

Supporting Information

Metal-Free approach towards efficient synthesis of FDCA using *p*-toluene sulfonic acid (*p*-TSA) derived heterogeneous solid acid catalyst and Oxone over Two Steps from HMF, Fructose and Glucose

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Instrumentation

¹H and ¹³C NMR were recorded on Bruker 400 MHz and Bruker 500 MHz instrument. GC was measured on Thermo Scientific Trace 1110 instrument using TG-624 column (6% cyanopropylphenylmethypolysilozane) and FID detector. GC-Mass was measured on Agilent 7890 BGC instrument using HP-5 MS column and EI source. Fourier transform infrared FTIR (Spectrum 400), The FTIR spectrum for the catalyst was obtained using the KBr pellet method. Powder X-ray diffraction P-XRD (Rigaku MiniFlex 600) was recorded using CuK α_1 (T=1.5 A°) as a radiation source with tube current and voltage of 40 mA and 40 kV. Thermogravimetric analysis TGA was done on Perkin Elmer Pyris 1 TGA instrument. The sample was heated till 500 °C at a rate of 10 °C/min. X-ray photo electron spectroscopy (XPS) was measured on Thermo K-alpha ESCA.

Spectral data for 2, 5-Diformylfuran:

¹H NMR (400 MHz, CDCl₃) δ 7.27 (s, 2H), 9.80 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 119.1, 154.2, 179.2; GC-MS: m/z 124, 95, 67, 50, 39, 28

Spectral data for FDCA

¹H NMR (500 MHz, D₂O): δ 7.12 (s, 2H); ¹³C NMR (125 MHz, D₂O): δ 118.3, 147.9 and 162.8. LC-Mass: 157 [M +1].

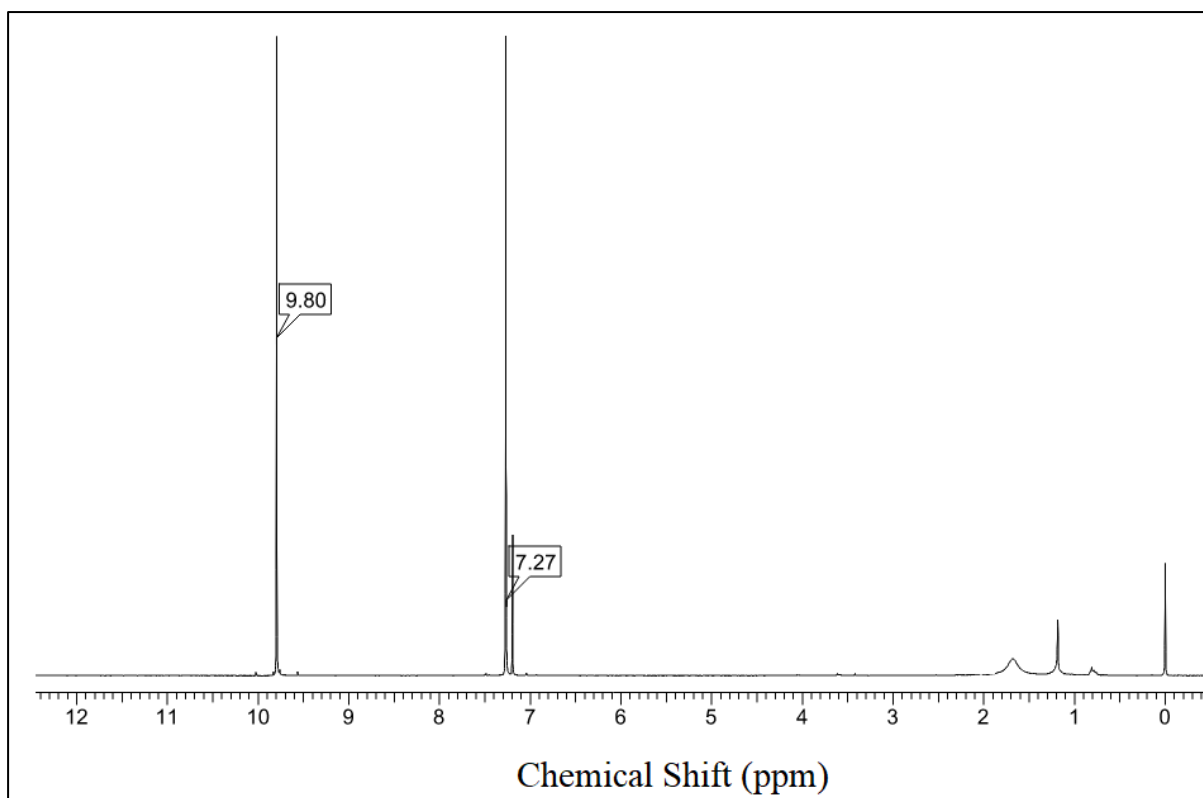


Figure S1: ^1H NMR (400 MHz, CDCl_3) of crude 2, 5-Diformylfuran

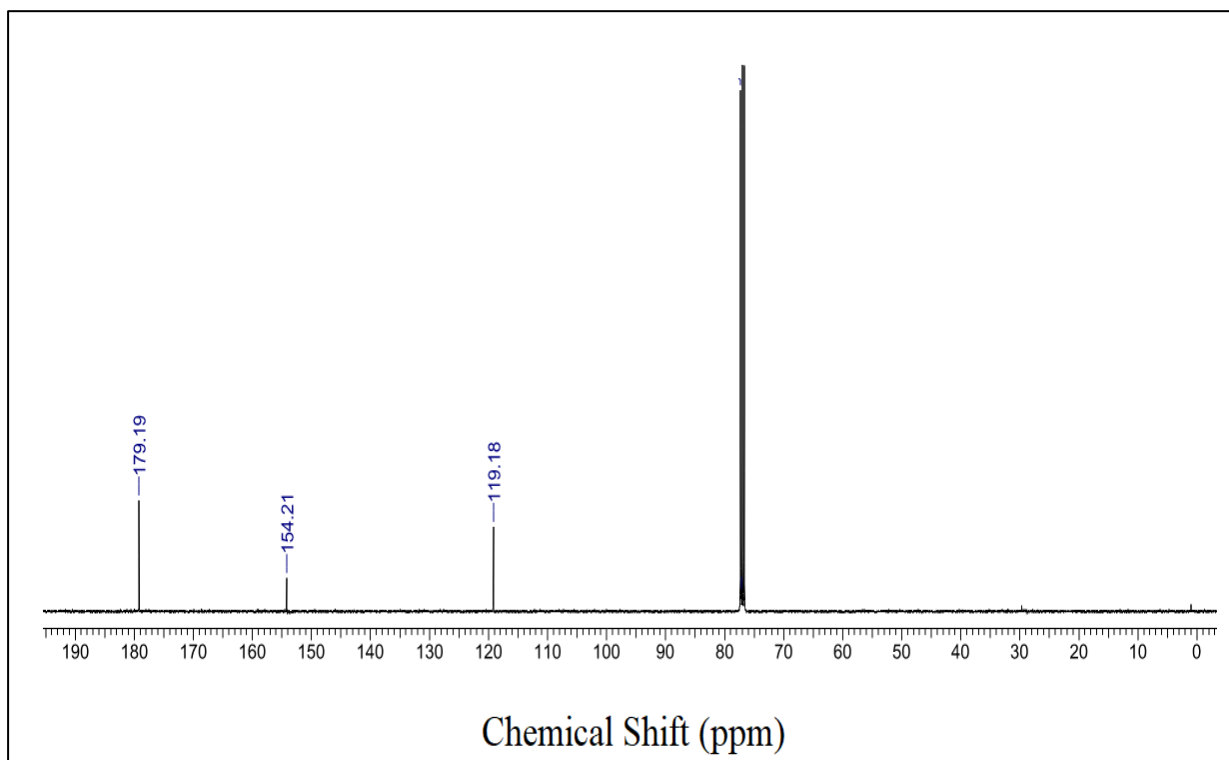


Figure S2: ^{13}C NMR (100 MHz, CDCl_3) of crude 2, 5-Diformylfuran

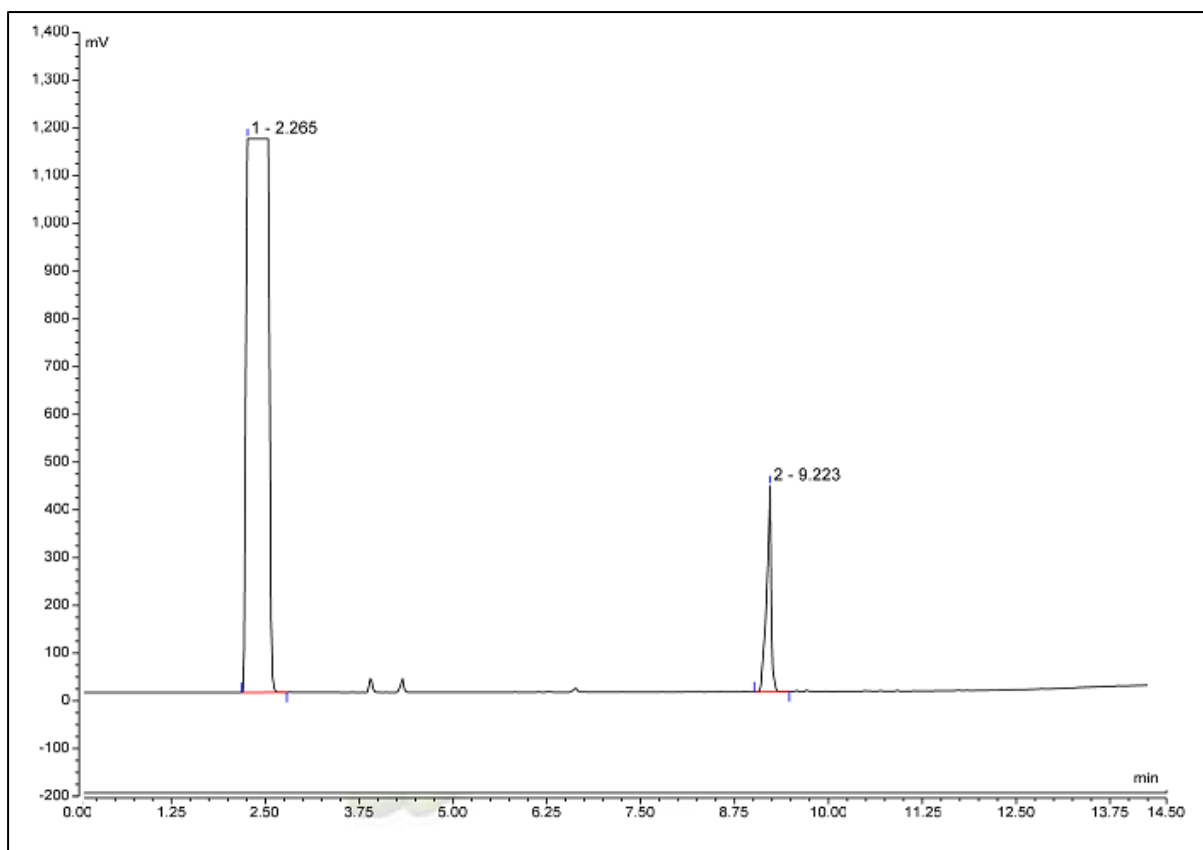


Figure S3: GC of crude 2, 5-Diformylfuran

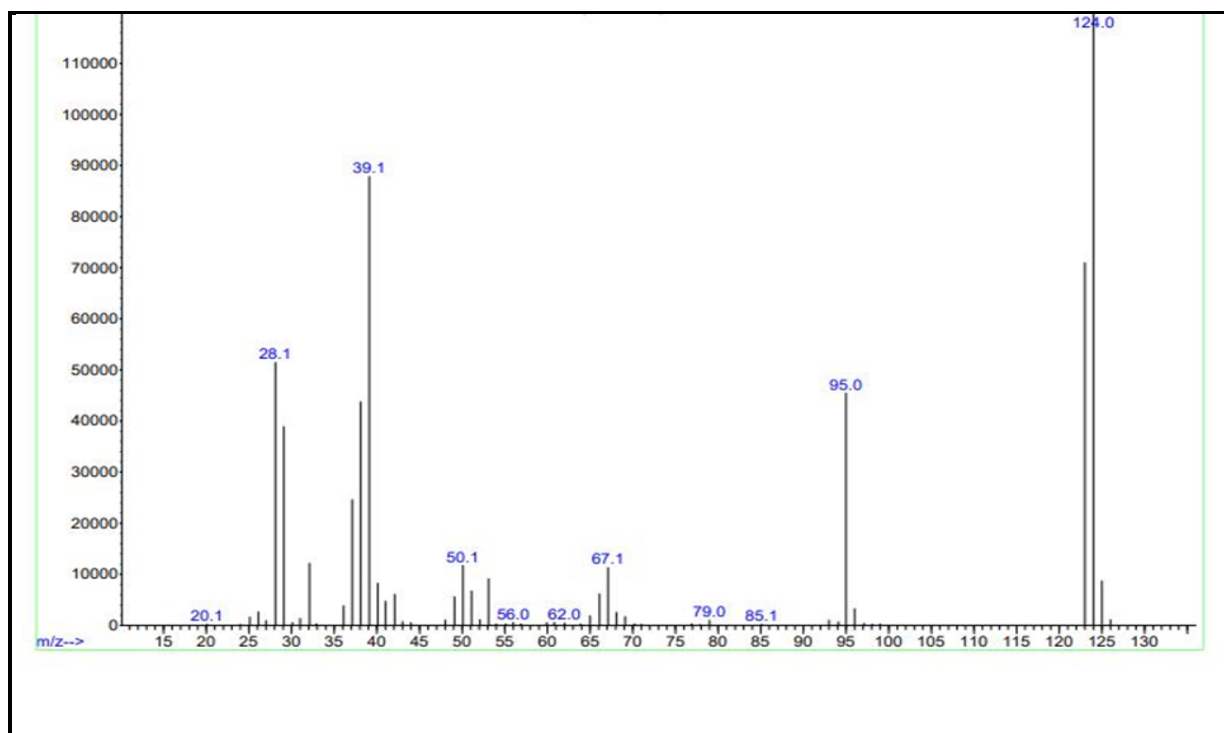


Figure S4: GC-MS of 2, 5-Diformylfuran

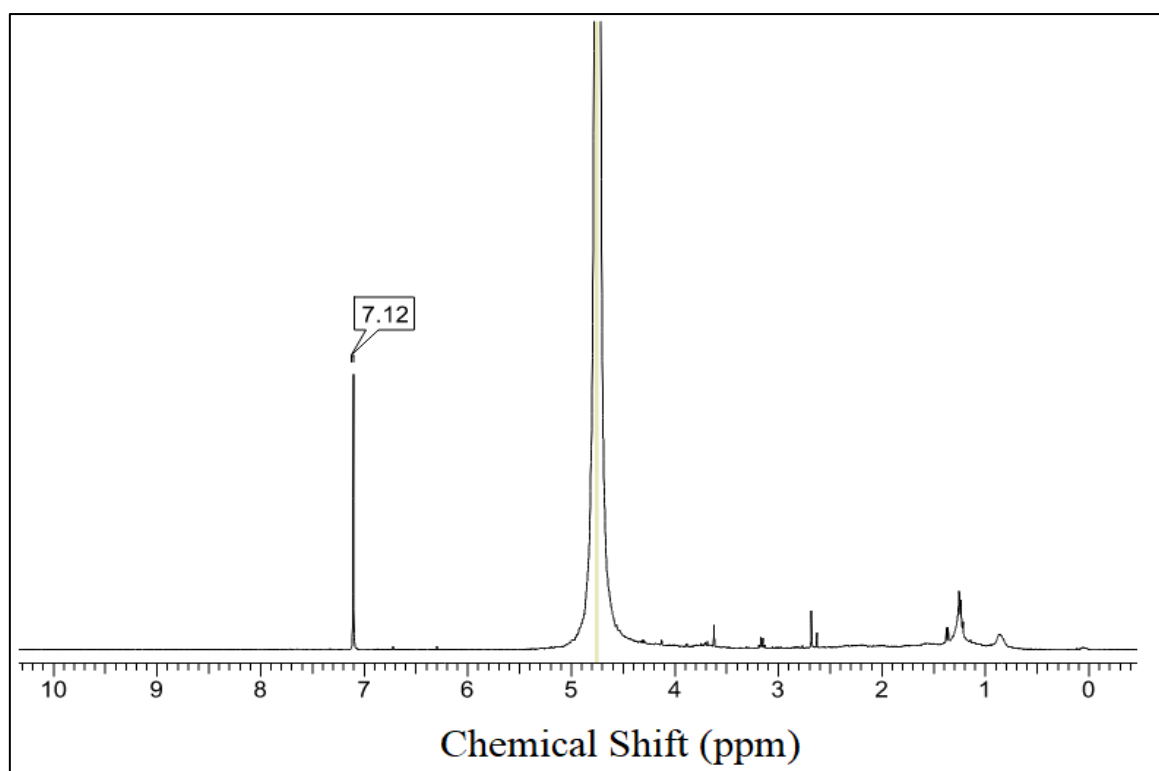


Figure S5: ¹H NMR (500 MHz, D₂O) of crude FDCA

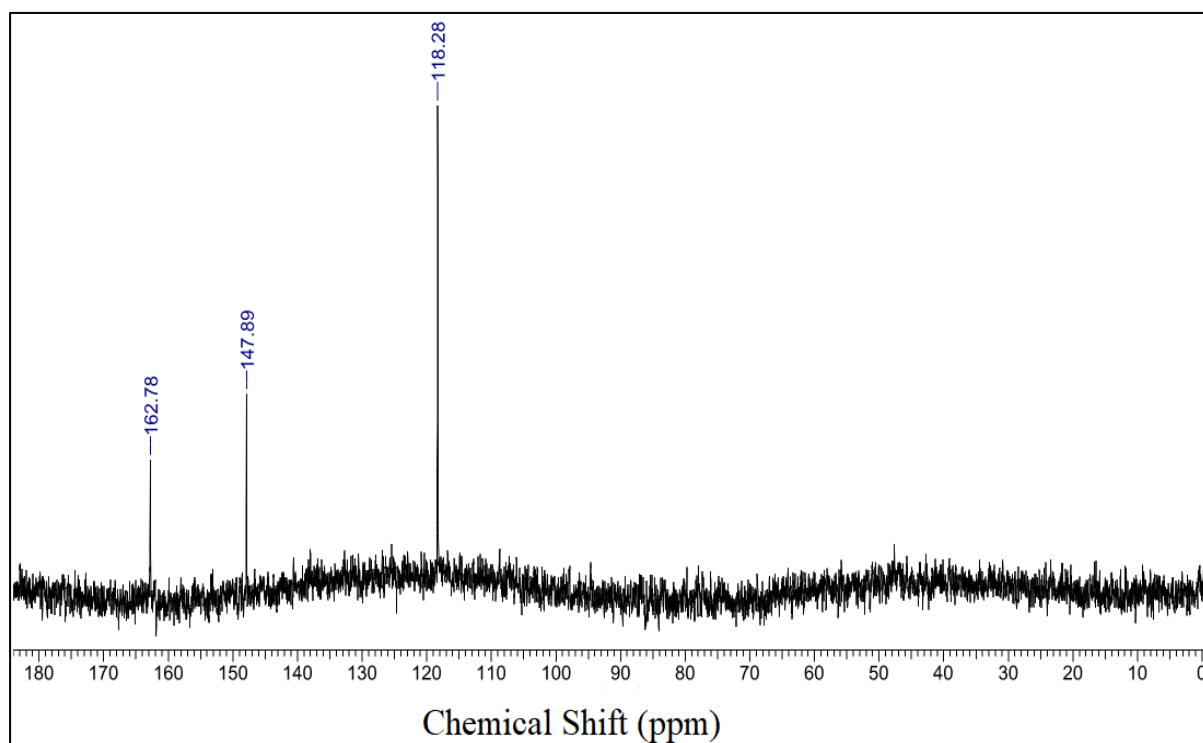


Figure S6: ¹³C NMR (125 MHz, D₂O) of crude FDCA

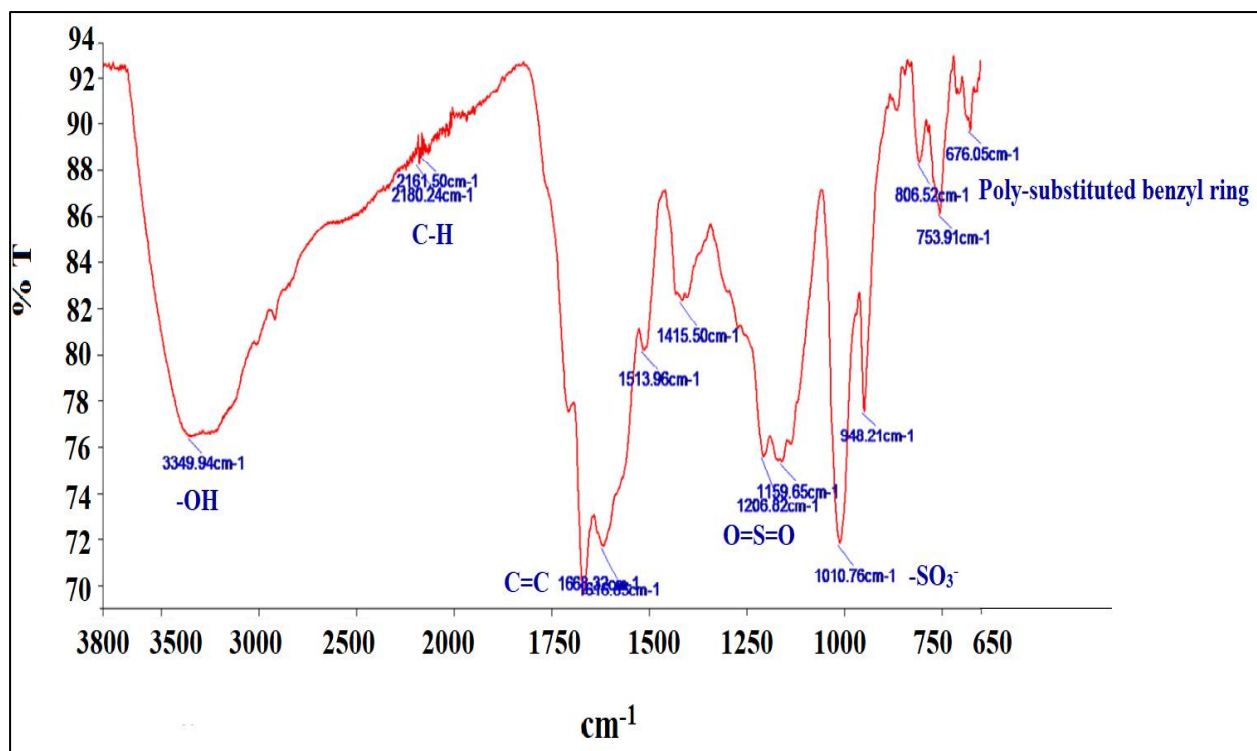


Figure S7: FT-IR of reused *p*-TSA-POM catalyst

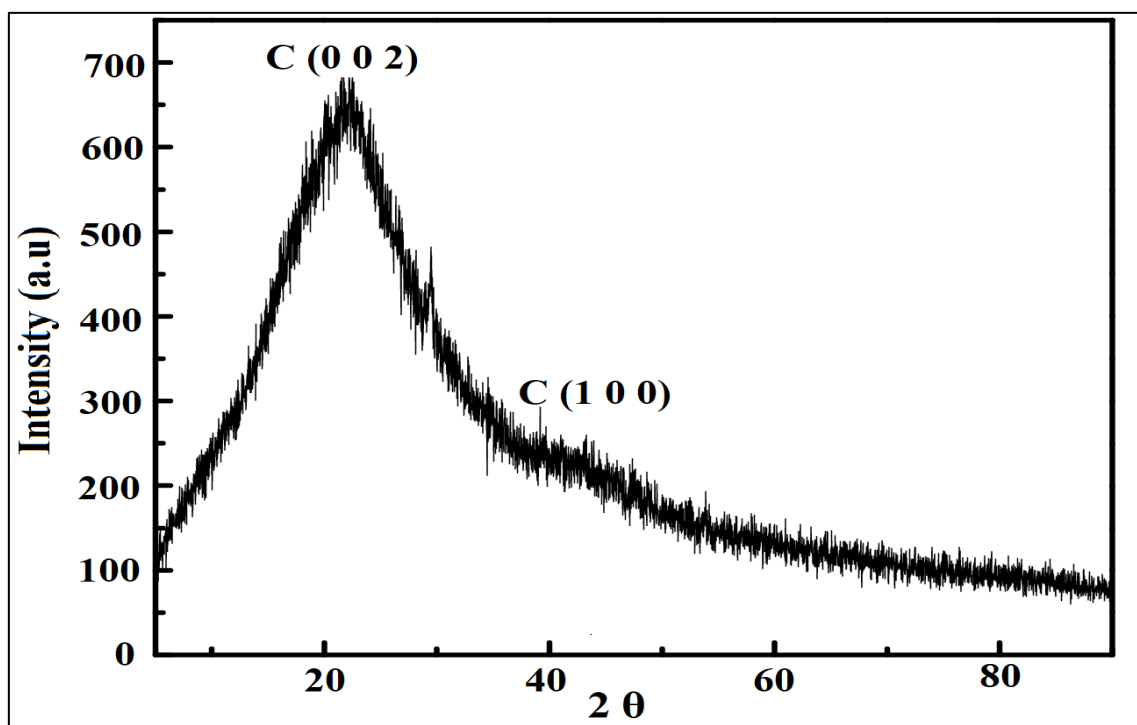


Figure S8: P-XRD of reused *p*-TSA-POM catalyst

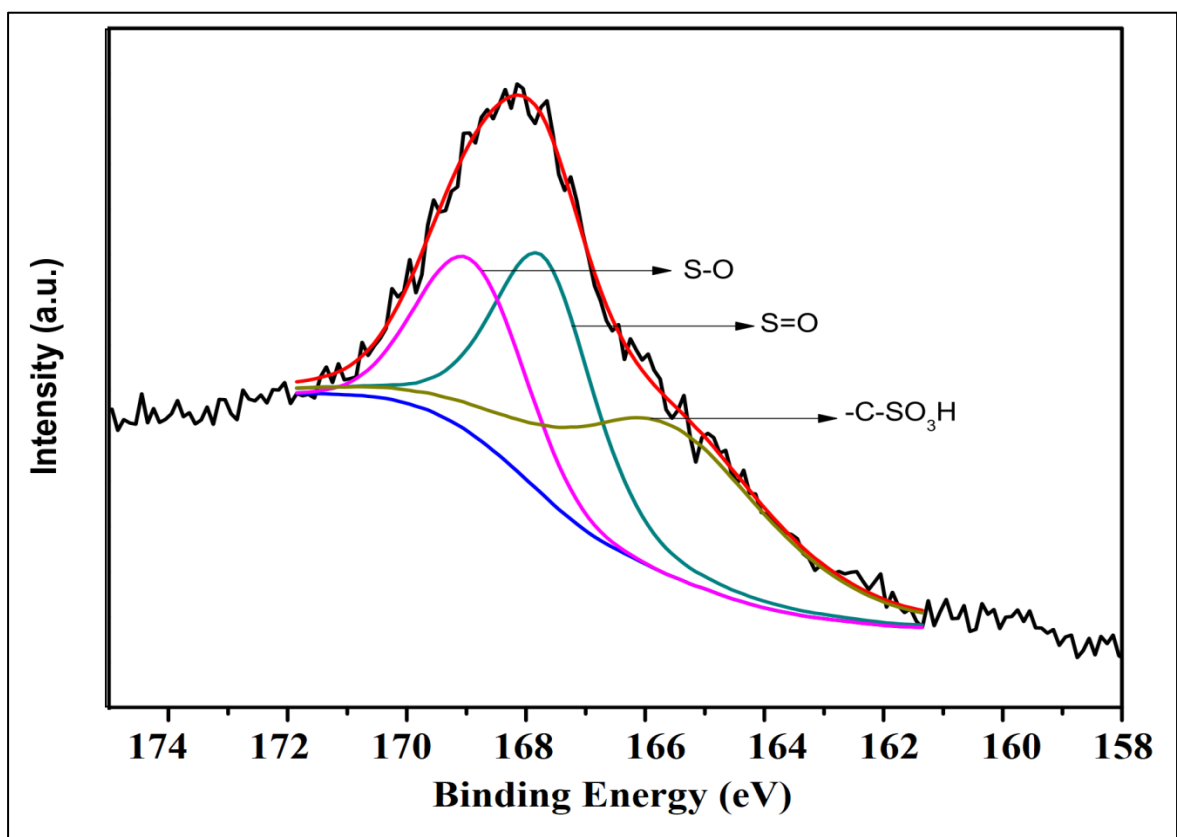
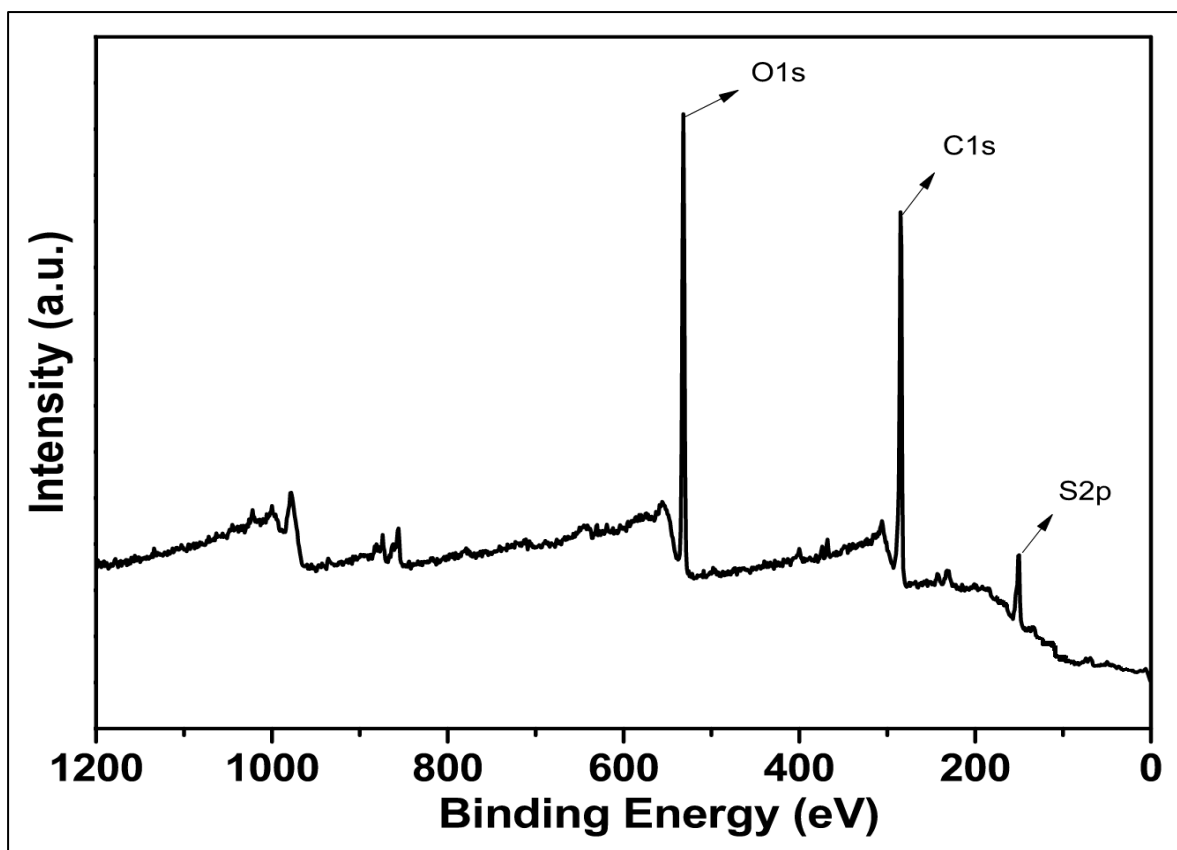


Figure S9: Survey & S 2p XPS spectrum of reused *p*-TSA-POM catalyst

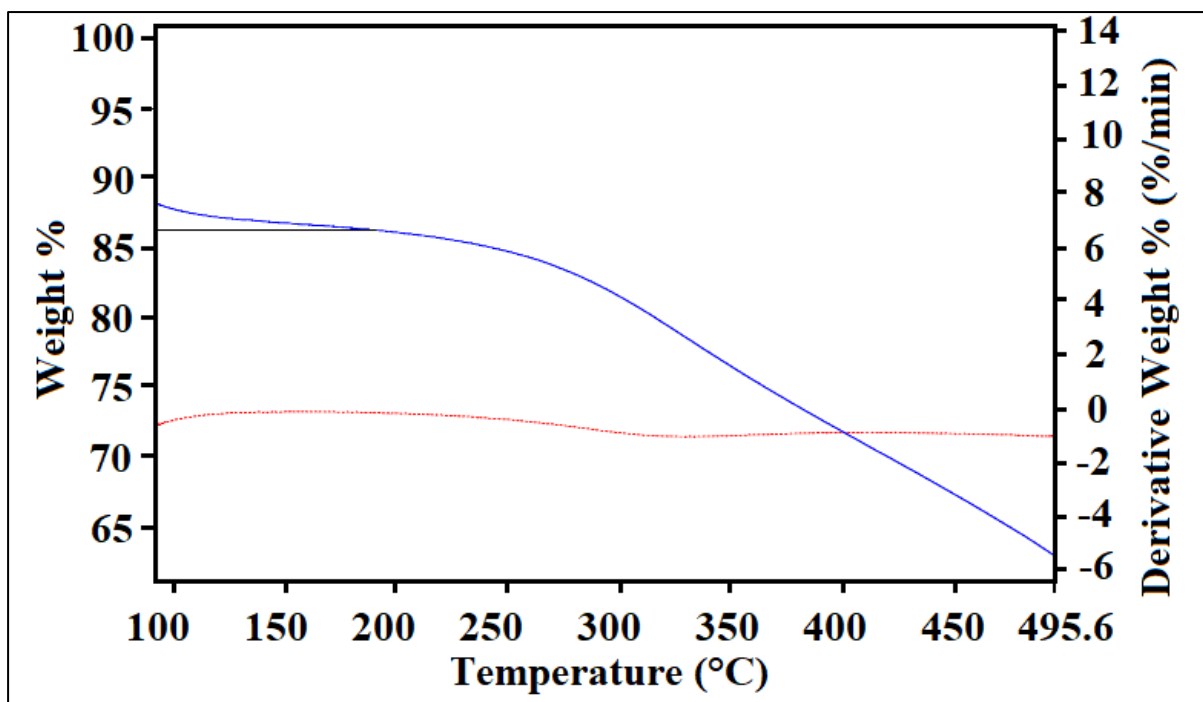


Figure S10: TGA of reused *p*-TSA-POM catalyst

Titration procedure for measuring acidity of the *p*-TSA-POM catalyst:

The measurement of the -SO₃H functional group: A sodium hydroxide solution (0.05 mol L⁻¹, 30 mL) was added to catalyst (0.25 g). The mixture was stirred for 60 min at room temperature under ultrasonic vibration. After centrifugal separation, the supernatant solution was titrated with hydrochloric acid (0.05 mol L⁻¹) using phenolphthalein as an indicator.