A one-pot Approach for conversion of Fructose to 2,5-diformylfuran by combination of Fe₃O₄-SBA-SO₃H 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$_2$O$_2$ (30 wt%), DMSO, HNO$_3$, H$_2$SO$_4$ were purchased from Sinopharm Chemical Reagent Co., Ltd. Pluronic 123, Fe$_3$O$_4$ 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$_3$O$_4$-SBA-SO$_3$H was prepared referring to our previous work. 2 g Fe$_3$O$_4$ 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$_2$O$_2$ (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$_2$SO$_4$ 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$_8$O$_{16}$·nH$_2$O and H$_{0.2}$K$_{0.8}$Mn$_8$O$_{16}$·nH$_2$O, 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$_3$O$_4$-SBA-SO$_3$H (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$_2$O 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 $^1$H NMR and $^{13}$C NMR spectra were shown as Fig. S11, S12.
4. Results

Table S1. Texture properties of K-OMS-2 and MnO₂

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_BET (m²/g)</th>
<th>Pore Vol (cm³/g)</th>
</tr>
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<tbody>
<tr>
<td>K-OMS-2</td>
<td>77.2106</td>
<td>0.451680</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.1324</td>
<td>0.000502</td>
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</table>

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Catalyst</th>
<th>Oxidant</th>
<th>Solvent</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5-HMF</td>
<td>K-OMS-2</td>
<td>O₂</td>
<td>DMSO</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>5-HMF</td>
<td>K-OMS-2</td>
<td>air</td>
<td>DMSO</td>
<td>20</td>
</tr>
</tbody>
</table>

* 2g 5-HMF, 2g K-OMS-2, 15mL solvents, 10mL/min air/O₂. React at 110°C for 6h. Selectivity of 2,5-DFF was 100%.

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**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 O₂.
Figure S2 N₂ adsorption–desorption isotherm of K-OMS-2.

Figure S3 N₂ adsorption–desorption isotherm of MnO₂.
**Figure S4** XPS patterns for K-OMS-2 and MnO₂.

**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$_3$O$_4$-SBA-SO$_3$H 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.