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Selective conversion of fructose into 5-ethoxymethylfurfural over green catalyst

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Abstract

In this study, selective formation of 5-ethoxymethylfurfural (EMF) from one-pot conversion of fructose in a co-solvent of ethanol with tetrahydrofuran over green SO_3H-CD carbon was investigated for the first time using an ultrasonic system. The maximum EMF yield of 74% with 100% fructose conversion was achieved in mild conditions. Moreover, the better selectivity and the longer recyclability (eight cycles) for EMF production via particular reactions such as fructose dehydration and etherification were obviously found while the formation of 5-hydroxymethylfurfual, ethyl levulinate or humins was inhibited using SO_3H-CD carbon, comparing to commercial catalysts such as Amberlyst-35, SiO_2-Tosic acid and Al_2O_3.

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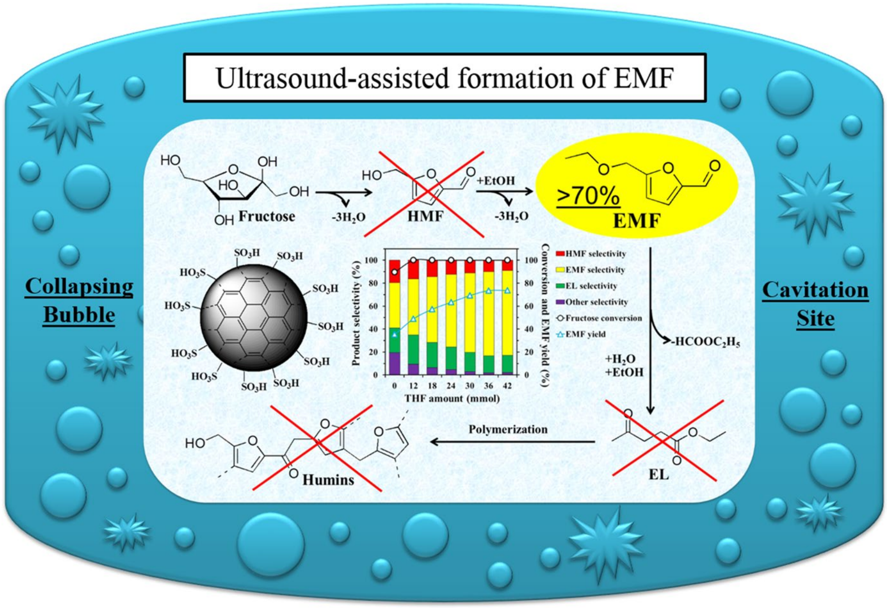
Graphical abstract



Keywords Fructose · 5-ethoxymethylfurfural · SO_3H-CD carbon · Selectivity · Recyclability

Introduction

In recent years, the conversion of carbohydrates into important chemical building blocks or petroleum-based industrial organic chemistry such as 5-ethoxymethylfurfural (EMF), levulinic acid, 5-hydroxymethylfurfual (HMF), ethyl levulinate (EL) and formic acid have attracted much attention since they can be easily found and obtained from biomass [1, 2]. Among of them, EMF is a strong potential chemical that can be applied as a blending/additive agent for diesel energy production [3]. Fructose has been substantiated as an effective feedstock for EMF production among all types of carbohydrates, which can be easily converted into HMF and EMF by homogeneous and heterogeneous Brönsted acid catalysts [4–7]. Yang et al. [8] reported that ~35% yield of EMF was obtained from fructose conversion using a commercial H_2SO_4 catalyst. Kraus et al. [9] found that by-products such as EL and humins were significantly suppressed while the yield of EMF was obviously increased by using SO_3H-functionalized ionic liquid. Moreover, some ionic liquids and Lewis acids such as 1-butyl-3-methylimidazolium and $AlCl_3$ are also identified as good catalysts for dehydration reaction [10, 11]. However, with their application in industrial process, several problems such as high corrosion to equipment, high toxicity to environmental and recycling difficulty always occur [12, 13]. From this point of view, heterogeneous acid catalysts can be considered since they are environmentally friendly [14]. To date, even many heterogeneous acid catalysts such as HPW/MCM-41 [15], SO_3H-polymeric material [16], and SO_3H-SBA-15 [17] are widely employed for EMF synthesis, but high production cost and long reaction time ($>$ 10 h), as well as two-step synthesis are still required. Therefore, it is necessary to develop the novel heterogeneous catalyst, which has lower cost, higher activity and better stability.

From this, we developed an SO_3H-CD carbon catalyst prepared through hydrothermal synthesis (in situ carbonization and sulfonation). Here, cyclodextrin (CD) consisting of an oligosaccharides structure (R-D-glucopyranose) was selected as a carbon source since formation of more polycyclic carbon was found, leading to the possibility of a high sulfonic amount functionalized on the carbon surface during carbonization-sulfonation [18]. The physical and chemical properties of the as-synthesized catalyst were investigated. Activity and selectivity of the catalyst were investigated on ultrasonic-assisted conversion from fructose into EMF in the co-existence of ethanol with tetrahydrofuran (THF) via various effects such as reaction time, reaction temperature, THF amount and catalyst amount. Moreover, the reusability of catalyst was also tested for eight cycles in optimum conditions, comparing to various commercial catalysts such as Amberlyst-35, SiO_2-Tosic acid and Al_2O_3. To the best of our knowledge, this research has not yet been reported in elsewhere. It is expected to provide highly effective catalyst and suitable system for EMF production with high yield and high selectivity.

Experimental

Catalyst synthesis

In situ hydrothermal carbonization and sulfonation were applied for the synthesis of SO_3H-CD carbon. In brief, a certain amount CD was dissolved into 40 mL of distilled water and vigorously stirred at 40 °C for 30 min. After homogeneous solution was obtained, 20 g of hydroxyethylsulfonic acid was then added and stirred for 1 h. Here, the weight ratio of hydroxyethylsulfonic acid to CD (4–1) was applied in this synthesis, which was obtained from our preliminary study based on highest acid amount on catalyst. The obtained solution was added into an autoclave (100 mL volume size) and heated at 180 °C for 4 h. Thereafter, the SO_3H-CD carbon (black precipitate) was filtered, washed several times with distilled water and ethanol to remove excess sulfate ions and finally dried in vacuum oven at 105 °C for 12 h.

Catalyst characterization

The X-ray diffraction (XRD) patterns were recorded on a Rigaku TTRAX III X-ray diffractometer using Cu Kα ($\lambda = 0.15418$ nm) radiation at 40 kV and 20 mA with a scanning range of 15°–75° at speed of 1°/min. N_2 sorption isotherm was obtained at

− 196 °C using Quantachrome Autosorb 1. Total surface area and pore size of catalyst were determined using the Brunauer–Emmett–Teller (BET) method and the Barrett–Joyner–Hallenda (BJH) method, respectively. The distribution of SO_3H group on catalyst, as well as morphology of carbon sphere were observed by a scanning electron microscope (SEM S-4800; Hitachi) equipped with a energy dispersive spectroscope (EDS). Total acid amount on the catalyst was determined using titration. Typically, 0.2 g of catalyst with an aqueous solution of NaOH (30 mL, 0.1 M) were mixed and stirred at ambient temperature for 1 h with a speed of 150 rpm. After centrifugal separation, the supernatant solution was titrated by an aqueous solution of HCl (0.01 M) using phenolphthalein as an indicator. Thermal decomposition of SO_3H group on catalyst was analyzed using a thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851).

Catalytic testing

The catalytic conversion of fructose into EMF was performed in a three-neck round bottom flask equipped with a reflux condenser and an ultrasonic probe, as well as a thermocouple thermometer. In each batch, the stirring speed and the frequency of the ultrasonic probe were fixed at 700 rpm and 20 kHz, respectively. A 0.5-mmol sample of fructose, 5 mL of ethanol, and required amount of THF and catalyst reactor was loaded into reactor. Then, the reaction was conducted at different temperatures and times in an oil bath. After finishing the reaction, the mixture product was cooled in an ice-bath, diluted and filtered with a 0.22 μm syringe filter. The separated spent catalyst was washed several times with distilled water and ethanol to remove the adsorbed by-products prior to reuse in the next run, and then dried at 105 °C for 12 h. The fructose and the formed products were analyzed by an Agilent 1200 HPLC chromatograph equipped with an Aminex HPX-87H column and refractive index detector. A 0.5-mM H_2SO_4 solution was used as the mobile phase at a flow rate of 0.6 mL/min and column temperature of 60 °C. The fructose conversion and yield and selectivity of each product were detemined based on external standard method and calculated using the following equations:

$$\text{Fructose conversion }(\%) = \frac{\text{Mole percentage of fructose reacted}}{\text{Mole percentage of initial fructose}}$$

$$\text{Product yield }(\%) = \frac{\text{Mole percentage of product produced}}{\text{Mole percentage of initial fructose}}$$

$$\text{Product selectivity }(\%) = \frac{\text{Mole percentage of product produced}}{\text{Mole percentage of fructose reacted}}$$

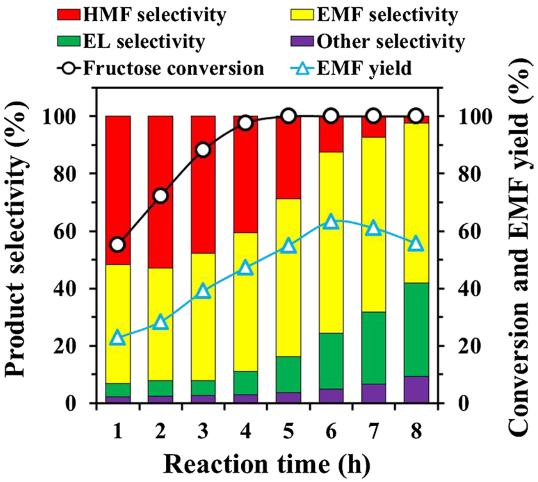


Fig. 1 Effect of reaction time (1–8 h) on EMF production derived from catalytic conversion of fructose over SO_3H-CD-carbon. Reaction conditions: 0.5 mmol of fructose, 24 mmol of THF, 5 mL of ethanol, 50 mg of catalyst and reaction temperature of 120 °C

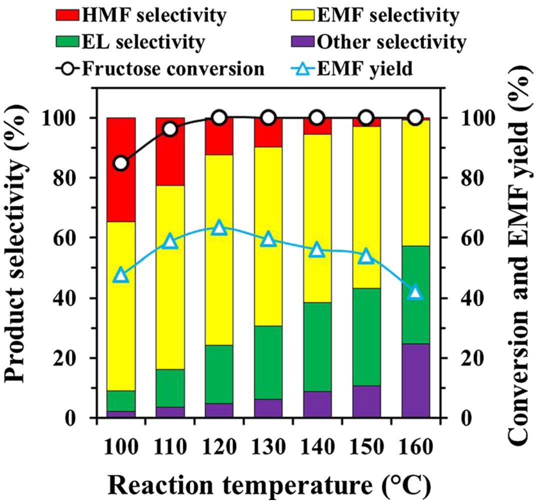


Fig. 2 Effect of reaction temperature (100–160 °C) on EMF production derived from catalytic conversion of fructose over SO_3H-CD-carbon. Reaction conditions: 0.5 mmol of fructose, 24 mmol of THF, 5 mL of ethanol, 50 mg of catalyst and reaction time of 6 h

Results and discussion

Catalytic conversion of fructose into EMF over SO_3H-CD carbon

Figures 1 and 2 show the effect of reaction time and reaction temperature on conversion of fructose in co-solvent using SO_3H-CD-carbon. As shown in Fig. 1, fructose conversion (100%) and EMF yield (63%) were achieved in 6 h via main consecutive reactions including the dehydration of fructose into HMF and etherification of HMF into EMF. However, yields of EMF were decreased to some extent with prolongation of reaction time beyond 6 h, suggesting that EMF was further converted into other undesired by-products such as EL and humins via ethanolysis-rehydration and polymerization as observing the EL and other products (humins or soluble polymers) selectivity increased [19, 20]. As indicated, these phenomena with similar trends were found with the result of reaction temperature (Fig. 2). Moreover, as shown in Fig. 2, the fructose was completely converted while best EMF selectivity was obtained at optimum reaction temperature of 120 °C. With the increase of reaction temperature from 120 to 160 °C, the EMF yield was continuously decreased to 42% even though the fructose conversion kept stable at 100%, indicating that too high of a temperature would cause the chain of side-reactions such as condensation, polymerization and decomposition, which could be clearly seen in the color change of liquid product from brown to black. In addition, this phenomenon might lead to the evaporation of ethanol from liquid phase, occurring the high viscosity in system with hindering the mass transfer of mixture. It should be mentioned here that SO_3H-CD-carbon was stable at reaction temperature range used in this study, which confirmed by TGA result in Fig. 3. As observed, the weight loss at temperature range of ~250 to ~500 °C was found, attributing to the decomposition of sulfonic group on catalyst [21]. The better selectivity for HMF production was found at short reaction time (~1 h) and low reaction temperature (~100 °C). The reaction route for synthesis of EMF and other products from fructose over acid catalyst are summarized in Fig. 4. Firstly, fructose was activated by Brönsted acid site of SO_3H-CD-carbon to form HMF with water. During this step, ethyl fructose might be possibly produced via ethanolysis and dehydration before HMF formation.Then, HMF would be activated by Brönsted acid sites and followed by an ethanol molecule to form EMF and water. Here, EL and humins always formed in several cases such as too long reaction time, too high reaction temperature and overloading the catalyst via several possible reaction pathways. For instance, epoxy groups of EMF were protonated with acid sites to form cyclic oxonium of EMF and followed by later encounters from the ring-opening reaction under a solution of ethanol and water to form EL, as well as polymerization of HMF, EMF and EL to from humins [22]. It is also possible that ultrasonic application may be related to the number of cavitation

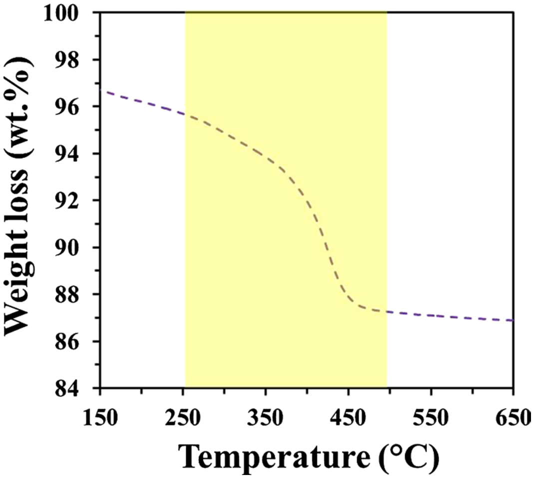


Fig. 3 TG curve of SO_3H-CD-carbon

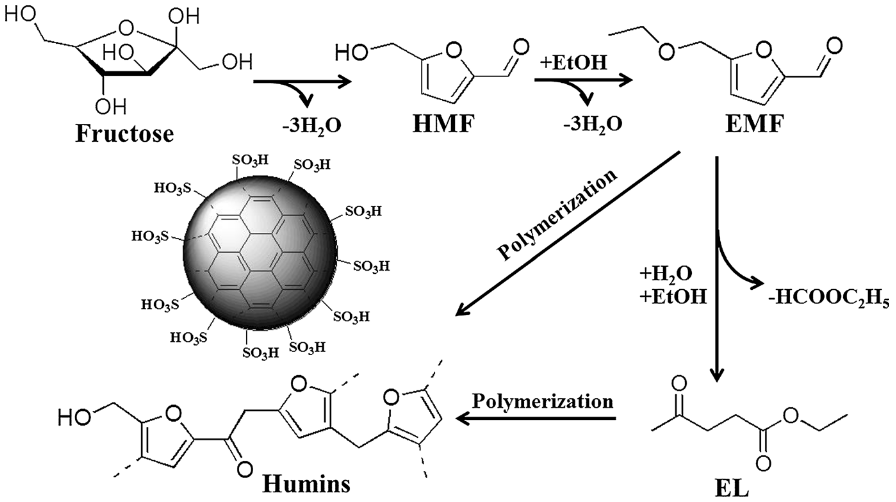
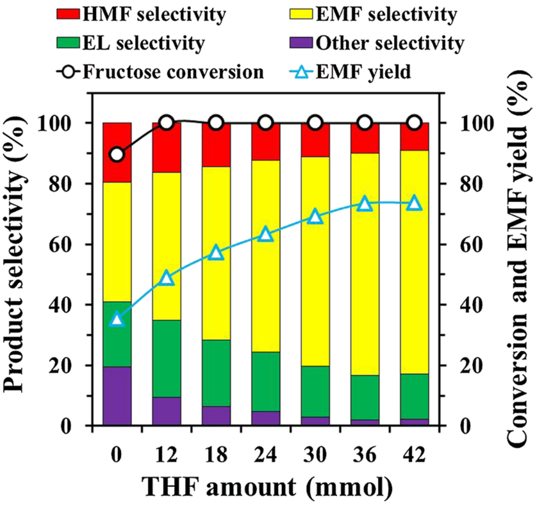


Fig. 4 Possible reaction pathways including dehydration, etherification, ethanolysis-rehydration and polymerization on conversion of carbohydrate into various products catalyzed by acid catalyst

bubbles formed in the medium, thus improving the EMF formation. Moreover, the energy generated due to cavitation is transferred to the reaction system, which could improve the process of interfacial area or mass transfer on the substrate towards a fast reaction rate.

The effect of THF amount on the conversion of fructose into EMF at 120 °C for 6 h is shown in Fig. 5. Interestingly, the increase of THF amount from 0 to 36 mmol resulted in promoting the formation of EMF while selectivity for EL and humins production was remarkably suppressed. The THF molecules could preferentially

Fig. 5 Effect of THF amount (0–42 mmol) on EMF production derived from catalytic conversion of fructose over SO_3H-CD-carbon. Reaction conditions: 0.5 mmol of fructose, 5 mL of ethanol, 50 mg of catalyst, reaction temperature of 120 °C and reaction time of 6 h



arrange themselves in the immediate vicinity of hydrogen atoms of the hydroxyl groups, enabling proton attack on fructose to initiate dehydration. The strong dehydration ability of THF due to its anhydrous nature might also shift the equilibrium to the product side and facilitate the water elimination from fructose. This might be also attributed to reduction of interaction between hydrophilic surface catalyst and EMF when more THF amount added in system, resulting in slowing the by-product formation [8, 16]. In other words, it limited the rehydration of EMF into EL. However, increasing the THF amount from 36 to 42 mmol did not significantly improve the EMF yield, indicating that optimum THF amount (36 mmol) and highest EMF yield (74%) were obtained. Figure 6 shows the effect of catalyst amount on conversion of fructose into EMF at 120 °C for 6 h. As expected, the EMF selectivity was obviously increased with increasing of catalyst amount up to 50 mg. However, a further increase in catalyst amount did not improve the EMF yield. This is attributed to the presence of an excessive amount of catalyst, which could lead to promoting the unexpected side-reactions, especially for ethanolysis-rehydration with the formation of other products as confirmed in EL and humins selectivity increase in Fig. 6. In addition, it presented the uneconomic process as well. The comparisons of one-pot synthesis of 5-ethoxymethylfurfural from fructose using SO_3H-CD-carbon with other literature are listed in Table 1. As expected and updated, the higher performance of our catalyst and system were clearly found. Here, the physical effects in terms of intense turbulence and microstreaming generated during the cavitation could play a dominating role in fructose conversion, resulting in faster reaction and higher EMF product when compared with the conventional system. This could provide a facile way for further development. The physicochemical properties of SO_3H-CD-carbon were also investigated since it exhibited high activity for EMF production in our system. Figure 7 shows the XRD patterns of catalysts. For pure CD-carbon and SO_3H-CD-carbon, two diffraction peaks at 15°–30° and 35°–50° appeared, corresponding to the presence of amorphous carbon composed

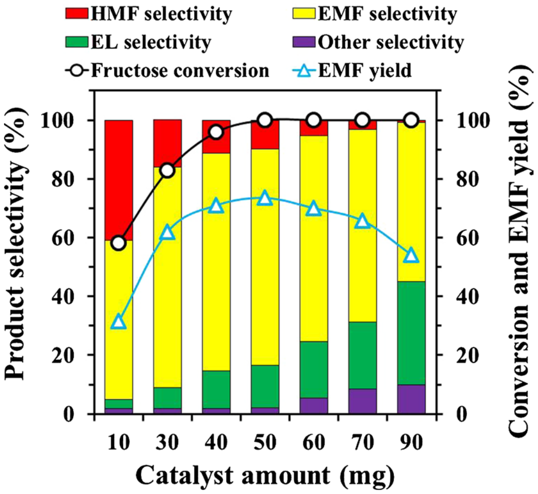


Fig. 6 Effect of catalyst amount (10–90 mg) on EMF production derived from catalytic conversion of fructose over SO_3H-CD-carbon. Reaction conditions: 0.5 mmol of fructose, 36 mmol of THF, 5 mL of ethanol, reaction temperature of 120 °C and reaction time of 6 h

Table 1 Comparison of maximum yield of EMF derived from fructose conversion using different catalysts

Catalysts	Conditions	EMF yield (%)	References
Imidazolium propanesulfonic acids	Reflux system: 130 °C for 80 min	55.0	[9]
$AlCl_3$	Reflux system: 100 °C for 11 g	71.2	[11]
MIL-101-SO_3H	Hydrothermal system: 130 °C for 15 h	67.7	[16]
Ar-SO_3H-SBA-15	ACE pressure glass system: 116 °C for 4 h	63.4	[17]
OMC-SO_3H	140 °C for 24 h	55.7	[26]
Fe_3O_4@C-SO_3H	Hydrothermal system: 140 °C for 24 h	67.8	[27]
SO_3H-CD-carbon	Ultrasonic system: 140 °C for 6 h	74.0	[This study]
SO_3H-CD-carbon	Reflux system: 140 °C for 24 h	39.5	[This study]

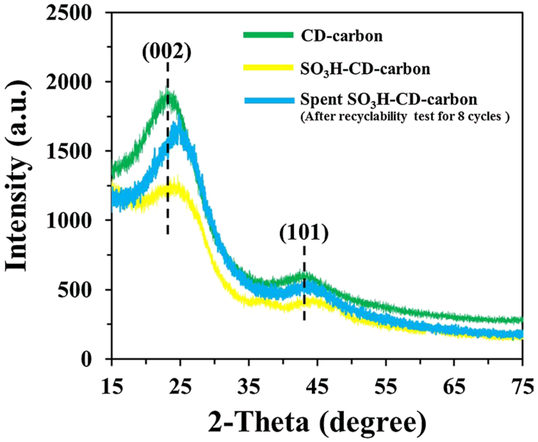


Fig. 7 XRD patterns of SO_3H-CD-carbon before and after reactions

of randomly oriented aromatic carbon sheets [23]. Moreover, the lower intensity of diffraction peak and the slight shifting of peak to higher 2θ angle were clearly found in SO_3H-CD-carbon when compared pure CD-carbon, suggesting to the functionalization of sulfonic groups on the sp^2 carbon network [24]. Figure 8 shows N_2 sorption isotherms of catalysts. All catalysts exhibited IUPAC type VI isotherms with hysteresis loops, corresponding to mesoporous carbon material [25, 26]. The SO_3H-CD-carbon also exhibited lower surface area, pore volume and pore size than CD-carbon, suggesting to the dispersion of sulfonic group on CD-carbon structure (Table 2). The existence of sulfonic group with its well distribution on CD-carbon

Fig. 8 N_2-sorption isotherms and pore-size distributions of SO_3H-CD-carbon before and after reactions

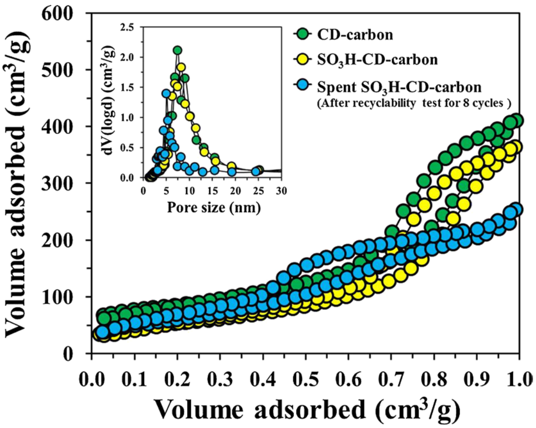


Table 2 Physicochemical properties of various catalysts before and after reactions

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	Acid amount (mmol/g)
CD-carbon	196	0.82	7.5	–
SO_3H-CD-carbon	162	0.68	6.9	1.82
Spent SO_3H-CD-carbon[a]	147	0.55	5.1	1.25
Amberlyst-35	50	0.39	30.0	5.20
Spent Amberlyst-35[a]	36	0.21	27.8	1.08
SiO_2-Tosic acid	279	0.54	9.7	0.80
Spent SiO_2-Tosic acid[e]	102	0.11	4.2	0.75
Al_2O_3	228	0.75	9.2	0.43
Spent Al_2O_3[a]	154	0.48	8.4	0.36

[a] Spent catalyst obtained after recyclability test for eight cycles

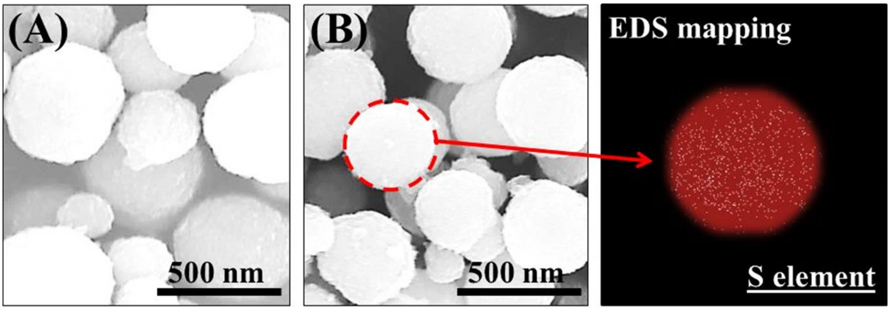


Fig. 9 SEM-EDS of **a** CD-carbon and **b** SO_3H-CD-carbon

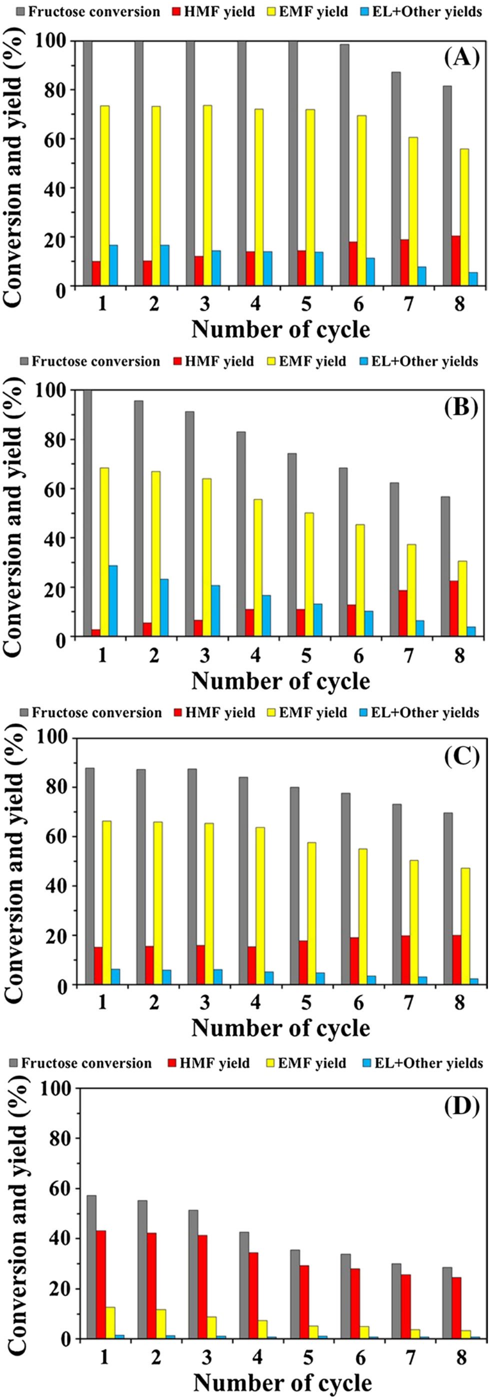
was clearly observed in SEM–EDS result (Fig. 9). Moreover, SO_3H-CD-carbon and pure CD-carbon also presented the same morphology of spherical shape.

Catalyst reusability and comparison between SO_3H-CD-carbon and commercial catalysts

The recycling of catalyst is an important parameter that can affect the overall EMF production process. After the optimum conditions were obtained from out system, the catalyst was reused for eight cycles on fructose conversion at 120 °C for 6 h. It should be mentioned here that a blank reaction test was also performed in this condition without using catalyst and the result found that no conversion of fructose into any products were occurred, indicating that the existence of acid catalyst was still necessary in this system. As shown in Fig. 10, no obvious reduction in catalytic performance based on EMF yield (~74%) was found over first to fifth reaction cycles. However, the slight decrease in EMF yield was observed since recycling test was carried out after fifth reaction cycle. This is attributed to leaching of the sulfonic group from the catalyst and the adsorption of humins by-product on catalyst surface which resulted in decrease of surface area and pore size of catalyst, as well as mass transfer of intermediates to inner of catalyst structure [27], confirming by the results of acid amount and textural properties of spent catalyst (Table 2). In other words, the ethanolysis-rehydration were initially suppressed. These result indicates that SO_3H-CD-carbon possessed excellent reusability and stability for five cycles.

Moreover, to evaluate the SO_3H-CD-carbon as a promising catalyst for further utilization in practical process, comparing its catalytic activity and reusability with various commercial solid acid catalysts was also investigated (Fig. 10). It is found that when Amberlyst-35, SiO_2-Tosic acid were applied for catalytic conversion of fructose, the highly obtained EMF yields were 69% and 66%, respectively. However, even Amberlyst-35 had higher acid amount than SO_3H-CD-carbon, but lower EMF yield still obtained, resulting from its excessive acid amount, promoting the formation of by-products. This is also believed that the interior layer of the SO_3H-CD-carbon sphere consisted of polyaromatic groups while the exterior layer consisted of hydrophilic groups such $-SO_3H$, phenolic –OH and –COOH groups, which could contribute to the mass transfer, as well as the synergetic effect, leading to better activity and stability [28, 29]. Furthermore, EMF yield was decreased to some extent after the first reaction cycle, suggesting that facile leaching of the sulfonic group in both catalysts, especially for Amberlyst-35, occurred while strong adsorption of hydrophilic oligomeric by-products was found as well, especially for SiO_2-Tosic acid, and these phenomena could be verified by physicochemical properties of fresh and spent commercial catalysts in Table 2. It should be mentioned here that the rapid deactivation of these commercial catalyst may be resulted from existence of highly hydrophilic properties, which favored to selectivity create an appropriate environment for water adsorption, leading to poor reusability. Thus, the regeneration process were further required for these spent commercial catalysts. In the case of Al_2O_3, a lowest yield of EMF (12.6%) was obtained, which might be explained by its low acid strength. However, better selectivity for HMF production

Fig. 10 Reusability of **a** SO_3H-CD-carbon, **b** Amberlyst-35, **c** SiO_2-Tosic acid and **d** Al_2O_3 on EMF production derived from catalytic conversion of fructose. Reaction conditions: 0.5 mmol of fructose, 36 mmol of THF, 5 mL of ethanol, 50 mg of catalyst, reaction temperature of 120 °C and reaction time of 6 h



was also found in Al_2O_3 when compared with other catalysts, probably due to only selective promoting of fructose dehydration in first step by Lewis acid site of Al_2O_3. Based on these results, SO_3H-CD-carbon could be considered as a promising catalyst for EMF production from one-pot conversion of fructose in practical process.

Conclusions

In summary, the fructose conversion into EMF catalyzed by SO_3H-CD-carbon was studied using an ultrasonic system. The SO_3H-CD-carbon also exhibited the reasonable properties such acid site concentration, surface area and pore size for selective production of EMF. The use of THF as co-solvent significantly resulted in suppressing the formation of EL and humins via EMF ethanolysis-rehydration and polymerization. The optimum conditions such as 0.5 mmol of fructose, 36 mmol of THF, 5 mL of ethanol, 50 mg of catalyst, reaction temperature of 120 °C and reaction time of 6 h were successfully achieved, providing a maximum EMF yield of 74%. The SO_3H-CD-carbon could be effectively reused for five cycles without reduction of EMF and regeneration.

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