Supplementary Information for

Graphene oxide as a facile acid catalyst for the one-pot conversion of carbohydrates into 5-ethoxymethylfurfural

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1. Experimental

1.1 Materials

Inulin (99%), sucrose (99%) and glucose (99%) were purchased from Tian Jin Hengxin chemical preparation Co., Ltd. Fructose (99%), HMF (99%) and HPW (analytical grade) were purchased from Amresco, J&K Scientific Company and Kermel chemical reagent company (Tianjin, China), respectively. Graphite powder was purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). H_2SO_4 (98 wt %) were bought from Xilong Chem. Co. Ltd (Guangzhou, China). $NaNO_3$ and $KMnO_4$ were from Kermel Chem. Reagent Co. Ltd (Tianjin, China). H_2O_2 (30 wt%) was from Dong Fang Chem. Co. (Tianjin, China). All other chemicals (analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the reagents were used as received without further purification.

1.2 Synthesis of graphene oxide(GO)

GO was prepared by the Hummers' method with post treatment of sonication and centrifugation. Typically, graphite powder (8000 meshes, 5 g) and $NaNO_3$ (2.5 g) were mixed with sulfuric acid (115 mL, 98 wt %) under magnetic stirring for 0.5 h, then the mixture was put into an ice bath before $KMnO_4$ (15 g) was slowly added, during which the temperature was kept below 20 °C. Subsequently, the reaction system was transferred to a water bath of 35 °C and maintained for 0.5 h. After that, 230 mL water was slowly added to the system. The diluted suspension was then stirred at 98 °C for 15 min, followed by another 700 mL of water added. And the reaction was terminated by the addition of H_2O_2 (50 mL, 30wt %). The mixture was filtered and washed with HCl (1 L, 1 $mol\cdot L^{-1}$) and a large amount of distilled water in sequence. The resulting solid was dried and dissolved. The graphite oxide suspension was ultrasonicated under 40 KHz for 60 min and centrifugated at 4000 rpm for 30 min, obtaining stable collosol of GO. The collosol of GO was dried at ambient temperature and got the powder of GO.

1.3 General reaction procedure

Typical procedure for etherification of HMF with ethanol (Table 1, entry 1): HMF (63.0 mg, 0.5 mmol), GO (20 mg) and ethanol (1 mL) were charged in a 5 mL stainless steel micro autoclave with a Teflon lining and sealed by a screw cap. The autoclave was then heated to 100 °C within ca. 25 min and maintained at 100 °C for 12 h. The autoclave was fitted with a magnet stir bar and filled with air under ambient pressure. After the reaction, the autoclave was cooled to room temperature and GO was separated by filtration. Typical procedure for conversion of carbohydrates into EMF in DMSO-ethanol solvent system: carbohydrate (0.5 mmol based on monosaccharide), GO (30 mg), ethanol (0.7 mL), DMSO (0.3 mL) were charged in a 5 mL stainless steel micro autoclave with a Teflon lining and sealed by a screw cap. The autoclave was then heated to 130 °C within ca. 25 min and maintained at 130 °C for 24 h. The autoclave was fitted with a magnet stir bar and filled with air under ambient pressure. After the reaction, the autoclave was cooled to room temperature and GO was separated by filtration.

1.4 Catalyst characterization

The catalyst was characterized by Infrared Fourier Transform spectroscopy (FT-IR) and the ammonia adsorption Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFT). FT-IR spectrum was recorded over the range from 400 to 4000 cm^{-1} on a FT-IR (Nexus) after the catalyst was evenly mixed with KBr powder. NH_3 adsorption was performed at room temperature. About 0.1 g of GO was spread on the bottom of a ceramic crucible to form a thin layer and evacuated for 1 h. NH_3 was then slowly introduced and kept airtight for 48 h. After that, the samples were heated at 120 °C for

1 h under vacuum to remove the physically adsorbed NH_3. The DRIFT characterization was performed on the Praying Mantis™ diffuse reflection accessory (Harrick Scientific Products INC) of a Bruker Vertex-70 Fourier transforminfrared spectrometer at room temperature. The DRIFT measurement lasted 2 min (from the sample loading to the spectrum recording). The spectrawere collected over the range of 750–3500 cm^{-1} with 64 scans and a resolution of 8 cm^{-1} using GO without adsorbing NH_3 as background.

1.5 products analysis

The reaction mixture was diluted with 95% ethanol and filtered with a 0.45 μm syringe filter prior to analysis. Quantitative analysis of raw materials and products was done by a Shi-madzu high-pressure liquid chromatograph (LC-10AT) equipped with a UV detector and an evaporative light-scattering detector. For the analysis of HMF, EMF and LAE, a 4.6 mm ID*250 mm Kromstar C18 reverse-phase column was used and the mobile phase consisted of deionized water and acetonitrile at a volume ratio of 7:3 at a flow rate of 0.6 mL/min. For the analysis of inulin, sucrose and fructose, a 4.6 mm ID*250 mm Shodex sugar column (SC1011) was used and distilled water was used as the mobile phase at a flow rate of 1.0 mL/min. The column temperature was maintained at 35 °C. All the raw materials and products were calculated based on external standard curves constructed with authentic standards. The crude product of EMF were separated and purified by chromatography on silica gel using ethyl acetate and petroleum (1:4) as eluent and finally were identified by LC-MS and NMR.

2. Reaction kinetics of HMF etherification to EMF at different temperatures.

We have constructed the kinetics profiles at different temperatures and calculated the activation energy for the purpose of better understanding the effect of temperature on the etherification of HMF to EMF. We supposed that the transformation of HMF to EMF is a 1st order process, and the ultimate product of HMF etherification is EMF only. Besides, we assumed that the degradation of EMF would not occur under our designed conditions (80~120°C, 0~6 h).

$$\text{HMF} \xrightarrow{\text{GO}} \text{EMF}$$

The reaction rate could be expressed as follows:

$$\frac{d[\text{EMF}]}{dt} = -\frac{d[\text{HMF}]}{dt} = k[\text{HMF}] \qquad (1)$$

$$-\ln[\text{HMF}] = kt + C \qquad (2)$$

[HMF] and [EMF] are molar concentration of HMF and EMF, and *k* is the rate constant for HMF conversion at a certain temperature. *t* is the reaction time, and *C* is an arbitrary constant.

$$X = \frac{[\text{HMF}]t0 - [\text{HMF}]}{[\text{HMF}]t0} \qquad (3)$$

$$[\text{HMF}] = [\text{HMF}]t0(1 - X) \qquad (4)$$

X is the conversion ratio of HMF. $[\text{HMF}]t0$ means the initial concentration of HMF. Based on the equation (2) and equation (4), the original equation will become:

$$-\ln(1 - X) = kt + C \qquad (5)$$

Therefore, we plotted figures with $-\ln(1 - X)$ as the *y*-axis and *t* as the x-axis, fitting the data linearly and evaluated reaction rate constants from the slopes, and the results are showed in Fig. S1.

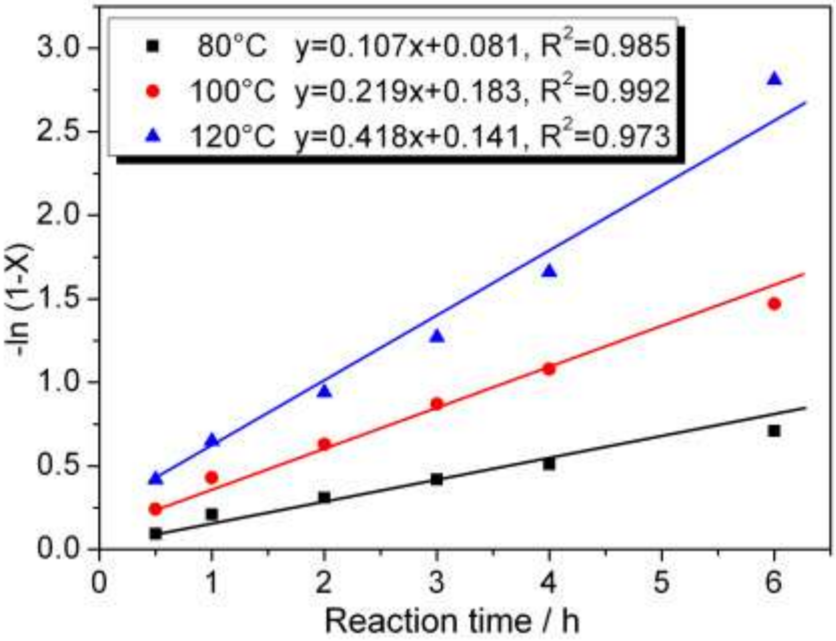

Fig. S1 The kinetics profiles of HMF etherification to EMF.

As shown in Fig. S1, there is an obvious increase of *k* when increase the reaction temperature. The value of *k* increased from 1.07 h^{-1} to 0.219 h^{-1} and 0.418 h^{-1} when the temperature increased from 80 °C to 100 °C and 120 °C, respectively, confirming temperature has a positive effect on promoting this reaction. Next, based on the rate constants we obtained, the activation energy (E_a) was calculated by the Arrhenius equation, and the apparent activation energy of the catalytic system was to be 39.93 kJ mol^{-1}.

3. Reusability study of fructose conversion to EMF over GO catalysis.

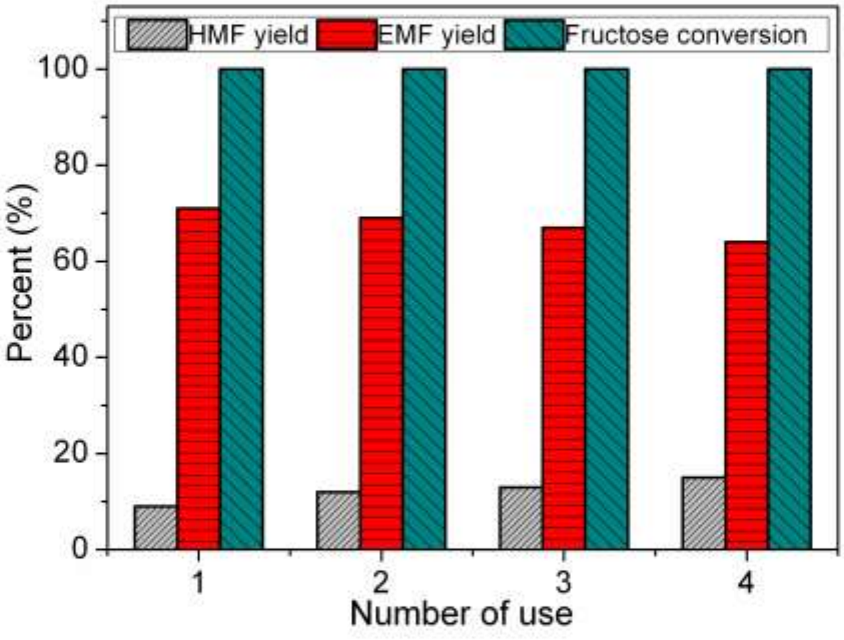

Fig. S2 Reusability study of fructose conversion to EMF over GO catalysis. Reaction conditions: 0.5 mmol fructose, 30 mg GO, 0.3 mL DMSO, 0.7 mL ethanol, T= 130 °C, t=24 h.

4.FT-IR spectra of GO

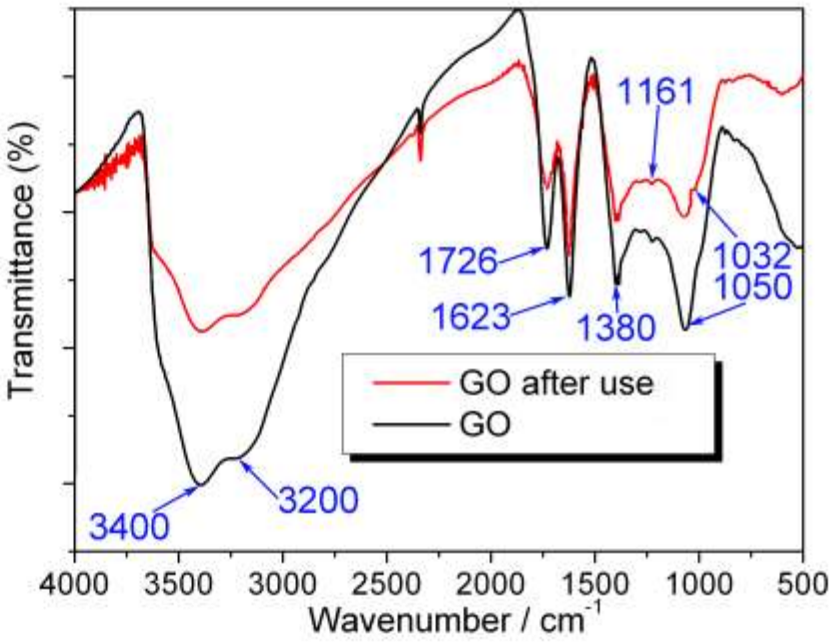

Fig. S3 FT-IR spectra of GO

Based on previous studies[1, 2], contributions from various oxygen functional groups on the as-synthesized GO can be clearly indicated by FT-IR spectroscopy. As depicted by Fig. S1, compared to the starting material of GO sample, the GO separated from the reaction mixture exhibited attenuated signals, which can be assigned to hydroxyls (O–H at $\bar{\nu}$=3200–3500 cm^{-1} and $\bar{\nu}$=1380 cm^{-1}, C–OH at $\bar{\nu}$=1050–1150 cm^{-1}), carboxyls (COOH at $\bar{\nu}$=1620–1730 cm^{-1} , $\bar{\nu}$=3000–3600 cm^{-1} and $\bar{\nu}$=1050-1200 cm^{-1}) as well as epoxides ($\bar{\nu}$=1280–1330 cm^{-1}). This result indicates that the GO catalyst undergoes partial reduction during the heat treatment for a long time. In addition, the bands at 1161 cm^{-1} (SO_3-H stretching) and 1032 cm^{-1}(O=S=O stretching in SO_3H) in the FT-IR spectrum indicate that the GO possesses SO_3H groups.[3]

5. DRIFT spectra of GO

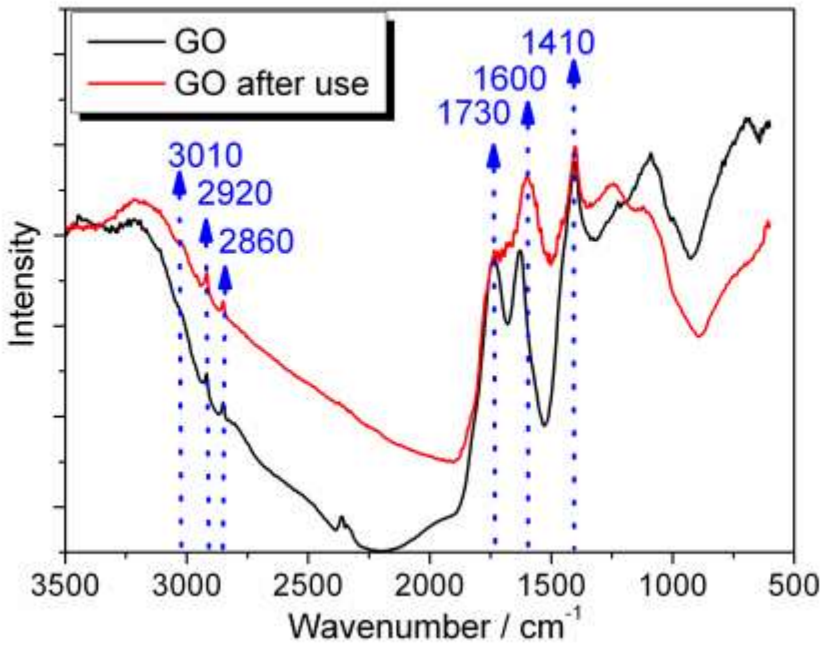

Fig. S4 DRIFT spectra of GO

Brønsted and Lewis acid sites can be distinguished by differentiating vibrational bands of the adsorbed basic probe molecules using Fourier transform infrared spectroscopy.[4-6] Thus, diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) was applied to differentiate the types of acid sites in GO by using NH_3 as a probe molecule. The bands at ~1410 and ~1730 cm^{-1} were attributed to NH_4^+ which was formed from NH_3 molecules reacted with Brønsted acid sites existed in GO. The band at ~1600 cm^{-1} was attributed to NH_3 co-ordinated to the Lewis acid sites in GO. After used, the signal at ~1600 cm^{-1} was increased while signals at ~1410 and ~1730 cm^{-1} were decreased. These results clearly indicated that Brønsted acid sites were reduced and Lewis acid sites were increased. It might due to the fact that a part of carboxyl groups as well as other oxygen containing groups were removed by the heat treatment during the catalysis reaction and that not only made some Brønsted acid sites lost but also increased some electron vacancies at the GO defects which created additional Lewis acid sites.

6. ^{1}H NMR ($CDCl_3$) of EMF

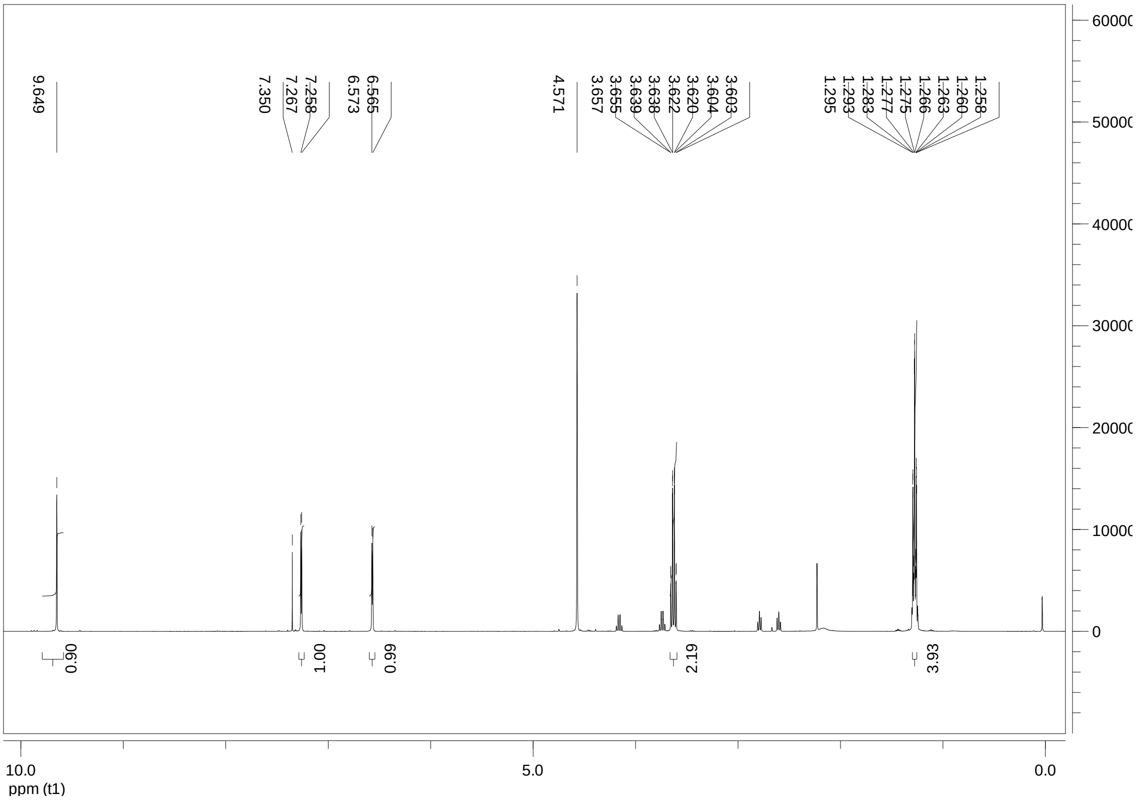

Fig. S5 ^{1}H NMR ($CDCl_3$) of EMF after purified by chromatography on silica gel

7. ^{13}C NMR ($CDCl_3$) of EMF

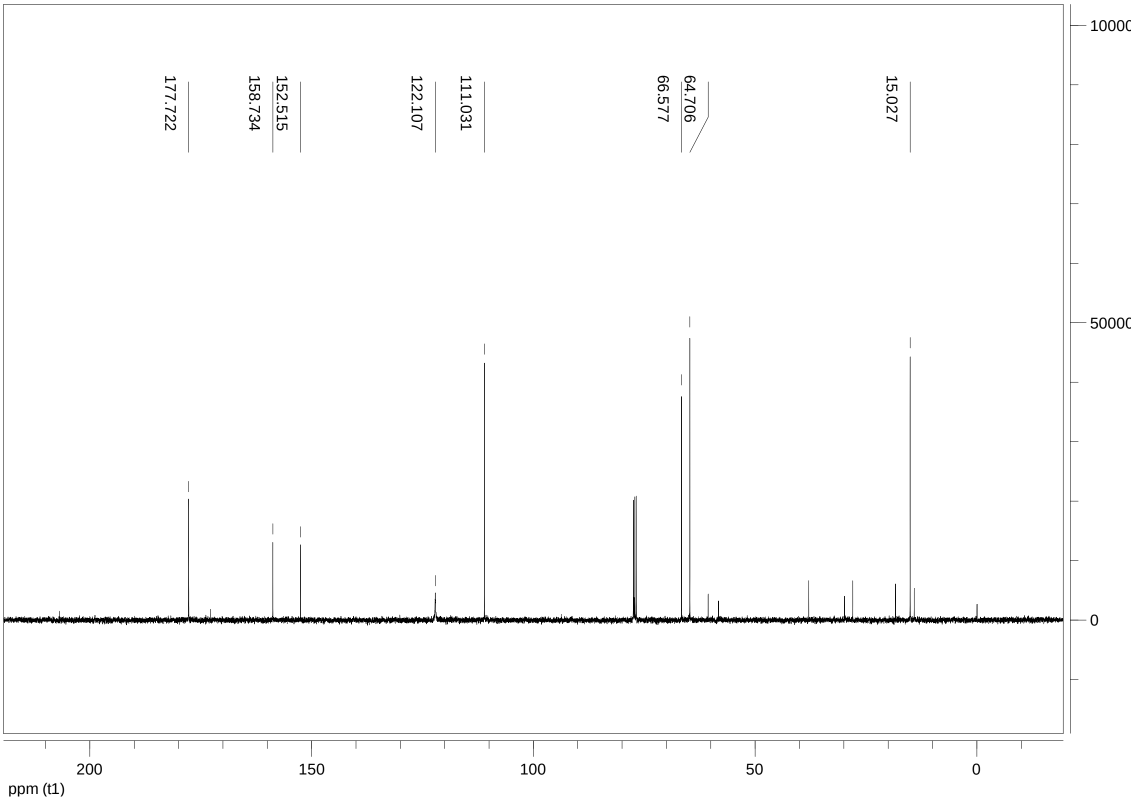

Fig. S6 ^{13}C NMR ($CDCl_3$) of EMF after purified by chromatography on silica gel

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