Electronic Supplementary Material (ESI) for Green Chemistry

A one-pot Approach for conversion of Fructose to 2,5-diformylfuran by combination of Fe_3O_4-SBA-SO_3H and K-OMS-2

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Supplemental Materials

1. Materials

The formation of 2,5-DFF from fructose was carried out in a glass tube equipped with a magnetic stirrer, molecular oxygen was simply introduced by an airway. Gas chromatography measurements were conducted on Agilent GC 4890D with a flame ionization detector. RTX-5 capillary column was used for separation. HPLC measurements were conducted on Water 2414 with a Refractive Index detector for fructose conversion detection.

Fructose, Potassium permanganate, manganese sulfate hydrate, Tetraethoxysilane, HCl, H_2O_2 (30 wt%), DMSO, HNO_3, H_2SO_4 were purchased from Sinopharm Chemical Reagent Co., Ltd. Pluronic 123, Fe_3O_4 NMPs, Naphthalenen, 3-mercaptopropyltrimethoxysilane were purchased from Aladdin Reagent Co., Ltd. 5-HMF and 2,5-DFF were purchased from TCI development Co., Ltd.

2. Catalysts preparation

Fe_3O_4-SBA-SO_3H was prepared referring to our previous work. 2 g Fe_3O_4 NMPs and 4 g Pluronic 123 were added to a round bottom flask which contained 200 mL 0.5 M HCl. After stirring for 2 h, 6.8 g tetraethoxysilane was added and the mixture was heat at 40 °C with stirring. 1.6 g 3-mercaptopropyltrimethoxysilane and 15 mL H_2O_2 (30 wt%) were added after 3h and the resulting mixture was stirred for 20 h at 40 °C. Then the obtained mixture was transferred to a Teflon-lined autoclave, the catalyst precursor was aged at 100 °C for 24 h. After filtration, 300 mL ethanol was employed to extract the block copolymer P123 in a Soxhlet extractor. Finally, the extracted material was washed with 1 M H_2SO_4 and a mixture of water and ethanol for several times and dried at 80 °C under vacuum. The amount of S in the catalyst was 4% (m/m), which was detected by ICP atomic emission spectrometry.

H-K-OMS-2 and K-OMS-2 were prepared referring to standard literature procedures. Potassium permanganate solution (225 mL, 0.4 M) was added to a mixture of manganese sulfate hydrate solution (67.5 mL 1.75 M) and concentrated nitric acid (6.8 mL), then the formed dark brown slurry was heated under reflux at 110 °C. 24h later, K-OMS-2 was obtained after filtered and washed with deionized water. The catalyst was dried at 110 °C for several hours before use. H-K-OMS-2 was synthesized by adding a subsequent process to the synthesis of K-OMS-2. That is, K-OMS-2 was stirred in a 1 M solution of nitric acid for several hours at 60-70 °C. The compositions of K-OMS-2 and H-K-OMS-2 were obtained by elemental analysis as $KMn_8O_{16}\cdot nH_2O$ and $H_{0.2}K_{0.8}Mn_8O_{16}\cdot nH_2O$, X-ray diffraction (XRD) and infrared (IR) studies were performed.

3. Reaction tests

The typical process for aerobic oxidation of 5-HMF to 2,5-DFF: 5-HMF (0.126 g, 1 mmol), K-OMS-2/H-K-OMS-2 (0.05-0.1 g) were charged into a tube, and 3 mL DMSO was added. The tube was heated at 110 °C for 6 h under 10 mL/min O_2. Then, the catalyst was filtered and the filtrate was detected by GC analysis with naphthalene as internal standard (Fig S10, ESI†).

The typical process for one-pot synthesis of 2,5-DFF: Fructose (0.18 g, 1 mmol) and Fe_3O_4-SBA-SO_3H (0.1 g) were added to 3 mL DMSO, the mixture was heated at 110 °C for 2 h. Then K-OMS-2 (0.1 g) was added without catalyst separation, the mixture was heated at 110 °C for another 6 h under molecular oxygen flow (10 mL/min). Fructose conversion and 5-HMF yield was detected by HPLC analysis, 2,5-DFF yield was detected by GC analysis.

Separation of 2,5-DFF from DMSO: After catalyst(s) was filtered and washed with DMSO for several times, 30 mL H_2O was added to the solution. Then, ethyl acetate (3×10 mL) was added for extracting 2,5-DFF from the solution. After combining the ethyl acetate layer, 5% NaCl aqueous (3×10 mL) was added for removal of the residual DMSO by extracting. Finally, the rest solution was dried with anhydrous $MgSO_4$, 2,5-DFF was obtained after condensing the solution. The ^1H NMR and ^{13}C NMR spectra were shown as Fig. S11, S12.

4. Results

Table S1. Texture properties of K-OMS-2 and MnO_2

Sample	S_{BET} (m^2/g)	Pore Vol (cm^3/g)
K-OMS-2	77.2106	0.451680
MnO_2	0.1324	0.000502

Table S2. Scale-up condition for aerobic oxidation of 5-HMF to 2,5-DFF[a].

Entry	Substrate	Catalyst	Oxidant	Solvent	Yield(%)
1	5-HMF	K-OMS-2	O_2	DMSO	70
2	5-HMF	K-OMS-2	air	DMSO	20

[a] 2g 5-HMF, 2g K-OMS-2, 15mL solvents, 10mL/min air/O_2. React at 110°Cfor 6h. Selectivity of 2,5-DFF was 100%.

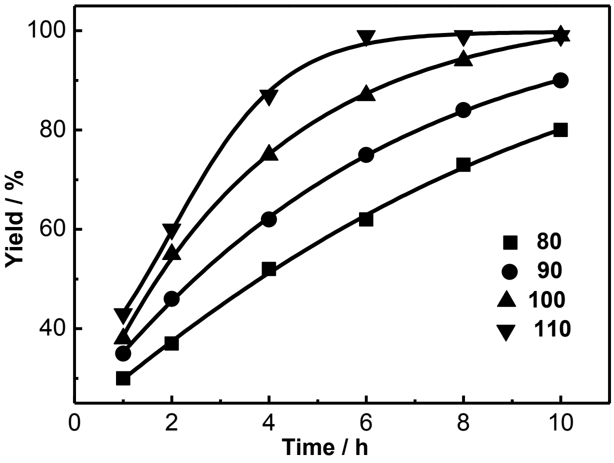

Fig. S1 Yields of 5-HMF under different temperature and different time. Reaction conditions: 1 mmol 5-HMF, 0.1 g K-OMS-2, 3 mL DMSO, 10 mL/min O_2.

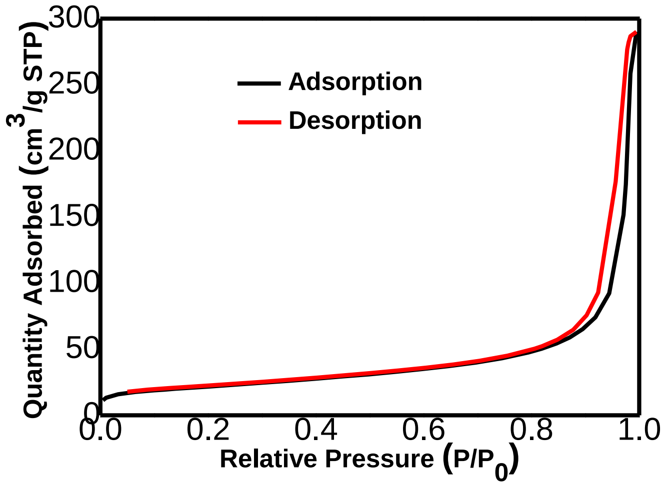

Figure S2 N_2 adsorption–desorption isotherm of K-OMS-2.

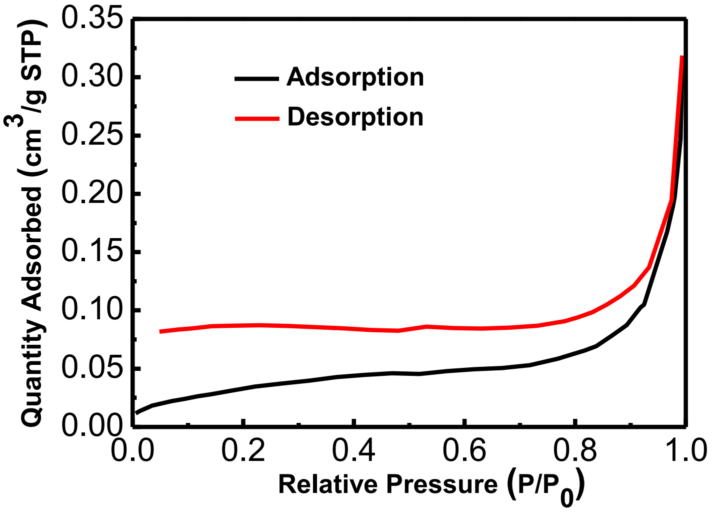

Figure S3 N_2 adsorption–desorption isotherm of MnO_2.

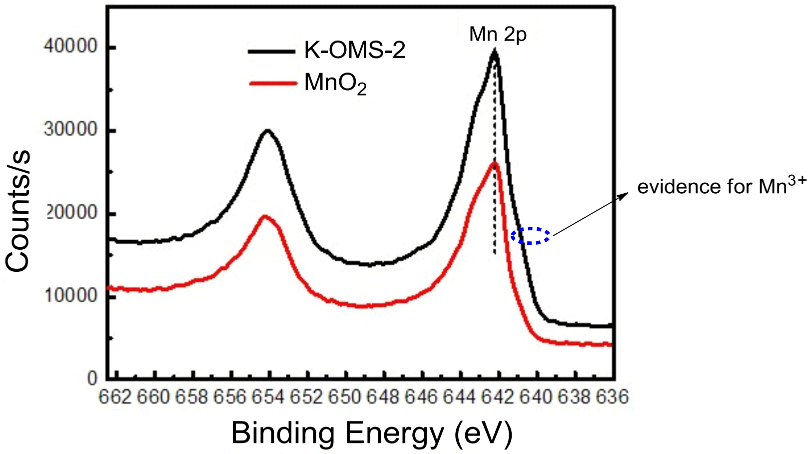

Figure S4 XPS patterns for K-OMS-2 and MnO_2.

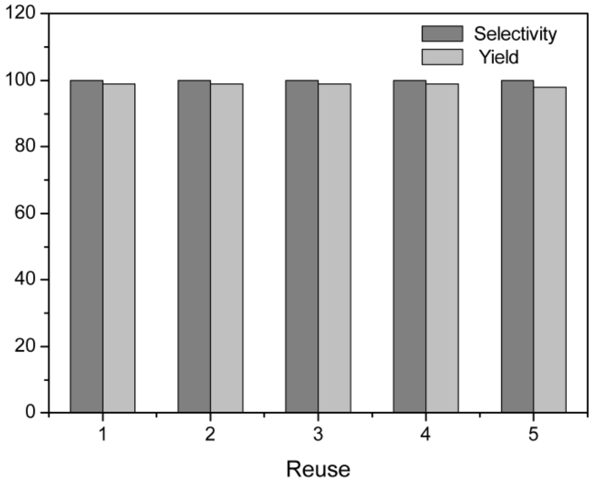

Fig. S5 Reuse of K-OMS-2 for oxidation of 5-HMF towards 2,5-DFF.

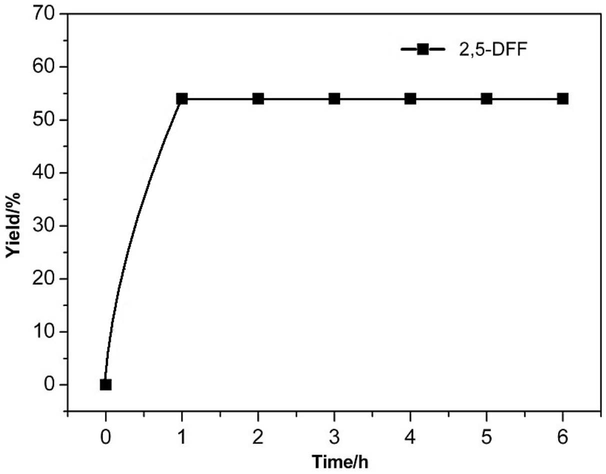

Fig. S6 Time course of product distribution after filtration of K-OMS-2 catalyst.

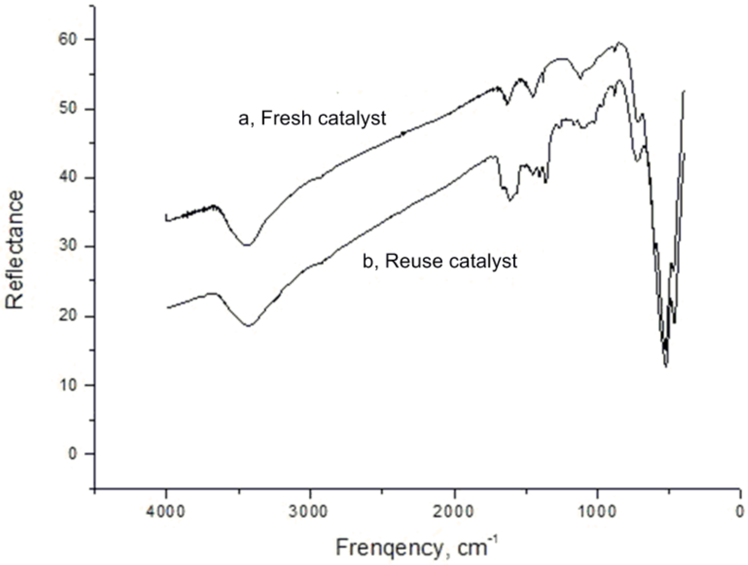

Figure S7 IR spectra for fresh (a) and reuse (b) K-OMS-2 catalyst.

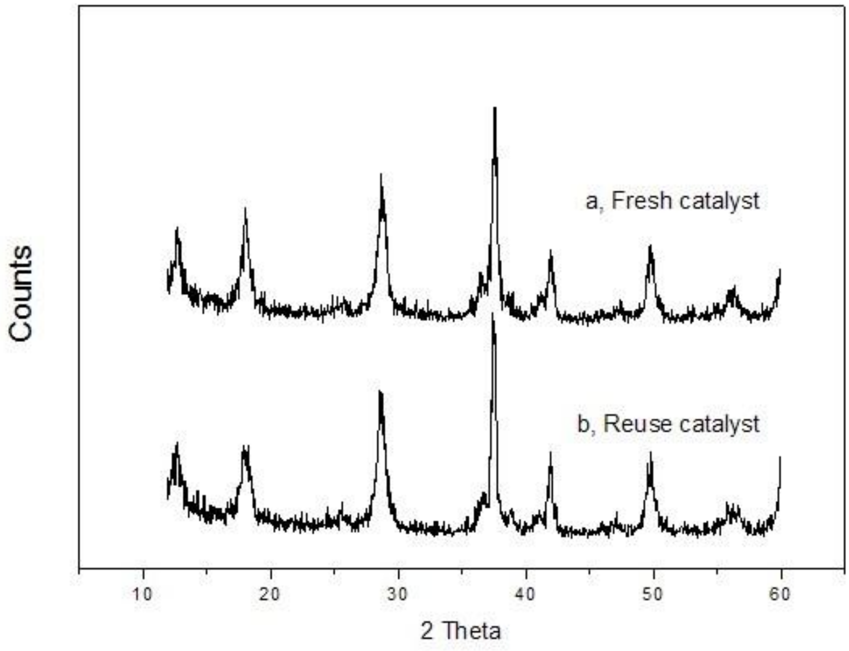

Figure S8 XRD patterns for fresh (a) and reuse (b) K-OMS-2 catalyst.

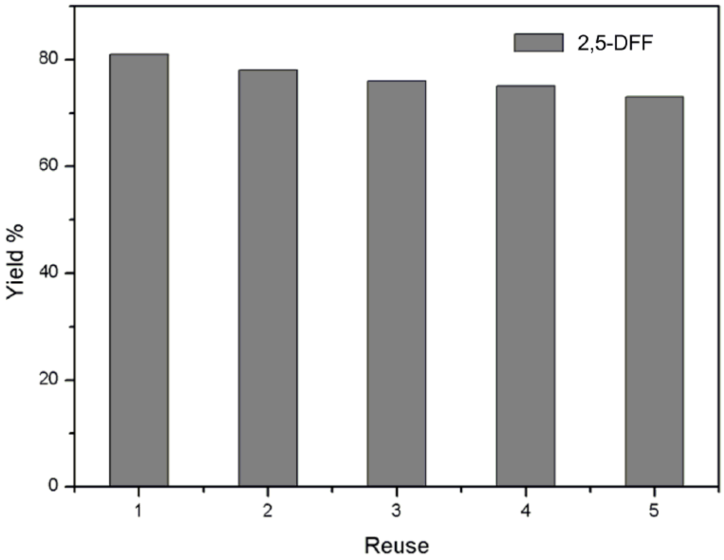

Fig. S9 Reuse of Fe_3O_4-SBA-SO_3H and K-OMS-2 for conversion of fructose to 2,5-DFF in one-pot reaction.

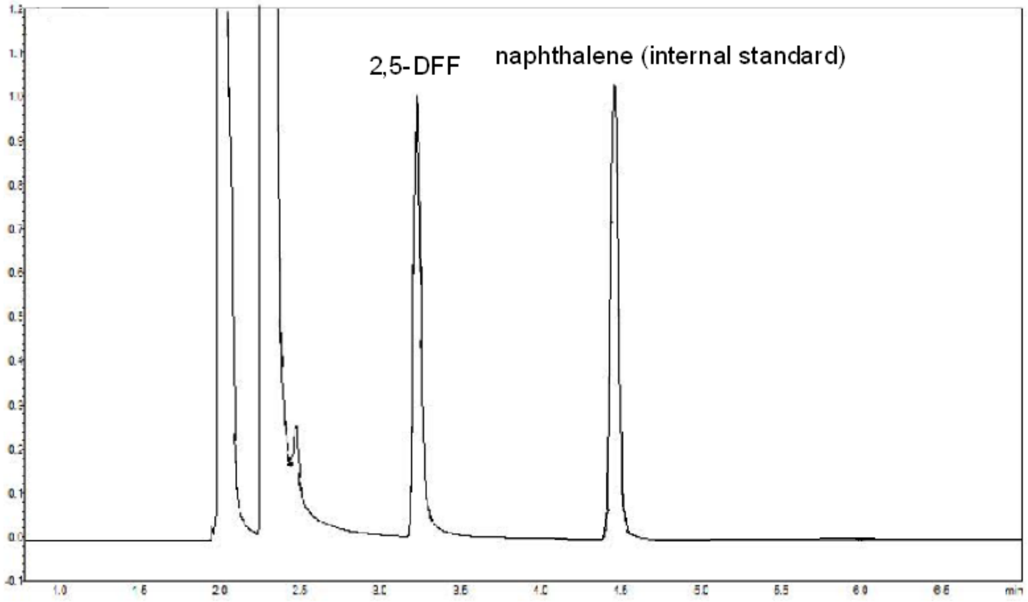

Figure S10 GC trace for one-pot synthesis of 2,5-DFF.

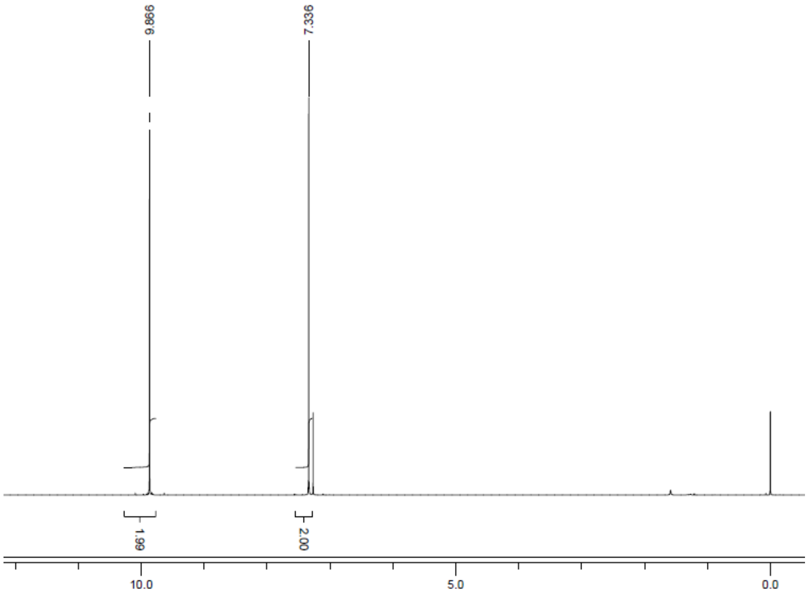

Figure S11 ^{1}H NMR ($CDCl_3$) of 2,5-DFF after separate from DMSO.

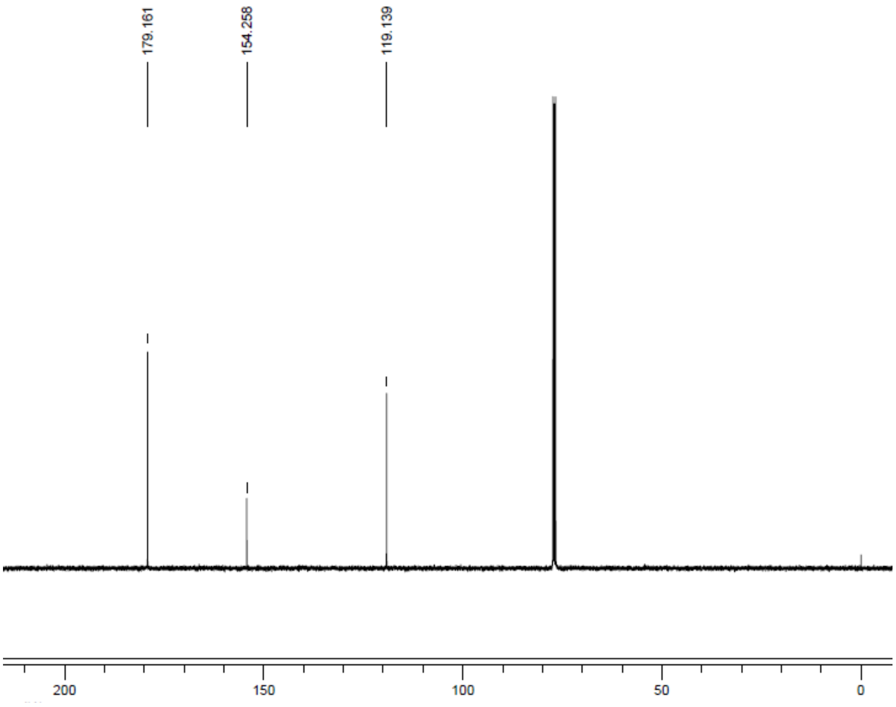

Figure S12 ^{13}C NMR ($CDCl_3$) of 2,5-DFF after separate from DMSO.