Stable Metal-Organic Frameworks for Applications in Heterogeneous Catalysis for Sustainable Chemistry

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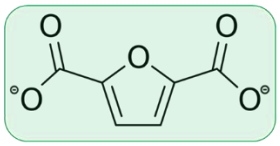
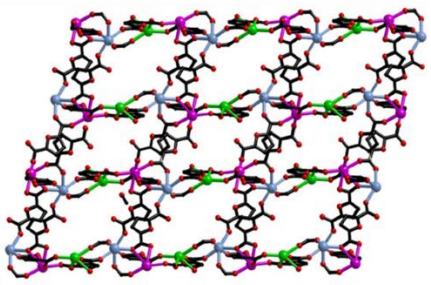
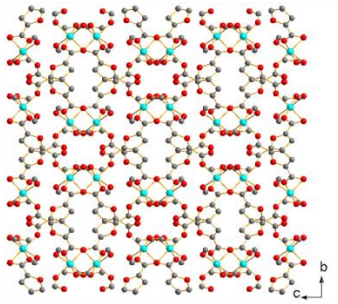
The field of metal-organic frameworks (MOFs) has grown rapidly and now includes a vast family of materials with extended solid structures, renowned for their tuneable porosity and ease of functionalisation. This chemistry makes use of metals from all parts of the Periodic Table, combined with ligands of diverse functionality that can be modified to give bespoke properties, either pre- or post-synthesis. The challenge remains to find materials with suitable stability for practical application and that are produced from sustainability sourced organic ligands to be used at scale.

We have investigated solution-stable MOF materials for acid-, redox- and electrocatalysis applications. This has spanned Lewis-acidic materials that contain the smaller lanthanoid cations (Yb and Y), and frameworks of iron(III) and Ni(II), to those doped with small amounts of the redox-active centre. We have applied these in the conversion of biomass-derived chemicals to useful products. This includes the acid-catalysed conversion of glucose to the platform molecule 5-hydroxymethylfurfural (5-HMF) and the subsequent oxidation of 5-HMF to 2,5-furandicarboxylic acid (FDCA). This leads to the consideration that FDCA might act as a ligand precursor to form novel dicarboxylate frameworks based on 2,5-furandicarboxylate (FDC), a ligand that has not yet been investigated widely in MOF chemistry, compared to other dicarboxylates.

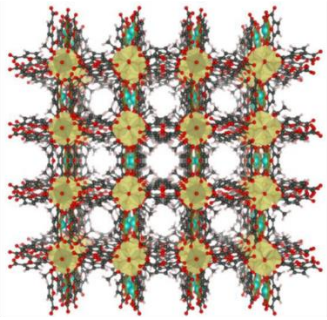




$\{[Y_3(FDA)_4(HFDA)(H_2O)_6]\cdot 3H_2O\}_n$



$Ni(FDC)(CH_3OH)_{1.5}(H_2O)_{0.5}(H_2O)_{0.35}$



$Fe_5NaO_3(FDC)_4(CH_3COO)_2$

Examples of new MOFs based on the 2,5-furandicarboxylate (FDC) ligand prepared in Warwick.

Structure solution of some of the new materials has been aided by 3D-electron diffraction, allowing analysis of microcrystals. Our new FDC MOFs (Y, Ni, Co and Fe) provide new materials with Lewis acidity for CO_2 fixation or redox-activity for further production of FDCA from 5-HMF. For many applications, the heterogeneous catalysts is most useful as a layer or coating and we have demonstrated this with the formation of mixed Co,Ni MOFs. These show remarkable robustness for use as electrocatalysts in alkali media (3 M KOH) for urea oxidation, which can be put use in a fuel cell to make use of waste urea as a fuel, or for other electrocatalytic transformations of waste materials.