Electronic Supplementary Material for Catalysis Science & Technology

Silica coated magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles supported phosphotungstic acid: a novel environment-friendly catalyst for the synthesis of 5-ethoxymethylfurfural

## from 5-hydroxymethylfurfural and fructose

Shuguo Wang, Zehui Zhang\*, Bing Liu and Jinlin Li

<sup>1</sup>Key Laboratory of Catalysis and Materials Sciences of the State Ethnic Affairs

Commission & Ministry of Education, College of Chemistry and Material Science,

South-Central University for Nationalities, Wuhan, 430074, China.

<sup>2</sup>Department of Biotechnology, Dalian Medical University, Dalian, 116044, PR China

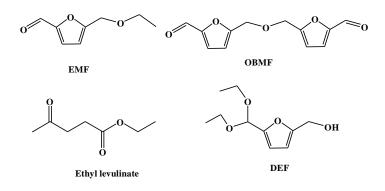
Fax: +86411-86110012; Tel: +86411-86110350

\* Corresponding author. Fax: +8627-67842752; Tel: +8627-67842752;

E-mail: zehuizh@mail.ustc.edu.cn

## Calculated the carbon balance for the synthesis of EMF by the etherification of HMF

The procedures for the synthesis of EME from HMF was described as in the test. The possible byproducts including ethyl levulinate (EL), the 5-(diethoxymethyl)-2-f uranmethanol (DEF), 5,5'(oxy-bis(methylene))bis-2-furfural (OBMF), the insoluble humins and others beyond our detection. After reaction, the reaction mixture was diluted, and analyzed by gas by gas chromatography. EL and OBMF were detected in our reaction during the synthesis of EMF from HMF at 100 °C and 120 °C. The insoluble humins were obtained by the filtration of the reaction mixture after removal of the catalyst by a permanent magnet.



Reaction	HMF	Percentage	Percentage	Percentage	Percentage	Percentage	Others
temperature	conversion	of HMF	of HMF	of HMF	of HMF	of HMF	(not
	(%)	used for	used for EL	used for	used for	Humins (%)	detected
		EMF (%)	(%)	OBMF (%)	DEF (%)		)
100 °C	97.9	83.6	5.8	2.3	ND	3.3	1.2
120 °C	98.9	57.8	21.3	3.5	ND	12.4	5.0

Table S1. Carbon balance calculation for the synthesis of EMF from HMF<sup>a</sup>

<sup>a</sup> Reaction conditions: HMF (126 mg, 1 mmol) and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-HPW (150 mg) were added into 5 mL of ethanol, then the reaction was carried out at desired temperature.

## Comaprsion with the characterization of the fresh catalyst and the reused catalyst

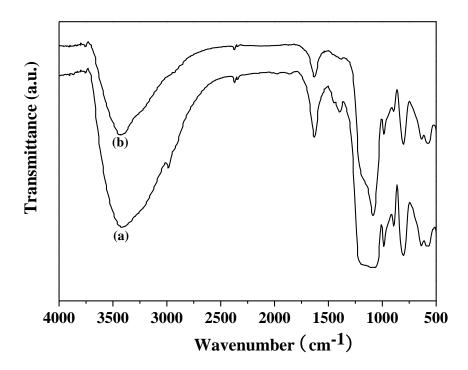


Fig. S1 IR spectra of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-HPW (a) Fresh (b) after reused for 5 times.

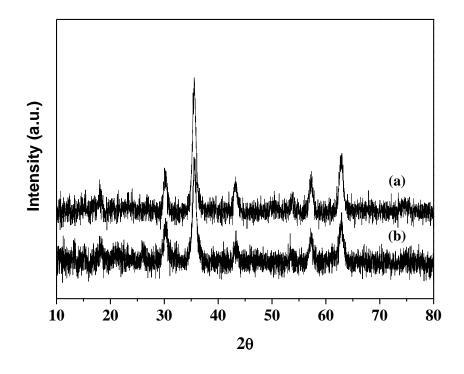


Fig. S2 XRD patterns of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-HPW (a) Fresh (b) after reused for 5 times.

## Recycling expriments for the synthesis of EMF from fructose

The recycling experiments of  $Fe_3O_4@SiO_2$ -HPW were also carried out in the reaction of the conversion of fructose to EMF. The reaction conditions were as follows: 180 mg of fructose and 150 mg of  $Fe_3O_4@SiO_2$ -HPW were added into 5 ml of ethanol, and the reaction was carried out 100 °C for 24 h. The recover and the recycling expriments were the same as described for the recycling expriments by the etherification of HMF, and the resluts were showed in Fig. S3. From the recycling results, it also indicated that the catalyst was stable without the loss of catalytic activity.

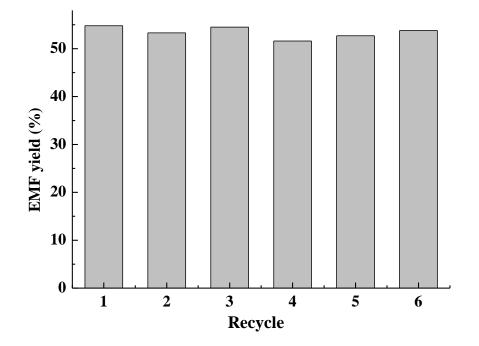


Fig. S3 The recycling expriments of  $Fe_3O_4@SiO_2$ -HPW by the synthesis of EMF from fructose.