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Synthesis of vanillin *via* a catalytically active Cu(II)-metal organic polyhedron

Cu(II)-MOP 1 was used for the first time in the catalytic conversion of *trans*-ferulic acid to vanillin. The generation of open Cu(II) metal sites within MOP 1 by activation, as well as sonication, revealed its catalytic potential.

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Crystalline Cu(II)-MOP **1** was employed for the first time in the catalytic conversion of *trans*-ferulic acid to vanillin. The generation of uncoordinated Cu(II) metal sites within MOP **1** by activation as well as sonication, revealed its catalytic potential that afforded a reaction yield of 60%. Complementary cyclic voltammetry experiments (CVs) demonstrated the formation of the complex Cu-H₂O₂, which supported the reaction mechanism proposed here.

Vanilla is one of the most valuable and popular flavouring substances in the world and is typically used in the food, nutraceutical, detergent, cosmetic, pharmaceutical and fine chemicals industries. The main natural sources of vanilla are the plants of the climbing orchids, *Vanilla planifolia* and *V. tahitensis*.¹ Although vanilla is considered a modern flavouring agent, the Mayan and Aztec civilisations first identified the use of vanilla to enrich chocolate flavour.² In fact, *Vanilla planifolia* was originally found in the subtropical forest in Mexico and some parts of Central America.^{2a}

Vanillin (3-methoxy-4-hydroxybenzaldehyde, C₈H₈O₃) is the main chemical constituent of vanilla, which is extracted from cured pods.³ The annual, worldwide production of vanilla is estimated to be approximately 1.2 × 10³ tonnes, and only 1%

corresponds to the natural extraction of vanillin.⁴ The manufacture of vanillin from the vanilla orchids is a difficult and very inefficient process. In fact, to produce 1 g of vanillin (from the vanilla orchids), 500 g of vanilla plants are needed.⁵ Therefore, the rest of its large-scale production is obtained from chemical synthesis or by acid hydrolysis of lignin.^{4,5} Unfortunately, chemical synthetic approaches to vanillin involve strong oxidising reagents and toxic solvents that are environmentally unfriendly. Certainly, biotechnological production of vanillin is significantly less harmful to the environment and industrially feasible. However, problems related to purification, time-consuming biotransformations and the use of potentially dangerous bacterial strains considerably restrain the use of these bio-processes.^{5,6}

Cleaner, milder and greener synthetic strategies towards the production of vanillic compounds have been recently proposed by transforming *trans*-ferulic acid to vanillin⁷ or vanillic acid⁸ using metal oxide catalysts. Our research group lately proposed the use of a metal-organic framework entitled HKUST-1 to catalytically and efficiently convert *trans*-ferulic acid to vanillin.⁹ Metal-organic frameworks (MOFs) have been shown to have very interesting heterogeneous-catalytic properties.¹⁰ Numerous research studies have been dedicated to the generation of different synthetic strategies for the preparation of catalytically active MOFs.¹¹ The incorporation of uncoordinated (catalytic active) metals into MOFs commonly involves the generation of vacant coordination sites on metal ions that are already occupied within the material by the removal of labile ligands.¹² In addition, heterogeneous catalysis arises in MOFs due to their intrinsic and robust porosity. By combining high surface areas and access to uncoordinated metal centres, very promising catalytic results have been achieved.^{11,12} On the other hand, non-porous, or very low surface area materials would be expected to be very poor catalytic materials.

Metal-organic polyhedra (MOPs, or molecular polyhedra, nanoballs or nanocages) are discrete molecular buildings constructed from the coordination of metal ions and organic

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ligands.¹³ To date, MOPs applications in fields such as chemical sensors, gas storage, drug delivery and catalysis have not been explored much due to easy aggregation of MOP molecules and the lower stability of their crystal lattice when compared to classic MOFs.¹³

Considering that applications of these discrete metal–organic materials could be uncovered by employing new approaches, we report the use of a porous metal–organic polyhedron (MOP) **1**, based on a carbazole–carboxylate ligand (H_2L^1 , Scheme S1†) and Cu(II) metal centres, as a catalyst in the oxidation of *trans*-ferulic acid to vanillin.

The carbazole–carboxylate ligand (H_2L^1 , 9*H*-carbazole-3,6-dicarboxylic acid) and MOP **1** (Fig. 1) were readily synthesised as previously reported¹⁴ with good yields of 79% and 67%, respectively. For this study, MOP **1** was characterised by PXRD experiments (Fig. S1 ESI†) and thermogravimetric analysis (TGA, Fig. S2, ESI†), which confirmed the purity of the samples. Once the purity of MOP **1** was established, the activation conditions of samples of **1** were studied by FTIR spectroscopy¹⁵ to efficiently generate uncoordinated metal sites. This is a fundamental step that determines access to the catalytic sites.⁹ MOFs provide very well ordered and regular access to those vacant sites due to their intrinsic permanent porosity (typically calculated by N_2 sorption experiments at 77 K) in contrast to nonporous, or very low porosity MOPs. However, we recently reported that MOP **1** exhibited a remarkable selectivity towards CO_2 over N_2 at cryogenic temperatures, which was achieved after the removal of terminal ligands (DMF and H_2O) at the Cu(II) metal sites.¹⁴

The net surface area of an activated sample of **1** (at 150 °C and 10^{-5} bar for 1 h) was measured in the present study using CO_2 as a probe gas at 196 K. Application of the standard Brunauer–Emmett–Teller (BET) model to adsorption data in the range $P/P_0 = 0.05–0.3$ gave a measured surface area of $341\text{ m}^2\text{ g}^{-1}$. This value is relatively higher than that for other MOPs examples,¹³ although it is lower than the remarkable example recently presented by Doonan in a series of hetero-bimetallic Pd(II)–Cu(II), Ni(II), and Zn(II) MOPs ($1100\text{ m}^2\text{ g}^{-1}$).¹⁶

MOP **1** is based on six dinuclear Cu(II) paddlewheel clusters $[Cu_2(O_2CR)_4]$, (Fig. 1), and each paddlewheel is coor-

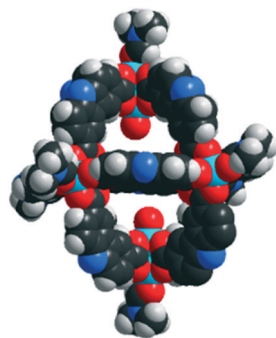


Fig. 1 Space filling view of the crystal structure of MOP **1**. Color-keys for the atoms: black (C), white (H), red (O), blue (N), and light blue (Cu).

ordinated to one DMF molecule in the outer part of the discrete assembly and one H_2O molecule within the cavity (Fig. 1).¹⁴

Thus, samples of **1** were thermally activated (under vacuum) and monitored by FTIR. First, an FTIR experiment was performed on the as-synthesised MOP **1** at 25 °C, non-activated **1** (Fig. S3, ESI†), where the broad adsorption band at 3250 cm^{-1} confirmed the presence of non-coordinated H_2O inside the material. At 3730 cm^{-1} , a typical sharp peak corresponding to a metal coordinated to H_2O (ref. 9, 15*a*, 17) was clearly noticeable in the spectrum (Fig. S3, ESI†). A DMF $\nu(CO)$ band coordinated to the Cu(II)-metal centre^{14,18} was observed at 1655 cm^{-1} in the spectrum (see Fig. S4, ESI†). Later, a freshly synthesised sample of **1** was activated at 150 °C under vacuum (10^{-3} bar, lower vacuum than previously reported⁹) for 1 h, without physical manipulation or exposure to air, which then cooled down to 25 °C. An FTIR spectrum showed the removal of DMF and H_2O molecules (Fig. S3 and S4, ESI†).

Given the fact that *trans*-ferulic acid is approximately $10.0\text{ \AA} \times 6.4\text{ \AA}$ in size, it appears very unlikely that this molecule could easily access the inside of the cavity of MOP **1**, estimated to be $10.8\text{ \AA} \times 9.8\text{ \AA}$ (from the X-ray crystal structure). Instead, we hypothesised that the activity of this catalyst could arise from the uncoordinated Cu(II)-metal sites on the outer part of **1** and this can be sufficient to oxidise *trans*-ferulic acid to vanillin. Then, a newly synthesised sample of **1** was activated (*vide supra*), and the catalytic experiment was carried out using the catalytic conditions in ethanol that we previously reported⁹ (Experimental ESI†). Gas chromatography (GC) exhibited a partial conversion of *trans*-ferulic acid to vanillin as the only product, and the purified sample (by column chromatography) gave a low reaction yield of approximately 15%. 1H NMR experiments confirmed the product purity and identity. In addition, it was not possible to completely recover all the catalyst and more importantly, copper species leached into the reaction solution, which were identified by inductively coupled plasma mass spectrometry (ICP-MS, ESI†) of the hot filtrate from the catalytic reaction. This is likely due to the partial solubility of MOP **1** in ethanol.

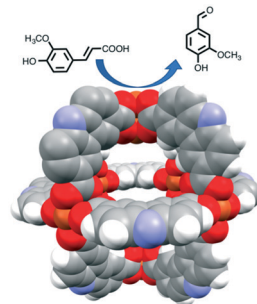
Therefore, we repeated the catalytic reaction, as previously described but using THF instead of ethanol. THF completely solubilised samples of *trans*-ferulic acid but, more importantly, did not dissolve samples of MOP **1**. After purification of the reaction solution by column chromatography, the product composition was confirmed with GC analysis and 1H and ^{13}C NMR spectroscopies (Fig. S5 and S6, respectively, ESI†), revealing a slightly better reaction yield of 30%. Using these conditions, the recovery of the catalyst was complete. Even though PXRD showed the loss of its crystallinity (which is characteristic of MOP materials,¹⁶ see Fig. S7, ESI†), ICP-MS experiments of the hot filtrate from the catalytic reaction revealed that no copper species leached into the reaction mixture (ESI†).

Even though the reaction yield was improved (from 15 to 30%) and the total recovery of the catalyst was achieved

(without any leaching of copper species), we explored other strategies to further improve this catalytic reaction. First, we rationalised that dry THF could be used since water is completely miscible in THF, and therefore these H₂O molecules could potentially re-coordinate the Cu(II) sites in MOP 1. When the catalytic reaction was performed again under the same conditions (*vide supra*), but using dry THF instead of “wet” THF, the reaction yield was approximately the same (31%). Although dry THF was used, there was water (due to the addition of H₂O₂, 50 wt% in H₂O) in the catalytic reaction. However, H₂O₂ coordinates better with the Cu(II) metal centres, as we previously observed,⁹ and thus, the catalytic process takes place. This phenomenon can be explained in terms of the nucleophilicity of the reacting species towards the Cu(II) metal sites since H₂O₂ shows a much higher reactivity than H₂O¹⁹ to coordinate with open Cu(II) metal centres over H₂O.

As an alternative approach to increase the transformation, we hypothesised that the severe aggregation of MOP 1 molecules, which typically occurs in these materials after activation, can lead to the blockage (inaccessibility) of active catalytic sites (Lewis-acid sites).²⁰ It is well known that the activity of a catalyst strongly depends on the particle size and surface area.²¹ In addition, it is possible to accelerate a reaction under ultrasound conditions as previously observed for the synthesis of lanthanide benzenetricarboxylates.²² In particular, in the field of MOFs/MOPs, Ahn and co-workers,²³ recently reported that the MOF material ZIF-8 (synthesised by sonochemical routes) exhibited a superior performance in the Knoevenagel condensation reaction. Thus, to reduce the possible aggregation (and increase reactivity), a newly synthesised sample of MOP 1 was activated (150 °C and 10⁻³ bar for one hour) and cooled to room temperature under N₂ atmosphere. Then, the activated catalyst was dispersed into dry THF and sonicated (ultrasonic bath; frequency of 42 kHz and total output power of 70 W) for 5 min. After the sonication was completed, the catalytic reaction was carried out and the reaction yield was found to considerably improve to 60%. In addition, the chemical composition (after purification) was confirmed by GC analysis, and ¹H and ¹³C NMR spectroscopies. Again, no copper species leached into the reaction mixture (ICP-MS). This reaction yield is comparable to the one obtained by Pagliaro *et al.*⁸ on the conversion of *trans*-ferulic acid to vanillic acid. Scheme 1 shows a proposed schematic representation of the catalytic process, in which the uncoordinated outer Cu(II) metal sites (of MOP 1) interact with *trans*-ferulic acid to produce vanillin. This schematic is further explained by a reaction mechanism (see below).

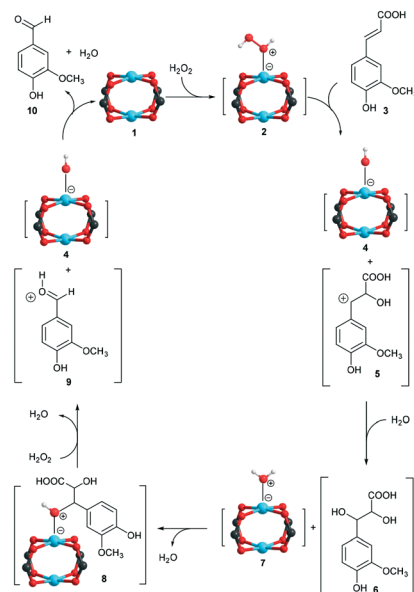
Once the optimal catalytic conditions were achieved, the recyclability of the catalyst was investigated. Thus, five catalytic experiments were performed on the same MOP 1 sample (activation and re-activation) showing a decrease in the conversion of *trans*-ferulic acid to vanillin with a final reaction yield of 40% (fifth reaction, ESI[†]). The chemical composition (vanillin) was confirmed by GC analysis and ¹H and ¹³C NMR spectroscopies, which confirmed that no copper species



Scheme 1 Schematic of the interaction of *trans*-ferulic acid with the uncoordinated outer Cu(II) metal sites, within MOP 1, to obtain vanillin.

leached into the reaction mixtures (ICP-MS) for each reaction. We rationalised that the decrease in the reaction yield is closely associated to MOP aggregation in 1, between catalytic cycles, making MOP 1 an inefficient, recyclable heterogeneous catalyst. This behaviour has been previously observed in MOPs. For example, MOP-SO₃H showed a sharp reduction in the catalytic conversion of styrene oxide from 48% to 2% after only one cycle.²⁴

A reasonable reaction mechanism to account for the conversion of *trans*-ferulic acid 3 into vanillin 10 is depicted in Scheme 2. This oxidation process is based on an electrophilic aromatic substitution, as it was considered by Baiker *et al.*²⁵ for the hydroxylation of benzene. Initial activation of hydrogen peroxide by Cu(II)-MOP 1 gave copper ion 2, which by transfer of HO⁺ to the vinyl system of *trans*-ferulic acid 3 gave carbocation 5, which should be favoured due to a stabilisation of the carbocation in the benzylic position. Nucleophilic attack of water onto the electrophilic carbon atom, after release of a proton, gave the diol-like compound 6, that



Scheme 2 Plausible reaction mechanism for the oxidation of *trans*-ferulic acid towards vanillin. Color-keys for the atoms: black (C), white (H), red (O), and blue (Cu).

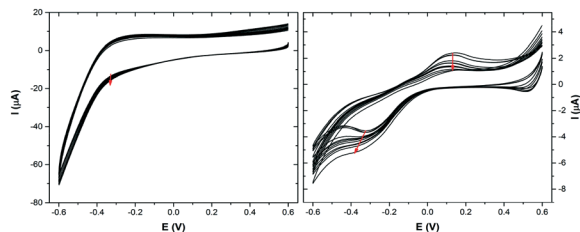


Fig. 2 CVs of the CPE (left) and MOP1@CPE (right), each with consecutive additions of H_2O_2 (from 0.02 to 1 mM) in 0.1 M KNO_3 .

provided vanillin **10** (60%) through the release of water and subsequent oxidation by a second molecule of hydrogen peroxide.

It is worth noting that oxalic acid and acetic acid were not detected as by-products, unlike previously observed in our earlier study using porous, coordination polymer HKUST-1.⁹ The presence of vanillin reported in the scheme was found in the bulk solution and it was confirmed by ESI-MS (HMRS, Fig. S8†). 4-Vinylguaiacol, vanillic acid or protocatechuic acid, were not detected in the bulk solution as we also observed in a previous study.²⁶

Finally, to support our oxidation mechanism using MOP 1 in the presence of hydrogen peroxide (H_2O_2), cyclic voltammetry experiments (CVs) were performed on MOP 1. Carbon paste electrodes (CPE) were constructed by preparing a 1 : 1 mass ratio mixture of activated carbon and an activated sample (150 °C and 10^{-3} bar for one hour) of MOP 1. Afterwards, mineral oil was added to form the paste, and it was mounted in a 2 mm diameter graphite transducer base. All CV experiments were carried out in 0.1 M KNO_3 at 100 mV min^{-1} in a potential range from -0.6 to 0.6 V.

The CVs from the CPE showed no difference in the presence of H_2O_2 (Fig. 2, left). When MOP 1 was introduced to the CPE (MOP1@CPE), the characteristic reduction and oxidation copper peaks were observed at -319 and -220 mV (reduction) and 142 mV (oxidation) (Fig. S9 ESI†). Upon the addition of H_2O_2 (from 0.02 to 1 mM), the reduction and oxidation peaks were displaced (Fig. 2, right). The cathodic peaks are associated with the reduction of Cu(II) to Cu(I) , and Cu(I) to Cu(0) , at -220 mV and -319 mV, respectively. Thus, the peak at -220 mV, which corresponds to the reduction of Cu(II) to Cu(I) , did not exhibit a significant change upon the addition of hydrogen peroxide. Conversely the peak at -319 mV (reduction of Cu(I) to Cu(0)) dominated the electrocatalytic irreversible reduction of H_2O_2 , as previously reported by Wang *et al.*²⁷ for HKUST-1.

Evidence of the complexation species ($\text{Cu-H}_2\text{O}_2$) can be obtained from the displacement of the reduction peak from -319 to -393 mV with the addition of H_2O_2 (0.1 mM) (Fig. S10 ESI†). In Fig. S10 ESI†, a sharp increase in the peak current up to 0.1 mM was observed, from which the potential remained without any further change (at -393 mV), and the current kept slowly increasing up to 1 mM. These two domains represent the formation of the $\text{Cu-H}_2\text{O}_2$ complex first and the H_2O_2 catalytic reduction second (Fig. S10 ESI†).

In summary, the use of a crystalline metal-organic polyhedron MOP 1, based on a carbazole-carboxylate ligand and Cu(II) metal centres, as a heterogeneous catalyst in the transformation of *trans*-ferulic acid to vanillin was successfully demonstrated. The generation of uncoordinated Cu(II) metal sites within MOP 1 (confirmed by FTIR), in combination with sonication of the activated catalyst, provided a reaction yield of 60%. The recovered catalyst was analysed by PXRD showing the loss of its crystallinity, which is characteristic of MOP materials, but ICP-MS experiments confirmed that no copper species leached into the reaction mixture. The reaction yield of the transformation was significantly improved from 30% to 60% when the activated catalyst was sonicated (ultrasonic bath). This treatment considerably reduced MOP aggregation in **1** and thus, promoted accessibility of active catalytic copper sites. After 5 experiments, the recyclability of the catalyst showed a decrease in the conversion of *trans*-ferulic acid to vanillin with a final reaction yield of 40%. Despite the lower yields after cycling, no copper species leached into the reaction mixtures, as shown by ICP-MS experiments. Cyclic voltammetry experiments (CVs) revealed the formation of the complex $\text{Cu-H}_2\text{O}_2$, which supported our proposed reaction mechanism.

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