Direct Conversion of Fructose To 5-Ethoxymethyl-furfural Catalyzed by Ultra Stable Y Zeolite

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5-Ethoxymethylfurfural (EMF) is a new type of biofuel with a high energy density and excellent fuel properties. One-pot production of EMF from renewable carbohydrate catalyzed by heterogeneous catalysts has the potential to be an attractive reaction pathway. In this study, fructose was directly converted to EMF in ethanol medium catalyzed by ultra stable Y zeolite (USY). The effects of different reaction conditions on EMF yields were investigated, and an optimum reaction condition was obtained by utilizing response surface methodology. Under the optimum reaction conditions, which were a temperature of 132 °C, substrate density of 60 g/L, and catalyst dosage of 2.1 wt%, a maximum EMF yield of 73.8 mol% with the prediction error of 1.6% was achieved in 25 min. Moreover, the reusability of USY and characterization were evaluated. This study demonstrated a promising strategy for EMF production from fructose.

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INTRODUCTION

With the depletion of fossil fuels and increasing attention on environmental pollution, the production of biofuels and value-added chemicals from biomass resources is becoming more attractive (Chang *et al*. 2012; Alam *et al*. 2018; Antonyraj and Haridas 2018). Among the various promising biofuels and value-added chemicals, 5-ethoxymethylfurfural (EMF) has been considered as a potential next-generation biofuel or fuel additive to replace petroleum. It not only has a high energy density of 8.7 kWhL^{-1}, which is comparable to that of gasoline (8.8 kWhL^{-1}) and diesel fuel (9.7 kWhL^{-1}), it also has the advantages of lower toxicity, good low-temperature fluidity, high boiling point (235 °C), and fine oxidation stability. Therefore, it has been evaluated and mixed with commercial diesel in engine tests, leading to promising results in terms of engine performance, and has been associated with a significant reduction of soot and SO*x* emissions. Apart from that, EMF also has been used as a flavor or aroma ingredient in wine or beer (Chang *et al*. 2018; Kong *et al*. 2018).

Recently, there has been remarkable interest in the synthesis of EMF from renewable carbohydrates (Deng *et al*. 2017; Chen *et al*. 2019a). Carbohydrates can be first converted into 5-hydroxymethyfurfural (HMF), then etherified to EMF (Gupta and Saha 2018). Although high EMF yields of 80 to 92 mol% can be obtained from HMF, the high cost of HMF and the challenge for the purification of HMF might limit the practicality of the two-step process (Wang *et al*. 2013a; Liu *et al*. 2014; Yuan *et al*. 2015). In comparison, direct conversion of carbohydrates into EMF is more attractive because only a simple one-pot process is needed without purification of intermediate products (Jia *et al*. 2013; Chen

et al. 2018; Chen *et al.* 2019b). Furthermore, different kinds of catalysts have been developed for the direct conversion process, such as homogenous acids, heterogeneous acids, and ionic liquid acids. High EMF yields can be obtained from carbohydrates catalyzed by homogenous acids (Liu *et al.* 2015; Zhao *et al.* 2015a; Li *et al.* 2018;). However, homogeneous catalytic systems have obvious drawbacks, such as difficult separation from products, waste generation, limited reusability, and equipment corrosion (Chang *et al.* 2015; Zhao *et al.* 2015b; An *et al.* 2017). To overcome such drawbacks, many heterogeneous catalysts, such as graphene oxide catalysts (Wang *et al.* 2013a), magnetic solid acids (Yin *et al.* 2015; Yao *et al.* 2016; Bai *et al.* 2018), heteropolyacids (Wang *et al.* 2013b), resins, metal and chlorides salts (Liu *et al.* 2013a; Wang *et al.* 2017; Xin *et al.* 2017; Guo *et al.* 2018; Yu *et al.* 2018; Yang *et al.* 2019), sulfonated functionalized solid acids (Liu *et al.* 2013b; Wang *et al.* 2017; Kumar and Srivastava 2019; Maneechakr and Karnjanakom 2019), and ionic liquid acids (Yadav *et al.* 2014; Guo *et al.* 2017) have been used in EMF production. However, more obstacles for heterogeneous catalysts still exist in the process, such as the complex preparation, high price, long reaction time, and the low substrate concentration. Thus, it is necessary to develop an economic and efficient catalyst and catalytic process.

Ultra-stable Y zeolite (USY) is a type of simple and easily available zeolite, which has been successfully used in industrial processes (Li *et al.* 2016). In the authors' previous studies, USY was efficiently used for the preparation of ethyl levulinate (EL) from carbohydrates (Xu *et al.* 2013, 2015). It is speculated that EMF as the precursor of EL, can also be generated by the catalysis of USY. Thus, the goal of this study was to investigate the conversion process of fructose into EMF with zeolite USY as the catalyst. The effects of reaction temperature, reaction time, substrate concentration, and catalyst dosage on the EMF yields were investigated, and the response surface method (RSM) was used to optimize the reaction conditions to maximize the EMF yield. Meanwhile, the reusability of USY was evaluated and characterized with the aid of X-ray powder diffraction (XRD), Fourier transform infrared (FTIR) characterization. The study gave insights into the effect of USY on the EMF synthesis, and provides a reference for the development of an economic and efficient catalytic process for EMF production.

EXPERIMENTAL

Materials

The EMF with a purity of over 99% was bought from Sigma-Aldrich (Shanghai, China). Ethyl levulinate (EL) with a purity of over 99% was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). The solid catalyst zeolite USY was procured from Nankai University Catalyst Co., Ltd. (Tianjin, China), and it was calcined for 4 h at 400 °C before use. Fructose was bought from Kermel Chemical Reagent Co., Ltd. (Tianjin, China), and ethanol was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents had analytical purity and were used without purification.

Methods

Catalytic reaction procedure

The experiments were performed in a 100-mL cylindrical pressurized stainless steel reactor with an electrical heating jacket and a magnetic stirrer. Typically, 40 mL ethanol solution, the certain amounts of catalyst, and fructose were added into the reactor. Then,

the reactor was heated to the set temperature with an initial stirring speed of 250 r min^{-1}. Timing began as the set temperature was reached, and the stirring speed was adjusted to 500 r min^{-1} at the same time. When the reaction time was reached, the reactor was immersed immediately in water to end the reaction. The reaction solution was filtered with a vacuum pump, and the filtrate was diluted with ethanol, centrifuging at 10,000 r min^{-1} for 30 min. The upper liquid and solid residues were collected for further analysis. In this study, RSM was applied to optimize the reaction conditions. A statistical analysis on the experimental data using Design Expert 7 software (Stat-Ease, Inc., Minneapolis, MN, USA) was performed.

Products analysis

The EMF and fructose were separated by an Aminex HPX-87H column (300 × 7.8 mm, 9 μm) at 65 °C, and the amounts were determined by a high-performance liquid chromatograph (HPLC, 1260; Agilent Technologies, Santa Clara, CA, USA) instrument equipped with a differential refractive index detector (G7162A). The mobile phase was 5 mmoL H_2SO_4 prepared with ultrapure water, and the flow rate was 0.6 mL min^{-1}. Moreover, the EL was separated by an HP-5MS capillary column (30 m × 0.32 mm × 0.50 μm) and analyzed by a gas chromatograph (GC, Trace 1300; Thermo Fisher Scientific, Shanghai, China) with a flame ionization detector. The starting temperature of the column was 60 °C. Then, it increased to 280 °C with a speed of 10 °C min^{-1} and was kept at 280 °C for 2 min. The flow rate of carrier gas (N_2) was maintained at 1.0 mLmin^{-1}, and the injector and detector temperatures were 240 and 250 °C, respectively. The conversion of fructose was calculated according to Eq. 1 and yields of EMF and EL were calculated using Eq. 2 and Eq. 3:

$$\text{Conversion of fructose (mol\%)} = \frac{Moles\ of\ residual\ fructose}{Moles\ of\ fructose\ in\ reaction} \times 100 \tag{1}$$

$$\text{Yield of EMF(mol\%)} = \frac{Moles\ of\ EMF\ formed}{Moles\ of\ fructose\ in\ reaction} \times 100 \tag{2}$$

$$\text{Yield of EL (mol\%)} = \frac{Moles\ of\ EL\ formed}{Moles\ of\ fructose\ in\ reaction} \times 100 \tag{3}$$

Catalyst characterization

The characterization of fresh and reused catalysts was analyzed by X-ray powder diffraction and Fourier transform infrared spectroscopy. The XRD patterns of the samples were performed using a BRUKER X-ray diffractometer (D8 Advance; Bruker, Germany) operated with a Cu Kα radiation source. Data was collected from 2θ between 4° and 60° with a step of 0.02° at a scanning speed of 3° min^{-1}. The FTIR spectra were conducted on a spectrometer (IR 960; Guangzhou Kexiao, Guangzhou, China) at a spectral resolution of 4 cm^{-1} in the wavenumber range of 500 to 4000 cm^{-1}.

RESULTS AND DISCUSSION

Effects of Reaction Conditions on EMF Production

The effects of different reaction parameters including fructose concentration, reaction time, reaction temperature, and USY dosage on the yields of EMF and EL were investigated. Figure 1a shows the effect of fructose concentration on the yields of EMF and

EL. The conversion of fructose was above 97.6% at different substrate concentrations. Meanwhile, the EMF yield increased from 56.7 mol% to 67.3 mol% as the fructose concentration increased from 20 g/L to 40 g/L. Nevertheless, further increase of fructose concentration resulted in a clear decrease of the EMF yield. Moreover, the EL yields were much lower than those of EMF, and the EL yield decreased slightly as the fructose concentration increased. These results indicated that the EMF formed from fructose was stable and only a small amount of EMF was converted to EL during the reaction process.
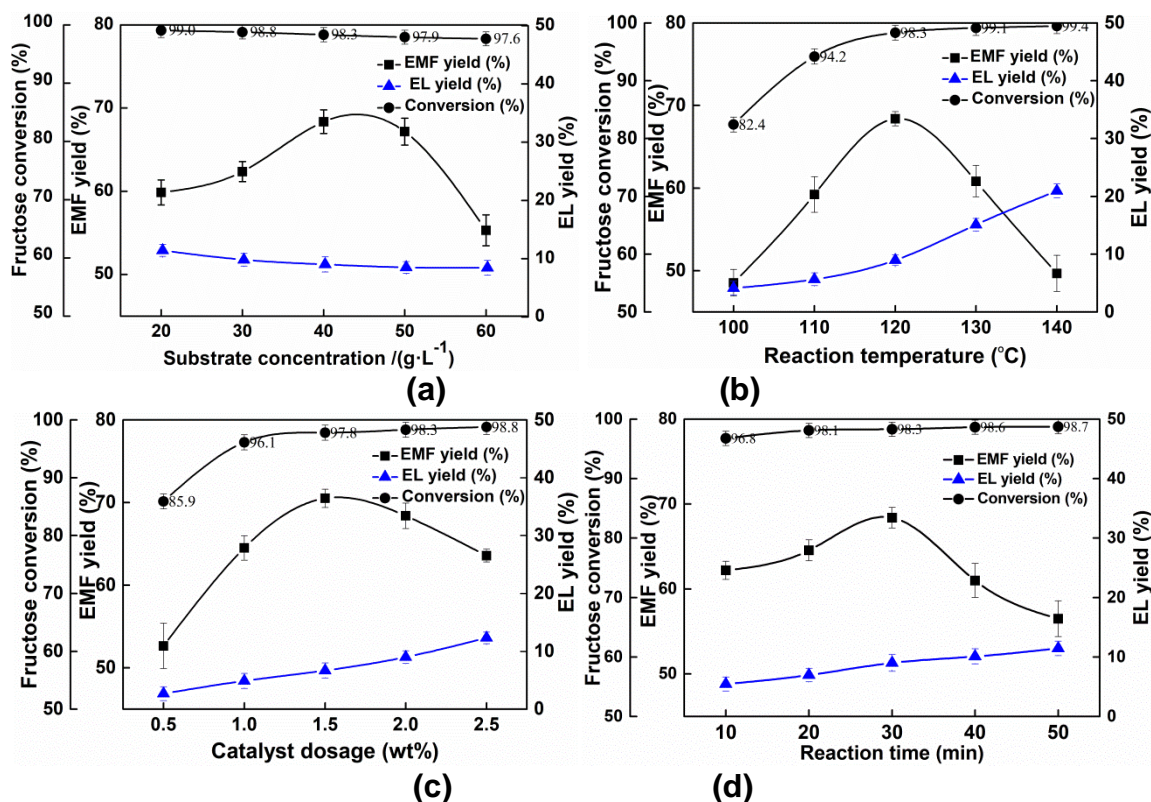

Fig. 1. Effects of different factors on EMF conversion from fructose in ethanol (reaction conditions: (a) 120 °C, 2.0 wt% USY, 30 min; (b) 2.0 wt% USY, 40 g/L fructose, 30 min; (c) 40 g/L fructose, 120 °C, 30 min; and (d) 120 °C, 2.0 wt% USY, 40 g/L fructose

The effect of reaction temperature on the conversion of fructose into EMF was investigated at the temperature range of 100 to 140 °C. As illustrated in Fig. 1b, the fructose conversion increased from 85.9% to 98.8% when the temperature increased from 100 °C to 140 °C, which implied that high temperature was beneficial for fructose conversion. When the reaction temperature was 100 °C, the EMF yield was less than 50 mol%. Moreover, the EMF yield increased with the increase of the reaction temperature, and the highest EMF yield of 67.3 mol% was obtained at 120 °C. Nevertheless, the EMF yield decreased as the reaction temperature exceeded 120 °C. In contrast, the EL yield increased as the reaction temperature increased, and it reached the maximum EL yield of 20 mol% at 140 °C. These results suggested that high temperature can enhance the EMF conversion into EL (Xu *et al*. 2015; Zhao *et al*. 2015a).

The effect of catalyst dosage on fructose conversion into EMF is shown in Fig.1c. Fructose conversion increased as the catalyst dosage increased. When the catalyst dosage increased to 1.5 wt%, a higher EMF yield of 70 mol% was achieved. However, more use

of the catalyst resulted in the decrease of the EMF yield and an increase in the EL yield. Meanwhile, the effect of reaction time on EMF formation is presented in Fig. 1d. The EMF yield rose first and then fell, and the maximum EMF yield was obtained at 30 min. With the prolonging of the reaction time, more EMF might be converted into EL, resulting in the decrease of the EMF yield.

Optimization of Reaction Conditions by RSM

Based on above results, RSM was further applied to optimize the reaction conditions. The reaction temperature, reaction time, substrate concentration, and catalyst dosage were chosen as the factors and the EMF yield was the response value. Design and data analysis of RSM experiments were calculated by Design Expert 8. Three levels of four factors are illustrated in Table 1, and the variables were coded according to Eq. 4,

$$x_i = (X_i - X_{i0}) / \Delta X_i \tag{4}$$

where x_i is the coded value, X_i is the actual value of the independent variables, X_{i0} is the actual value of the center point, and ΔX_i is the value of the step change.

Table 1. Factors and Levels of the RSM

Independent variable	Symbol		Levels		
	Uncoded	Coded	-1	0	1
Temperature (°C)	X_1	x_1	100	120	140
Time (min)	X_2	x_2	10	30	50
Substrate (g·L^{-1})	X_3	x_3	20	40	60
Catalyst dosage (wt%)	X_4	x_4	0.5	1.5	2.5

The statistical treatment and the test variables with the measured response values (Y), expressed as EMF yield, are shown in Table 2. The application of RSM yielded the quadratic Eq. 5, which represented the EMF yield as a function of reaction temperature, reaction time, substrate concentration, and catalyst dosage:

$$Y = 69.80 + 9.05x_1 + 2.83x_2 - 1.08x_3 + 7.15x_4 - 0.70x_1x_2$$
$$+ 11.98x_1x_3 - 9.57x_1x_4 + 5.37x_2x_3 - 6.55x_2x_4 + 9.48x_3x_4$$
$$- 15.49x_1^2 - 3.53x_2^2 - 3.70x_3^2 - 10.79x_4^2 \tag{5}$$

Table 2. Reaction Conditions for Direct Conversion of Fructose to EMF

Experiments	Temperature (°C)	Time (min)	Substrate (gL^{-1})	Catalyst Dosage (wt%)	EMF Yield Y (mol%)
1	100	30	60	1.5	33.3
2	120	50	60	1.5	64.6
3	120	30	60	2.5	66.4
4	140	10	40	1.5	70.7
5	100	50	40	1.5	54.5
6	120	30	60	0.5	39.9
7	120	30	40	1.5	72.5
8	140	30	60	1.5	72.0
9	140	30	20	1.5	45.3
10	120	30	40	1.5	71.5
11	120	50	40	2.5	62.3
12	120	30	40	1.5	68.0
13	120	10	20	1.5	67.7
14	140	50	40	1.5	57.5
15	120	30	40	1.5	69.5
16	100	30	40	0.5	15.0
17	100	30	40	2.5	53.3
18	100	30	20	1.5	54.5
19	120	30	20	0.5	65.4
20	120	50	20	1.5	56.5
21	120	10	40	2.5	66.2
22	120	30	20	2.5	54.0
23	140	30	40	2.5	49.3
24	140	30	40	0.5	49.3
25	100	10	40	1.5	24.9
26	120	50	40	0.5	59.2
27	120	10	60	1.5	54.3
28	120	30	40	1.5	67.5
29	120	10	40	0.5	36.9

A regression analysis was performed to determine whether there were significant relationships between the responses and the variables. The values of Student's t-test and P-values, which reflect the significance of coefficients, are listed in Table 3. The first-order main effect of reaction temperature (x_1) and catalyst dosage (x_2) were highly significant with P-values smaller than 0.0001. Likewise, both of the quadratic main effect of temperature (x_1^2) and catalyst dosage (x_4^2) were also highly significant (P < 0.0001), suggesting that the reaction temperature and catalyst dosage played crucial rules in the conversion of fructose into EMF. Moreover, some of the interaction coefficients (x_1x_2, x_1x_3, and x_1x_4) were found as significant terms with P-values of less than 0.001, indicating that the reaction temperature had a significant interactive effect with the other three factors. Meanwhile, the interactive effect of substrate concentration and catalyst dosage was also significant as was evident from its P-value (0.001). According to the F-values in Table 3, the effects of various factors on EMF yield can be determined as follows: the reaction temperature was as significant as catalyst dosage > reaction time > substrate concentration.

Table 3. Significance of Regression Coefficient for EMF Yield

Source	Sum of Squares	df	Mean Square	F-Value	P-value > F
Model	5726.89	14	409.06	19.72	< 0.0001
x_1	982.83	1	982.83	47.39	< 0.0001
x_2	95.77	1	95.77	4.62	0.0496
x_3	13.87	1	13.87	0.67	0.4272
x_4	613.47	1	613.47	29.58	< 0.0001
x_1x_2	457.96	1	457.96	22.08	0.0003
x_1x_3	573.60	1	573.60	27.66	0.0001
x_1x_4	366.72	1	366.72	17.68	0.0009
x_2x_3	115.56	1	115.56	5.57	0.0333
x_2x_4	171.61	1	171.61	8.27	0.0122
x_3x_4	359.10	1	359.10	17.31	0.0010
x_1^2	1556.70	1	1556.70	75.05	< 0.0001
x_2^2	80.79	1	80.79	3.90	0.0685
x_3^2	89.00	1	89.00	4.29	0.0573
x_4^2	755.42	1	755.42	36.42	< 0.0001

Df: degrees of freedom

The second-order model for EMF yield was also evaluated by analysis of variance (ANOVA) (Table 4). The ANOVA of quadratic regression model demonstrated that the model was highly significant with an evidential low probability value from the F-test ($P < 0.0001$). The model could fit the experimental results well, as the lack of fit test demonstrated no inadequacy in the model ($P > 0.05$). In addition, the regression coefficient $R^2 = 0.96$ indicated a close agreement between experimental and predicted values of the EMF yield (Fig. 2).

Table 4. ANOVA of RSM Regression Analysis

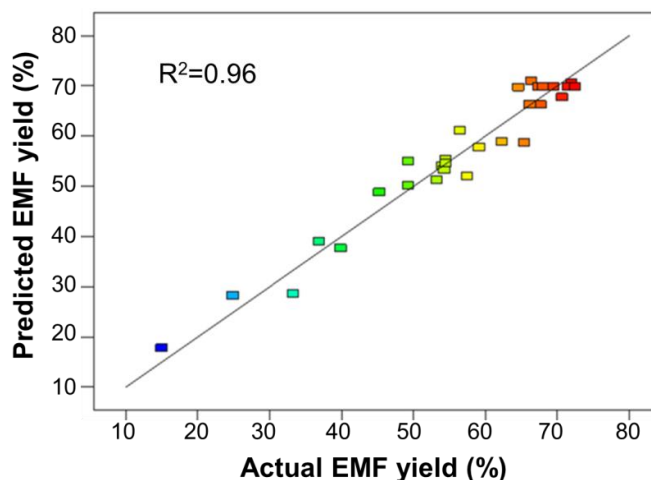| Source	Sum of Squares	df	Mean Square	F-Value	P-value > F
Model	5726.89	14	409.06	19.72	< 0.0001
Residual	290.37	14	20.74		
Lack of Fit	271.58	10	27.16	5.78	0.0528
Pure Error	18.80	4	4.70		
Cor Total	6017.26	28			
R^2	0.96				

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Fig. 2. Relationship between predicting values and experimental values

The 3D response surface plots are shown in Fig. 3 to explain the interaction of the variables. These graphs were drawn by imposing two other variables at their zero levels, which clarified both the main and interactive effects of these factors. When the reaction temperature was at a low level, the EMF yield increased with the increase of the reaction time. However, when the reaction temperature was higher, the EMF yield decreased with the prolonging of the reaction time (Fig. 3a).

Similarly, under the condition of high temperature, the EMF yield decreased as the catalyst dosage increased, suggesting that higher temperature was not beneficial to the EMF production (Fig. 3c). However, when substrate concentration was at a high level, increasing temperature improved the conversion of fructose into EMF (Fig. 3b). Therefore, the reaction temperature had a significant interactive effect on reaction time, catalyst dosage, and substrate concentration, which can be indicated by the surface confined in the smallest ellipse in the contour diagrams. Meanwhile, the low P-values (0.0003, 0.0001, and 0.0009) also confirmed this finding.

In addition, the catalyst dosage had a significant effect on the EMF yield, and the mutual interaction of catalyst dosage with other three variables is shown in Figs. 3c, 3e, and 3f. It can be seen from Fig. 3e that when the catalyst dosage was at a low level, the reaction time had little effect on the EMF yield. However, when the catalyst dosage was at a high level, the EMF yield increased first and then decreased with the increase of the reaction time. Moreover, as shown in Fig. 3f, when a low substrate concentration was used, a higher EMF yield was obtained with low catalyst dosage. Higher catalyst dosages can result in the decrease of EMF yield. The effects of reaction time on the EMF yield are shown in Figs. 3a, 3d, and 3e. Under most reaction conditions, the EMF yield first increased and then decreased with the increase of the reaction time, indicating that there was a suitable reaction time for the conversion process.
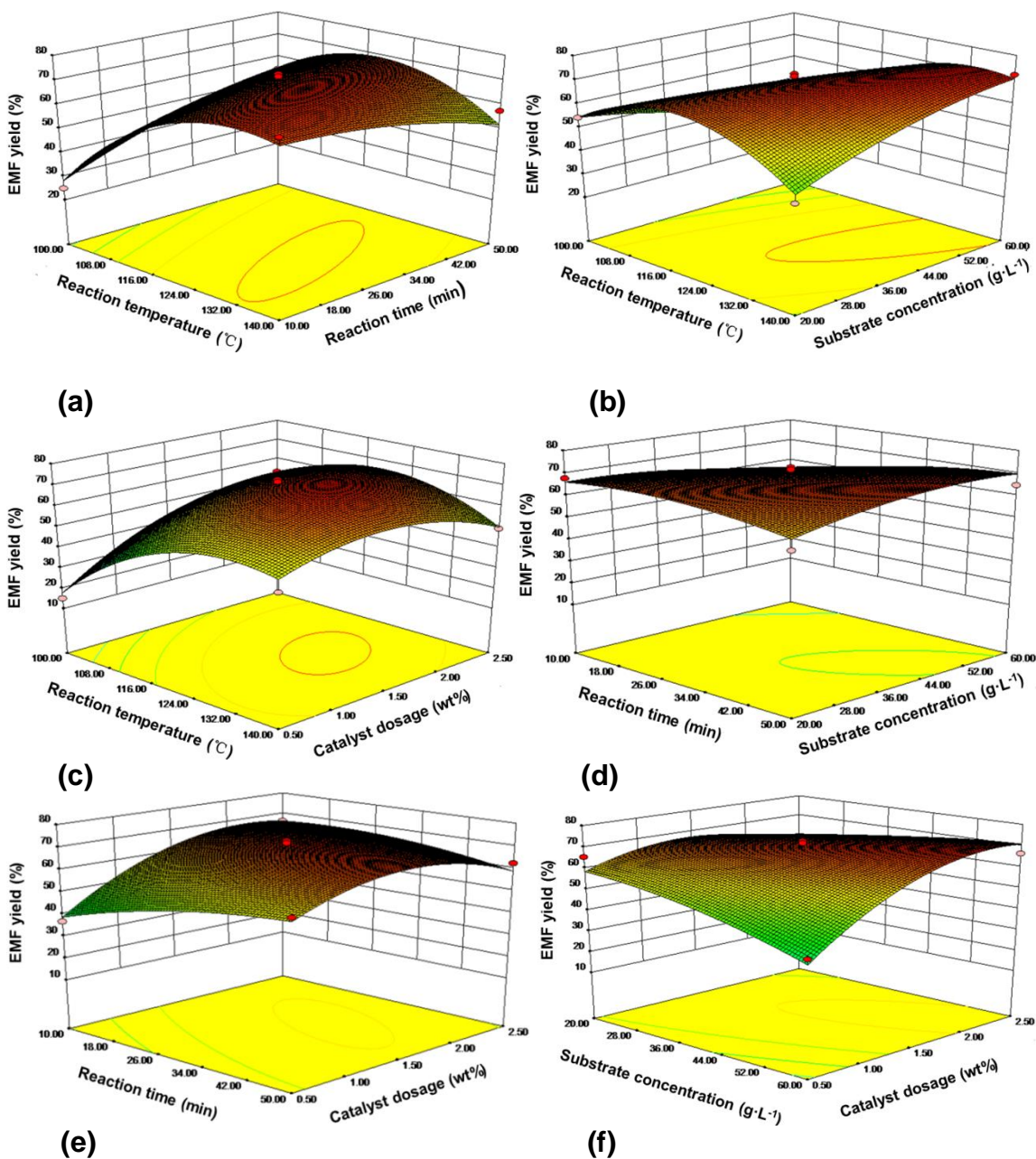
Fig. 3. 3D plots of EMF yield *versus* different variables

To optimize the reaction conditions in the RSM approach, a desirability function was implemented. The optimum conditions for the EMF yield were reaction temperature of 131.9 °C, reaction time of 24.5 min, substrate concentration of 60 g/L, and catalyst dosage of 2.1 wt%. Under the optimum reaction conditions, the predicted EMF yield was 75.0 mol%. To confirm the results, three verification experiments were performed under the reaction conditions of reaction temperature of 132 °C, reaction time of 25 min, substrate concentration 60 g/L, and catalyst dosage of 2.1 wt%, and the corresponding EMF yields were 72.2 mol%, 74.3 mol%, and 74.8 mol%, respectively. Thus, a mean yield of EMF of 73.8 mol% was obtained, which was close to the predicted value. Meanwhile, 12.3 mol% EL yield and 99.5% fructose conversion were obtained.

Reusability of USY

To test recycling properties of USY, the used USY was separated by filtration and washed with deionized water, then calcined at 400 °C for 4 h. The recovered USY was employed again for the catalytic tests. As shown in Fig. 4, the initial EMF yield was 73.8 mol%, and the EMF yield decreased slowly with the increase of cycles. After five cycles, the EMF yield decreased to 44.0 mol%, likely due to the reduction of the catalyst recovery and the carbon deposit (Chang *et al*. 2015). The gradual darkening of the recovered USY also confirmed the finding (Fig. 5). Further research is needed to reduce carbon deposition and improve the reusability of USY.
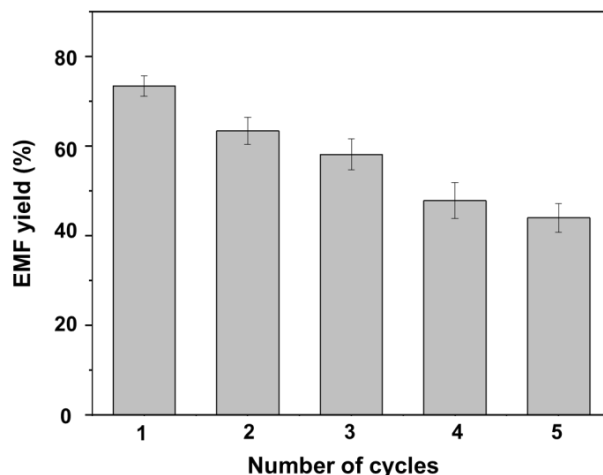

Fig. 4. Reusability of catalyst; reaction conditions: 60 g/L fructose, 132 °C, 25 min, catalyst dosage 2.1 wt%

Fig. 5. The change of color of USY

Fresh USY and reused USY were further characterized by FTIR and XRD to evaluate the structural changes of the USY. As shown in Fig. 6a, the FTIR spectra of USY showed typical peaks around 3431 cm^{-1}, which was the characteristic peak of hydroxyl vibration. The characteristic peaks at 1051 cm^{-1}, 816 cm^{-1}, and 457 cm^{-1} can be observed as the bands of Si-O bonds, which indicated that the Si/Al ratio of reused zeolite USY were

similar to that of the fresh USY. In addition, the XRD patterns of the USY are illustrated in Fig. 6b. The typical peaks around 2θ angles of 6.24°, 10.18°, 11.96°, 15.74°, 18.79°, 20.48°, 23.78°, 27.21°, and 31.6° can be observed after five recycles, which signified that the structure of the reused catalyst was still maintained well.
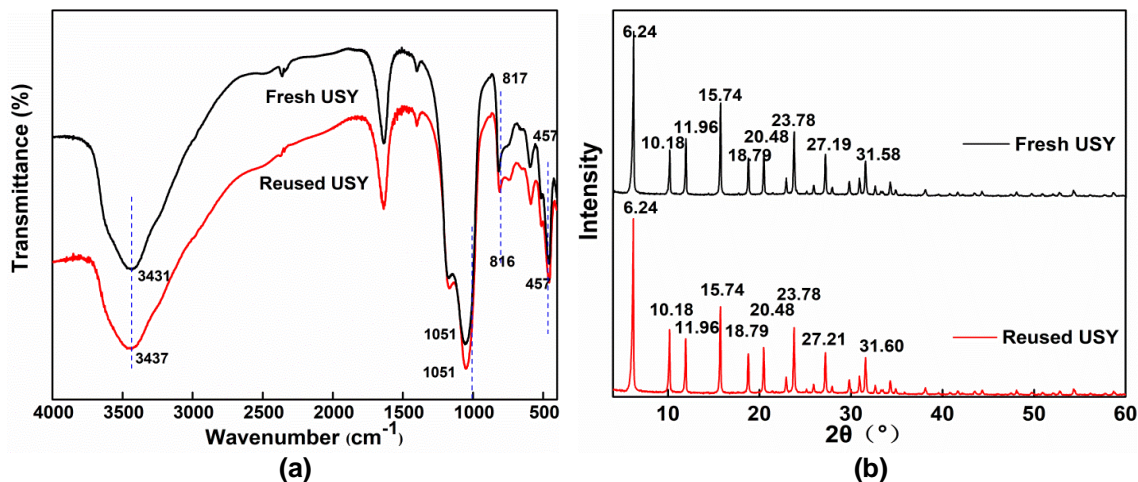

Fig. 6. FTIR spectra (a) and XRD (b) pattern of fresh and reused catalyst; reaction conditions: 60 g/L fructose, 132 °C, 25 min, catalyst dosage 2.1 wt%

Comparison with Previous Studies

The comparison of this study with recently published reports on the EMF yields from fructose catalyzed by different solid catalysts is summarized in Table 5. More than 10 h were needed to achieve a higher EMF yield for most studies. As shown in Table 5, the reaction time of 12 h was required to achieve the highest EMF yield of 77.3 mol% catalyzed by Amberlyst-15 (Zuo *et al*. 2018). Such a long reaction time may result in the increase of the production cost and energy consumption. In comparison, a higher EMF yield of 73.8 mol% was obtained in 25 min in this study, indicating that the reaction process had higher efficiency. These results suggested that zeolite USY can be used as an efficient solid catalyst for direct conversion of fructose into EMF.

Table 5. Comparison with Previous Studies

Fructose (gL^{-1})	Catalyst	Reaction Conditions	EMF Yield (mol%)	Reference
30	Sulfonated organocatalyst	140 °C, 18 h	68.8	Dai *et al.* (2019)
30	Amberlyst-15	100 °C, 12 h	77.3	Zuo *et al.* (2018)
36	OMC-SO$_3$H	140 °C, 24 h	55.7	Wang *et al.* (2017)
36	MIL-101-SO$_3$H(100)	130 °C, 15 h	67.7	Liu *et al.* (2016)
90	AlCl$_3$·6H$_2$O/BF$_3$·(Et)$_2$O	110 °C, 3 h	55.0	Jia *et al.* (2013)
36	AlCl$_3$	100 °C, 11 h	71.2	Liu *et al.* (2013a)
50	Cellulose sulfuric acid	100 °C, 12 h	72.5	Liu *et al.* (2013b)
60	Zeolite USY	120 °C, 25 min	73.8	This study

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CONCLUSIONS

1. EMF can be efficiently produced from fructose catalyzed by zeolite USY with short reaction time and high fructose concentration.

2. Under the optimum reaction conditions of a reaction temperature of 132 °C, fructose concentration of 60 g/L, USY dosage of 2.1 wt%, and reaction time of 25 min, a maximum EMF yield of 73.8 mol% can be obtained.

3. The recycling test showed the structure of USY was kept stable after repeated runs.

ACKNOWLEDGMENTS

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