

[Supporting Information]

A Renewable HSO₃/H₂PO₃-Grafted Polyethylene Fiber Catalyst: An Efficient Heterogeneous Catalyst for the Synthesis of 5-Hydroxymethylfurfural from Fructose in Water

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1. Experimental Section

Preparation of the co-grafting acrylonitrile with vinyl sulfonic acid or vinylphosphonic acid monomers on polyethylene fibers (HSO₃-fiber and H₂PO₃-fiber)

High surface area polyethylene fibers (~0.75 g) were sealed in the double-layered plastic bags previously placed under an inert, N₂, atmosphere and electron beam irradiated using a RDI Dynamitron electron beam machine, over dry ice using the following parameters: beam energy – 4.9 MeV; beam current – 1.00 mA; approximate total dose – 200 kGy; total irradiation time – about 22 min.

After irradiation, the samples were placed under a nitrogen atmosphere in a glove bag where they were transferred to a solution containing 56.7 mL of DMSO, 162 mL of acrylonitrile and either 55.5 mL vinylsulfonic acid sodium salt with 25% H₂O or 55.4 mL of vinyl phosphonic acid in a reaction flasks, previously nitrogen degassed for at least 1 h. The fibers in the solution were placed in an oven at 60 °C overnight. The fibers were then filtered and washed with DMF, then rinsed with methanol, dried in a vacuum oven at 50 °C overnight to give an approximated degree of grafting of ~157 % for the HSO₃-fiber and ~280 % for the H₂PO₃-fiber.

$$\% \text{ DOG} = ((\text{wt}_{\text{AG}} - \text{wt}_{\text{BG}}) / \text{wt}_{\text{BG}}) \times 100$$

wt_{AG} - dry weight after grafting

wt_{BG} - dry weight before grafting

The elemental analysis of the grafted fibers reveals a composition of approximately C 70 %, H 8.8 %, N 15 %, O 2.5 % and S 0.2 % for the grafted HSO₃-fiber and C 71 %, H 8.1 %, N 16.9 %, O 4.5 % and P 0.24 % for the grafted H₂PO₃-fiber. Before using the fibers they were treated with 2.5 % H₂SO₃, (~15 mL for every 1.5 mg of grafted fibers) at 80 °C for 1 h and rinsed with deionized water until the pH of the rinsing water was 7.

Materials Characterization

The grafted PE fiber catalyst was characterized by FT-IR (Bio-Rad Excalibur FTS-3000) after being evenly mixed with KBr powder and the spectrum was recorded over the range from 500 - 3500 cm^{-1} . The solid state NMR was measured on a Bruker AVANCE 400 spectrometer at 11 kHz. Scanning electron microscope (SEM) experiments were conducted on HITACH HD2000 microscopes with an accelerating voltage of 200 kV. Elemental analysis of the samples was done by EAI-Elemental Analysis Inc. and Galbraith; CHNO analyzed by combustion. Sulfur was determined by titration or combustion and Phosphorus by ICP. The analysis of HMF was carried out by means of a reversed phase HPLC system (Shimadzu CBM-10AW VP) equipped with a C18 column (250 mm \times 4.6 mm \times 5 μm). The mobile phase was water at a flow rate of 1.0 mL/min and the detection wavelength was 300 nm and the samples were diluted with water. The consumption of fructose was confirmed by the phenol-sulfuric acid method.^[1] A mixture containing 0.1 mL of the reaction sample (water-soluble portion), 0.9 mL of deionized water, 1 mL of 5% phenol (freshly distilled) and 5 mL of 98% concentrated sulfuric acid was prepared. The analysis was performed on an Evolution 600 UV-vis spectrophotometer at about 490 nm. The concentration of fructose in the reacted solution was calculated based on the standard curve obtained with fructose.

Adsorption experiments of fructose and HMF for catalyst

0.3 g of each solid acid catalyst was immersed in 3.5 mL of deionized water containing 0.23 g of fructose or 0.1 g of HMF. After shaking for 24 h at room temperature, the mixture was filtered and the supernatant solution was analyzed by UV-vis spectrophotometer and HPLC, while the adsorbed amount can be calculated by subtracting the concentration of equilibrium solution from the initial concentration.

Catalytic test for dehydration of fructose to HMF

The dehydration of fructose to HMF over the solid acid catalysts was performed in a 50 mL round-bottom flask equipped with a magnetic stirrer containing 8.6 wt % (0.35 g) of catalyst, 5.6

wt % (0.23 g) of fructose, and 3.5 mL of distilled water at 120 °C. Each aliquot of reaction mixture was filtered and the supernatant liquid was analyzed by HPLC based on the standard curve obtained with HMF (external standard method). After each reaction (6 h), the catalyst was collected by filtration, washed with ethanol and 1 M HCl solution for several times to remove any byproduct, then washed to neutral with water and dried. Then another reaction batch started as a new recycle with the used catalyst. This process was repeated for several times, and the catalytic performance in each recycle was recorded.

Estimation of Yields of Levulinic Acid

Mass spectrometry was used to estimate the yields of levulinic acid at reaction times of 3, 6, 10, and 20 h in the experiment for Figure 2a based on the yields of HMF through a semi-quantitative method. Since the yields of HMF were known from HPLC, we used HMF, observed at m/z 127 in positive-ion mode in mass spectrum, as the internal standard to estimate the yield of levulinic acid (observed at m/z 117 in positive-ion mode) in the same reaction mixture. Mass spectrometry was performed using a JEOL (Peabody, MA, USA) orthogonal time-of-flight (TOF) mass spectrometer (model JMS-T100LC) with an IonSense (Danvers, MA, USA) direct analysis in real time (DART) source in positive-ion mode. Helium gas was used for the DART source at a flow rate of 4 L/min and heated to be 300 °C. The mass acquisition range was m/z 100-300 with a spectra recording interval of 0.1 s. Five standards were prepared in aqueous solutions with the varying concentration ratio of levulinic acid to HMF. The concentration of HMF in these five standards was constant (2.5 wt%). Each standard was examined by DART-TOFMS for five times. The average intensity ratio of ions at m/z 117 (levulinic acid) to m/z 127(HMF) was plotted against the concentration ratio of levulinic acid to HMF. The mass spectra of the reaction mixtures taken at 3, 6, 10, and 20 h were analyzed by mass spectrometry in the same manner. Based on the yields of HMF at four different reaction times determined by HPLC, the relative yields of levulinic acid in the reaction mixtures were calculated using the calibration curve and are shown in Figure S6. Clearly, the yield of levulinic acid did not change much after 6 h, suggesting that the further hydration of HMF was indeed restrained.

2. Figures

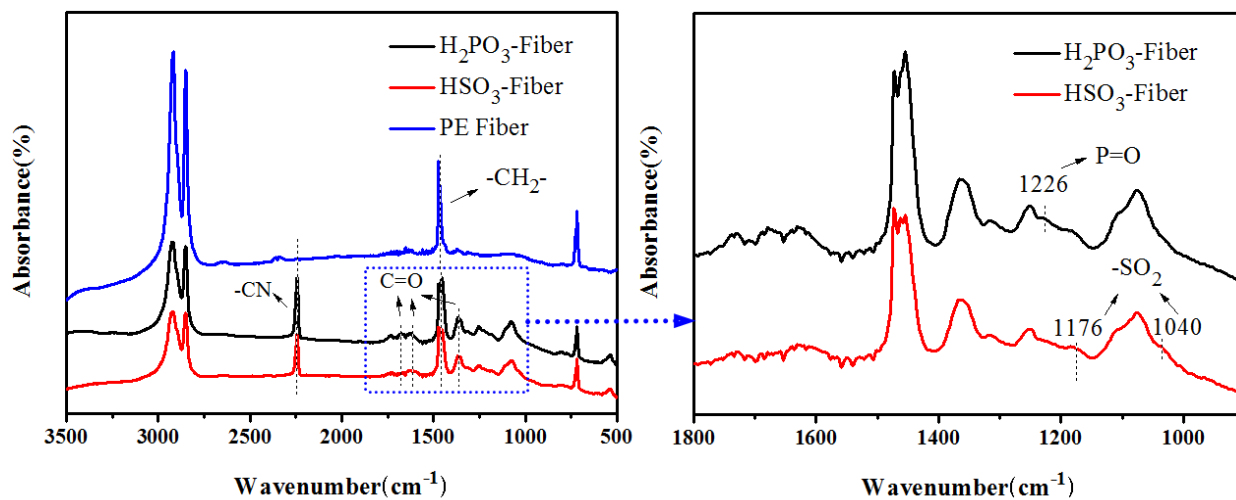


Figure S1. FT-IR spectra of (a) PE fiber, H₂PO₃-fiber and HSO₃-fiber and (b) zoomed in the region of H₂PO₃-fiber and HSO₃-fiber focusing on the absorbance of the P=O and -SO₂ groups.

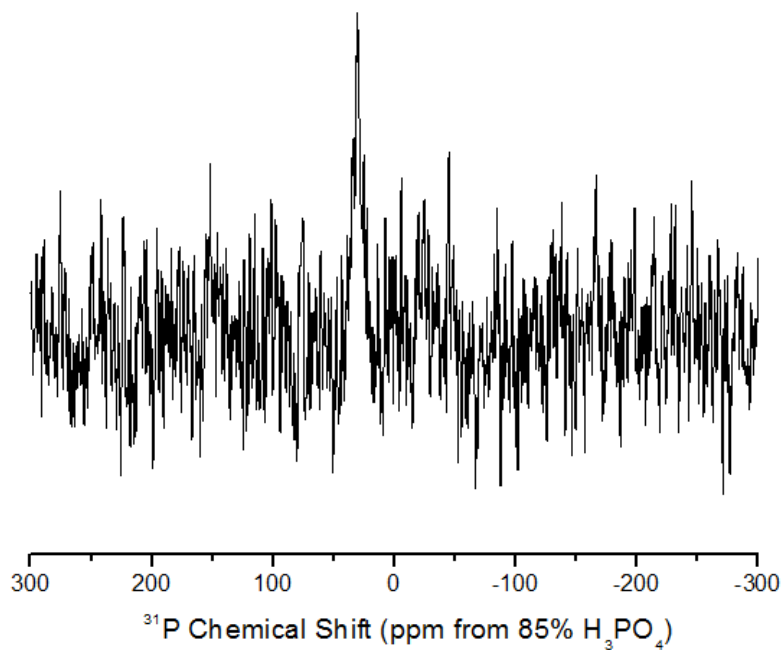


Figure S2. ³¹P solid-state MAS-NMR spectrum of H₂PO₃-fiber.

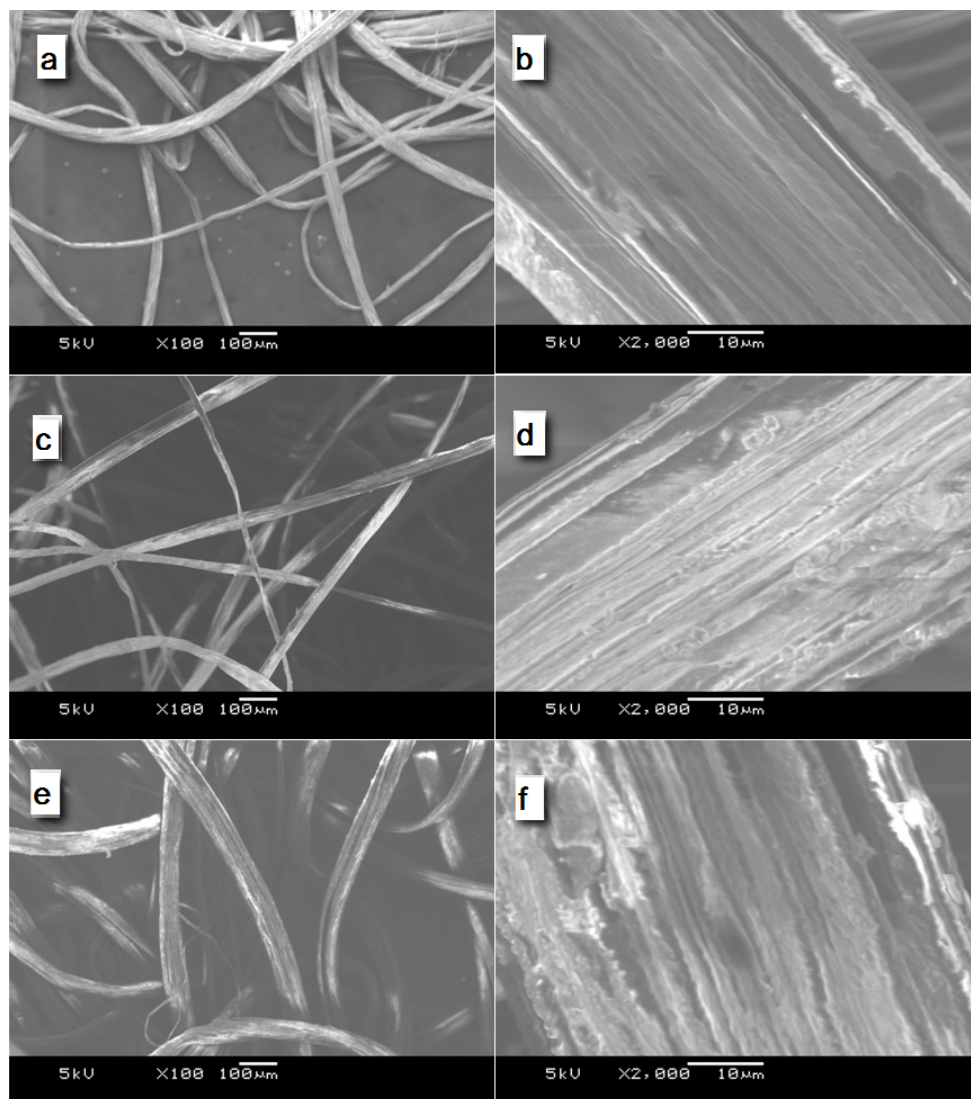


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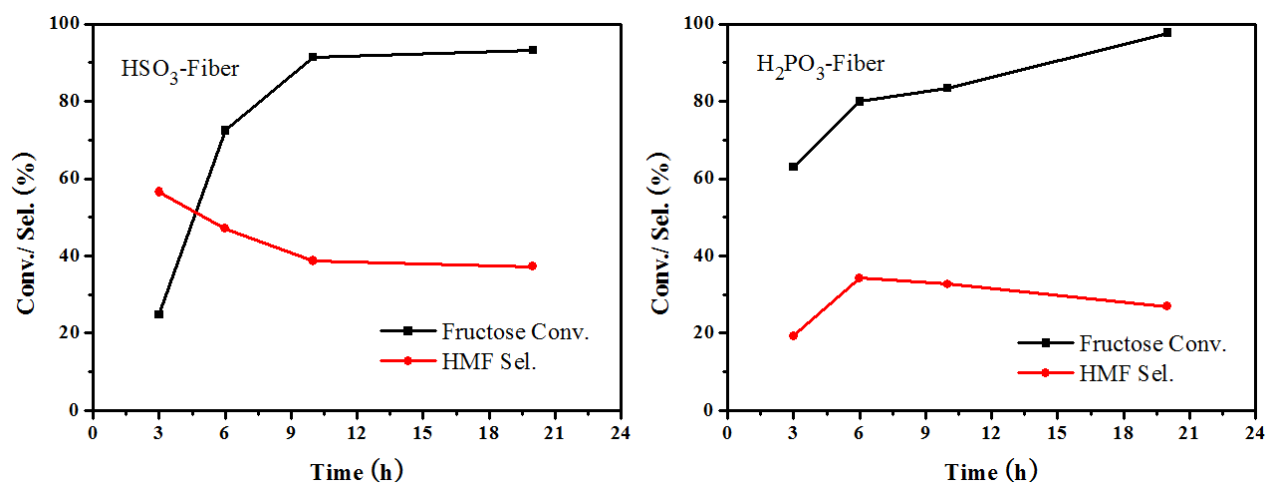


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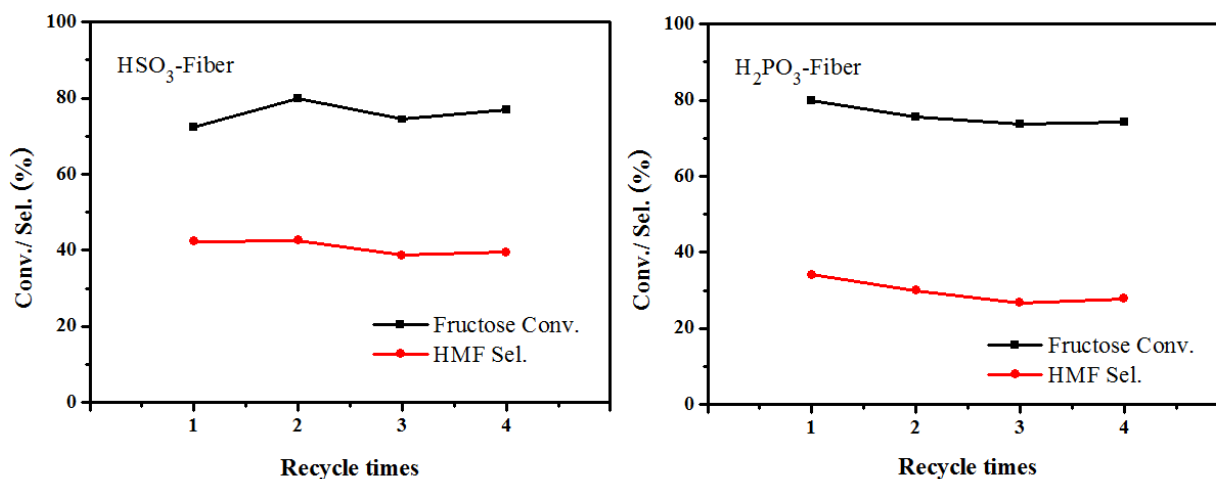


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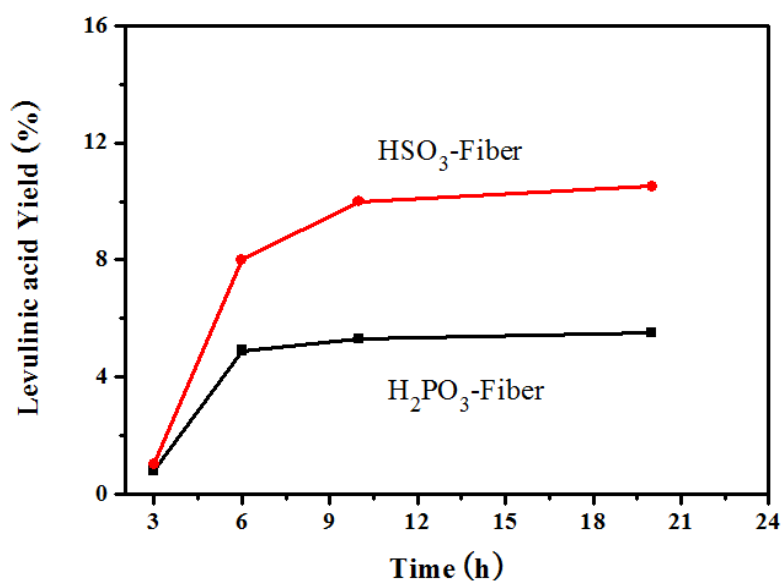


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3. Tables

Table S1. The elemental compositions of the fresh catalysts. (Pretreatment method: the sample was dried to constant weight at 80 °C under vacuum, at this point to be held for three hours and then handled under nitrogen)

| Catalyst | S (wt%) | P (wt%) | O (wt%) | carboxylic acid density (mmol/g) | sulfonic / phosphonic acid density (mmol/g) |
|---------------------------------------|------------|------------|------------|-------------------------------------|--|
| HSO ₃ -fiber | 0.20 | | 2.97 | 0.83 | 0.063 |
| H ₂ PO ₃ -fiber | | 0.19 | 4.54 | 1.32 | 0.061 |

Table S2. The elemental compositions (Pretreatment method: the sample was washed by ethanol and water several times and dried to constant weight at 80 °C under vacuum, at this point to be held for three hours and then handled under nitrogen) and catalytic performances of the catalysts after being reused for four times.

| Catalyst | S (wt%) | P (wt%) | O (wt%) | carboxylic acid density (mmol/g) | HMF yield (%) |
|---------------------------------------|------------|------------|------------|-------------------------------------|------------------|
| HSO ₃ -fiber | 0.20 | | 2.97 | 0.83 | 30 |
| H ₂ PO ₃ -fiber | | 0.19 | 4.55 | 1.32 | 21 |

4. References

[1] Dubois, M.; Gilles, K. A.; Hamilton, J. K.; Rebers, P. A.; Smith, F. *Anal. Chem.* **1956**, *28*, 350–356.