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Oxidation of 5-Hydroxymethyl Furfural to 2,5-Furan Dicarboxylic Acid Under Mild Aqueous Conditions Catalysed by MIL-100(Fe) Metal-organic Framework

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Abstract: *We present the use of the redox active MIL-100(Fe) metal-organic framework (MOF) as a catalyst for the oxidation of 5-hydroxymethyl furfural (HMF) into 2,5-furan dicarboxylic acid (FDCA) in water. The MOF is synthesised in water alone under mild hydrothermal conditions and ^1H NMR is used to analyse the products of HMF oxidation. The MOF in combination with the co-catalyst TEMPO provides a total selectivity of desired products of 74% with a maximum FDCA yield of 57% seen after 24 hours at only 70 °C. The catalyst is recycled ten times with no loss in activity and no evidence of a reduction to the crystallinity of the MOF.*

Introduction

The production of chemicals and feedstocks from renewable resources has become increasingly important as the move away from fossil resources accelerates. One such chemical, FDCA, was designated as one of the top 12 value-added chemicals derived from biomass by the US Department of Energy.[1] The interest into FDCA is derived from the possibility of it substituting benzene-1,4-dicarboxylic acid (terephthalic acid) as a monomer in the production of polyethylene terephthalate (PET), to instead produce poly(ethylene 2,5-furandicarboxylate) (PEF) by copolymerisation with ethylene glycol.

Over 50 million tonnes of PET is produced annually and terephthalic acid is produced industrially exclusively by the oxidation of *para*-xylene, a by-product of the catalytic reforming of petroleum.[2] It is hoped that PEF could replace PET not only since it can be sourced renewably, but also due to its improved thermal behaviour.[3-5] However, this requires the discovery of effective ways of manufacturing FDCA ideally using mild and benign conditions that are scalable for manufacture.

FDCA can be produced by the oxidation of HMF, which has itself gained a great deal of interest[6] over recent years as it can be produced from glucose in a two-step isomerisation-dehydration reaction via fructose.[7-10] The oxidation of HMF is commonly reported to proceed via one of two pathways with three potential intermediates; DFF, HMFCA and FFCA, as shown in Scheme 1.[6]
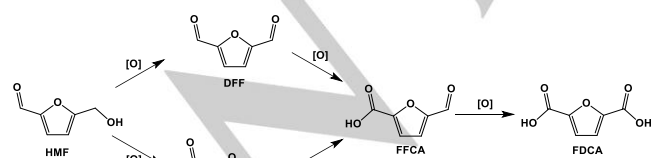
Scheme 1. Schematic representation of the oxidation of HMF to FDCA via the intermediates 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) and 5-formyl-2-furancarboxylic acid (FFCA). The three sequential oxidations occur via two potential routes through either DFF or HMFCA.

Research into the catalytic oxidation of HMF into FDCA has increased rapidly in recent years. Subramaniam *et al.* demonstrated that a combination of Co^{3+}, Mn^{2+} and Br^- ions in acetic acid solution formed bromide radicals which gave good yields of FDCA but required high temperatures and pressures of 160 °C and the use of toxic reagents which can contaminate the FDCA.[11] Mixed metal oxides,[12-16] TiO_2 supported Au and Pt,[17, 18] and carbon supported Pt, Ru and Rh[19, 20] have also been very promising, but require forcing conditions and high pressures of oxygen which can lead to the formation of side products.[21] Despite the growing interest in the production of FDCA, the field is missing a highly efficient benchmark catalyst that can be produced on a large scale and used under environmentally benign conditions.

Metal-organic frameworks (MOFs) have become extremely popular over recent decades as their high surface areas and tuneability have allowed them to find uses in a wide variety of applications such as gas separation and drug delivery.[22] Their ease of functionalisation such as incorporation of acid sites or redox sites has also led to a great deal of research into their use as catalysts.[22] Despite this, there have been very few reports on the use of MOFs as catalysts for the oxidation of HMF.[23]

Results and Discussion

In this work, we present the first use of the redox active MOF, MIL-100(Fe) as a recyclable oxidation catalyst for the oxidation of HMF to FDCA in water. MIL-100(Fe) has the chemical formula $Fe_3O(H_2O)_2(X)(BTC)_2$, where BTC is the organic linker benzene-1,3,5-tricarboxylate, and the counterion, X, can vary depending on the synthesis employed. The MOF was first reported in 2007 by Férey and co-workers and is a thermally and hydrothermally robust MOF with an open framework and considerable porosity.[24] The MOF was originally synthesised on a small scale under harsh conditions with the use of both nitric and hydrofluoric acid (X = F-) but has since been synthesised in water alone (X = OH-).[25] The high stability and surface area of MIL-100(Fe), combined with the high density of redox active sites, have the potential to make it an extremely efficient oxidation catalyst even under relatively mild reaction conditions.

MIL-100(Fe) was synthesised hydrothermally by modification of literature syntheses such that the use of HNO_3 and HF acids was not required. Whilst omission of the acids from the synthesis is known to reduce the BET surface area of the MOF, it also leads to a more scalable and green synthesis.[26] The successful synthesis of MIL-100(Fe) was confirmed by a combination of powder XRD and TGA (Figures S1 and S2), and a BET surface area of 1158 m^2/g was recorded. This surface area is comparable to those previously reported for MIL-100 (Fe) which range from 1150 - 2550 m^2/g.[26]
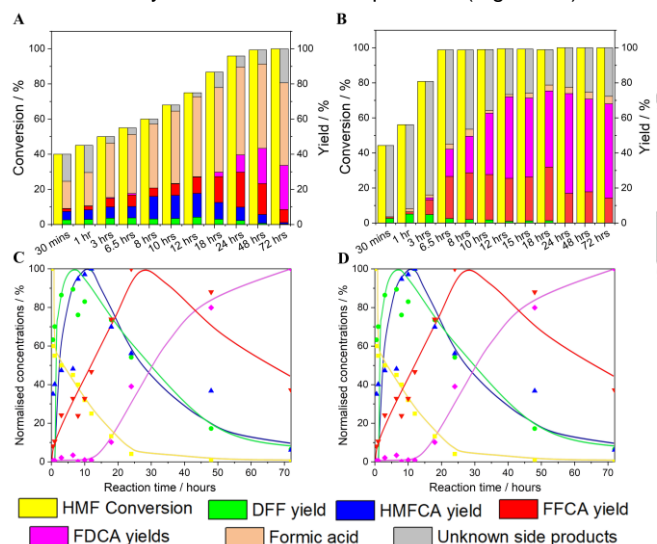
The catalytic reactions were carried out under aqueous conditions using tert-butyl hydroperoxide (^tBuOOH) oxidant. The choice of ^tBuOOH was made because MIL-100(Fe) was found to be extremely stable in aqueous solutions of the peroxide, especially compared to other peroxides such as Na_2O_2 and H_2O_2. It is also considered to be relatively environmentally friendly since

its degradation products are water and tert-butanol.[27] The use of oxygen gas, although more desirable at atmospheric pressure, can lead to significant concerns when pressurised, and especially on industrial scales. ^{t}BuOOH has been used as an oxidant alongside MOF catalysts previously because MOFs are generally less stable in other peroxides, and it is compatible with both aqueous and organic solvents.[28-30] An assigned ^{1}H NMR spectrum is shown in Figure S3 for reference.

After heating HMF (1.2 mmol, 5 wt%) at 60 °C in the presence of ^{t}BuOOH and the MIL-100(Fe) catalyst, it was found that the HMF had been almost completely consumed with a conversion of 99.8% after 72 hours (Figure 1A). The total selectivity towards the oxidation products peaked at 43% after 48 hours, whilst the FDCA yield peaked at 25% after 72 hours. A further 48% of the converted HMF was found to have formed formic acid, a product of the ring opening rehydration of HMF.[31] The ring opening can be catalysed by Lewis acid sites, which are present within the MIL-100(Fe) structure in the form of coordinatively unsaturated Fe(III) sites.[32] By replacing HMF in turn for each of the intermediates between HMF and FDCA (Figure S4), it was found that HMF, HMFCA and DFF each underwent the ring opening and subsequent decomposition, as was seen with HMF, in competition with their oxidation. FFCA was found to be oxidised selectively towards FDCA whilst FDCA was found to be stable under the reaction conditions proving that once made, it would not decompose or react over time.

Varying the reaction temperature, or the concentration of peroxide used, was not found to alter the selectivity towards FDCA, and high yields of formic acid were found in each case. Substitution of ^{t}BuOOH with alternative oxidising agents such as persulfates and other peroxides led to either a reduction in selectivity or complete decomposition of the catalyst. In contrast, the replacement of ^{t}BuOOH with an autogenous pressure of oxygen gas resulted in a low HMF conversion of around 10% and a low selectivity towards the desired products (Figure S5).
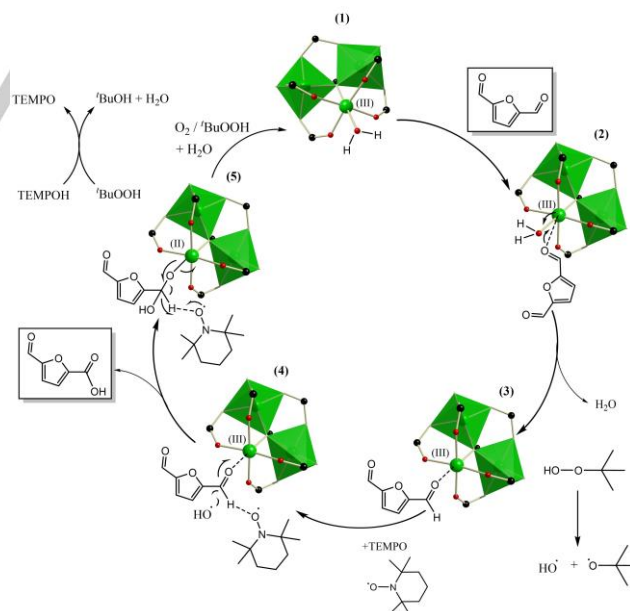
With the aim of increasing the selectivity of the MIL-100(Fe) catalyst towards FDCA, the addition of the co-catalyst, TEMPO, into the reaction was investigated. TEMPO is known to promote the oxidation of alcohols and aldehydes,[33, 34] and with the addition of one equivalent of the co-catalyst, it was found that the conversion of HMF increased dramatically, with almost 100% HMF conversion after just 6.5 hours (Figure 1B). The selectivity of the reaction towards FDCA also increased significantly, whilst the ring opening and decomposition to formic acid was greatly reduced. At the optimal reaction temperature of 70 °C, a selectivity towards the oxidation products at 74% and a maximum FDCA yield of 56% (Figure S6). Interestingly, the intermediate HMFCA was not observed when TEMPO was used, and this is attributed to TEMPO's preferential oxidation of alcohols over aldehydes.

Plotting the normalised concentration of each of the desired reaction products over time (Figures 1C and 1D), clearly shows how the reaction proceeds through each of the intermediates both with and without the addition of TEMPO. The beneficial effect of the co-catalyst is also highlighted, with the production of FDCA predominantly occurring at between 5 and 10 hours with TEMPO, compared between 18 and 72 hours without.

The increased selectivity towards the oxidation products with TEMPO was discussed previously in the synthesis of DFF over MIL-100 and HKUST-1 catalysts,[35, 36] and an adapted proposed mechanism for the oxidation of HMF to DFF over MIL-100(Fe) is depicted in Figure 2. It is the terminally bound neutral water molecule within the Fe-trimer of MIL-100 that is proposed to be the active site for the oxidation of HMF. The weakly coordinated water can be displaced for the neutral HMF molecule without any need for charge balancing. Once bound to the active site, the reaction is proposed to proceed by proton transfer from the HMF molecule leading to reduction of the Fe(III) to Fe(II). This is then followed by synergistic activation of the C-O within HMF by the MOF, and C-H activation by TEMPO leading to the oxidation of the HMF to DFF and the formation of TEMPOH. This is in good agreement with mechanisms described in literature for other catalysts and is consistent with current data.

Figure 1. *A Conversion of HMF and selectivity towards known products over time. Reaction conditions: 3 ml of 5 wt% HMF aqueous solution heated together with 30 mg MIL-100(Fe) catalyst and 8 eq ^{t}BuOOH at 60 °C for the stated duration. **B** Conversion of HMF and yield of known products by MIL-100(Fe) catalyst and TEMPO co-catalyst over time. Reaction conditions: 3 ml of 5 wt% HMF aqueous solution heated together with 30 mg MIL-100(Fe) catalyst, 1 eq TEMPO and 8 eq ^{t}BuOOH at 70 °C for the stated duration. **C** The time dependent oxidation of HMF over MIL-100(Fe) without TEMPO cocatalyst. The concentrations of each of the major reaction products is normalised such that its maximum concentration during the reaction is 100% and trendlines have been added as a guide to the evolution of the reaction. **D** The time dependent oxidation of HMF over MIL-100(Fe) with TEMPO cocatalyst. The concentrations of each of the major reaction products is normalised such that its maximum concentration during the reaction is 100% and trendlines have been added as a guide to the evolution of the reaction.*

Figure 2. *The proposed mechanism for the oxidation of HMF to DFF over MIL-100(Fe) catalyst and TEMPO co-catalyst. The active site of MIL-100(Fe) within a single Fe₃ cluster is depicted, with Fe ions in green, oxygen in red and the carbons of the BTC linkers in black. Reformation of TEMPO cocatalyst after the reaction is also depicted.*

The subsequent catalytic oxidation of the aldehyde group in DFF to the acid, forming FFCA, in combination with TEMPO has not been studied to the best of our knowledge. The co-catalyst is generally considered to be selective for the oxidation of alcohols,[34, 37] but in this case TEMPO was found to significantly increase the selectivity towards FFCA and FDCA in the oxidation of DFF. In our proposed mechanism, the oxidation of DFF over MIL-100(Fe) and TEMPO (Figure 3) is proposed to proceed in a similar way to that of the oxidation of HMF. After binding of the substrate to the MOF's active site, synergistic C-H and C=O bond activation by TEMPO and the MOF respectively activates the aldehyde allowing the addition of hydroxide and the formation of the acid group. This leads to the reduction of the Fe(III) in the MOF, and the reduction of TEMPO to TEMPOH. The re-oxidation of TEMPOH can be facilitated in the same way, by reduction of the oxidant ^{t}BuOOH.

With the impressive catalytic activity of MIL-100(Fe) in combination with TEMPO as a co-catalyst, a series of reference reactions were carried out where the MIL-100(Fe) was replaced with either Fe_2O_3, a solution of homogeneous $FeCl_3$, commercial Basolite® F300 or MIL-100(Al) (Figure S7). $FeCl_3$ was found to be highly active, giving 100% HMF conversion after 24 hours, but it is far less selective for FDCA (25% yield vs 57% with MIL-100(Fe)), and this is attributed to the lack of a clearly defined active site selective for FDCA. Fe_2O_3 showed much lower conversion, as well as lower selectivity towards the desired products than when using MIL-100(Fe). This can be explained by the significantly reduced surface area and therefore lower availability of the redox active sites within the oxide compared to the MOF, as well as the very different surface chemistry of the two solids. The higher selectivity with the MOF can be attributed to the synergistic activity of the MOF and TEMPO co-catalyst which may not be possible in the dense oxide.
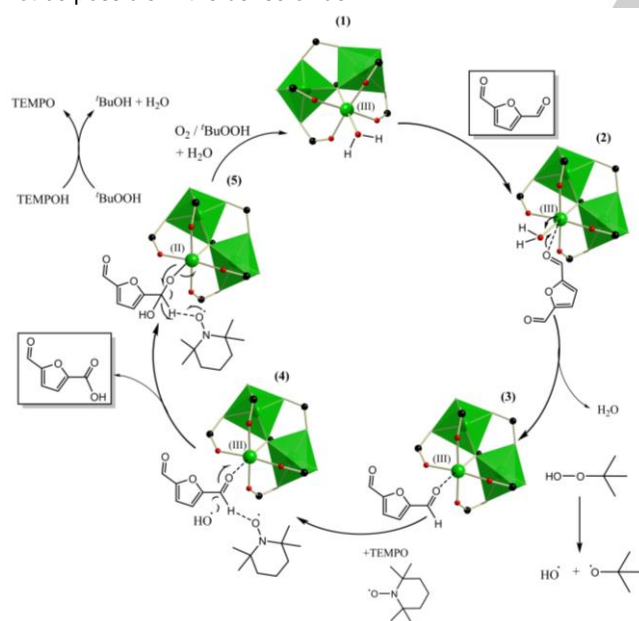

Figure 3. The proposed mechanism for the oxidation of DFF to FFCA over MIL-100(Fe) catalyst and TEMPO co-catalyst. The active site of MIL-100(Fe) within a single Fe_3 cluster is depicted, with Fe ions in green, oxygen in red and the carbons of the BTC linkers in black.

One significant advantage of using MIL-100(Fe) over other materials or MOFs is the fact that it is commercially available. MIL-100(Fe) is sold under the name 'Basolite F300' and is produced by BASF. Although it does have the MIL-100 structure, Basolite® F300 is poorly crystalline compared to many hydrothermally produced samples including ours (Figure S8). In our experience, the more crystalline the catalyst sample, the better it performed. Basolite F300 has also be shown previously to be much less

crystalline than MIL-100(Fe), and to significantly less porous, with a measured porosity of around 840 m^2g^{-1}.[38] Basolite F300 followed this trend, with considerably lower selectivity (50%) towards the desired reaction products and a yield of only 27% FDCA.

MIL-100(Al), which shares the same structure as the Fe version, is not redox active and so provides an insight into the effect of the redox active metal site. MIL-100 also contains Lewis acidic sites in the form of coordinatively unsaturated metal ions, and these can lead to side reactions taking place. It was thought that the Al(III) version of the MOF would also facilitate these side reactions, without oxidation of HMF, which requires the redox activity. The results showed very low conversion of HMF over MIL-100(Al) of about 18%, with no obvious signs of any side products in the resulting ^{1}H NMR spectrum. This conversion may be a result of the polymerisation of HMF into humins, which is known to occur at elevated temperatures in the presence of acid sites.[39] These humins are insoluble polymers which therefore do not appear in solution NMR. This indicates that the unknown side products from the MIL-100(Fe) catalysed reactions are likely to be at least partially due to humins, although these are difficult to quantify.

The recyclability of a catalyst is vital if it is to be useful on large and industrial scales. The long-term stability of MIL-100(Fe) was investigated by successive recovery and reuse of the catalyst, comparing its activity and selectivity after each cycle (Figure 4A). The HMF conversion and product yields were found to remain relatively constant over ten reaction cycles, and powder XRD of the washed MOF after the final cycle confirmed that the structure of the MOF was maintained (Figure 4B). In addition, recycling of the catalyst at incomplete conversion (~ 90% after 6 hrs) showed no significant changes in the product distribution and there was no evidence of deactivation of the MOF (Figure S9). Notable in the powder XRD of the MOF after catalysis is the reduction in relative intensity of the low angle reflections, which is evidence of blocking of the pores of the MOF. This is likely to be due to an accumulation of species from the reaction within the pores of the MOF that remain trapped after the mild post catalysis washing and this was further indicated by a significant reduction in the surface area after catalysis (37 m^2/g). These trapped species may account for a proportion of the unknown products of the reaction, but these proved difficult to remove from the MOF structure, despite attempted washing with various solvents. This pore blocking clearly does not have a significant effect on the activity of the catalyst however, indicating that the catalysis is limited to the surface of the material. This would be unsurprising given the proposed mechanism in which the MOF, TEMPO, the oxidant, and the substrate are required for the oxidation to occur, and the simultaneous diffusion of all into the MOF is unlikely to take place.
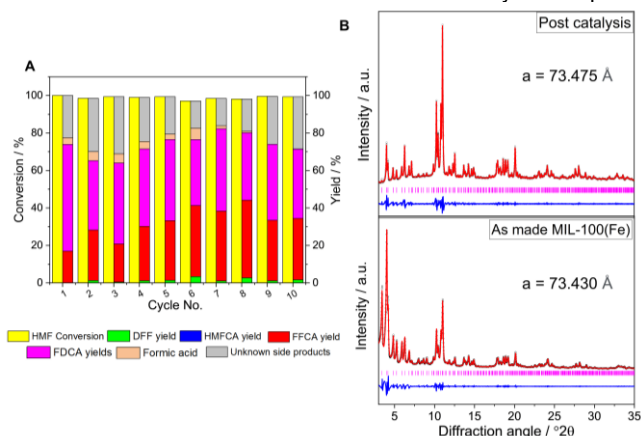
Figure 4. (A) HMF conversion and product distribution after each of ten consecutive reaction cycles reusing the same catalyst. Recycling was carried out by removal of the reaction solution, and this was replaced with fresh solution of HMF, TEMPO, ^{t}BuOOH without washing of the catalyst. Reaction conditions: 3 ml of 5 wt% HMF aqueous solution heated together with MIL-100(Fe) catalyst,

1 eq TEMPO and 8 eq tBuOOH at 70 °C for 24 hours each cycle. (B) Fitted powder XRD patterns of MIL-100(Fe) catalyst before and after the fifth reaction cycle.

The ratio of FDCA/FFCA in the final product appeared relatively constant in each of the recycles. To test whether the accumulation of FFCA and FDCA in the reaction was causing deactivation of the catalyst, FDCA was deliberately added from the start of the reaction to simulate product inhibition. The results (Figure S10) showed that the yield of oxidation products was much lower (~50%) after addition of FDCA, with an FDCA yield of around 22%. This strongly suggested that the build-up of acid within the reaction solution deactivated the MOF and prevented the oxidation of the final aldehyde of FFCA. A final investigation into the effect of washing the catalyst was carried out by recycling the catalyst without any washing (Figure S11). This was found to have no effect on the product distribution of the recycle reaction suggesting that a concentration of acid sites within the reaction mixture leads to the inhibition of the MOF, but that the inhibition can be reversed by removal of the reaction products. This indicates that separation of the products from the catalyst would prevent the inhibition and lead to greater selectivity towards FDCA.

Conclusion

This work presents a MOF catalyst for the oxidation of HMF to FDCA in water. A strong emphasis was placed upon the use of environmentally benign conditions, and MIL-100(Fe), which was synthesised in water, was found to be an efficient, robust, and recyclable MOF catalyst. In combination with the co-catalyst TEMPO, the MOF facilitated the complete conversion of HMF in 24 hours and, under optimum reaction conditions, a maximum yield of 57% FDCA and 17% FFCA was achieved to give a total selectivity of 74%. Mechanisms for both the alcohol and aldehyde oxidations were proposed, and these highlight the synergistic activity of the MOF and TEMPO. Compared to other proposed catalysts for the oxidation of HMF using TEMPO as a co-catalyst, this work is the only example in which water is used as the solvent, and most other reported catalysts operate under pure oxygen, often above 1 atms. (Table S1 and S2). It is also noteworthy that many catalysts for HMF oxidation only report the formation of DFF and not the subsequent formation of FFCA and FDCA. The materials that presently offer the best selectivity towards FDCA are enzymes or electrocatalysts: MIL-100(Fe) offers significant advantages over these approaches, being easily prepared, non-toxic, and performs extremely well under mild reaction conditions in water. This work therefore demonstrates a step towards the scalable and green synthesis of high value chemicals. Future work must include mechanistic studies to verify the redox chemistry proposed in the catalysis mechanism, in order to then design future optimised catalysts.

Experimental Section

Synthesis of MIL-100(Fe)

MIL-100(Fe) was prepared by addition of iron (III) chloride hexahydrate (10.8 g, 40 mmol) and 1,3,5-benzenetricarboxylic acid (5.56 g, 26.5 mmol) to 100 ml of deionised water. The solution was then stirred for 5 minutes before being transferred to a 200 ml polytetrafluoroethylene-lined (PTFE) autoclave and heated to 130 °C for 5 days. After cooling, the material was collected by centrifugation, washed twice with DMF, twice with water and finally twice with methanol, before being dried at 70 °C in air. After drying, approximately 10 g of pale orange powder was obtained.

Catalytic Reactions without TEMPO Co-catalyst

The catalyst (30 mg) was weighed into a 7 ml reaction tube along with 3 ml of 5 wt % (150 mg) aqueous HMF solution. To this, 8 equivalents tBuOOH (1.32 ml, Alfa Aesar 70% aqueous solution) was added. Finally, a magnetic stirrer bar was added, and the tube was sealed, heated to 70 °C and held for 24 hours under

constant stirring. After the time had elapsed, the solution was cooled quickly in cold water, and then an exact amount of dioxane (NMR standard, approximately 100 mg) was weighed into the reaction tube. A sample of the solution was then filtered using a 40µm filter and added to an NMR tube for analysis along with D2O solvent.

For reactions with high yields of FFCA and FDCA, which are relatively insoluble in water, the addition of a base was required to ensure the complete dissolution of the products. This caused dissolution of the MOF catalyst and prevented its recovery and so the solution was split to avoid the loss of all of the catalyst. In this case, approximately 1 ml of the reaction solution was separated off after the addition of dioxane. To this 1 ml portion, approximately 30 mg of Na2CO3 was added and the solution stirred for 5 mins to allow complete dissolution of the FFCA and FDCA. An NMR sample was then prepared, again by filtering of the solution through a 40 µm filter. The reaction solution was then centrifuged, and the liquid portion poured off to leave the solid catalyst. The solid was then washed twice with water and collected both times again by centrifugation before being dried at 70 °C in air.

Catalytic Reactions with TEMPO Co-catalyst

The catalyst (30 mg) was weighed into a 7 ml reaction tube along with 3 ml of 5 wt % (150 mg) aqueous HMF solution. To this, 1 equivalent TEMPO (188 mg, 1.2 mmol) and 8 equivalents tBuOOH (1.32 ml, Alfa Aesar 70% aqueous solution) was added. Finally, a magnetic stirrer bar was added, and the tube was sealed, heated to 70 °C and held for 24 hours under constant stirring. After the time had elapsed, the solution was cooled quickly in cold water, and then an exact amount of dioxane (NMR standard, approximately 100 mg) was weighed into the reaction tube. A sample of the solution was then filtered using a 40µm filter and added to an NMR tube for analysis along with D2O solvent. The addition of TEMPO appeared to aid the solubility of the products in water and so basic workup of the reaction solution was not required. The reaction solution was then centrifuged, and the liquid portion poured off to leave the solid catalyst. The solid was then washed twice with water and collected both times again by centrifugation before being dried at 70 °C in air.

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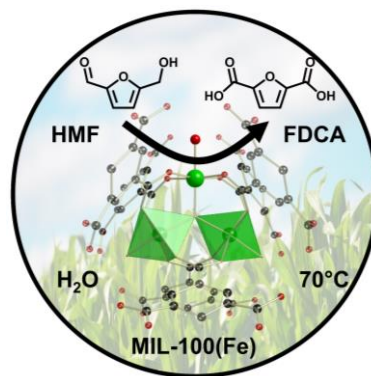
The highly stable MOF, MIL-100(Fe) can be synthesised in water alone and acts as a recyclable redox active catalyst for the oxidation of HMF to FDCA with no loss in activity after ten cycles. This is the first example of the use of a MOF for the complete conversion of HMF to FDCA.

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