

## Supporting Information

### Experimental section

**Materials:** all starting materials are commercially available and were used as received, unless otherwise indicated. Fructose (99%) was purchased from Alfa Aesar. *iso*-propanol (99.9%), hydrogen chloride (37%), acetic acid (glacial) were purchased from Merck. HMF (99%), FDCA (97%), DFF (97%), HFCA (97%), V<sub>2</sub>O<sub>5</sub> (99.6%), fumed SiO<sub>2</sub> (surface area 380 m<sup>2</sup> g<sup>-1</sup>), oxalic acid (98%), 4-tert-butylphenol (99%) were purchased from Aldrich. The other chemicals not stated here were purchased from Sigma-Aldrich or Merck.

**Product analysis:** analysis of the reactant and product in the dehydration of fructose to HMF and HMF oxidation to MA was carried out using HPLC (Agilent Technologies, 1200 series) with UV and refractive index (RI) detector. Reactant and product were separated on an Agilent Hi-Plex H column (7.7 × 300 mm, 8 μm). The effluent was a solution of H<sub>2</sub>SO<sub>4</sub> (0.0001 M), flow rate 0.7 ml min<sup>-1</sup>, 25 °C. The retention times were 9.2 min, 22.1 min, 24.9 min, 31.0 min, 36.4 min, and 44.5 min for maleic acid, FDCA, HFCA, FFCA, HMF, and DFF, respectively. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Bruker AV-400 (400 MHz) spectrometer. Chemical shifts are reported in ppm with reference to tetramethylsilane with the solvent resonance as the internal standard.

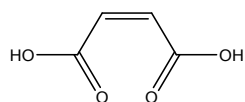
**Catalysts characterization:** powder X-ray Diffraction (XRD) was conducted using a Bruker automatic diffractometer (Bruker D8 ADVANCE) with monochromatized Cu-Kα radiation (λ = 0.15406 nm) at a setting of 40 kV. The TEM images were obtained with a FEI Tecnai F20 transmission electron microscope.

**Catalyst preparation:** calculated amount of V<sub>2</sub>O<sub>5</sub> was dissolved in 3 wt% oxalic acid solution. This precursor solution was then impregnated onto SiO<sub>2</sub> at room temperature. The material was dried overnight and then calcined at 450 °C for 4 h in air.

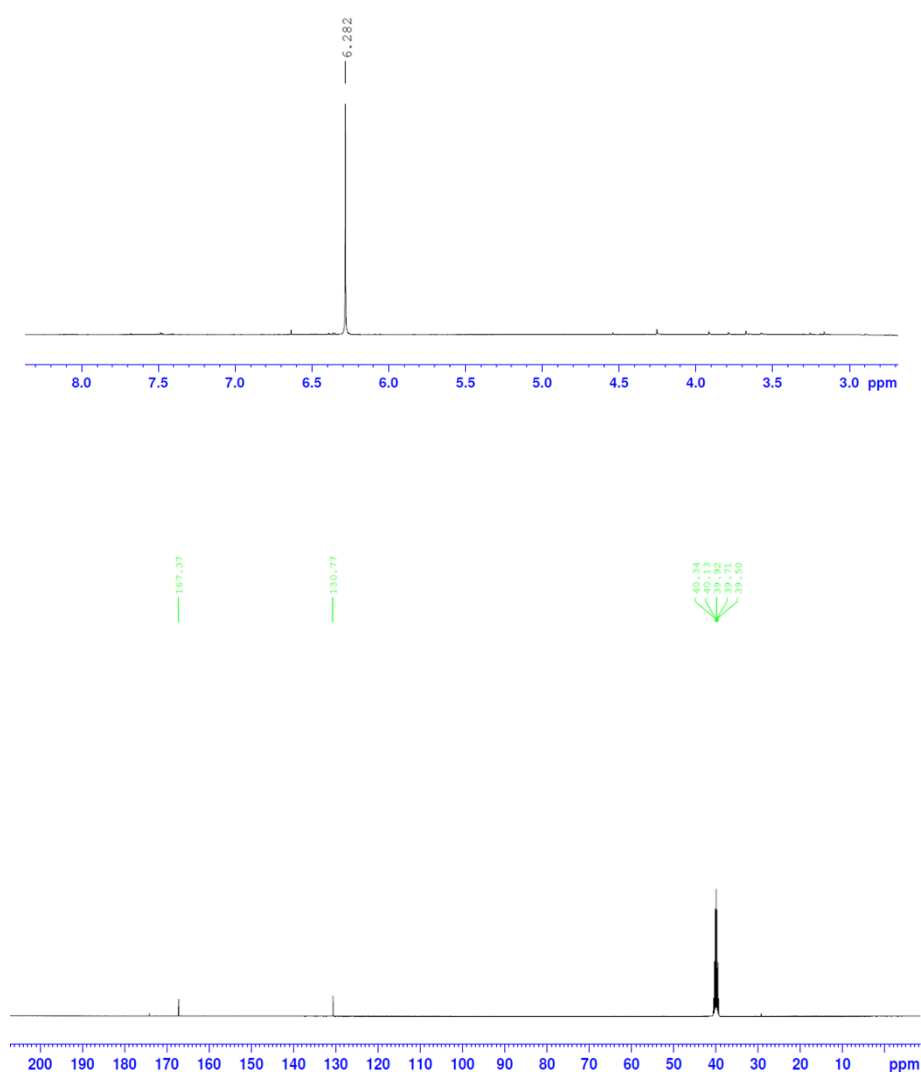
**HMF oxidation to MA:** HMF (0.252 g, 2.0 mmol), acetic acid (10.0 ml), and V<sub>2</sub>O<sub>5</sub> catalyst (9.0 mg, 2.5 mol%) were charged into a Parr reactor with glass liner. The reactor was sealed and pressurized with 5 bar O<sub>2</sub> and then heated at 100 °C for 4 h. The reactor was cooled to room temperature and depressurized. The catalyst was separated by centrifuge and the reaction mixture was analyzed by HPLC to determine the conversion and yield.

**The direct conversion of Fructose to MA:** For the first step fructose dehydration to HMF, fructose (0.36 g, 2 mmol), HCl (37 wt%, 8.4 ul, 5 mol%), and IPA (4 ml) were charged in to the reactor and heated at 100 °C for 3 h. After that the IPA solvent was

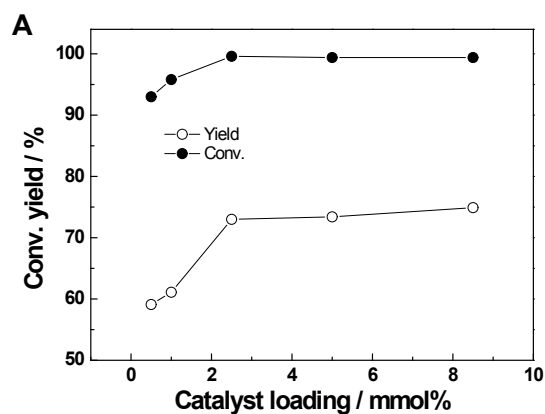
removed by evaporation under reduced pressure to give the crude HMF product. For the second step HMF oxidation to MA, AcOH (10 ml), 5%V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> (36 mg, 0.5 mol%) or V<sub>2</sub>O<sub>5</sub> (9 mg, 2.5 mol%) were directly charged into the reactor. The reactor was pressurized with 5 bar O<sub>2</sub> and then heated at 100 °C for 4 h. The reactor was cooled to room temperature and depressurized. The catalyst was separated by centrifuge and the reaction mixture was analyzed by HPLC to determine the conversion and yield.



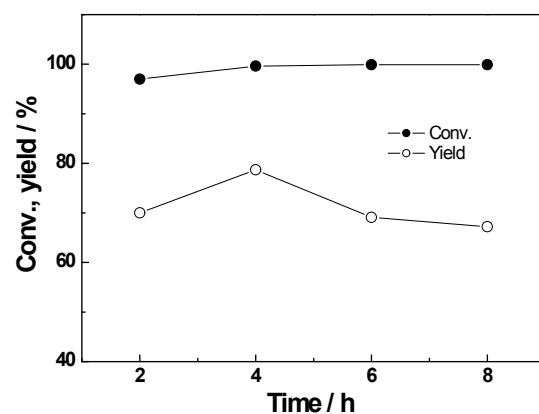
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ),  $\delta = 6.282$ ;  $^{13}\text{C}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ),  $\delta = 130.77, 167.37$



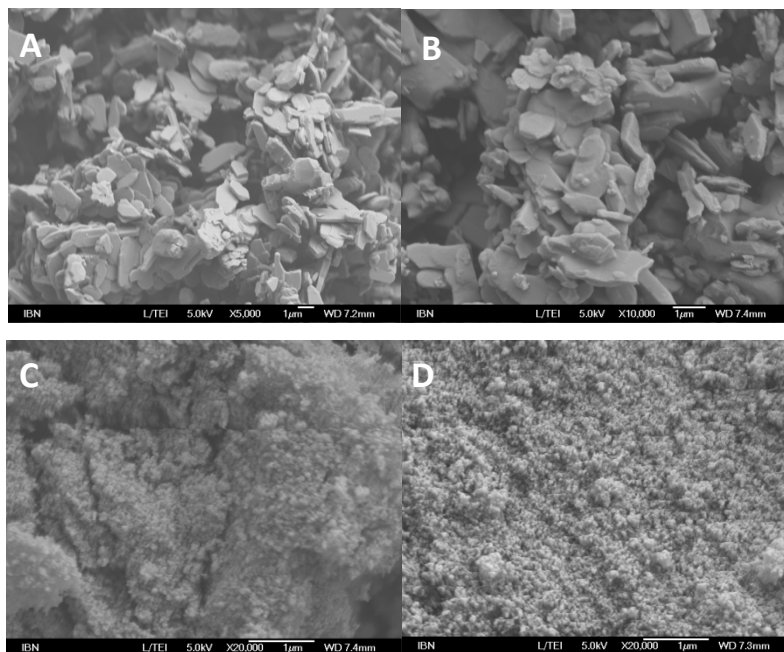
**Fig. S1.** NMR spectra of maleic acid from the hydrolysis of HMF oxidization product. Procedure for HMF oxidation: HMF 0.252 g (2.0 mmol); acetic acid 10.0 ml; catalyst 30.0 mg (8.2 mol%); 100 °C, 4 h,  $\text{O}_2$  10 bar. After the reaction, the catalyst was separated by filtration, then 10 ml water was added to the filtrate and the mixture was stirred at 50 °C for 2 h in a flask. The solvent was then removed by evaporation to give solid maleic acid product.



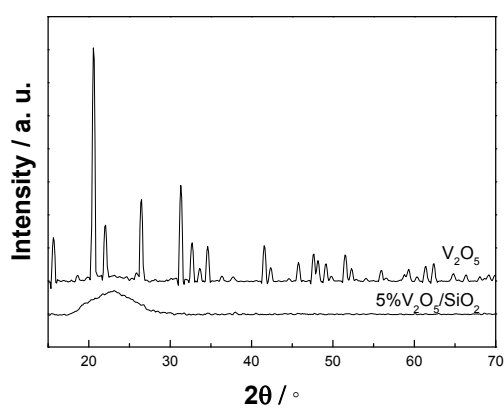
**Fig. S2.** Varying the loading amount of  $V_2O_5$  catalyst in HMF oxidation to MA. HMF 0.252 g (2.0 mmol); acetic acid 10.0 ml;  $O_2$  10 bar, 100 °C, 4 h. Yields include maleic anhydride and maleic acid.



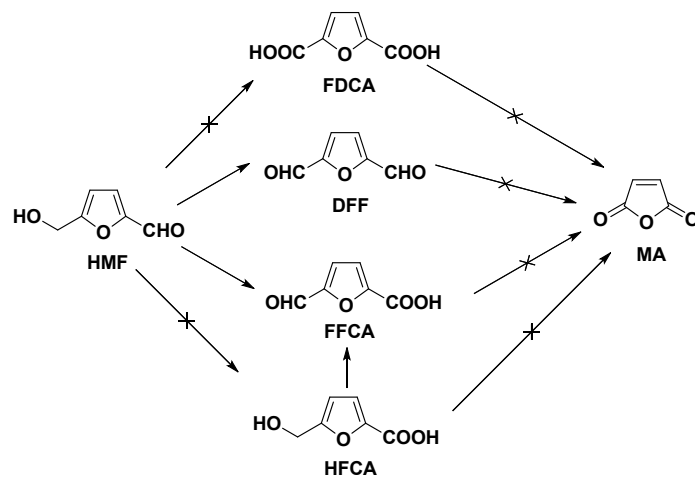
**Fig. S3.** The effect of reaction time on HMF oxidation to MA over the  $V_2O_5$  catalyst. HMF 0.252 g (2.0 mmol); acetic acid 10.0 ml;  $V_2O_5$  catalyst 9.0 mg (2.5 mol%),  $O_2$  5 bar,  $T = 100$  °C. Yields include maleic anhydride and maleic acid.



**Fig. S4.** SEM image of (A) fresh  $V_2O_5$  catalyst, (B) used  $V_2O_5$  catalyst, (C) fresh 5%  $V_2O_5/SiO_2$  catalyst, and (D) used 5%  $V_2O_5/SiO_2$  catalyst.



**Fig. S5.** XRD patterns of used  $V_2O_5$  and 5%  $V_2O_5/SiO_2$  catalysts.



**Fig. S6.** Mechanism study for MA formation from HMF. Under typical reaction conditions (HMF 0.252 g, 2.0 mmol; acetic acid 10.0 ml; catalyst 9.0 mg, 8.2 mol%; O<sub>2</sub> 5 bar; 100 °C, 4 h), DFF was detected at < 5% yield, FFCA was detected at trace amount (< 0.5% yield), FDCA and HFCA were not detected. To find out the possible intermediate products for MA formation, FDCA, DFF, FFCA, and HFCA were tested under the same reaction conditions for HMF oxidation, however, the conversions were very low and MA was not detected. When HFCA was used as raw material, FFCA was obtained at 10% yield.

**Table S1.** HMF oxidation over  $V_2O_5$ ,  $SiO_2$ , 5% $V_2O_5/SiO_2$ , and the mechanical mixture of  $V_2O_5$  and  $SiO_2$ .<sup>[a]</sup>

Entry	Cat. (weight, mg)	$V_2O_5$ [mol%]	Conv. [%]	Yield [%]	
				MA <sup>[b]</sup>	DFF
1	5% $V_2O_5/SiO_2$ (36)	0.5	99	70	2
2	$V_2O_5$ (1.8)	0.5	96	59	6
3	$V_2O_5$ (1.8)+ $SiO_2$ (34)	0.5	90	56	12
4	$SiO_2$ (34)	-	2	-	-

[a] Reaction conditions: HMF 0.252 g (2.0 mmol); acetic acid 10.0 ml;  $O_2$  5 bar, 100 °C, 4 h. [b] Yields include maleic anhydride and maleic acid.

**Table S2** The effects of  $H_2O_2$  and 4-tert-butylphenol addition on HMF oxidation to MA.<sup>[a]</sup>

Additive	Amount	Catalyst	Conv. %	Yield of MA <sup>[b]</sup> / %	Yield of DFF / %
$H_2O_2$ (35%)	0.5 ml	-	80.5	37.2	14.2
	1.0 ml	-	82.9	51.6	11.0
	2.0 ml	-	96.9	68.0	3.88
4-tert-butylphenol	0.05 g	$V_2O_5$	75.1	47.0	14.7
	0.1 g	$V_2O_5$	69.1	20.2	16.4
	0.2 g	$V_2O_5$	48.3	0.0	5.25

[a] Reaction conditions: HMF 0.252 g (2.0 mmol); acetic acid 10.0 ml;  $V_2O_5$  catalyst 9.0 mg (2.5 mol%);  $O_2$  5 bar, 100 °C, 4 h. [b] Yields include maleic anhydride and maleic acid.