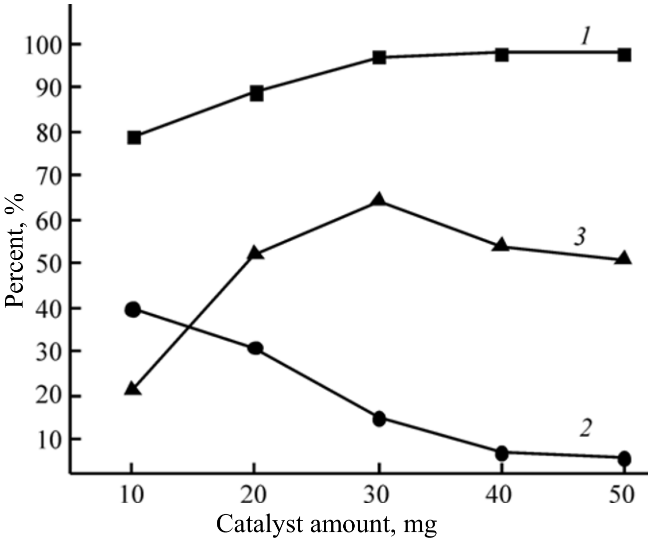

Fig. 6. Effect of the catalyst amount on the on the synthesis of EMF from fructose: (*1*) fructose conversion, (*2*) HMF yield, and (*3*) EMF yield. Reaction conditions: solvent 5.0 mL; fructose 1 mmol; temperature, 100°C; time, 10 h.

With HY zeolite, which is a weak solid acid catalyst, the HMF conversion only achieved 10 % and the yield of EMF was as low as 8.5% (Table 1, entry 3). As a strong solid acid catalyst we tested a SO_3H-functionalized NKG-9 ion-exchange resin. As expected, the HMF conversion was achieved 100% and the EMF yield was as high as 82.8% (Table 1, entry 4). However, the structure of NKG-9 ion-exchange resin was seriously destroyed, and the catalyst was pulverized after reaction and, therefore, quite difficult to separate and recycle. The yield of EMF in the Fe_3O_4@C-catalyzed reaction was negligible (<1%) (Table 1, entry 5). At the same time, with our synthesized catalyst Fe_3O_4@C-SO_3H, the yield of EMF increased to 85.6% at the HMF conversion of 97.0% (Table 1, entry 6). This result demonstrates that Fe_3O_4@C-SO_3H efficiently catalyzes the synthesis of EMF by the etherification of HMF, and it showed the best catalytic activity among all the tested catalysts. As shown in Table 1, -SO_3H was the active catalytic species in Fe_3O_4@C-SO_3H, and homogeneous H_2SO_4, too, efficiently catalyzed the etherification of HMF to EMF: the yields of EMF and HMF conversions with Fe_3O_4@C-SO_3H and H_2SO_4 were close to each other (Table 1, entries 1 and 6). However, Fe_3O_4@C-SO_3H, unlike H_2SO_4, is insoluble in ethanol and, what is more important, the use of Fe_3O_4@C-SO_3H prevents inevitable loss of the catalyst in the separation process. In conclusion, Fe_3O_4@C-SO_3H not only showed the highest catalytic activity among all the tested catalysts, but also offered superior advantages in terms of catalyst recycling.

The effect of the catalyst amount in the dehydration of fructose and the etherification of HMF to EMF was studied (Fig. 6). Initially, in the dehydration of fructose step, fructose conversion increased when more catalyst was used. At a low catalyst amount of 10 mg, HMF was the main product (yield 40%), and the yield of EMF was only 21%. As seen in Fig. 6, the catalyst amount had a high effect on the conversion of HMF to EMF: the conversion increased with increasing amount of the solid acid catalyst. The yield of EMF also increased as the catalyst amount increased from 10 to 30 mg. As seen in Fig. 6, the yield of EMF reached a maximum of 64.2% when the amount of solid acid catalyst increased to 30 mg. However, the yield of EMF decreased to 53.9%, when the catalyst amount further increased to 40 mg. This result can be attributed to the fact that excess catalyst accelerated additional side reactions that converted EMF into ethyl levulinate and humins. Therefore, the amount of the Fe_3O_4@C-SO_3H catalyst, which ensures a high yield of EMF in the reaction in study, is 30 mg.

Besides fructose, such fructose-based disaccharide and polysaccharide as sucrose and inulin were also

Table 2. One-pot conversion of carbohydrates in ethanol–DMSO[a]

Entry no.	Substrate	Temperature, °C	Conversion, %	HMF yield, %	EMF yield, %
1	Fructose	80	97.9	29.5	47.9
2	Fructose	100	98.4	9.8	64.2
3	Fructose	120	98.5	7.3	50.4
4	Sucrose	100	100.0	5.2	31.2
5	Inulin	100	100.0	3.7	50.1

[a] Reaction conditions: substrate 1 mmol hexose unit; solvent 5 mL (ethanol 4.0 mL, DMSO 1.0 mL); catalyst 30 mg; time 10 h.

employed as the starting reactants for the synthesis of EMF. As seen in Table 2, no sucrose was detected after 10 h at 100°C. The yield of HMF was 5.2%, and the yield of EMF was 31.2% from sucrose after 10 h at 100°C (Table 2, entry 4). It was found that the yield of EMF from sucrose was lower than that from fructose [42]. One sucrose molecule comprises one fructose and one glucose molecule [43]. When glucose was used as the starting reactant to this reaction, the major product was ethyl glucoside. These results indicate that the one-pot synthesis of EMF from glucose is difficult, and only the fructose molecule in sucrose can be converted to HMF and EMF. Interestingly, a good yield of EMF (50.1%) was obtained from the inulin polysaccharide (Table 2, entry 5). These results show that the synthesized catalyst not only catalyze the dehydration and etherification reactions, but also the hydrolysis of inulin into fructose.

Finally, the stability and reusability of the Fe_3O_4@C-SO_3H catalyst was studied both in the etherification of HMF to EMF and one-pot synthesis of EMF from fructose under the conditions described in the experimental section. The spent Fe_3O_4@C-SO_3H catalyst could be readily separated from the reaction mixture by an external magnetic field and, after washing and drying, used in a subsequent run. In the recycling experiments with the one-pot synthesis of EMF from fructose, the yield of EMF was stable around 60% thought over six runs, providing further for the stability of the Fe_3O_4@C-SO_3H catalyst. Compared to centrifugation or filtration, the recovery of the used catalyst by an external magnetic field obviously allows one to avoid the loss of catalyst in the recycling experiments.

CONCLUSIONS

In summary, we have developed a novel magnetically-recoverable SO_3H-functionalized carbonaceous catalyst Fe_3O_4@C-SO_3H for the synthesis of the liquid biofuel EMF by one-pot conversion of fructose-based carbohydrates or conversion of HMF. The yield of EMF in the one-step conversion of fructose in an ethanol−DMSO solvent system was as high as 64.2%. The prepared catalyst also showed a remarkable catalytic activity for the conversion of HMF to EMF with a high yield of 85.6%. The Fe_3O_4@C-SO_3H catalyst could be readily recovered from the reaction mixture by an external magnetic field and reused several times without loss of its catalytic activity. Along with the synthesis EMF from HMF and fructose-based carbohydrates, the environmentally friendly catalyst Fe_3O_4@C-SO_3H has enormous potential for other acid-catalyzed reactions.

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