

Research Article

Catalytic Cascade Dehydration-Etherification of Fructose into 5-Ethoxymethylfurfural with SO₃H-Functionalized Polymers

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A series of SO₃H-functionalized polymers were prepared and employed as heterogeneous catalysts for one-pot transformation of fructose into 5-ethoxymethylfurfural (EMF) that is considered to be one of potential liquid biofuels. A high EMF yield of 72.8% could be obtained at 110°C for 10 h, and the polymeric acid catalysts could be recycled for five times without significant loss of catalytic performance.

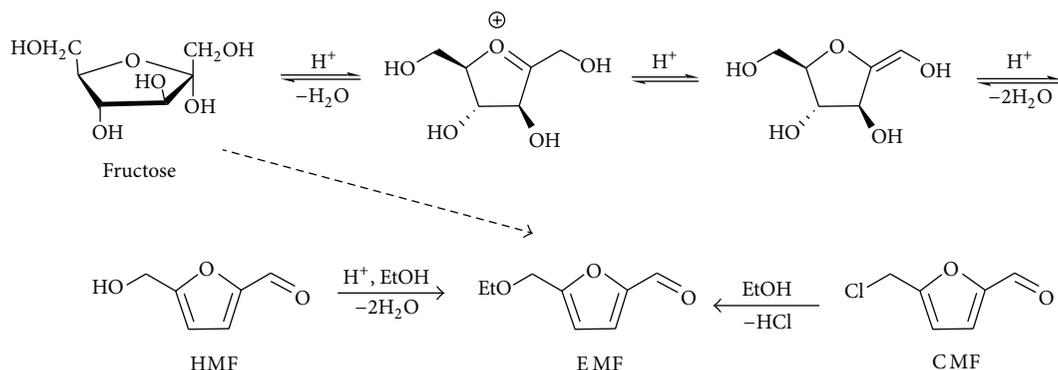
1. Introduction

With the increasing concerns about the depletion of fossil resources, environmental pollution, and global warming, biomass which is abundant, widespread, and an ideal substitute for unsustainable resources has attracted worldwide attention [1]. Much effort has been made to develop processes for the efficient conversion of biomass resources into biofuels and value-added chemicals [2–6]. Amongst the existing alternatives, 5-hydroxymethylfurfural (HMF), furfural and other furanic derived products have received wide attention and showed great potential in the replacement of fuels and chemicals currently produced from fossil resources [7]. In particular, 5-ethoxymethylfurfural (EMF) has high energy density of 8.7 kWh/L, which is thereby proposed to be one of potential liquid biofuels [8].

In the presence of metal chlorides, mineral acids, or solid acids, EMF could be synthesized from 5-chloromethylfurfural (CMF), HMF, and carbohydrates such as fructose (Scheme 1). As one of the initiators, Mascall and Nikitin [9] reported that CMF might emerge as a central intermediate in the conversion of carbohydrate-based material into EMF. Starting from HMF, Che et al. [10] illustrated that H₄SiW₁₂O₄₀/MCM-41 nanospheres were efficient for production of EMF with selectivity of 84.1% at HMF conversion of 92.0%. In contrast to Brønsted acids facilitating for

the formation of ethyl-4-oxopentanoate, solid catalysts with strong Lewis acid sites (e.g., introduction of ZrO₂ into SBA-15 or presence of extraframework isolated Al³⁺ sites in MCM-41) could afford a higher yield to EMF (up to 76%) with HMF conversion of 100% at 140°C for 5 h [11]. With respect to one-pot catalytic conversion of carbohydrates into EMF, reaction systems containing AlCl₃, FeCl₃, NH₄Cl, or H₃PW₁₂O₄₀ were capable of successively catalyzing dehydration of fructose to HMF and etherification of HMF with ethanol to EMF [12–18]. From an economical and environmental point of view, heterogeneous catalysts were further developed for the sequential dehydration-etherification of carbohydrates into EMF. Silica coated magnetic Fe₃O₄ nanoparticles and K-10 clay supported phosphotungstic acid were demonstrated to be efficient for the synthesis of EMF from fructose, giving a maximum EMF yield of 54.8% and 61.5%, respectively [19, 20]. Two different types of solid acid catalysts (i.e., Brønsted acid Amberlyst 131 and Lewis acid zeolite Sn-BEA) were simultaneously employed for conversion of glucose to EMF, and a moderate yield of EMF (31%) could be achieved in ethanol in a single reactor at 90°C [21].

Besides, sulfonic acid functionalized catalysts were illustrated to exhibit highly efficient catalytic performance for selective conversion of fructose into EMF. Kraus and Guney [22] found SO₃H-functionalized ionic liquids used together with hexane resulting in a 54% isolated yield from fructose



SCHEME 1: Synthesis of EMF from CMF, HMF, and fructose.

at 100°C for 80 min. Using silica supported sulfonic acid as a heterogeneous catalyst, EMF could be obtained in a high yield of 63.1% from fructose at 100°C for 24 h [23]. A cellulose sulfuric acid was also synthesized and used as an efficient and environmentally friendly biosupported catalyst for the synthesis of EMF from fructose, giving a high EMF yield of 72.5% through one-pot reaction at 100°C within 12 h [24]. It should be noted that a much higher EMF yield of 90.5% could be obtained from fructose with the presence of methylimidazolebutylsulfate phosphotungstate ($[MIMBS]_3PW_{12}O_{40}$) at 90°C for 24 h [25]. In the present study, a series of SO_3H -functionalized polymers were hereby prepared and further employed for the catalytic conversion of fructose into EMF in one-pot.

2. Experimental Part

2.1. Materials. Azobisisobutyronitrile (AIBN), 1-vinylimidazole, 1,3-propanesultone, $H_3PW_{12}O_{40}$ (PW), fructose, EMF (98%), and HMF (98%) were purchased from Shanghai Aladdin Industrial Inc.; acetone, methanol, ethanol (99.5%), HCl, H_2SO_4 , and CF_3COOH were purchased from Chongqing Chuandong Chemical Reagent Company. All chemicals were of analytical grade and used as received, unless otherwise noted.

2.2. Preparation of Poly(VMPS)-PW and Poly(VMPS)-Cl. Firstly, poly(VMPS) was synthesized as reported in the previous literature [26]. Then, an aqueous solution of $H_3PW_{12}O_{40}$ (4 g, 1.39 mmol) or HCl (4.17 mmol) was added to the solution of Poly(VMPS) (0.88 g, monomer molar quantity was 4.17 mmol) dispersed in methanol, followed by stirring of the mixture at 60°C for 24 h. On completion, water and methanol were removed in vacuum to afford the final product poly(VMPS)-PW (or poly(VMPS)-Cl) as a solid [27].

For comparison, three other solid acidic ionic liquid polymers DVB- $[C_3vim][CO_2CF_3]$, DVB- $[C_3vim][Cl]$, and DVB- $[C_3vim][HSO_4]$ were also prepared from divinylbenzene (DVB) and corresponding Brønsted acidic ionic liquids $[SO_3H(CH_2)_3vim][X]$ ($X = CO_2CF_3, Cl,$ and HSO_4) respectively, according to the reported procedures [28, 29]. As illustrated in Figure 1, all the prepared solid catalysts consist of SO_3H functionalized ionic liquids and corresponding polymers.

2.3. Catalyst Characterization. XRD patterns were recorded with Rigaku D/Max-2200 X-ray powder diffractometer using Ni-filtered $Cu K\alpha$ radiation source. FT-IR spectra were measured on a Nicolet 360 FT-IR instrument (KBr discs). TG analysis was performed with a Netzsch STA449C Jupiter instrument in dry air at a heating rate of 10°C/min. NH_3 -TPD was carried out on an AutoChem 2920 chemisorption analyzer.

2.4. Typical Procedure for Catalytic Transformation of Fructose into EMF. The synthesis of EMF from fructose was performed in a sealed tube (Ace, pressure limit: 20 bar) under magnetic stirring. In a typical procedure, to a stock solution of fructose (50 mg) dissolved in ethanol (2 mL), a SO_3H functionalized polymer (10 mg) was introduced. The resulting mixture was stirred magnetically and heated with an oil bath at a certain temperature for a specific time. After the reaction and separation of the catalyst, the obtained solution was decanted into a volumetric flask using ethanol as diluents and analyzed by high performance liquid chromatography.

2.5. Analysis Methods. HMF and EMF were analyzed by high-performance liquid chromatography (HPLC; Agilent 1100, USA) fitted with a Lichrospher C18 column and an ultraviolet (UV) detector at 280 nm. The column oven temperature was set at 30°C, and the mobile phase was 0.1 wt% acetic acid/acetonitrile (85/15, v/v) at a flow rate of 1.0 mL/min.

The concentration of HMF and EMF was calculated based on the standard curve obtained with the standard substances. HMF yield (X, mol%) and EMF yield (Y, mol%) were calculated as follows:

$$X(\%) = (\text{mole concentration of HMF}) / (\text{mole concentration of initial fructose}) \times 100\%$$

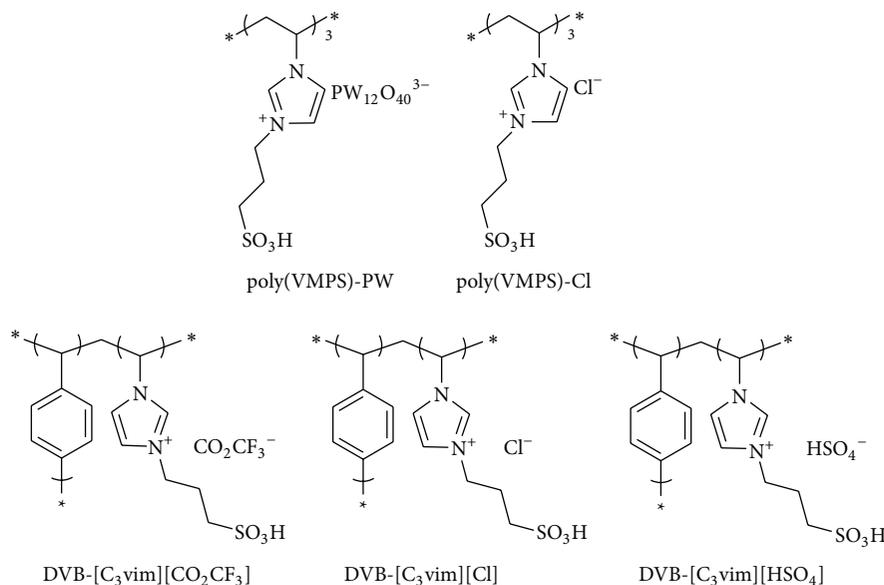
$$Y(\%) = (\text{mole concentration of EMF}) / (\text{mole concentration of initial fructose}) \times 100\%$$

2.6. Recycling of Catalysts. The catalyst was recovered by centrifugation, washing with acetone for three times, and drying at 60°C for 2 h. The recovered catalyst was directly used for the next run.

TABLE 1: Acid properties of the different carboxylic acids modified Zr-Mo oxides catalysts^a.

Sample	NH ₃ desorption peaks (area %)			Total NH ₃ adsorption (mol/g)
	<150°C	150–300°C	300–500°C	
DVB-[C ₃ vim][CO ₂ CF ₃]	5.3	0	94.7	0.019
DVB-[C ₃ vim][Cl]	6.9	0	93.1	0.021
DVB-[C ₃ vim][HSO ₄]	0	38.9	61.1	0.033
poly(VMPS)-Cl	0	0	100	0.024
poly(VMPS)-PW	0	0	100	0.010

^aDetermined by adsorption and TPD of NH₃.

FIGURE 1: General structures of the prepared $\text{-SO}_3\text{H}$ functionalized polymers.

3. Results and Discussion

3.1. Catalyst Characterization. FTIR spectra and XRD patterns on the prepared $\text{-SO}_3\text{H}$ functionalized polymers were performed (Figures 2(a) and 2(b)). In Figure 2(a), two significant bands at 1166 cm^{-1} and 1040 cm^{-1} are attributable to the asymmetric and symmetric stretching vibrations of $\text{S}=\text{O}$, respectively. As to poly(VMPS)-PW, 1080 cm^{-1} ($\text{P}-\text{O}_a$), 975 cm^{-1} ($\text{W}=\text{O}_d$), 898 cm^{-1} ($\text{W}-\text{O}_b-\text{W}$) (corner-sharing), and 810 cm^{-1} ($\text{W}-\text{O}_c-\text{W}$) (edge-sharing) are assigned to a Keggin structure of $\text{PW}_{12}\text{O}_{40}^{3-}$ [30]. Although, the XRD pattern of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ displays a series of featured diffraction peaks (Figure 2(b)), XRD patterns for poly(VMPS)-PW as well as poly(VMPS)-Cl only show broad diffraction peaks, indicating the loss of the long-range crystal order for the polymeric ionic hybrid and the rearrangement of the Keggin anions during the self-assembly of polymeric cations with heteropolyanions [30].

Figure 2 also demonstrates the TG analysis of poly(VMPS)-PW and poly(VMPS)-Cl. In both samples, the decomposition temperatures are above 300°C (Figure 2(c)). As the temperature increases to over 350°C , the PW-based catalyst sample (poly(VMPS)-PW) exhibits much

better thermal stability compared with Cl-based sample (poly(VMPS)-Cl).

To determine the distribution of acid strength and the relative acid amount for the catalysts, the NH_3 -TPD was carried out and the profiles were revealed in Figure 3. The peak maximums of all the catalyst samples appear at the temperature ranging from 300 to 500°C , implying that the acidic centers of the sample are related to medium strong acid sites of $\text{-SO}_3\text{H}$ groups. It is worth noting that even though all the catalysts are functionalized with ionic liquids bearing SO_3H groups, the acid strength as well as acid density is greatly influenced by both polymers and anions (Table 1). Obviously, DVB-[C₃vim][HSO₄] catalyst was found to exhibit the highest acid density with different acid strengths.

3.2. Catalytic One-Pot Dehydrative Etherification of Fructose into EMF with Various $\text{-SO}_3\text{H}$ Functionalized Polymeric Catalysts. Initially, various $\text{-SO}_3\text{H}$ functionalized polymeric catalysts were prepared and further employed to evaluate their catalytic performance for one-pot dehydrative etherification of fructose into EMF, and the results are summarized in Figure 4. $\text{-SO}_3\text{H}$ functionalized DVB polymers were demonstrated by NH_3 -TPD to possess relatively

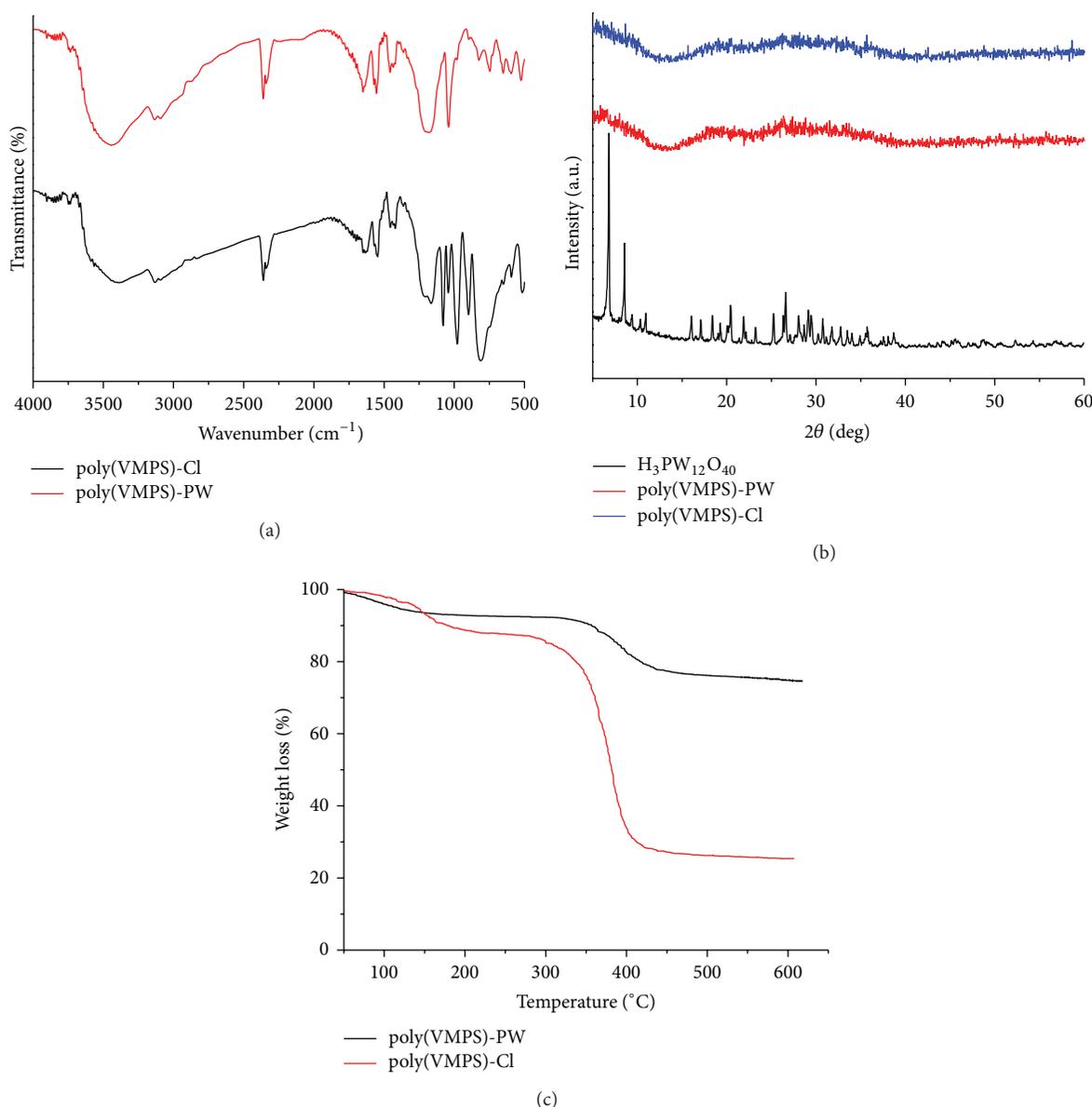


FIGURE 2: FTIR spectra (a), XRD patterns (b), and TG analysis (c) of powder samples.

higher acid density as compared with poly(VMPS)-PW and poly(VMPS)-Cl, which were well illustrated by the corresponding relatively higher fructose conversions (>95%). Nevertheless, DVB polymers supported sulfonate catalysts only exhibited moderate reactivity in terms of EMF yields (up to ~36%) and low HMF yields (around 4%) directly generated from fructose. In contrast, a high EMF yield of 48.9% together with 5.3% HMF yield was obtained when using a solid-liquid biphasic system consisting of the catalyst poly(VMPS)-PW and ethanol. While poly(VMPS)-Cl exhibited relatively lower catalytic activity, which might be attributed to the poor mass transfer of the catalyst since it was attached onto the bottom surface of the flask reactor at high reaction temperature. Besides HMF and EMF as well as humins formed during the process of catalytic conversion of fructose with SO₃H-functionalized polymers, a certain amount of ethyl levulinate

and 5-ethoxymethylfurfural diethyl acetal were also detected by HPLC [31].

3.3. Effect of Reaction Temperature and Time on One-Pot Dehydrative Etherification of Fructose into EMF. Since poly(VMPS)-PW was investigated to exhibit the best catalytic performance of all the screened catalysts, the effect of reaction temperature and time on the synthesis of EMF from fructose was further carried out with the same catalyst. Reactions were conducted at reaction temperature of 90, 110, and 130°C within reaction time of 1, 4, 7, 10, and 15 h, respectively, and the results are shown in Figure 5. It was demonstrated that EMF yields were gradually increased to 60.7% and 71.3% with the increase of reaction time from 1 to 15 h at reaction temperature of 90 and 110°C, respectively. Nevertheless, at the higher temperature of 130°C, the maximum EMF yield could

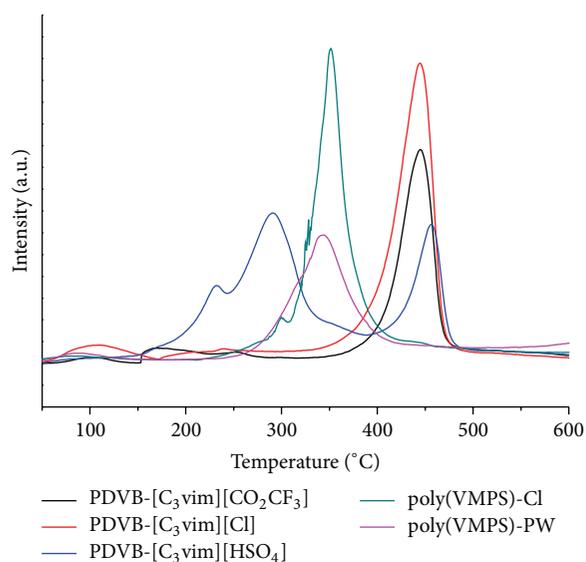


FIGURE 3: NH_3 -TPD profiles of sample powders.

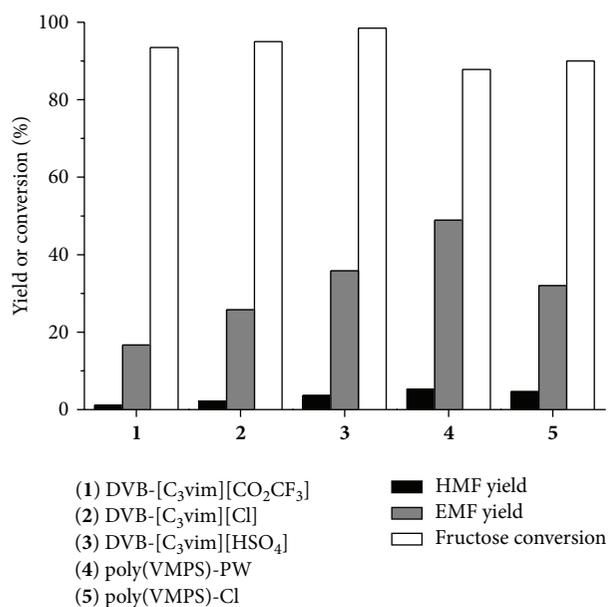


FIGURE 4: Catalytic dehydrative etherification of fructose in ethanol to EMF with various catalysts at 110°C for 7 h.

be obtained in 60.1% for 4 h, which was then slowly decreased to 31.2% for 15 h. It was noted that the yield of HMF only increased with the relatively lower reaction temperature of 90°C at the early reaction stage and the increasing rate for EMF yield was slowed down or even reduced after a long reaction period, indicating that much more side products were formed at high temperature of 130°C or after a long reaction time. Taking above discussions into consideration, reaction temperature of 110°C and reaction time of 10 h were selected as the optimized reaction conditions and employed for the following studies.

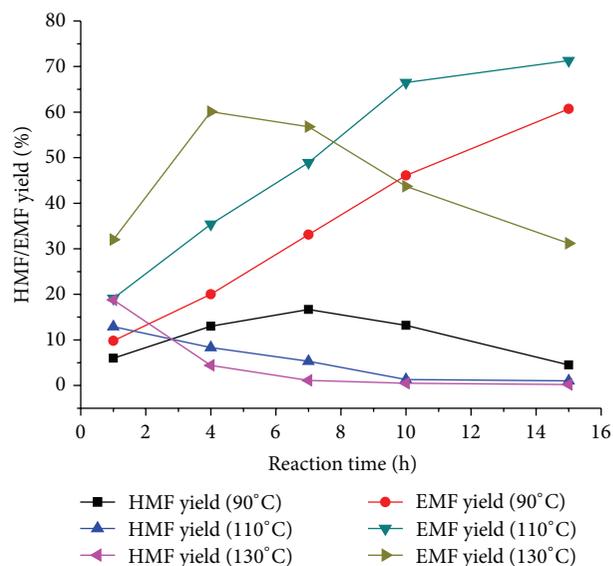


FIGURE 5: The effect of reaction temperature and time on catalytic one-pot dehydrative etherification of fructose in ethanol to EMF with poly(VMPS)-PW.

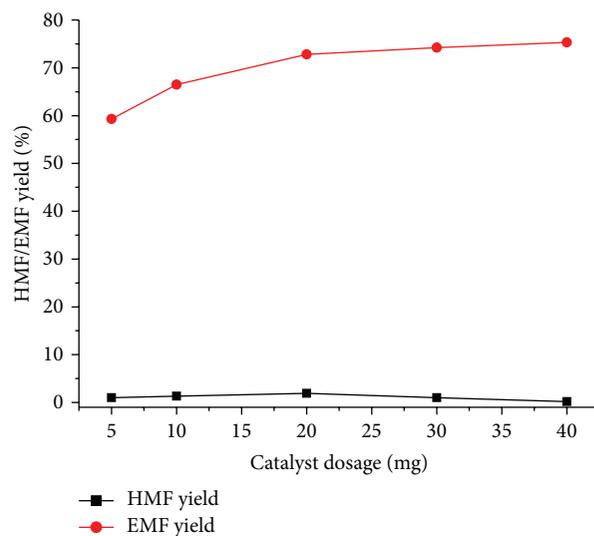


FIGURE 6: The effect of catalyst loading on one-pot dehydrative etherification of fructose in ethanol to EMF with poly(VMPS)-PW at 110°C for 10 h.

3.4. Effect of Catalyst Loading on One-Pot Dehydrative Etherification of Fructose into EMF. The effect of catalyst loading on direct dehydrative etherification of fructose into EMF was also investigated, and the results are illustrated in Figure 6. It was clearly shown that increasing the catalyst dosage of poly(VMPS)-PW from 5 mg to 20 mg correspondingly resulted in a significant increase in EMF yield from 59.3% to 72.8% at 110°C for 10 h, which should be ascribed to the increased availability and number of active sites. Simultaneously, the tendency in HMF yield with the increase of catalyst dosage implied the gradually enhanced conversion of fructose and HMF. From an economical and environmental

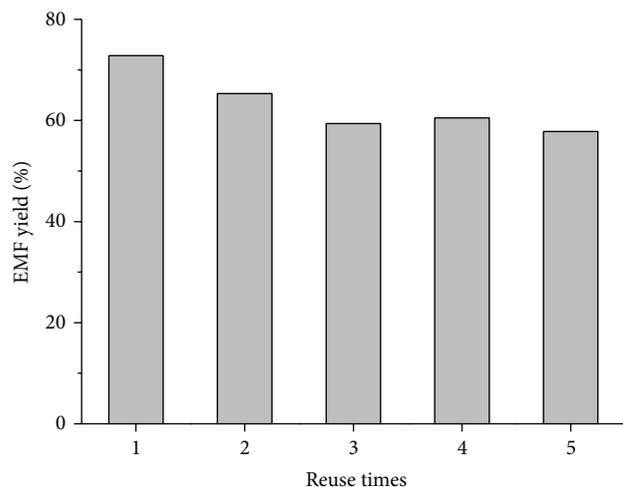


FIGURE 7: Recycle experiments for catalytic transformation of fructose into EMF with the catalyst poly(VMPS)-PW at 110°C for 10 h.

point of view, 20 mg might be an appropriate catalyst loading for the one-pot dehydrative etherification of fructose into EMF with high yield.

3.5. Reusability of Poly(VMPS)-PW for One-Pot Conversion of Fructose into EMF. Catalyst recycling is one of essential aspects for practical applications. The study on reusability of poly(VMPS)-PW for one-pot conversion of fructose into EMF was carried out at 110°C for 10 h. After the reaction of each run, the catalyst was recovered by centrifugation, washing with acetone for three times and drying at 60°C for 2 h. The recovered catalyst was directly used for the next run, and these steps were repeated five times. As shown in Figure 7, the EMF yields were remained around 60% within every cycle. These results indicated that the $-SO_3H$ functionalized polymeric catalyst could be effectively separated and reused for the one-pot cascade dehydration-etherification reaction.

4. Conclusions

In summary, the SO_3H -functionalized polymeric catalyst was efficient for direct conversion of fructose into EMF, and a maximum EMF yield of 72.8% was achieved at 110°C within 10 h. Moreover, the heterogeneous catalyst could be reused several times with no significant reduction in catalytic reactivity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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