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{[Cu₃Lu₂(ODA)₆(H₂O)₆]·10H₂O}ₙ: the first heterometallic framework based on copper(II)/lutetium(III) for the catalytic oxidation of olefins and aromatic benzylic substrates†

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The catalytic performance of the novel framework {[Cu₃Lu₂(ODA)₆(H₂O)₆]·10H₂O}ₙ was tested in the oxidation of alkenes and benzylic hydrocarbons, using *tert*-butyl hydroperoxide (TBHP) and molecular oxygen (O₂) as oxidants. Excellent conversions were obtained with O₂ under solvent-free conditions, in the absence of a co-catalyst, for cyclohexene (95%) and for cumene (91%).

Heterogeneous catalysis was one of the earliest proposed applications for crystalline metal–organic frameworks (MOFs), and it was also one of the early demonstrated applications. In 1994, the cyanosilylation of various aldehydes, using a cadmium-based MOF as a catalyst, was reported,[1] and many more examples can be found in the literature to date.[2,3] MOFs provide powerful platforms to immobilize multiple functional sites within a single crystal, and this makes them potential materials to be probed as heterogeneous catalysts. This fact can be amplified by using two different metal ions to build MOF catalysts. In spite of this, the application of heterometallic MOFs as catalysts has been much less explored in comparison with homometallic ones. With this in mind, we started a study on the catalytic properties of a series of MOFs with the general formula {[Cu₃Ln₂(ODA)₆(H₂O)₆]·*x*H₂O}ₙ (Ln^{III} = lanthanide ion, H₂ODA = 2,2′-oxydiacetic acid).[4]

The chemistry of compounds based on the 2,2′-oxydiacetic acid ligand is currently well documented. The coordination modes of this ligand have allowed a large variety of compounds derived from transition metal ions, lanthanide ions or both to be obtained.[5–12] For example, the review done by Kremer *et al.*[10] reports a series of compounds with lanthanide(III) ions, and heterometallic combinations using transition metal ions and lanthanide ions. The authors analyzed the thermodynamic properties, magnetism and thermal stability of these compounds. However, this review does not mention homo- or heterometallic compounds of lutetium. In general, the catalytic properties of lutetium-based compounds have not been extensively studied, and are not well detailed in the literature. There are few examples of the catalytic performance of lutetium. For example, the hydroformylation of 1-octene was studied using a mixture of (C₂H₂)₂LuCl/NaCo(CO)₄ or (C₂H₂)₃Lu/0.5Co₂(CO)₈.[13] The observed conversion was greater than 50%, and the products obtained were *n*-aldehydes and iso-aldehydes. More recent studies have used lutetium(III) ions to change the catalytic site in DNA and modify the sequence of a specific protein.[14] To the best of our knowledge, there are no studies that demonstrate the catalytic properties of heterometallic MOFs based on copper(II)/lutetium(III). Our group synthesized a new heterometallic MOF based on the ODA ligand and copper(II) and lutetium(III) ions, {[Cu₃Lu₂(ODA)₆(H₂O)₆]·10H₂O}ₙ (CuLuMOF), and investigated its catalytic activity in alkene and aromatic benzylic substrate oxidation. Thus, we herein report the catalytic study related to this novel heterometallic framework.

The synthesis of {[Cu₃Lu₂(ODA)₆(H₂O)₆]·10H₂O}ₙ (CuLuMOF) was done starting from ODA in the acidic form and the metal chloride at a controlled pH value (see the ESI† for details). After 48 hours, light blue crystals were obtained, which were suitable for single crystal X-ray diffraction. The CuLuMOF framework crystallizes in the *P*6/*mcc* space group. The molecular structure contains Lu^{III} ions coordinated by three tridentate ODA ligands, forming the building block [Lu(ODA)₃]³⁻. The central atom is surrounded by nine oxygen atoms, with its coordination geometry being better described

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as a distorted tricapped trigonal prism. The six carboxylate oxygen atoms form a trigonal prism (Lu–O2 at 2.336 Å), with three ether oxygen atoms as capping ones at a longer distance (Lu–O1 at 2.415 Å). Each $[Lu(ODA)_3]^{3-}$ unit is connected to six Cu^{II} atoms *via* single *syn–anti* μ-carboxylato-*O-O′* bridges; copper(II) ions are six-coordinated. They are surrounded by four carboxylate oxygen atoms (Cu–O average distance is 1.953 Å), which define the equatorial plane, and two water molecules at longer distances (2.457 Å). Thus, Cu^{II} exhibits an elongated octahedral geometry. As a result of this connectivity, a 2D honeycomb pattern is formed in the (001) plane (Fig. 1a and b). Columnar hexagonal channels are then formed along the *z* direction. Detailed crystallographic data are given in Tables 1S(A–D).† Besides, CuLuMOF was characterized by elemental and thermogravimetric analyses (ESI†).

The initial catalytic reactions were done following the conditions described by our group in previous reports.[4,15] $\{[Cu_3Lu_2(ODA)_6(H_2O)_6]\cdot 10H_2O\}_n$ was found to be an active catalyst in the oxidation of styrene and cyclohexene with TBHP, both in 1,2-dichloroethane (DCE) and *n*-decane media. The oxidation of cyclohexene produced cyclohexene oxide (A), 2-cyclohexenol (B), 2-cyclohexenone (C) and 1,2-cyclohexenediol (D) (Scheme 1S†). When the reaction was done using DCE as a solvent, the conversion after 24 h was 60%, and the main product was 2-cyclohexenone (57%). The oxidation of styrene under the same experimental conditions produced styrene oxide (a), benzaldehyde (b), 1-phenylacetaldehyde (c) and 1,2-phenylethanediol (d) as products (Scheme 1S†). The conversion was 75%, and the main product was 1-phenylacetaldehyde (45%). The corresponding yields for both substrates are given in Table 1. The effect of the solvent was studied by changing the reaction medium from DCE to *n*-decane; an increase in the conversion of approximately 10% was observed for both substrates (Fig. 2S†). It is important to mention that the main products in both oxidation reactions remained the same. The catalyst was analyzed by X-ray powder diffraction after the catalytic re-

action; the crystallinity of the catalyst remained unchanged, as observed in Fig. 3S and 4S.† The ICP results indicated that the amount of copper(II) was less than 0.01% in the filtered reaction solution of cyclohexene, and less than 0.05% in the filtered reaction solution of styrene. These data revealed that the catalyst is robust and that leaching is insignificant. These catalytic results were compared with those previously reported, using isostructural MOFs as catalysts, $\{[Cu_3Ln_2(ODA)_6(H_2O)_6]\cdot 10H_2O\}_n$ (Ln = La^{III}, Gd^{III} or Yb^{III}) (Fig. 5S†).[4] As compared to the reported catalysts, CuLuMOF was the most active among the series in the oxidation of olefins (Fig. 2). The results reported in this study are in agreement with those obtained from DFT calculations for CuLuMOF, in relation to the catalytic performance of this family of frameworks. Thus, the conversion increases as the lanthanide series progresses from lanthanum(III) to lutetium(III), favoring the catalytic cycle as has been explained in our previous work.[4] The catalytic performance of the heterometallic CuLnODA catalysts, including the lutetium-based catalyst, was shown to be better than that of the homometallic copper(II) catalyst, CuMOF.[4]

Molecular oxygen is an ideal reagent as it is a naturally occurring oxidant, which does not give any unwanted reduced products, thus simplifying the purification of products.[16]

Therefore, the performance of the CuLuMOF catalyst was also studied by changing the reaction conditions to a solventless medium and using molecular oxygen as an oxidant, in order to obtain more environmentally friendly conditions. In a typical experiment, the substrate and catalyst were added to the reactor (0.001 mol% of Cu per mole of substrate). The reactions were carried out under solvent-free conditions in the absence of a co-catalyst, and the temperature of the reaction was 120 °C with an oxygen pressure of 5 bar, using a batch reactor. After the reactor was charged with 5 bar of oxygen, the reactor was sealed, placed in a silicone oil bath and left to react at 120 °C. After the reactor was cooled, the remaining oxygen was released and the catalyst was recovered by filtration. Excellent results were obtained by modifying the reaction conditions; the conversion of cyclohexene increased from 60% for a time interval of 24 h (TBHP/DCE) to 95% for 4 h of reaction time (O_2/solvent-less). The main product for both reactions remained 2-cyclohexene, with a selectivity close to 55%. Good results at shorter reaction times were also observed for the rest of the studied cycloalkenes (Table 2) (Scheme 2S†). It is important to remark that the reactions done at 120 °C imply the removal of the coordinated water molecules bonded to copper(II) (Fig. 1b and 1S†), thus making this Lewis acid center accessible to molecular oxygen.[17] Different conversions were observed depending on the number of carbon atoms in the ring; when cyclohexene was used as the substrate the major conversion among the studied cycloalkenes (95%) was observed. The selectivity also changed with the nature of the cycloalkane, with the main product being a conjugated ketone for C6 and C7, and an epoxide for C8. The yield of epoxide increased as the number of carbons increased from C6 to C8. The stabilization of the double

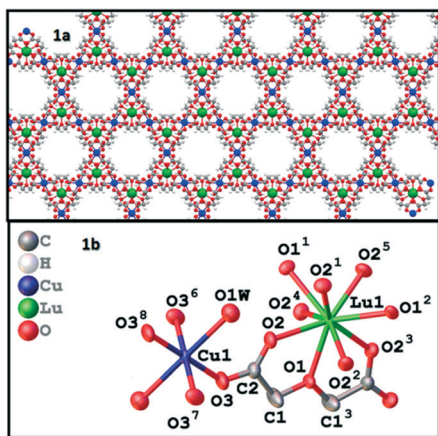**Fig. 1** (a) View of the *ab* plane of $\{[Cu_3Lu_2(ODA)_6(H_2O)_6]\cdot 10H_2O\}_n$ (CuLuMOF) (blue (copper), green (lutetium), red (oxygen), grey (carbon), white (hydrogen)). (b) ORTEP view and labeling scheme for $\{[Cu_3Lu_2(ODA)_6(H_2O)_6]\cdot 10H_2O\}_n$.

Table 1 Oxidation of cyclohexene and styrene using CuLuMOF as a catalyst

	Conversion (%)	Solvent	TON/TOF (h^{-1})	Main reaction products	Selec. (%)
Cyclohexene	60	1,2-DEC	10 827/451	Cyclohexenone	57
				Cyclohexenol	30
				Cyclohexene oxide	5
Cyclohexene	69	n-Decane	12 451/519	Cyclohexenone	55
				Cyclohexenol	28
				Cyclohexene oxide	6
Styrene	75	1,2-DCE	13 534/564	Styrene oxide	31
				Benzaldehyde	24
				Phenylacetaldehyde	45
Styrene	88	n-Decane	15 880/662	Styrene oxide	12
				Benzaldehyde	30
				Phenylacetaldehyde	43

Reaction conditions: catalyst (0.0165 mmol), substrate (40 mmol), TBHP (40 mmol), 75 °C and 24 h reaction time. Ratio S/C = 2400/1 or 0.001 mol% of copper per mole of substrate. TON is calculated as moles of products per mole of active site (Cu^{II} ions); TOF is calculated as moles of products per mole of active site (Cu^{II} ions) per hour (TOF was calculated using the time reported in the table).

bond has an important role in the formation of the products, with the alkene position being the most active for cyclooctene, and the allylic position being the most active for cyclohexene (Table 2).[18,19]

The previously reported catalyst CuLaMOF presents similar results for the aerobic oxidation of cyclohexene.[20] However, a conversion of 75% was obtained after only 6 h of reaction, while by using CuLuMOF under identical reaction conditions the same conversion was reached in 2 h. These results can be compared with those reported by Parra da Silva et al.,[21] who used 3 nm average diameter calcinated CuO NPs as a catalyst in the aerobic oxidation of cyclohexene, at 100 °C and 4 bar of O_2. The results for a reaction interval of 2 h were 65% conversion and 45% selectivity to ketone, lower than those obtained using CuLuMOF.

The activation of oxygen probably begins by the formation of radical species, as suggested by Santiago-Portillo et al.[22] TGA analysis indicates that free positions on the copper(II) ions are generated by the removal of ligand water molecules from the first coordination sphere (ESI†). These positions permit the interaction of molecular oxygen with the catalyst, generating radical species. The presence of radical species was verified by incorporating 5 mol% of anthraquinone into the reaction mixture as a radical trap, since it is known to inhibit the action of radical species,[22] and observing a null conversion of cyclohexene to the corresponding cyclohexenone

under these experimental conditions. On the other hand, the conversion of cyclohexene was not altered by the addition of DMSO to the reaction mixture, which is known to be reactive with the hydroxyl radical. Thus, it was possible to infer that the hydroxyl radical did not play an important role in the formation of the -ol/-one products.[23–25]

The performance of CuLuMOF as a catalyst was also studied using aromatic benzylic hydrocarbon compounds (cumene and indan) (Schemes 3S and 4S†). The conversion after 4 h of reaction was 91% for cumene and 60% for indan; the respective ketone being the main product in both cases (74% for acetophenone and 49% for indanone) (Table 2). These results are very interesting due to the fact that the performance of catalysts based on copper(II) or lutetium(III) in oxidation reactions of benzylic compounds has not been extensively studied. One of the examples of the use of a heterogeneous copper(II) catalyst that can be cited is the oxidation of cumene using CuO at 100 °C with 1 atm of molecular oxygen. The reported conversion of cumene was 56% after 7 h of reaction with a selectivity of 69% for cumyl hydroperoxide. Such a high selectivity to hydroperoxide cannot be considered as positive, since this species is considered hazardous.[26,27] Moreover, the use of copper(II) salts such as $CuCl_2 \cdot 2H_2O$ and $Cu(acac)_2$ needs an activator or a co-catalyst to proceed with the oxidation of cumene at 90 °C using molecular oxygen as an oxidant. The conversion for both salts is only 29% with a selectivity of 58% for acetophenone.[28] The use of [Cu(pymo)₂]MOF (pymo: 2-hydroxypyrimidinolate) and [Cu(im)₂]MOF (im: imidazole) for the aerobic oxidation of cumene revealed a better catalytic performance for the second MOF catalyst. For 4 h of reaction, ca. 57 and 71% conversions were obtained, respectively. For these two catalysts, the results indicated that the yield of the products shows dependence on the geometry of the copper center, which was determined by the nature of the ligands. [Cu(pymo)₂]MOF has also been reported as a catalyst for the aerobic oxidation of another benzylic substrate, tetralin, with a conversion of 51.5%. This copper(II)-based catalytic system produces hydroperoxide

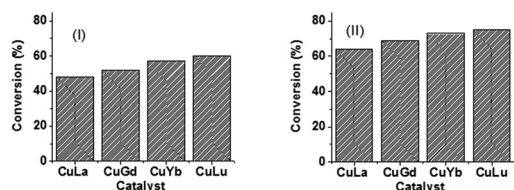**Fig. 2** (I) Conversion of cyclohexene after 24 h of reaction; (II) conversion of styrene after 24 h of reaction in the presence of the different catalysts. Reaction conditions: 1,2-dichloroethane as solvent, TBHP (70% in water) as an oxidant, 75 °C, ratio S/C = 2400/1 or 0.001 mol% of copper per mole of substrate.

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Table 2 Aerobic oxidation of cycloalkenes and aromatic benzylic hydrocarbons using CuLuMOF as a catalyst

	Conversion (%)	Time (h)	TON/TOF (h⁻¹)	Main reaction products	Selec. (%)
Cyclohexene	75	2^a	13 534/6767	Cyclohexenone	55
				Cyclohexenol	25
				Cyclohexene oxide	9
Cyclohexene	95	4	17 143/4286	Cyclohexenone	60
				Cyclohexenol	20
				Cyclohexene oxide	4
Cycloheptene	58	4	10 466/2617	Cycloheptenone	45
				Cycloheptenol	15
				Cycloheptene oxide	35
Cyclooctene	35	4	6316/1579	Cyclooctenone	10
				Cyclooctene oxide	90
Cumene	91	4	16 421/4105	Acetophenone	74
				Cumyl hydroperoxide	23
Indan	60	4	10 827/2707	Indanone	49
				Indanol	31

Reaction conditions: catalyst (0.0041 mmol), substrate (10 mmol), O_2 atmosphere (5 bar), 120 °C and reaction time depending on the substrate in order to achieve the indicated conversion. Ratio S/C = 2400/1 or 0.001 mol% of copper per mole of substrate. ^{a} Complete consumption of oxygen occurs at this reaction time. TON is calculated as moles of products per mole of active site (Cu^{II} ions); TOF is calculated as moles of products per mole of active site (Cu^{II} ions) per hour (TOF was calculated using the time reported in the table).

as the main product with less than 10% of tetralone after 15 h of reaction.[29] The oxidation of indan was reported using Cu(OH)$_2$, CuCl$_2$ or Cu(TPIP)$_2$ (TPIP: tetraphenylimidodiphosphinate) as a catalyst.[30] The chloride and hydroxide species gave a similar low conversion of 27%, but with a selectivity of 75% for indanone. On the other hand, the use of Cu(TPIP)$_2$ as a catalyst permitted the conversion to increase to 49%, but the main product was indanyl-1-hydroperoxide (31%), instead of the ketone.[30]

To the best of our knowledge, the only heterometallic MOF based on copper(II) and lanthanide(III) ions used as a catalyst for the oxidation of aromatic benzylic compounds is CuLaPDC (PDC: 3,5-pyridindicarboxylate).[19] The reported catalysts based on copper(II) or copper(II)/lanthanum(III) present a lower conversion than the reported catalyst in this work, using CuLuMOF with molecular oxygen as an oxidant, under solvent-free conditions.

Conclusions

The present work reports a new heterometallic metal organic framework, $\{[Cu_3Lu_2(ODA)_6(H_2O)_6]\cdot10H_2O\}_n$ (CuLuMOF) with an active catalytic performance in the oxidation of olefins and aromatic benzylic hydrocarbon compounds, using tert-butyl hydroperoxide or molecular oxygen as an oxidant. The lutetium(III) ions enhance the oxidation reactions by increasing the catalytic properties of the copper(II) ions. The change to more environmentally friendly solvent-free conditions, using molecular oxygen as the sole oxidant since the presence of a co-catalyst is not needed, exhibited better results than those previously reported for heterogeneous copper(II) catalysts. The best catalytic performance of CuLuMOF was obtained for cyclohexene with a conversion of 95%, and for cumene with a conversion of 91% after four hours of reaction.

Conflicts of interest

There are no conflicts to declare.

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