Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

SUPPPORTING INFORMATION

Cu-MOFs as active, selective and reusable catalysts for oxidative C-O bond coupling reactions by direct C-H activation of formamides, aldehydes and ethers

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1. CHARACTERIZATION OF THE MOFs

1.1. [Cu(2-pymo)$_2$]·2.25 H_2O

Elemental analysis. Calcd for $CuC_8H_{10.5}N_4O_{4.25}$: C, 32.6; H, 3.6; N, 19.0; Cu, 21.6. Found: C, 32.4; H, 3.4; N, 19.0; Cu, 22.2.

Fig. S1. Thermogravimetric analysis (air flux, 10º/min)

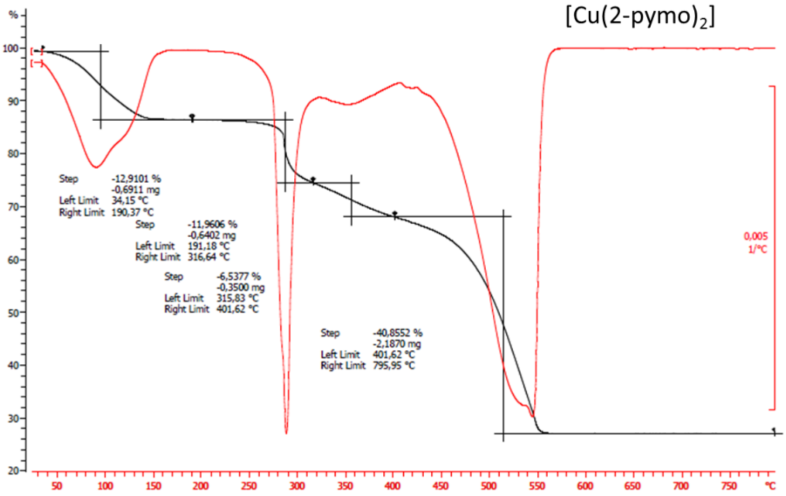


Fig. S2. FTIR (ATR)

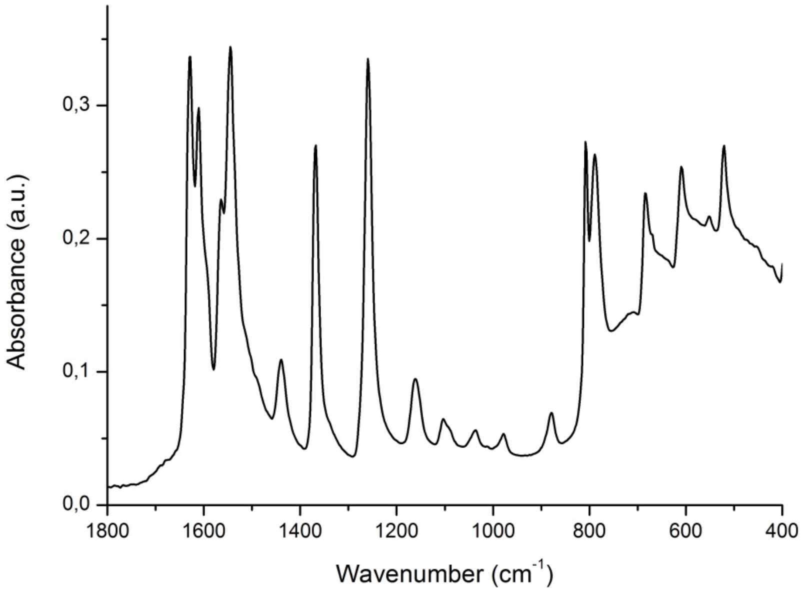


Fig. S3. XRD (Cu Kα radiation)

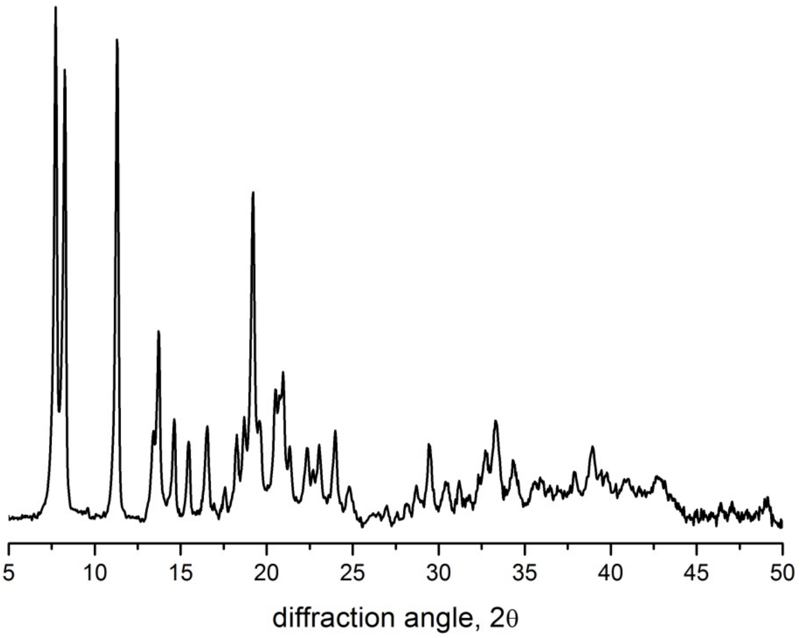
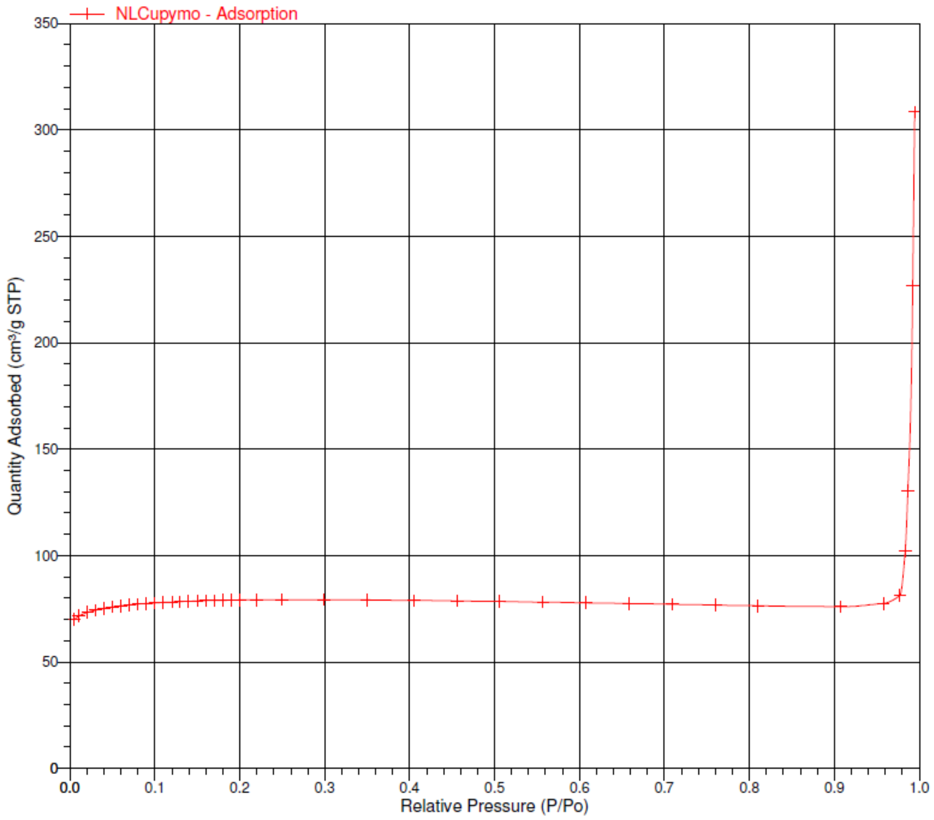


Fig. S4. N_2 adsorption isotherm



S_{BET} = 258 m^2/g

V_p = 0.48 cm^3/g

1.2. [Cu(im)$_2$]

Elemental analysis. Calcd for Cu($C_3H_3N_2$)$_2$: C, 36.5; H, 3.1; N, 28.3; Cu, 32.1.

Found: C, 36.1; H, 3.5; N, 27.2; Cu, 32.4.

Fig. S5. Thermogravimetric analysis (air flux, 10º/min)

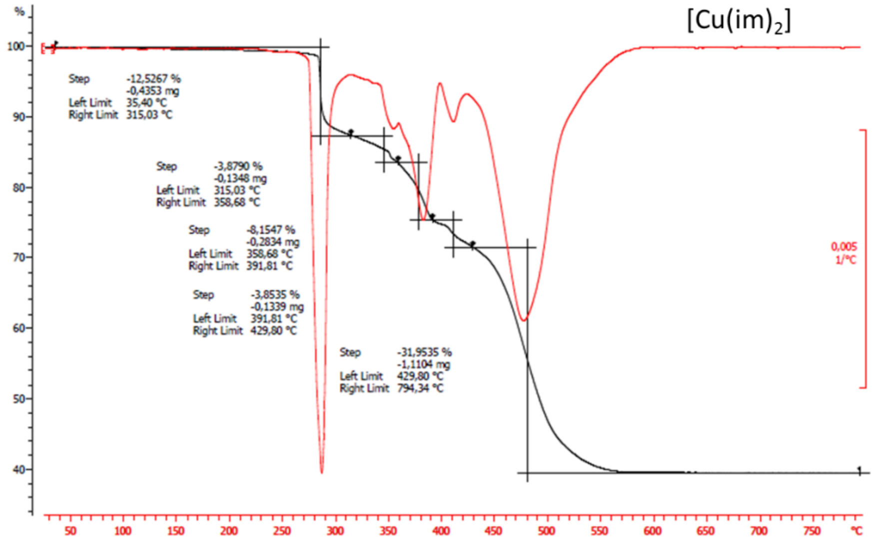


Fig. S6. FTIR (ATR)

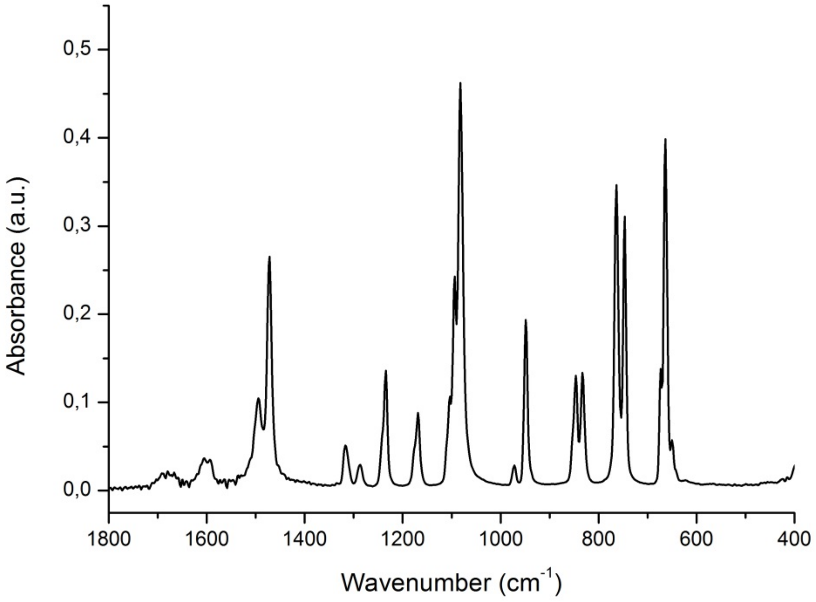


Fig. S7. XRD (Cu Kα radiation)

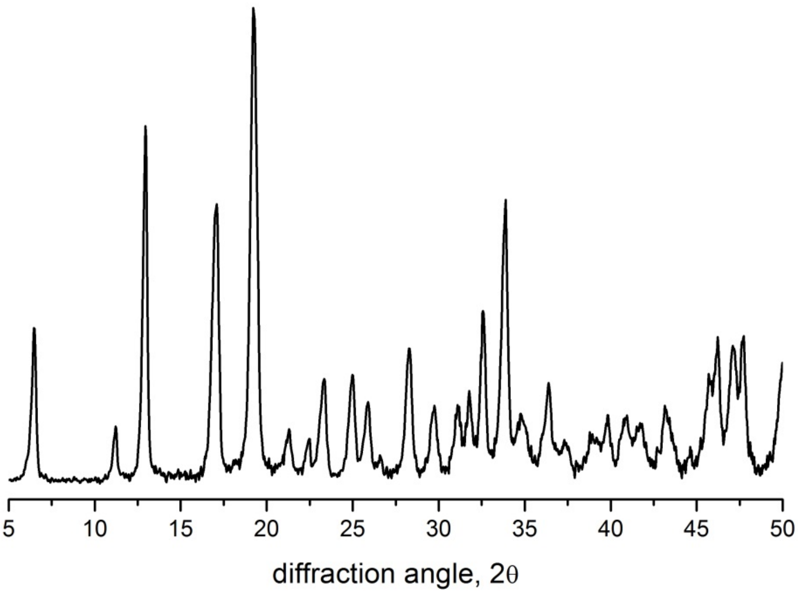
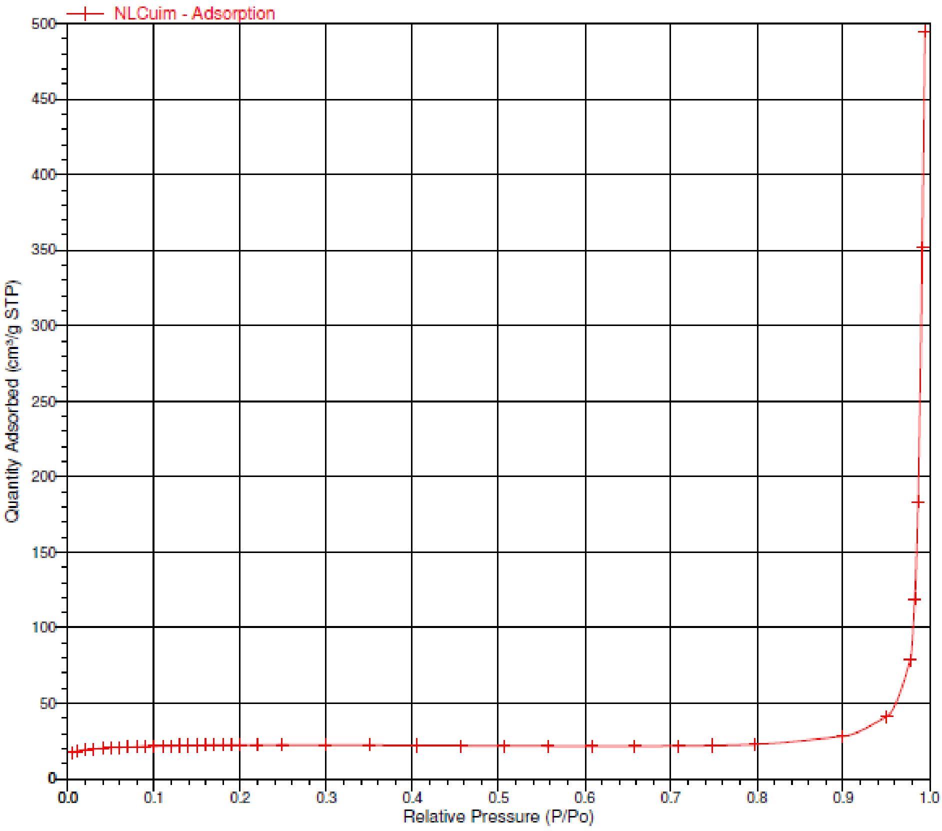


Fig. S8. N_2 adsorption isotherm



S_{BET} = 74 m^2/g

V_p = 0.77 cm^3/g

1.3. [$Cu_3(BTC)_2 \cdot 3H_2O$]

Elemental analysis. Calcd for $Cu_3C_{18}H_{12}O_{15}$: C, 32.7; H, 1.8; Cu, 28.9. Found: C, 32.4; H, 1.6; Cu, 28.6.

Fig. S9. Thermogravimetric analysis (air flux, 10º/min)

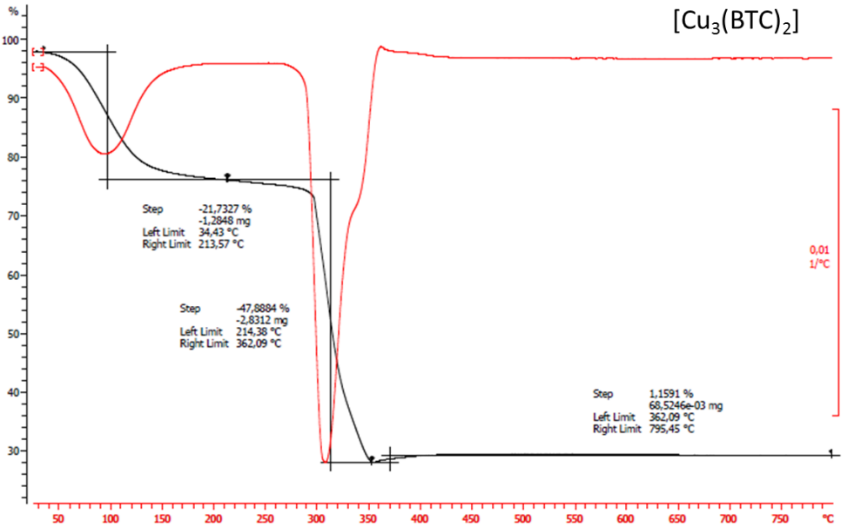


Fig. S10. FTIR (ATR)

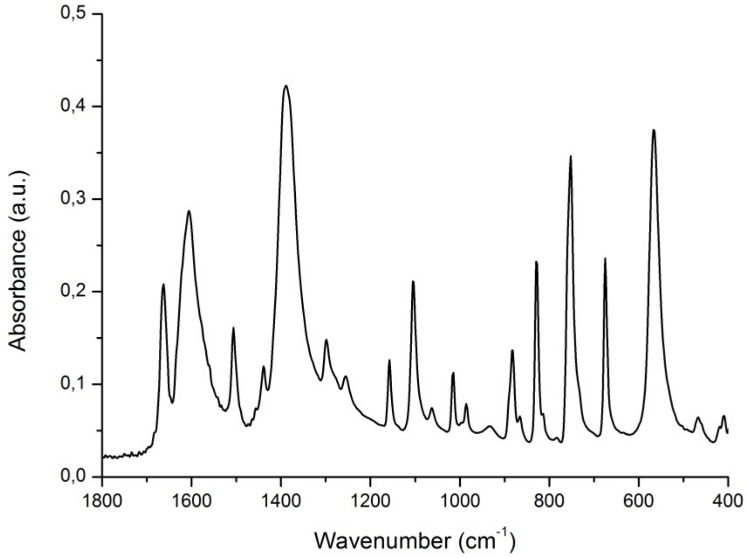
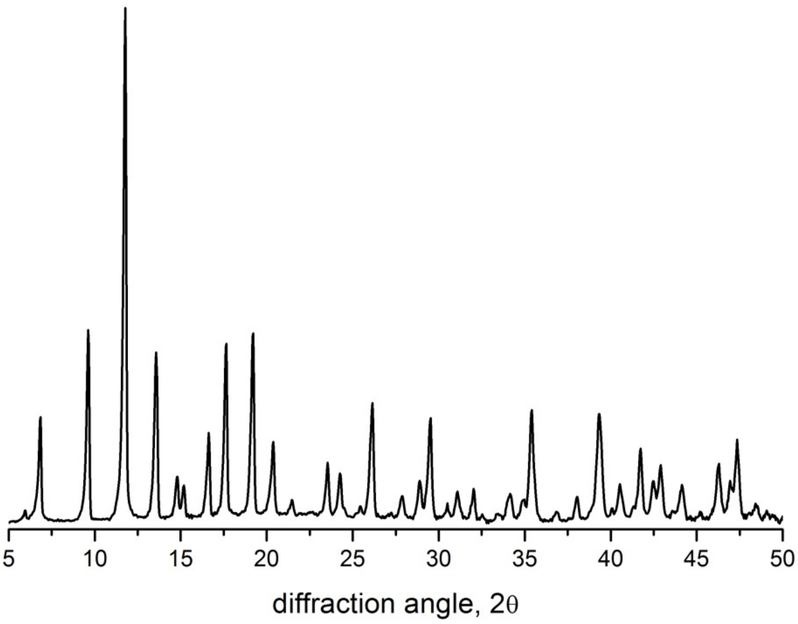


Fig. S11. XRD (Cu Kα radiation)



1.4. [Cu(BDC)·dmf]

Elemental analysis. Calcd for $CuC_{11}H_{11}NO_5$: C, 43.9; H, 3.7; N, 4.6; Cu, 21.1. Found: C, 43.3; H, 3.7; N, 4.6; Cu, 22.2.

Fig. S12. Thermogravimetric analysis (air flux, 10º/min)

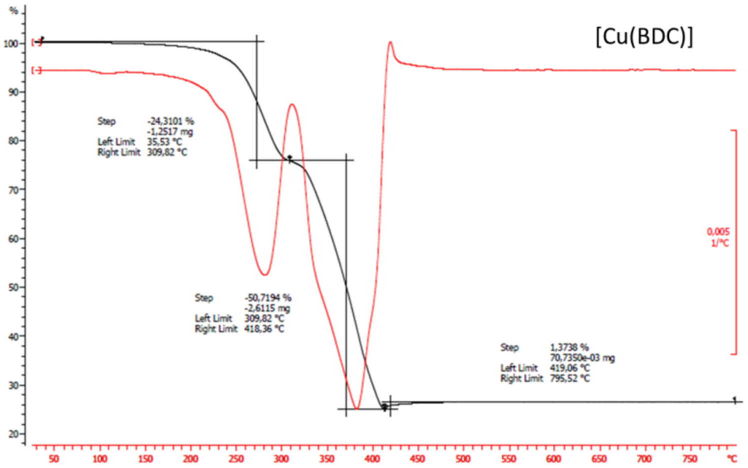


Fig. S13. FTIR (ATR)

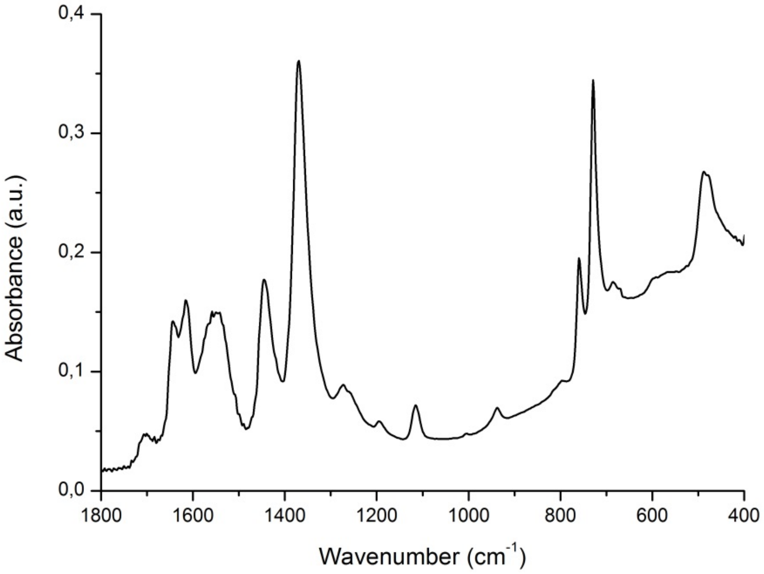
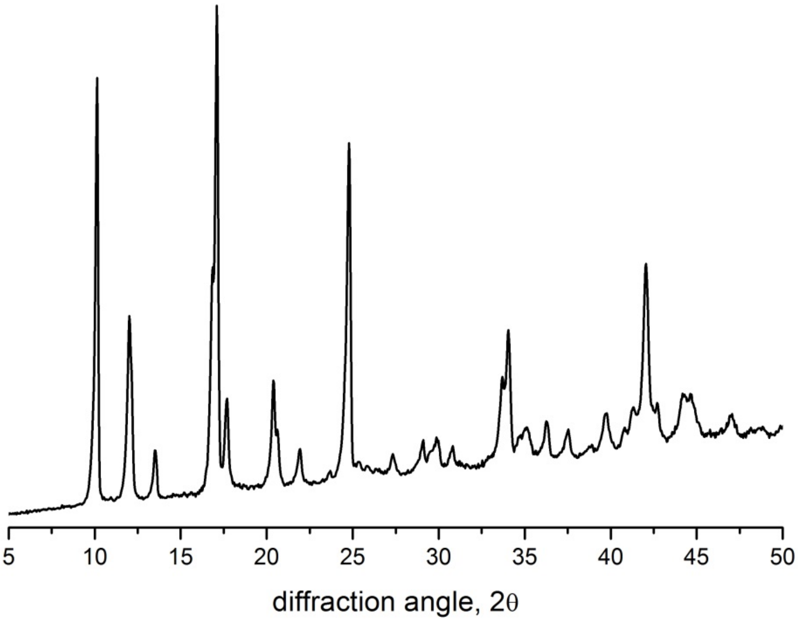


Fig. S14. XRD (Cu Kα radiation)



2. PREPARATION OF CU-CONTAINING ZEOLITES

Zeolites USY and ZSM-5 were commercial samples obtained from Zeolyst International. Prior to ion exchange, all zeolites were rinsed with a 0,04 M solution of $NaNO_3$ in order to have the materials in the sodium form. The metal exchange was carried out by immersing the Na-zeolites in an aqueous solution of the desired amount of $Cu(CH_3COO)_2{\cdot}4H_2O$, with a zeolite/liquid ratio of 10 g/l and under stirring for 24 h at room temperature. After that, the zeolite was filtered and washed, and then calcined at 823 K for 3 hours. Figures S15 and S16 show the XRD (Cu Kα radiation) of the calcined samples.

Fig. S15. XRD (Cu Kα radiation) of Cu- USY

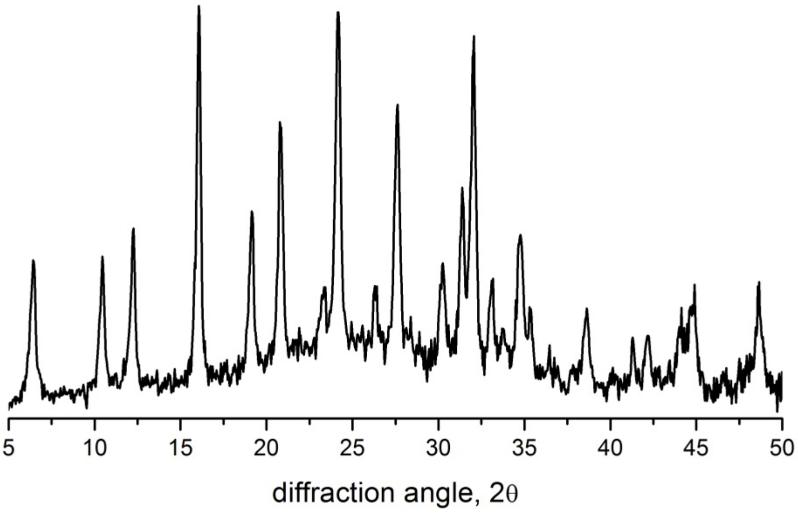
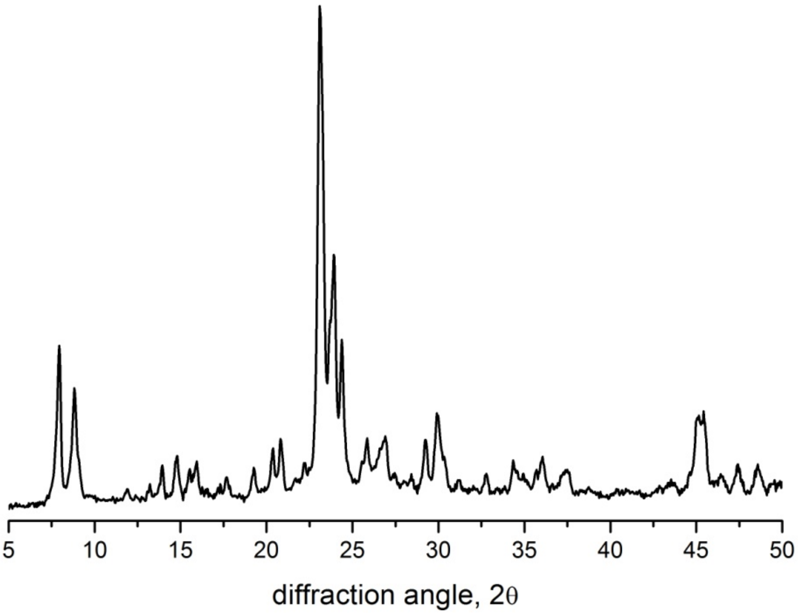


Fig. S16. XRD (Cu Kα radiation) of Cu- ZSM-5



3. COMPARISON OF FRESH AND USED MOFs

Fig. S17. XRD (Cu Kα radiation) of fresh [Cu(2-pymo)$_2$] and after catalyzing the oxidative coupling of 2-hydroxyacetophenone and DMF (3rd catalytic cycle)

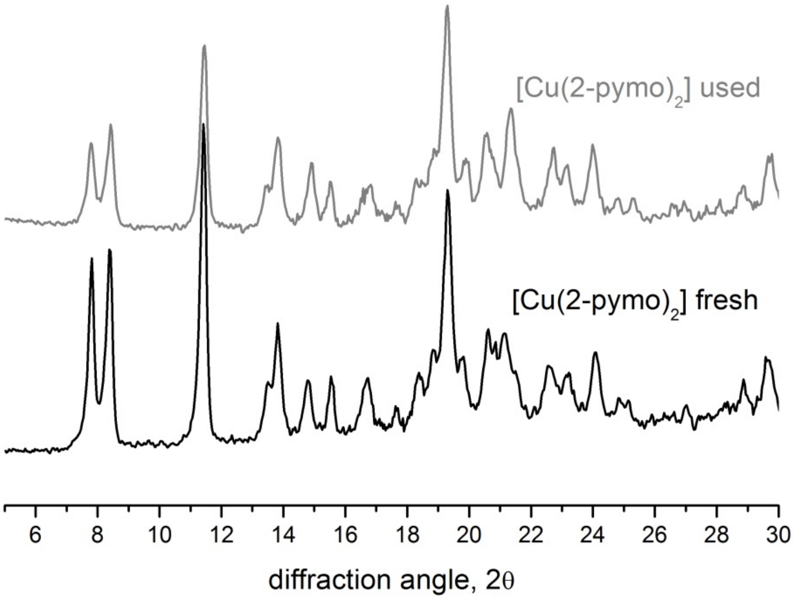


Fig. S18. XRD (Cu Kα radiation) of fresh [Cu(im)$_2$] and after catalyzing the oxidative coupling of 2-hydroxyacetophenone and DMF (3rd catalytic cycle)

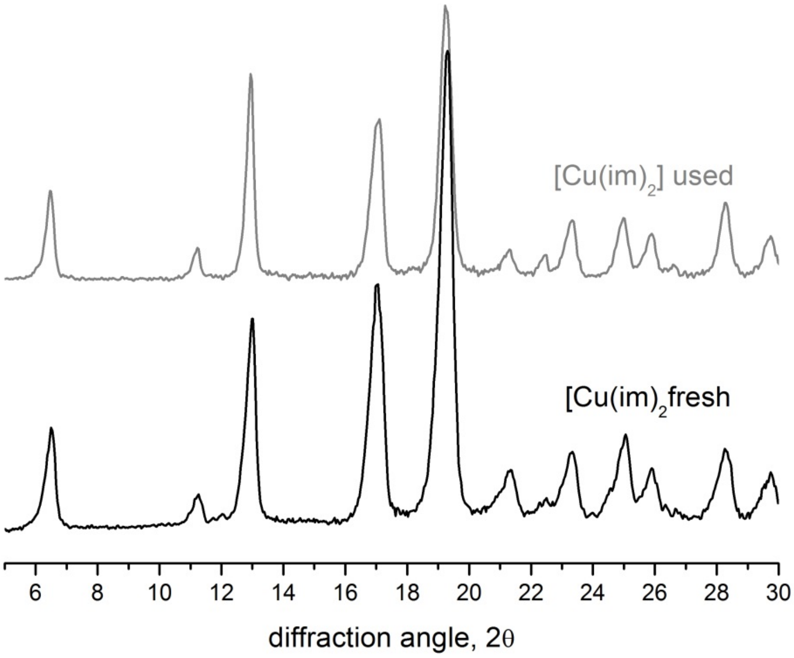


Fig. S19. Hot filtration test during the reaction of 2-hydroxyacetophenone and DMF in the presence of [Cu(2-pymo)$_2$].

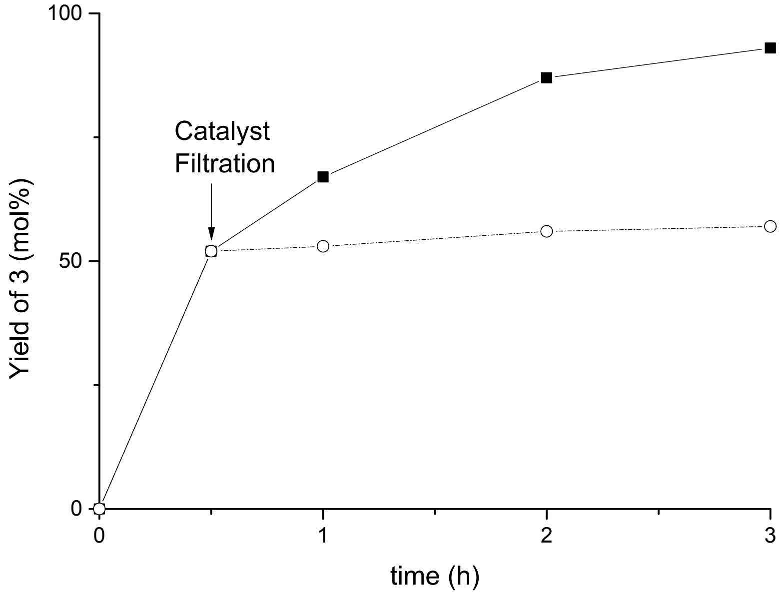


Figure S20. Progressive degradation of the structure of [Cu(2-pymo)$_2$] during the oxidative coupling of 2-hydroxyacetophenone and dioxane. XRD pattern (Cu Kα radiation) of fresh [Cu(2-pymo)$_2$] and the material recovered after the first and fourth catalytic runs.

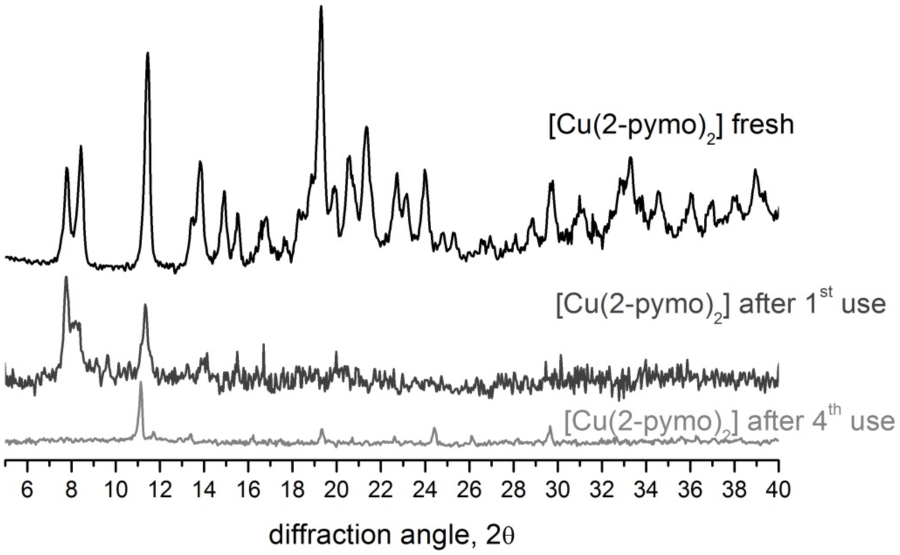


Figure S21. Progressive degradation of the structure of [Cu(2-pymo)2] during the oxidative coupling of 2-hydroxyacetophenone and dioxane. TGA (air flux, 10º/min) of the material recovered after the first catalytic run (compare with Fig. S1).

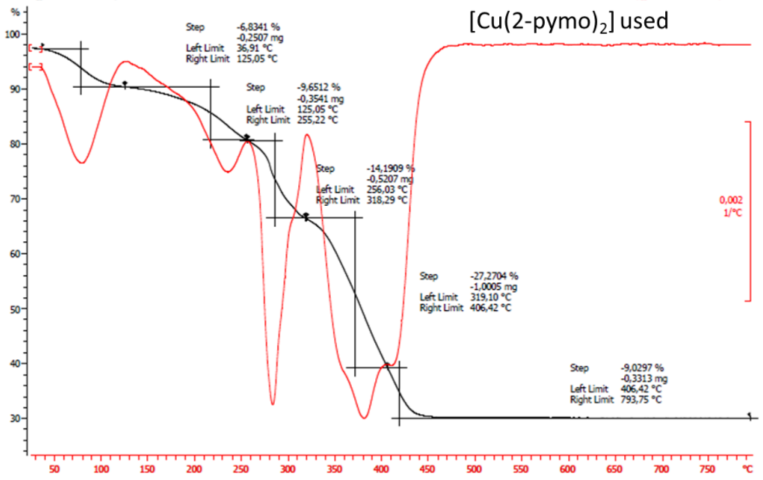


Figure S22. Progressive degradation of the structure of [Cu(2-pymo)2] during the oxidative coupling of 2-hydroxyacetophenone and dioxane. FTIR of fresh [Cu(2-pymo)$_2$] and the material recovered after the first catalytic run. Adsorption of reaction products on the MOF is evidenced by the band at ca. 1700 cm^{-1}.