Electronic Supplementary Information

Greener synthesis of Cu-MOF-74 and its catalytic use for the generation of vanillin

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1. Experimental

All reagents and solvents were used as received from commercial suppliers without further purification. Powder X-ray diffraction (PXRD) data were collected under ambient conditions on a Bruker AXD D8 Advance diffractometer operated at 160 W (40 kV, 40 mA) for Cu K α 1 (λ = 1.5406 Å). Thermal gravimetric analysis (TGA) was performed under N₂ at a heating rate of 2 °C/min using a TA Instruments Q500HR analyser. Inductively coupled plasma mass spectrometry was conducted on a Varian model ICP spectrometer. Scanning Electron Microscopy images (SEM), were recorded using a JEOL Scanning Electron Microscope, JSM-7600F using secondary electrons at 15 kV current in high vacuum. Energy Dispersive Spectroscopy (EDS) analysis were carried out with an Oxford Instruments, INCA X-act Silicon Drift Detector operated at 5 kV.

2. TGA plot



Fig. S1: Thermal gravimetrical analysis of as-synthesised Cu(II)-MOF-74.

2. PXRD: Le Bail fitting



Fig. S2: Cu-MOF-74 Le Bail fitting. PXRD pattern was fitted using the FullProf program[1] (Le Bail method).[2]

3. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Each of the 5 hot filtrates (coming from the catalytic reactions) were combined with OPTIMA grade nitric acid (180 μ L) and OPTIMA grade sulphuric acid (180 μ L). The mixture was heated to 90 °C for 2 h in an open container in a dust-free environment. The resulting solutions were diluted to 5.0 mL using 2% OPTIMA grade nitric acid. These stock solutions were diluted to 1:100 (v/v) with 2% nitric acid and analysed relative to a 50 ppb germanium internal standard on a Varian model ICP spectrometer using He collision gas mode.

Results

Analysis was done in CCT mode. The instrument passed its performance check. No analytes were observed to have tripped to analogue at any concentration measured and thus no cross calibration was necessary. A good calibration line was obtained for all elements. The washout samples were fine, indicating that there is no problem with carryover in this experiment. Cu was found on prepared sample with a concentration equivalent to 3.3 mg L^{-1} .

4. ¹H-NMR and ¹³C-NMR Spectra



Fig. S3: ¹H-NMR spectrum of vanillin after column chromatography purification on silica gel.



Fig. S4: ¹³C-NMR spectrum of vanillin after column chromatography purification on silica gel.



5. Proposed Mechanism for the Oxidation of trans-ferulic Acid

Scheme S1: Proposed mechanism for the oxidation of *trans*-ferulic acid with Cu-MOF-74.

The reaction mechanism for the oxidation of *trans*-ferulic acid presented takes into account the partial decomposition of the Cu(II) catalytic centre, leading to the formation of copper(II) oxalate 14. This was identified from the PXRD data (Fig. S4), nonetheless in the pattern we can observe the presence of an additional amorphous phase, this can be attributed to the decomposed Cu-MOF-74. Cu-MOF-74 after catalytic reaction FTIR spectra showed a broad band at 1690 cm⁻¹ assigned to the carboxylic acid, a significant blue shift from the coordinated MOF v_a (COO) at 1551 cm⁻¹(Fig. S5).



Fig. S5: Cu-MOF-74 after catalytic reaction PXRD pattern, matching the copper(II) oxalate hydrate reflections (PDF entry No. 00-021-0297).



Fig. S6: FTIR spectra of the as-synthesised Cu-MOF-74 (green) and Cu-MOF-74 after catalytic reaction (red).

6. Computational Studies



Fig. S7: Geometry optimisation of structure 1 showing the coordination bond distances.



Fig. S8: Geometry optimisation of structure 2 showing the coordination bond distances and the hydrogen bond distances.



Fig. S9: Geometry optimisation of structure 4 showing the coordination bond distances and the hydrogen bond distances.



Fig. S10: Geometry optimisation of structure 7 showing the coordination bond distances and the hydrogen bond distances.



Fig. S11: Geometry optimisation of structure 8 showing the coordination bond distances and the hydrogen bond distances.



Fig. S12: Geometry optimisation of structure 8 (another view) showing the hydrogen bond distances.

7. SEM images of Cu-MOF-74



Fig. S13: As-synthesised Cu-MOF-74 SEM micrographs.



Fig. S14: As-synthesised Cu-MOF-74 SEM micrographs, featuring the MOF nanoparticles.



Fig. S15. SEM micrographs of the as-synthesised Cu-MOF-74 (left) and Cu-MOF-74 after the catalytic reaction (right).



Fig. S16. As-synthesised Cu-MOF-74 SEM micrograph with EDS mapping.



Fig. S17. Cu-MOF-74 after catalytic reaction SEM micrograph with EDS mapping.

8. References

[1] T. Riosnel, J. Gonzalez-Platas and J. Rodriguez-Carvajal, *WinPlotr and FullProf suite program, version 3.00.*, 2015; https://www.ill.eu/sites/fullprof (june, 2017).

[2] Y. Laligant, A. Le Bail and F. Goutenoire, *Ab Initio* Structure Determination of Lanthanum Cyclotetratungstate α -La₂W₂O₉ from X-ray and Neutron Powder Diffraction. *J. Solid State Chem.* 2001, **159**, 223-227.