Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Selective Aerobic Oxidation of Furfural to Maleic Anhydride with Heterogeneous Mo-V-O Catalysts

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Experimental section

Materials: all starting materials are commercially available and were used as received, unless otherwise indicated. Furfural (> 98%), acetic acid (glacial), ammonium monovanadate (99%), and ammonium heptamolybdate (99%) were purchased from Merck. V_2O_5 (99.6%), WO_3 (99.9%), MoO_3 (99.5%), H_2O_2 (28%) 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 oxidation of furfural 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_2SO_4 (0.0001 M), flow rate 0.7 ml min^{-1}, 25 °C. The retention times were 8.7 min and 58.4 min for maleic acid and furfural, respectively. ^{1}H and ^{13}C NMR spectra were obtained using a Brucker 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 SEM images were obtained with a JEOL JSM 7500 scanning electron microscopy. FTIR spectra were collected on the PerKinElmer Spectrum 100 FT-IR Spectrometer.

Catalyst preparation: The Mo-V-O catalysts were prepared by decomposing the ammonium salts of the metal precursors. Stoichiometric amounts of ammonium monovanadate and ammonium heptamolybdate were dissolved in DI water and then evaporated to dryness. The combination was calcined at 275 °C for 4 h in air and then at 325 °C for 4 h in Ar.

Furfural oxidation to MA: furfural (192 mg, 2 mmol), acetic acid (10 ml), and catalyst (66 mg, 5 mol%) were charged into a Parr reactor with glass liner. The reactor was sealed and pressurized with 20 bar O_2 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.

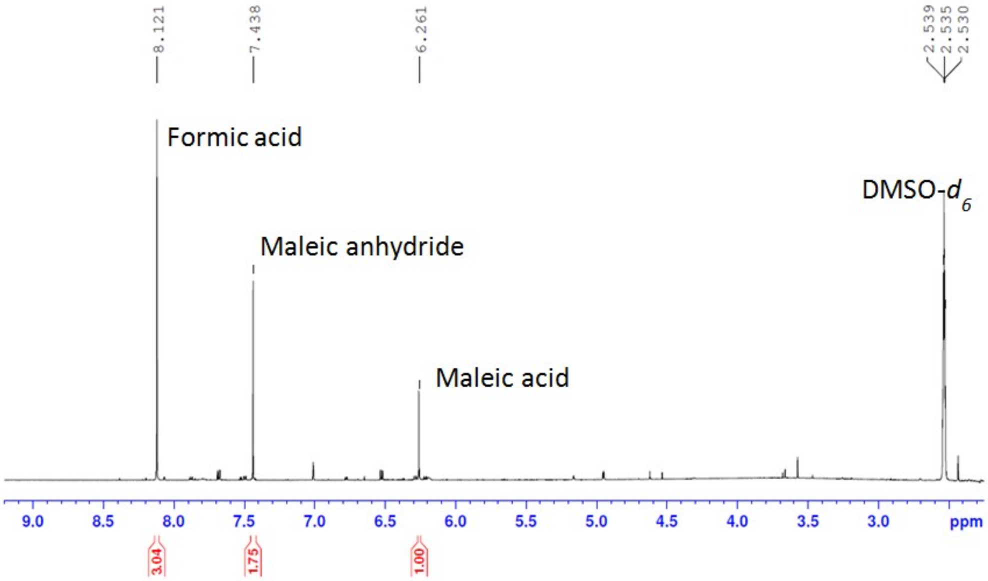
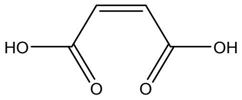
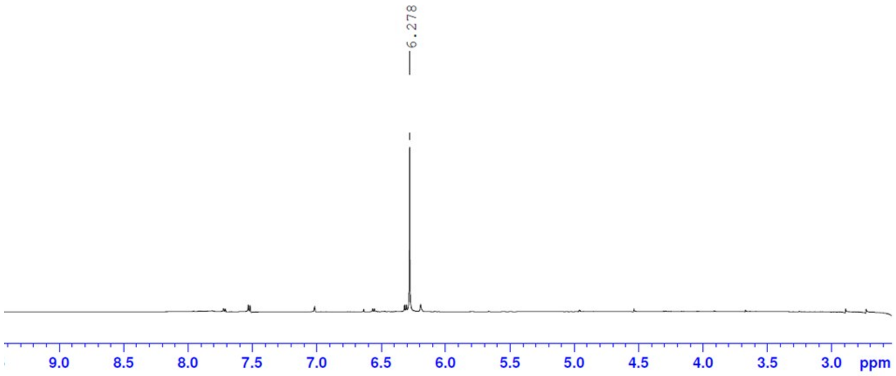


Fig. S1. The ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of furfural oxidation products. Reaction conditions: furfural, 2 mmol; Mo_4VO_{14} catalyst, 30 mg; acetic acid, 10 ml; O_2, 20 bar; 120 °C, 16 h.



^{1}H NMR (400 MHz, DMSO-d_6), δ = 6.28; ^{13}C NMR (400 MHz, DMSO-d_6), δ = 130.68, 167.23



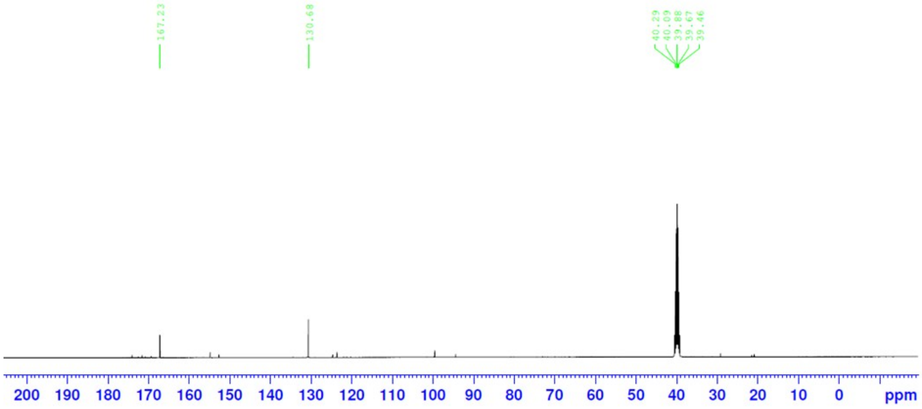


Fig. S2. NMR (400 MHz, DMSO-d_6) spectra of maleic acid from the hydrolysis of furfural oxidization product. Reaction conditions: furfural, 2 mmol; Mo_4VO_{14} catalyst, 30 mg; acetic acid, 10 ml; O_2, 20 bar; 120 °C, 16 h. After the reaction, the catalyst was separated by filtration, then 10 ml water was added to the filtrate and the mixture was stirred at 50 °C for 3 h in a flask. The solvent was then removed by evaporation to give solid maleic acid product.

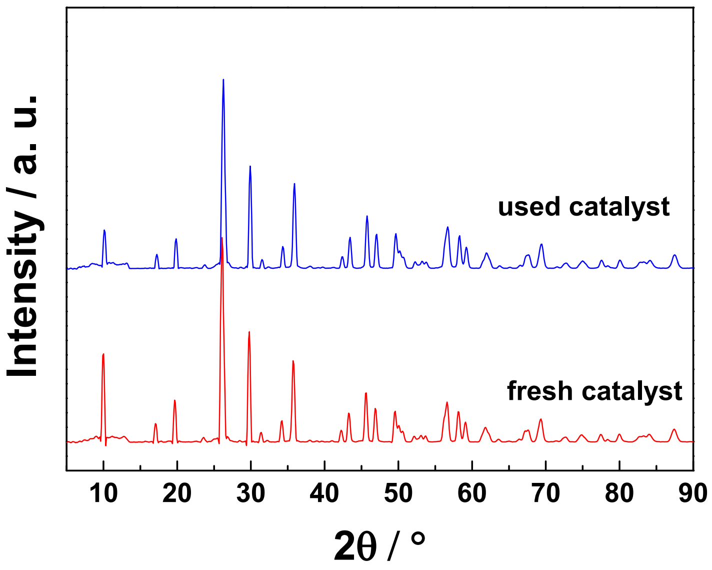


Fig. S3. XRD patterns of the fresh and used Mo_4VO_{14} catalysts.

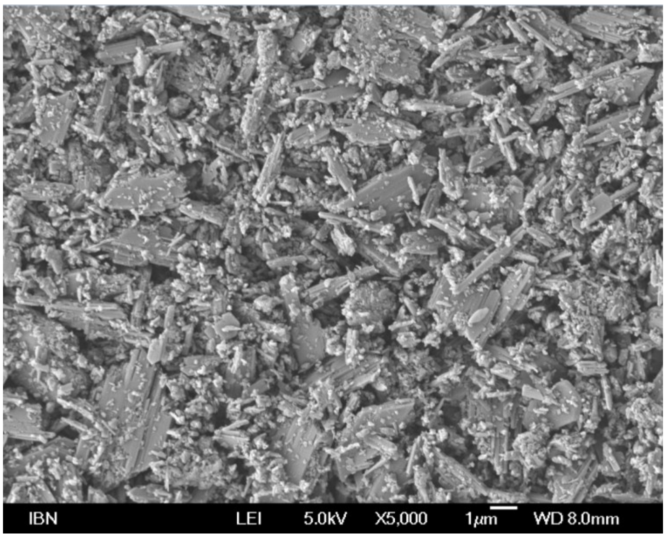


Fig. S4. SEM image of the recovered Mo_4VO_{14} catalysts after 5 runs of reaction.

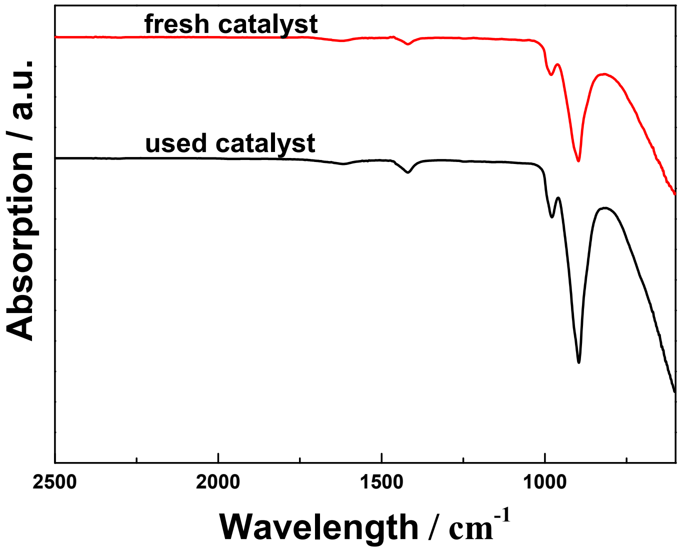


Fig. S5. FT-IR spectra of the fresh and used Mo_4VO_{14} catalysts.

Table S1. The leak of vanadium and molybdenum from the Mo_4VO_{14} catalyst in the recycle experiment.[a]

Run sequence	V leak (%)	Mo leak (%)
1	15.0	3.0
2	12.3	2.9
3	8.4	1.8
4	7.0	1.3
5	3.9	0.6

[a] Reaction conditions: furfural 2 mmol, acetic acid 10 ml, O_2 20 bar, 100 °C, 4 h.

Table S2. HMF oxidation over various vanadium catalysts.[a]

Catalysts (mg)	Conv. (%)	MA Yield (%)[c]
MoO_3 (57.6) + V_2O_5 (9.1)	84	40
MoO_3 (57.6) + VO_2 (9.1)	60	19
Mo_4VO_{14} (66.0)	93	65
W_4VO_{14} (59.0)[b]	16	0

[a] Reaction conditions: furfural 2 mmol, acetic acid 10 ml, O_2 20 bar, 100 °C, 4 h. [b] 120 °C, 16 h. [c]Yields include maleic anhydride and maleic acid.

Table S3. The effects of H_2O_2 and 4-tert-butylphenol addition on furfural oxidation to MA.[a]

Additive	Amount	Catalyst	Conv. (%)	MA Yield (%)
H_2O_2	2.0 ml	-	98	54
4-tert butylphenol	0.2 g	Mo_4VO_{14}	12	0

[a] Reaction conditions: furfural, 2 mmol; Mo_4VO_{14} Catalyst, 5 mol%; acetic acid, 10 ml; O_2, 20 bar; 100 °C, 4 h. [b] Yields include maleic anhydride and maleic acid.