Efficient synthesis of 5-ethoxymethylfurfural from biomass-derived 5-hydroxymethylfurfural over sulfonated organic polymer catalyst

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Herein, we investigated catalytic potential of a functionalized porous organic polymer bearing sulfonic acid groups (PDVTA-SO₃H) to the etherification of 5-hydroxymethylfurfural (HMF) to 5-ethoxymethylfurfural (EMF) under solvent-free conditions. The PDVTA-SO₃H material was synthesized via post-synthetic sulfonation of the porous co-polymer poly-divinylbenzene-co-triallylamine by chlorosulfonic acid. The physicochemical properties of the PDVTA-SO₃H were characterized by FT-IR, SEM, TG-DTG, and N₂ adsorption isotherm techniques. PDVTA-SO₃H had high specific surface area (591 m² g⁻¹) and high density of −SO₃H group (2.1 mmol g⁻¹). The reaction conditions were optimized via Box–Behnken response surface methodology. Under the optimized conditions, the PDVTA-SO₃H catalyst exhibited efficient catalytic activity with 99.8% HMF conversion and 87.5% EMF yield within 30 min at 110 °C. The used PDVTA-SO₃H catalyst was readily recovered by filtration and remained active in recycle runs.

1. Introduction

With the inevitable depletion of non-renewable energy sources such as fossil fuels, as well as the increasing demand for energy, the development and utilization of green and renewable new energy sources has become urgent. Abundant renewable biomass is a green and environmentally friendly energy source that is a key alternative to fossil energy sources such as petroleum and coal for the production of chemicals and liquid fuels. In the past several decades, significant effort has been devoted to synthesizing various valuable chemicals from biomass. 5-Hydroxymethylfurfural (HMF) is an important biomass-derived platform chemical and a valuable precursor for the synthesis of biofuels and value-added chemicals. Because of its good solubility and reactivity, HMF can be further transformed into products such as 2,5-furandicarboxylic acid, 2,5-dimethylfuran, γ-valerolactone, and n-butyl levulinate.

An etherified product of HMF, 5-ethoxymethylfurfural (EMF), has been identified as a potential next-generation biodiesel candidate to improve and replace current petroleum-based fuels because of its high miscibility in diesel fuel. Its high energy density (8.7 kW h L⁻¹) is comparable with that of standard gasoline (8.8 kW h L⁻¹) and diesel fuel (9.7 kW h L⁻¹), and is significantly higher than that of the well-known biofuel bioethanol (6.1 kW h L⁻¹). The use of EMF also decreases the release of contaminants such as soot, SOₓ, and NOₓ in engine tests when compared with the use of traditional transportation fuels. Furthermore, ethyl levulinate (EL), a by-product formed during the EMF production process, also has significant biodiesel characteristics. Therefore, the synthesis of EMF from biomass-derived feedstock represents a promising strategy for the effective utilization of renewable biomass resources for biofuels.

Several catalytic routes have been developed to date for the synthesis of EMF from carbohydrates or biomass. For example, Wang et al. reported that a 55.7% yield of EMF was obtained from fructose with sulfonic acid functionalized ordered mesoporous carbon (OMC-SO₃H) as a catalyst after 24 h at 140 °C. Dai et al. employed a double-hydrogen-bonded sulfonated polymer catalyst (D-SPC) at 140 °C, and EMF was obtained from fructose in a 68.8% yield within 18 h. Other catalysts such as deep eutectic solvents, [BMIM][HSO₄], and Ar-SO₃H-SBA-15 have also been studied for the synthesis of EMF from hexose. While converting hexose to EMF has the advantage of being a low cost, one-pot process, direct synthesis of EMF from carbohydrates still has some disadvantages, such as a long reaction time, high catalyst loading, and low EMF yield. The selective synthesis of EMF from HMF is a feasible approach for overcoming those disadvantages because it provides a shorter reaction time, lower catalyst loading, high selectivity, and solvent-free reaction conditions.

An acid catalyst is the key parameter for the conversion of biomass to EMF or other platform compounds. Catalysts are generally divided into homogeneous catalysts and heterogeneous catalysts. Homogeneous acid catalysts such as H₂SO₄, HCl, and H₂PO₄...
and benzenesulfonic acid, which have high catalytic activity, have traditionally been used to catalyse the conversion of biomass to EMF. However, homogeneous acid catalysts suffer from serious drawbacks such as difficulty in separating the catalyst from the reaction mixture and poor catalyst recycling, as well as equipment corrosion. Heterogeneous catalysts can overcome these disadvantages to a certain extent. They are typically separable, recyclable, more thermally stable, and less corrosive to equipment. Heterogeneous catalysts have been widely used in the conversion of carbohydrates, especially in esterification and etherification reactions, because of their Brønsted acidity and high proton mobility, as well as their ability to accept and release electrons.

Sulfonic acid (SO₃H) functionalized materials have generally been found to be efficient solid acid catalysts for the synthesis of EMF. For example, Amberlyst-15, a strongly acidic sulfonated ion-exchange resin which has been employed for EMF production, shows remarkably high catalytic performance, but these commercial resins are costly and have low thermal stability owing to their fragile organic framework. Sulfonated carbonaceous-based materials with relatively high thermal stability, including sulfonated organic polymer and biomass-derived amorphous carbon, are more eco-friendly and cost effective. Sulfonic acid catalysts, such as magnetic cellulose-derived carbonaceous solid acid (MCC-SO₃H), S-PANI-FeVO₄, and PU-Cat, are a novel class of solid acid catalysts that have been widely used in the synthesis of EMF in recent years. However, a common problem with these sulfonic acid solids is their low surface area. SO₃H groups in bulk amorphous carbon may not be accessed by the reactants, leading to low catalytic activity. These materials are characterized by high surface area, large uniform pores, high thermal stability, and the capability to control the surface hydrophilic/hydrophobic balance as well as the strength and concentration of acid sites, and therefore are promising catalysts for acid-catalysed reactions such as the synthesis of EMF. More broadly, solid acids with SO₃H acid sites and tuneable surface properties appear to have a large potential for the valorisation of biomass.

A sulfonic acid functionalized organic porous polymer (PDVTA-SO₃H) was prepared and applied for the etherification of HMF to EMF. The effects of reaction time, reaction temperature, and catalyst amount on the yield of EMF were investigated first, and the reaction conditions were further optimised by response surface methodology (RSM). The reusability of PDVTA-SO₃H was also evaluated. The results demonstrate that the PDVTA-SO₃H catalysts have great potential for the efficient synthesis of the renewable liquid-fuel EMF.

2. Experimental section

2.1. Materials

HMF (97%), EL (99%), and divinylbenzene (DVB, monomer) were purchased from Shanghai Macklin Biochemical Co., Ltd. EMF (97%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Triallylamine (TAA, monomer), azobisisobutyronitrile (AIBN, radical initiator), and chlorosulfonic acid were obtained from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of the catalyst

2.2.1. Synthesis of PDVTA. PDVTA was prepared by solvothermal co-polymerization of DVB and TAA according to a known method. In a typical synthesis, 4.28 mL DVB (24 mmol) and 1.05 mL TAA (6 mmol) were added to a 100 mL round-bottom flask, then 50 mL dry acetone was added and the mixture stirred for 30 min under a nitrogen atmosphere. Subsequently, 0.1 g AIBN (0.6 mmol) as a radical polymerization initiator was added to the mixture. The mixture was stirred for 12 h at 40 °C under a nitrogen atmosphere before being autoclaved at 120 °C for 24 h without stirring. The obtained solid was soaked and washed thoroughly with acetone to remove residual chemicals and impurities. The product was dried at 60 °C under vacuum to afford a white powder.

2.2.2. Synthesis of PDVTA-SO₃H. Functionalized PDVTA materials were obtained by a sulfonation process. PDVTA powder (1 g) and 40 mL anhydrous dichloromethane were mixed in a 100 mL three-necked round-bottom flask. The flask was immersed in an ice-water bath and the mixture was continuously stirred at 500 rpm for the duration of the reaction. After dispersing evenly, a mixture of 5 mL chlorosulfonic acid and 10 mL anhydrous dichloromethane was then added slowly and the reaction stirred for 4 h under a nitrogen atmosphere. Ethanol was then slowly added dropwise to the violet slurry until there were no bubbles. Finally, the sulfonic acid functionalized catalyst was filtered, washed several times with ethanol, and vacuum dried at 60 °C overnight.

2.3. Catalyst characterization

FT-IR spectra were obtained on a Thermo Nicolet infrared spectrophotometer using a KBr pellet. Thermogravimetric and differential thermogravimetric (TG/DTG) curves were recorded on a TGA4000-FTIR Frontier Analyzer (Perkin Elmer) with a heating rate of 10 °C min⁻¹ from room temperature to 800 °C under a nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific K-Alpha spectrometer with a monochromatized AlKα source (1486.6 eV) at a constant analyzer pass energy of 12 eV and 6 mA. Nitrogen sorption isotherms were measured with an ASAP 2400 apparatus (Micromeritics, USA). The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation, pore volumes were calculated using the t-plot method, and pore sizes were calculated using the Brunauer–Joyner–Halenda (BJH) method based on the adsorption branch of the isotherms. The morphologies of the samples were investigated by SEM (Carl Zeiss Sigma-HD, Germany). The catalysts were coated with gold before SEM observations.

2.4. Acidity titration

The amount of H⁺ in the PDVTA-SO₃H was determined by acid-base titration with a standardised aq. NaOH solution using phenolphthalein as the indicator. Unlike acidity determination for a common inorganic acid, PDVTA-SO₃H was not dissolved in water. For this analysis, 0.1 g of previously dried PDVTA-SO₃H was stirred in 50 mL of saturated NaCl solution at room
temperature for 24 h whereupon the $\text{H}^+$ was completely released into the solution by exchange with $\text{Na}^+$. The released $\text{H}_3\text{O}^+$ was then titrated by a standardised $\text{NaOH}$ solution. The titration was stopped when the colourless liquid immediately turned to light red. The amount of $\text{H}_3\text{O}^+$ was equal to the amount of consumed $\text{NaOH}$.

2.5. Synthesis of EMF from HMF

Etherification of EMF from HMF was conducted in a stainless-steel autoclave with a Teflon lining at autogenous pressure. HMF (126 mg, 1.0 mmol), ethanol (5 mL), and a specified amount of catalyst were added to a 50 mL autoclave reactor. The mixture was magnetically stirred at 300 rpm. The reactor was heated to a specified temperature. After the desired reaction time, the reactor was cooled in an ice-water bath to terminate the reaction, and small aliquots withdrawn from it were passed through a 0.2 $\mu$m pore polytetrafluoroethylene membrane (Millipore) filter for GC analysis.

Analysis of EMF and HMF was conducted on a gas chromatograph (Nexis GC-2030) fitted with a capillary column (30 m, 0.25 mm inner diameter, 0.25 $\mu$m film thickness), employing a hydrogen carrier gas and a flame ionization detector. The GC parameters were: injection volume 1.0 $\mu$L, split ratio 1 : 40, injection port and detector temperatures, 250 °C. The temperature program was set as 100 °C for 1 min, 100−120 °C (10 °C min$^{-1}$), 120−180 °C (20 °C min$^{-1}$), 180 °C for 2 min. The chemical species were identified by matching the retention times to known standards.

3. Results and discussion

3.1. Characterization of the catalyst

The chemical structures of PDVTA and PDVTA-SO$_3$H were characterized by FT-IR analysis (Fig. 1). Both spectra show bands at 1630 and 1508 cm$^{-1}$ that could be assigned to the C=C stretching vibration, while the absorbance at 2923 cm$^{-1}$ was attributed to the aromatic C−H stretching vibration.
For the S 2p XPS peaks of PDVTA-SO3H sample, the peaks to 402.0 eV can be also attributed to the added of stretching vibration, demonstrating that the SO3H groups were the full surface survey of PDVTA-SO3H, in which the single O X-ray photoelectron spectroscopy (XPS). Fig. 2a demonstrates that changes the original electronic environment of graphitic N. A

\[ \text{In addition, the observed O 1s spectra showing strong peak at } 532.5 \text{ eV, 402.0 eV, 284.5 eV and 170.2 eV respectively. As seen from Fig. 2b, the peak centered at 400.0 } \text{eV is typically assigned to C–N of graphitic N. After sulfonation, the shift of N 1s XPS peaks to 402.0 eV can be also attributed to the added of } -\text{SO3H that changes the original electronic environment of graphitic N. In addition, the observed O 1s spectra showing strong peak at 532.5 eV could be ascribed to O–S in the sulfonic group (Fig. 2c). For the S 2p XPS peaks of PDVTA-SO3H sample, the peaks centered at 168.9 and 170.2 eV were ascribable to graft–SO3H groups (Fig. 2d). The above results further confirmed that –SO3H groups were firmly bonded to the polymer framework. These results indicated that this PDVTA materials were successfully functionalized with –SO3H groups.}

The porosity and surface characteristics of the as-prepared PDVTA and PDVTA-SO3H were derived from N2 adsorption–desorption isotherms, and the profiles are presented in Fig. 3. Both PDVTA and PDVTA-SO3H displayed typical IV-type N2 sorption isotherms with a significant hysteresis loop in a wide range of relative pressure (0.45< P/P0 <0.95), demonstrating their meso porosities. Moreover, a large amount of nitrogen uptake was observed in the low-pressure region (below 0.1 bar). This suggests the existence of appreciable amounts of interparticle micropore voids in these organic polymers. Pore size distribution curves were obtained by the BJH method, taking adsorption branches into account (Fig. 4). The materials have considerable microporosity, which is primarily distributed at 0.73 nm. This is a unique property of these materials, and may have a positive impact on the catalytic activity. As listed in Table 1, the parent PDVTA material possessed a high BET surface area and pore volume of 774 m2 g−1 and 0.54 cm3 g−1, respectively. PDVTA-SO3H exhibits similar adsorption behaviour to PDVTA, including a BET surface area of 591 m2 g−1 and a pore volume of 0.41 cm3 g−1. Obviously, PDVTA-SO3H has decreased surface area, pore volume, and average pore diameter, indicating the modified functional groups exist in the pores, which is in good agreement with the pore size distribution.

The thermal stability of PDVTA and PDVTA-SO3H were investigated by TG/DTG analysis, and the results are shown in Fig. 5. The weight loss detected below 100 °C was attributed to the removal of adsorbed water and volatile components. From approximately 200–300 °C, the weight loss could be ascribed to desorption of decomposed sulfonic acid groups. The sharp peaks occurring at 430 and 450 °C were attributed to the successive destruction of the PDVTA and PDVTA-SO3H polymer framework, respectively, indicating the thermal stability of the carbon materials slightly increases after acid treatment. Additional weight loss at 650 °C signified the thorough decomposition of the benzene ring building block. The as-prepared PDVTA-based solid acidic catalyst had reliable thermal

Table 1 Physicochemical properties of PDVTA and PDVTA-SO3H

| Catalyst    | BET surface area/m2 g−1 | Pore volume/cm3 g−1 | Micropore volume/cm3 g−1 | Pore size/ nm |
|-------------|-------------------------|---------------------|--------------------------|---------------|
| PDVTA       | 774                     | 0.54                | 0.07                     | 3.6           |
| PDVTA-SO3H  | 591                     | 0.41                | 0.09                     | 3.4           |

Fig. 3 Nitrogen adsorption–desorption isotherms for the synthesized PDVTA and PDVTA-SO3H.
stability within temperatures below 250 °C, indicating it is sufficiently stable at the reaction temperature required for the conversion of HMF to EMF.

The surface morphologies of the as-prepared PDVTA and PDVTA-SO₃H were observed by scanning electron microscopy (Fig. 6). All the PDVTA-based carbon materials were composed of similar irregular amorphous carbon particles within a size range of 10–20 nm and have a flaky or lamellar structure.

3.2. Catalytic performance

The catalytic etherification of HMF to EMF was carried out in an autoclave using heat and autogenous pressure with ethanol as both reactant and reaction medium. The results are listed in Table 2. The major reaction products observed are EMF and EL. EMF is derived from the etherification of HMF via acid catalysis, while EL is formed stoichiometrically from the hydration of EMF, as shown in Scheme 1. A control experiment performed without any catalyst showed negligible production of EMF. When catalysed by PDVTA, the HMF conversion was only 22.8% and the EMF yield was only 6.2%. The PDVTA-SO₃H catalyst clearly accelerated the conversion of HMF, achieving a high conversion of HMF and an 87.5% yield of EMF. This shows that the incorporation of SO₃H into PDVTA facilitated the etherification reaction, leading to EMF as the major product with very high selectivity. Commercially available Amberlyst-15 and the homogeneous sulfonic acid P-TSA were used for comparison with PDVTA-SO₃H because they all have an aromatic ring directly attached to the SO₃H group. Although the active sulfonic acid sites of these catalysts were similar in nature, the catalytic activity of PDVTA-SO₃H was higher than that of Amberlyst-15 and P-TSA. In addition, P-TSA is soluble in ethanol and could not be recycled. The efficient catalytic activity of PDVTA-SO₃H was most likely due to the existence of an appropriate pore diameter as well as an appropriate number of Brønsted acid sites. According to the pore size distribution of
PDVTA–SO$_3$H, it can be seen that a portion of the pores inside the catalyst are 0.73 nm in diameter, which is larger than the HMF molecular size of 0.71 nm and less than that of EMF. This pore size is conducive to stabilizing the synthesis of EMF by reducing the probability of EMF further transforming into the by-product EL. This suggests acid catalysis occurs both on the surface and inside of the catalyst.

3.3. Optimisation of EMF production

3.3.1. Experimental design. A RSM with a Box–Behnken design was adopted to optimise the PDVTA–SO$_3$H-catalysed EMF production from HMF when multifactorial reaction variables were fully considered. The Box–Behnken design with three variables (reaction time, reaction temperature, and catalyst dosage) was applied according to the results from the single factor experiments and included 17 sets of experiments. The response chosen was the yield of EMF. The values that were chosen for the variables are presented in Table 3. The central point experiment was repeated five times in order to determine the variability of the results and assess the experimental error. The experiments were conducted in random order to minimize errors resulting from possible systematic trends in the variables.

3.3.2. Model analysis. The complete experimental design matrix and responses are shown in Table 4. A multiple regression analysis of the experimental data was performed according to the RSM, then a second-order polynomial equation was established to describe the mathematical relationship between EMF yield and the test variables based on the coded values.

$$Y = 84.48 + 1.66X_1 + 5.01X_2 + 2.40X_3 - 4.03X_1X_2 + 0.15X_1X_3 - 1.95X_2X_3 - 1.10X_1^2 - 3.15X_2^2 - 0.63X_3^2$$ (1)

$Y$ is the EMF yield, and $X_1$, $X_2$, and $X_3$ are the coded factors of the test variables time, temperature, and PDVTA–SO$_3$H dosage, respectively.

The values of the regression coefficients and the analysis of variance (ANOVA) of the experimental results are given in Table 5. The $F$-value of 83.62 and $P$-value lower than 0.0001 of the model imply that the model is highly significant. The lack of fit

Table 2  Etherification of HMF into EMF over various catalysts$^a$

| Entry | Catalyst    | HMF conv./% | EMF yield/% | EMF sel./% | EL sel./% |
|-------|-------------|-------------|-------------|------------|-----------|
| 1     | —           | 7.0         | 0.1         | 2.0        | 0.7       |
| 2     | PDVTA       | 22.8        | 6.2         | 27.0       | 4.5       |
| 3     | PDVTA-SO$_3$H | 99.8        | 87.5        | 87.7       | 12.3      |
| 4     | P-TSA$^a$  | 99.5        | 82.9        | 83.3       | 16.7      |
| 5     | Amberlyst-15 | 85.4        | 70.8        | 82.9       | 7.1       |

$^a$ Reaction conditions: HMF (1 mmol, 0.126 g), ethanol (5 mL), and catalyst (42.5 mg), 110 °C, 30 min. $^a$Corresponding amount of sulfonic acid.

Table 3  Independent variables and the corresponding levels

| Independent variable | Units | Code | Level |
|----------------------|-------|------|-------|
| Reaction time        | min   | $X_1$| 30 45 60 |
| Reaction temperature | °C   | $X_2$| 90 100 110 |
| Catalyst dosage      | mg   | $X_3$| 30 40 50 |
was not significant, with an $F$-value of 1.22 and $P$-value of 0.4110, suggesting the model had good predictability. Moreover, the regression coefficient $R^2$ for the model was 0.9908, and the predicted $R^2$ value (0.9220) is in reasonable agreement with the adjusted value (0.9789). The signal to noise ratio is adequate for each response because the adequate precision of 32.283 is greater than 4. In addition, Fig. 7 depicts an excellent correlation between the experimental EMF yields and the predicted EMF yields obtained using the mathematical model for the entire range of values. Therefore, there is a real relationship among the selected variables, and the mathematical model can be applied to predict and analyse the conditions of the actual experiment.

Furthermore, the $P$-value suggests that all linear ($X_1, X_2, X_3$) parameters had a significant effect on the formation of EMF ($P < 0.05$) because the $P$-values were as low as <0.0001. The results derived from the ANOVA demonstrated that the three individual variables tested, reaction time, reaction temperature, and PDVTA-SO$_3$H dosage, were crucial parameters, as seen by their effects on the response variables. The first order main effect of reaction temperature ($X_2$) was significant, which suggests that temperature plays a crucial role in EMF production. Using the $F$-value, the effect of the various factors on EMF yield are reaction temperature $>$ catalyst dosage $>$ reaction time. To explain the interaction between the variables and determine the optimal level of maximum response for each variable, three-dimensional response surfaces and two-dimensional contour plots of the model were created, as shown in Fig. 8. Each figure presents the impact of two variables while the other factor was fixed at zero. When the catalyst dosage was lower, the yield of EMF increased with the increase of reaction temperature, but when the reaction time was longer, the EMF yield decreased with the increase of temperature. At the same time, it was also observed that the EL increased under the high temperature condition, indicating that the excessive reaction temperature will aggravate the occurrence of the side reaction, which was unfavorable to the formation of EMF.

### Table 4 Results of the Box–Behnken design for the reaction optimisation

| Entry | $t(X_1)/$min | $T(X_2)/^\circ$C | Catalyst dosage($X_3$)/mg | EMF yield/% |
|-------|--------------|------------------|---------------------------|-------------|
| 1     | 30(−1)       | 90(−1)           | 40(0)                     | 69.6        |
| 2     | 60(1)        | 90(−1)           | 40(0)                     | 81.5        |
| 3     | 30(−1)       | 110(1)           | 40(0)                     | 87.0        |
| 4     | 60(1)        | 110(1)           | 40(0)                     | 82.8        |
| 5     | 30(−1)       | 100(0)           | 30(−1)                    | 78.9        |
| 6     | 60(1)        | 100(0)           | 30(−1)                    | 81.4        |
| 7     | 30(−1)       | 100(0)           | 50(1)                     | 83.8        |
| 8     | 60(1)        | 100(0)           | 50(1)                     | 86.9        |
| 9     | 45(0)        | 90(−1)           | 30(−1)                    | 71.2        |
| 10    | 45(0)        | 110(1)           | 30(−1)                    | 85.8        |
| 11    | 45(0)        | 90(−1)           | 50(1)                     | 79.5        |
| 12    | 45(0)        | 110(1)           | 50(1)                     | 86.3        |
| 13    | 45(0)        | 100(0)           | 40(0)                     | 84.2        |
| 14    | 45(0)        | 100(0)           | 40(0)                     | 83.7        |
| 15    | 45(0)        | 100(0)           | 40(0)                     | 84.1        |
| 16    | 45(0)        | 100(0)           | 40(0)                     | 85.4        |
| 17    | 45(0)        | 100(0)           | 40(0)                     | 85.0        |

### Table 5 Regression coefficients and analysis of the model for EMF yield

| Source | Sum of squares | $F$-value | $P$-value | $prob>F$ | Significance |
|--------|----------------|-----------|-----------|----------|--------------|
| Model  | 401.09         | 83.62     | <0.0001   |          | Significant  |
| $X_1$  | 22.11          | 41.49     | 0.0004    |          |              |
| $X_2$  | 201.00         | 377.16    | <0.0001   |          |              |
| $X_3$  | 46.08          | 86.47     | <0.0001   |          |              |
| $X_1X_2$ | 64.80      | 121.60    | <0.0001   |          |              |
| $X_1X_3$ | 0.090      | 0.17      | 0.6934    |          |              |
| $X_2X_3$ | 15.21      | 28.54     | 0.0011    |          |              |
| $X_1^2$ | 5.12          | 9.60      | 0.0173    |          |              |
| $X_2^2$ | 41.85         | 78.52     | <0.0001   |          |              |
| $X_3^2$ | 1.66          | 3.11      | 0.1211    |          |              |
| Lack of fit | 1.78      | 1.22      | 0.4110    |          |              |
| $R^2$  | 0.9908         |           |           |          |              |
| $R^2$ adjusted | 0.9789 |           |           |          |              |
| $R^2$ predicted | 0.9220 |           |           |          |              |
| Adequate precision | 32.383 |           |           |          |              |
Based on eqn (1) and using the software’s numerical optimisation function, the maximum predicted EMF yield was 87.6% for the optimal conditions of a 30 min reaction time, 42.5 mg catalyst dosage, and 110 °C reaction temperature. Three experiments were carried out under the optimal conditions to verify the prediction, and an average EMF yield of 87.5% was obtained. This shows that the experimental data are in good agreement with the model, indicating that the model for the synthesis of EMF from HMF was adequate.

3.4. Catalytic etherification of HMF by different alcohols

To study the applicability of the PDVTA-SO$_3$H catalyst to the catalytic etherification of HMF with other alcohols, catalytic reactions were carried out using the optimised conditions described in Section 3.3. As listed in Table 6, methanol, ethanol, $n$-propanol, isopropanol, tert-butanol, and benzyl alcohol were used as the alcohol substrates. The product distributions indicate that HMF etherification proceeds similarly in these solvents, with the corresponding 5-alkoxymethylfurfural being the major product. Notably, a high yield can be obtained when using a simple alcohol, although in the case of methanol more by-products were produced at this reaction temperature than had been produced at the same temperature using ethanol, leading to lower selectivity and yield. The use of branched alcohols like isopropanol and tert-butanol largely delays the reaction progress, which, in association with the existing steric hindrance and possibly inadequate reaction temperature, prohibits the efficient progress of the reaction in the pore space of PDVTA-SO$_3$H.

3.5. Comparison of the activity with other reported catalysts

The catalytic performance of PDVTA-SO$_3$H is, to the best of our knowledge, better than that of other acid catalysts that have been reported for the etherification of HMF to EMF (Table 7). For example, Yuan et al.$^{34}$ reported that Fe$_3$O$_4$@C-SO$_3$H catalysed an 88.4% yield of EMF from the etherification of HMF with

Fig. 8 3D and contour plots of EMF yield versus different variables.
PDVTA-SO$_3$H catalyst could be sufficiently separated from the reaction mixture by centrifugation. The catalyst was recovered, washed with ethanol three times, and dried at 60 °C before the next usage. As seen from Fig. 9, the recovered PDVTA-SO$_3$H remained catalytically active for each recycle run, although the HMF conversion decreased from 99.8% to 75.3% after four uses. The FT-IR analysis of the spent catalyst confirmed that there was no obvious structural change (Fig. 1), suggesting that the SO$_3$H groups were essentially preserved. To explore the cause of the catalyst deactivation, the amount of H$^+$ in the used catalyst after the fourth recycle run was measured by titration, and it was found that the amount of H$^+$ declined compared with the fresh catalyst (from 2.1 mmol g$^{-1}$ to 0.9 mmol g$^{-1}$), indicating that the loss of catalytic activity may be a result of SO$_3$H leaching or poisoning. As further proof, the spent catalyst was analysed by elemental analysis, showing almost constant carbon content but a decrease in sulphur content by 0.4 mol g$^{-1}$. This suggests that functional groups might be shedding from the PDVTA-SO$_3$H. The deactivated catalyst could be easily regenerated by simple treatment in diluted HCl solution at 50 °C for 1 h, after which a HMF conversion of 95.2% was regained in a subsequent recycling experiment (Fig. 9, run 5). Therefore, the loss of catalytic activity may be due to poisoning of the SO$_3$H active sites.

### 4 Conclusions

EMF was efficiently synthesized from HMF by the catalyst PDVTA-SO$_3$H. The impacts of catalyst amount, temperature, and reaction time on the synthesis of EMF were further investigated in Box–Behnken design experiments based on RSM, with the model predicting a maximum EMF yield of 87.6% at 110 °C and 42.5 mg PDVTA-SO$_3$H in 30 min. The PDVTA-SO$_3$H catalyst is a promising candidate for the heterogeneous etherification of HMF to EMF and other biomass-based acid-catalysed reactions.

### Conflict of interest

There are no conflicts to declare.

### Acknowledgements

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (21600682), Scientific Research Fund of Hunan Provincial Education

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**Table 6** Expanded catalytic etherification experiments using different alcohols$^a$

| Entry | Alcohol | Ether | Yield/% |
|-------|---------|-------|---------|
| 1     | H$_2$C$\text{OH}$ | | 70.7 |
| 2     | HOH    | | 87.5 |
| 3     | HOH    | | 75.0 |
| 4     | H$_2$C$\text{OH}$ | | 53.7 |
| 5     | HOH    | | 32.1 |
| 6     | OH     | | 35.5 |

$^a$ Reaction conditions: 1 mmol HMF5, mL alcohol, 42.5 mg catalyst30, min, and 110 °C.

**Table 7** Comparison of the etherification of HMF to EMF with reported different catalysts

| Entry | Catalyst | $T/°C$ | $t/h$ | EMF yield/% | ref. |
|-------|----------|--------|-------|-------------|------|
| 1     | Fe$_2$O$_3$@C-SO$_3$H | 100    | 12    | 88.4        | 34   |
| 2     | C-SO$_3$H | 100    | 6     | 71.0        | 35   |
| 3     | PDVTA-SO$_3$H | 110    | 0.5   | 87.7        | This work |

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**Fig. 9** Recyclability of the catalytic system.
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