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Novel Copper(II)-Lanthanum(III) Metal Organic Framework as Selective Catalyst for the Aerobic Oxidation of Benzylic Hydrocarbons and Cycloalkenes.

P. Cancino,^{a,b} A. Vega,^{b,c} A. Santiago-Portillo,^d S. Navalon,^d M. Alvaro,^d P. Aguirre,^a E. Spodine,^{*a,b} H. García,^{*d}

The synthesis and structure of a novel heteronuclear Cu^{II} and La^{III} metal organic framework (MOF), having pyridinedicarboxylic acid (CuLa-MOF) is reported. The obtained MOF of formula $[Cu_{0.5}La_2(HPDC)(PDC)_2(SO_4)(H_2O)_2]H_2O]_n$ (PDC: 3,5-pyridinedicarboxylate), has a 3D non-porous lattice with a single type of octahedrally coordinated Cu^{II} and two distinct nonacoordinated La^{III} ions, sulphate being a linker between the Cu^{II} and La^{III} centers. The CuLa-MOF exhibits catalytic activity to promote the aerobic autooxidation of benzylic hydrocarbons, and the aerobic oxidation of cycloalkenes. Comparison with the homogenous catalyst, $Cu(OAc)_2$, shows that the CuLa-MOF, as a heterogeneous catalyst, exhibits similar activity, but the solid is recyclable with some minor decrease in the activity from the first to the second catalytic cycle, after which a steady activity is observed, as determined by the coincidence of the temporal evolution of the reaction.

Introduction

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Metal organic frameworks (MOFs) or coordination polymers are a relatively new class of crystalline porous materials with potential application in catalysis.^[1] These organic-inorganic hybrid materials are formed by nodes of metal ions or metal clusters, interacting with bi- or multi-podal organic linkers such as aromatic polycarboxylates. Nowadays, there is a vast number of MOFs with different topologies, morphologies and compositions, which are used for different purposes.^[2] Potential applications of these materials include gas storage,^[3,4] fluid separation,^[4,5] biomedicine,^[6] sensing,^[7] photocatalysis^[8] and catalysis^[9] among others.

In this context, there is a great current interest in exploiting the potential that MOFs offer as heterogeneous catalysts for organic reactions, particularly to promote aerobic oxidations.^[10] Aerobic oxidations of hydrocarbons are processes of large industrial importance for the manufacture of bulk chemicals and commodities,

- a Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Sergio Livingstone P 1007, Santiago, Chile. E-mail: espodine@uchile.cl
- b CEDENNA, Av. Libertador Bernando O'Higgins 3363, Santiago, Chile
- c Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andrés Bello, Quillota 980, Viña del Mar, Chile
- d Instituto de Tecnología Química and Departamento de Química, Universidad Politécnica de Valencia, Av. De los Naranjos s/n, 46022 Valencia, Spain. E-mail: hgarcia@qim.upv.es
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used as starting compounds in polymers and fine chemicals such as in fragrances, agrochemicals, glues or medicines.^[11] Preparation of these compounds in absence of organic solvents, and using only molecular oxygen as oxidizing reagent, is a continued target for the development of green processes, more efficient and selective, and with the generation of lesser amounts of toxic residues and byproducts.^[12] The use of heterogeneous catalysts can contribute to achieve this target by promoting aerobic oxidations and allowing an easy separation of the products from the catalyst that eventually can be recovered and recycled.

MOFs can have robust frameworks stable under reaction conditions, decreasing the percentage of metal leaching into the organic solution. MOFs have been successful heterogeneous catalysts mainly for liquid-phase reactions.[13,14] Partial success has been obtained using MOFs as support of radical initiators such as NHPI [15] or TEMPO [16,17] able to perform oxidations with molecular O2. In other cases, MOFs have been used as catalysts for oxidation reactions using H₂O₂^[18,19] or organic peroxides such as TBHP ^[19-24] as oxidants or as radical initiators in combination with molecular O2. Other related reactions employ organic aldehydes, such as isobutyraldehyde^[25] or thimethylacetaldehyde^[23], which with O₂ and with a proper metal catalyst can act as peracid precursors, have been carried out using organic solvents. Howerver, there are also some examples showing the ability of using MIL-101(Cr or Fe),^[26], Co-^[27,28] or Cu-containing MOFs^[29] as catalysts under solvent-free conditions with the exclusive use of molecular O₂ as oxidant. Regardless these achievements there is still room to develop active, selective and stable MOFs able to promote oxidation reactions using exclusively molecular oxygen in the absence of any organic promoter.

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Less common are the heterogeneous catalysts based on lanthanide(III) ions. For example, lanthanide(III) based MOFs with arenedisulfonate ligands have been used as catalysts in the oxidation of organic sulfur containing compounds and alkanes.^[30] Moreover, lanthanide carboxylates MOFs, as heterogeneous catalysts for oxidation of olefins, have recently been reported in 2011 and 2012 by Sen *et al.*.^[31] However, to the best of our knowledge heteronuclear copper(II)-lanthanide(III) MOFs have not been reported to date as catalysts in oxidation reactions of benzylic and cycloalkene substrates.

In the present work we report the synthesis of a new heterometallic Cu^{II} and La^{III} coordination polymer (CuLa-MOF) of formula $\{[Cu_{0.5}La_2(HPDC)(PDC)_2(SO_4)(H_2O)_2]\cdot H_2O\}_n$ that shows catalytic activity for the aerobic oxidation in free-solvent conditions of benzylic substrates and cycloalkenes, without any aldehyde or hydroxylimide as co-oxidant.

Experimental Section

Reagents

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All the reagents were of analytical grade and supplied by Sigma Aldrich. Benzylic substrates were distilled immediately before use in the catalytic reactions, in order to remove possible radical quenchers or avoid the initial presence of hydroperoxides.

Synthesis of {[Cu_{0.5}La₂(HPDC)(PDC)₂(SO₄)(H₂O)₂]·H₂O}_n

 $\{[Cu_{0.5}La_2(HPDC)(PDC)_2(SO_4)(H_2O)_2]\cdot H_2O\}_n$, was obtained by hydrothermal synthesis. Briefly, 1 mmol of 3,5 pyridindicarboxylic acid (H₂PDC), 0.25 mmol of lanthanum oxide (La₂O₃) and 0,5 mmol of copper sulfate pentahydrate (CuSO₄·5H₂O) were mixed with 8 mL of water in a Teflon vessel. The reaction mixture was heated at 170 ºC for 72 h in a Parr autoclave. Then, the reaction mixture was cooled for 10 h till room temperature. The products were filtered off and dried at room temperature. Blue crystals, together with a blue microcrystalline solid were obtained; the crystals were separated manually from the bulk product, being suitable to single crystal X-ray diffraction. The bulk product identified was as ${[Cu_{0.5}La_{2}(HPDC)(PDC)_{2}(SO_{4})(H_{2}O)_{2}]\cdot H_{2}O}_{n}$ powder by X-ray diffraction. Yield: 30%. Elemental analysis (Calc %): C: 26.4 ; H: 1.7 ; N: 4.5 ; S: 3.4 ; Cu: 3.4% ; (Exp %): C: 25.8 ; H: 1.5 ; N: 4.3 ; S: 3.3 ; Cu: 3.3%.

Single Crystal X-Ray Diffraction

The data were collected on a Bruker Smart Apex diffractometer at 293 K, using separations of 0.3° between frames, and 10 s by frame. Data integration was made using SAINTPLUS.^[32] The structure of $\{[Cu_{0.5}La_2(HPDC)(PDC)_2(SO_4)(H_2O)_2]\cdot H_2O\}_n$ was solved by direct methods using XL SHELXTL^[33] and completed (non-H atoms) by Fourier difference synthesis. Refinement until convergence was obtained using XL SHELXTL and SHELXL97.^[34] All hydrogen atoms were calculated in idealized positions on geometric basis and refined with restrictions. Table 1 summarizes the methods used and displays the main structural parameters obtained for $\{[Cu_{0.5}La_2(HPDC)(PDC)_2(SO_4)(H_2O)_2]\cdot H_2O\}_n$.

CCDC 1417605 contains the supplementary crystallographic data for $\{[Cu_{0.5}La_2(HPDC)(PDC)_2(SO_4)(H_2O)_2] \cdot H_2O\}_n$. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif, or from the

Elemental analysis

The C, N, S and H contents were determined using a Carlo-Erba EA-1108 microanalyzer, and the Cu analysis was done using an atomic absorption spectrophotometer, Shimadzu model AA-6200.

Thermogravimetric analysis

The thermogravimetric analyses were done on a NETZCH Iris equipment. The TGA curves were registered in the 20-700°C range, under nitrogen atmosphere (20 mL/min) using a 10°C/min heating rate.

X-Ray powder diffraction (XRPD)

The X-ray powder diffraction patterns were recorded in the refraction mode using a Philips X'Pert diffractometer using the Cu Ka radiation ($\lambda = 1.54178$ Å) as the incident beam, PW3050/60 (2h) as Goniometer, PW 1774 spinner as sample stage, PW 3011 as detector, incident mask fixed with 10 mm. PW3123/10 for Cu was used as a monochromator. PW3373/00 Cu LFF was used as X-ray tube with power scanning of 45 kV and 40 mA current. The sample powder was loaded into a holder and levelled with a glass slide before mounting it on the sample chamber. The specimens were scanned between 2 and 70° with the scan rate of 0.02 s⁻¹.

Table 1. Crystallographic Parameters for ${[Cu_{0.5}La_2(HPDC)(PDC)_2(SO_4)(H_2O)_2] \cdot H_2O}_n$

Empiric formula	$C_{42}H_{28}CuLa_4N_6O_{36}S_2\cdot 2(H_2O_{36})$
Formula weight	1912.05
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	PI
a (Å)	9.4008 (5)
b (Å)	11.5017 (6)
<i>c</i> (Å)	13.7959 (7)
α (deg)	108.560 (1)
β (deg)	106.079 (2)
γ (deg)	97.892 (2)
Volume (ų)	1316.50 (12)
Z	1
Density (Mg m ⁻³)	2.412
ิ (mm⁻¹)	3.775
F(000)	919
Fit quality on F ²	1.039
Final R indices (I > 2σ(I))	0.0278
	0.0296
Indices (all data)	0.0765
	0.0782

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Nitrogen sorptometry

The surface area of {[Cu_{0.5}La₂(HPDC)(PDC)₂(SO₄)(H₂O)₂]H₂O}_n was measured using the Brunauer-Emmett-Teller (BET) method on a Micromeritics ASAP 2010 equipment after degassing the sample. The result of the physical characterization of the catalyst by N₂ sorptometry show that the specific area is approximately 0.0147 m²g⁻¹ and the pore volume 0.0137 cm³g⁻¹, with the adsorption isotherm being of type III according to the IUPAC classification (Figure S1).

Catalytic reactions

In a typical reaction, 20 mmol of organic substrate was placed into the two neck bottom flask (25 mL capacity) together with 20 mg of catalyst. These mixtures were stirred at 120 °C under molecular oxygen atmosphere (1 atm) for the required time. For cyclooctene, cycloheptene and cyclohexene the reactions were carried out in closed reinforced glass vessels that can stand a pressure of 5 bars. After the reaction time, the catalyst was filtered through a Nylon filter (0.2 μ m) and extracted with toluene, and the reaction mixture analyzed by GC. Nitrobenzene was used as an external standard. The products were identified by GC and GC-MS, using available commercial samples. As previously reported, the corresponding hydroperoxides were analyzed by adding an excess of triphenylphosphine to aliquot samples, and quantifying the corresponding trihphenylphosphine oxide formed due to the presence of hydroperoxide.^[26,35] Mass balances based on the initial moles of indane were higher than 95 %.

The reusability of the catalyst was tested for the oxidation of indane or cyclooctene. After the reaction time, the reaction mixture was filtered off, the catalyst dried and reused directly without further treatment for a subsequent run with fresh indane or cyclooctene. The absence of active species leached from the solid to the solution was assured by the Sheldon's hot filtration test. In this case, the reaction was initiated under the typical oxidation conditions indicated above and the solid catalyst filtered at the time required for a conversion around 40 %. Then, the clear solution was allowed to react further at 120 °C in the absence of any solid.

Results and Discussion

Structural description

The heteronuclear copper(II)-lanthanum(III) metal organic framework, ${[Cu_{0.5}La_2(HPDC)(PDC)_2(SO_4)(H_2O)_2]H_2O_n}$ (HPDC: monoacid 3,5-pyridinedicarboxylate; PDC: 3,5pyridinedicarboxylate) crystallizes in the triclinic system with space group PI. The coordination environment around $\mbox{Cu}^{\mbox{\tiny II}}$ is well described as slightly elongated octahedral. The $\mbox{Cu}^{\mbox{\tiny II}}$ atom lies on a crystallographic inversion center, occupying a special position of type $b \left[00\frac{1}{2}\right]$. Its first coordination sphere is completed by two oxygen atoms from two different sulfate groups, in a trans configuration, that are equivalent (Cu1-O16; Cu1-O16ⁱ), and four N atoms from four deprotonated pyridine dicarboxylic ligands (PDC²⁻) (Cu1-N1; Cu1-N2; Cu1-N1ⁱ; Cu1-N2ⁱ) as shown in Figure S2. On the other hand, there are two different La^{III} centers, both being nonacoordinated. The coordination around La1 is completed by seven oxygen atoms from six PDC²⁻ ligands (La1-O1; La1-O2; La1-O3ⁱⁱ; La1-O4ⁱⁱⁱ; La1-O8^{iv}; La1-



Figure 1. a) View along [100], b) View along [010], c) View along [001] directions. Legend: Cyan: Cu; green: La; yellow: S; red: O; grey: C; blue: N; white: H.

O10; La1-O11^v), a water molecule (La1-O1W), and sulfate oxygen atom (La1-O13), as shown in Figure S3. In contrast, coordination around La2 is defined by five oxygen atoms from four PDC²⁻ ligands (La2-O1; La2-O5; La2-O9^{vi}; La2-O11^v; La2-O12^v), three oxygen atoms from two sulfate ions (La2-O13; La2-O14ⁱ; La2-O15) and one water molecule (La2-O2W), as shown in Figure S4.

The carboxylic acid ligands are found in two different forms in the structure: partially protonated (HPDC⁻) or totally deprotonated (PDC²⁻). These carboxylate groups present diverse coordination modes: tridentate, coordinating one La^{III} atom as chelate (O1-La1-O2), and another La^{III} center in a monodentate bridging mode (La1-O1-La2). Besides, the carboxylate group of HPDC⁻ is bonded in a monodentate form to a La^{III} center (La2-O5). In contrast, the oxygen atom O7 of one of these carboxylate groups does not present coordination with any metallic center; the charge is compensated by hydrogen bond interactions between the deprotonated carboxylic group and two water molecules coordinated with two neighboring La^{IIII} ions (O7-O1w = 2.704(4); O7-O2w = 2.602(4) Å).

The extended framework defines a 3D system, being a nonporous structure. The inorganic polymer grows along the a, b and caxes, thus forming a covalent three dimensional structure. The connectivity is through the carboxylate and sulfate groups, which act as bridges between the Cu^{II} and La^{III} centers (Figure 1).

The calculated X-ray powder diffractogram (XRPD) pattern obtained from the single crystal parameters matches the experimental pattern of bulk $\{[Cu_{0,5}La_2(HPDC)(PDC)_2(SO_4)(H_2O)_2]H_2O\}_n$ (Figure 2a). Thus, the results confirm that the compound used in the catalytic experiments exactly corresponds to the species whose structure was obtained from single crystal XRD data.



 $\label{eq:Figure 2. (a) XRD pattern of $ [Cu_{0.5}La_2(HPDC)(PDC)_2(SO_4)(H_2O)_2]H_2O\}_n$, simulated (1) and experimental (2). (b) Thermogram of $ [[Cu_{0.5}La_2(HPDC)(PDC)_2(SO_4)(H_2O)_2]H_2O\}_n$. }$

The thermal stability of the catalyst was studied by thermogravimetric analysis (TGA) (Figure 2b). The compound presents a weight loss of 1.5 % in the 20 to 165 °C temperature range, corresponding to crystallization water molecules. The coordinated water molecule is lost at 205 °C. A temperature-programed decomposition (TPD) showed that the loss weight between 205 - 360 °C corresponds to CO₂ molecules from the carboxylic groups of the PDC²⁻ ligands. Finally, between 360 – 700 °C a weight loss of approximately 40 % corresponds to the total decomposition of the organic material and the breaking down of the sulfate group that begins at 438 °C. At 700 °C the weight loss is not complete; the remaining mass corresponds to Cu and La oxides formed in the thermic decomposition process.

Catalytic activity

After characterizing the new CuLa-MOF, the catalytic activity of the novel material for the aerobic oxidation of hydrocarbons was evaluated. Aimed at this purpose, the catalytic activity of CuLa-MOF was initially explored for benzylic oxidation of a series of aromatic hydrocarbons, and subsequently, the activity for the epoxidation of three cycloalkenes was determined.

Aerobic oxidation of indane was efficiently promoted by CuLa-MOF using 0.05 Cu mol % at 120 ºC. Figure 3 shows the temporal evolution of indane conversion and the major products formed (see Figure S5 for other minor products also observed). As can be seen, the corresponding indanyl hydroperoxide appears as primary oxidation product, as well as the benzylic ol/one products. During the course of the reaction, the selectivity of the hydroperoxide decreases and indanone becomes the major product with selectivity above 80 % for complete indane conversion. These selectivity values are better than those previously reported using MIL-101(Fe) and similar to those of MIL-101(Cr), as catalysts for the aerobic oxidation of indane under similar reaction conditions.^[26] It is worth commenting that attempts to activate the catalyst at 120 °C under vacuum did not result in an increase of the catalytic activity. This observation is not unexpected considering the chemical structure of the CuLa-MOF were Cull as active center is not coordinated with water molecules, whose removal to liberate some coordination positions around the metal center is among the main reasons for catalyst activation.^[26] The fact that thermal activation of CuLa-MOF is not needed represents an advantage compared to other reported MOF catalysts such as MIL-101(Cr)^[21,22,26,36] or MIL-101(Fe)^[21,26,36,37] that typically require thermal activation to remove water or solvent molecules coordinated to the active metal centers.^[38]



Figure 3. (a) Time conversion plot for the aerobic oxidation of indane using CuLa-MOF as catalyst during four consecutive uses. (b) Time selectivity plot of the main products observed for the aerobic oxidation of indane using CuLa-MOF as catalyst. Reaction conditions: Catalyst (20 mg, 0.05 mol % Cu), substrate (20 mmol), 120 °C, O₂ atmosphere. Legend a): 1st use (\blacksquare), 2nd use (\bigcirc), 3th use (\square) and 4th use (\triangle). Legend b): 1-indanyl hydroperoxyde (\bigcirc), indanone (\square), indanol (\blacktriangle) and hydroperoxide+indanol+indanone (\bullet).

Importantly, CuLa-MOF can be recovered from the reaction mixture and reused four consecutive runs under the same conditions. It was observed that the catalyst undergoes a certain deactivation from the first to the second cycle, but then it maintains essentially the same activity for the third and fourth cycle. Interestingly, the selectivity towards hydroperoxide/ol/one is similar within ± 10 % for all the four runs, being over 90 % for conversions lower than 70 % and, then, decreasing to about 80 % for complete conversion. When using CuLa-MOF as catalyst, 1-indanone represents about 80 % of the product mixture at complete conversion.

This selectivity data compares favorably respect to the use of MIL-101(Fe) or MIL-101(Cr) as catalysts under similar reaction conditions.^[26] For these two MIL-101 MOFs the selectivity to 1-indanone at full indane conversion represents about 65 and 40 % for Fe and Cr, respectively.^[26] This difference in selectivity could be explained considering that the reaction occurs on the surface of the CuLa-MOF catalyst, due to the negligible internal porosity (CuLa-MOF surface area < 5 m² g⁻¹). In the case of MIL-101(Fe) or MIL-101(Cr) the reaction takes place in the cavities of these MOFs and, therefore, the occurrence of over oxidation is more likely in these cases. Interestingly, the selectivity of CuLa-MOF is also higher respect to the use of homogeneous radical initiators such as TBHP or AIBN where selectivity at full indane conversions were lower than 60 %, therefore showing the beneficial role of CuLa-MOF to promote the selective aerobic oxidation.^[26]

Stability of CuLa-MOF under the reaction conditions was supported by XRPD; comparing the diffraction pattern of the fresh catalyst with that of the three and four times used catalyst, no significant variations were observed (Figure 4a). In addition, chemical analysis of Cu^{II} by quantitative inductively coupled plasma (ICP) measurements in the liquid phase after the first use shows the presence of about 1.5 % (10.5 μ g) of the initial amount of Cu^{II} (0.7 mg) present in the fresh catalyst dissolved in the solution. Then, the Cull leaching decreases from the first to the forth use with values of 0.9, 0.6 and 0.2 wt% of Cu respect to the fresh catalyst. Control experiments, in which the amounts of leached Cu^{II} in the different catalyst cycles were evaluated as homogeneous catalyst to promote benzylic oxidation of indane, showed that these amounts of Cu^{II} leached contribute in fact in a certain percentage to the aerobic oxidation when CuLa-MOF is used as solid catalyst (Figure 4b). However, experiments using the Cu^{II} leach resulted in significantly slower conversion reaction rates (Figure 4b) and lower selectivities (Figure S6) respect to experiments in which CuLa-MOF was used as

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Figure 4. (a) XRPD of fresh (A), three (B) and four times used catalyst (C). (b) Time conversion plot for the aerobic oxidation of indane the heterogeneous CuLa-MOF catalyst (close symbol) and the homogeneous Cu(OAc)₂ catalyst (open symbols). Legend panel (b): CuLa-MOF (\blacksquare); Amount of Cu employed as homogeneous catalyst corresponding to the 1.5 (\square), 0.8 (Δ) and 0.3 wt% (o) of the leached Cu from the solid catalyst to the solution. Reaction conditions: Catalyst (20 mg, 0.05 mol % for CuLa-MOF or the indicated amounts of Cu(OAc)₂), substrate (20 mmol), 120 °C, O₂ atmosphere (1 atm).

catalyst. For example, the combined selectivity to hydroperoxide/ol/-one using CuLa-MOF was found to be 97 % at 60 % conversion while using the corresponding amount of Cu(OAc)₂ equivalent to that found in the leachates, the selectivity was below < 80 % at the same conversion (Figure S6).

The stability of CuLa-MOF as catalyst is higher than that reported for a commercial Cu-MOF, namely Basolite C 300 (Cu₃(BTC)₂, (BTC: 1,3,5-benzenetricarboxylate), this catalyst becomes transformed in metallic Cu nanoparticles when used for the aerobic oxidation of thiols to disulfides.^[39]

Related with catalyst stability, a productivity test using a large amount of indane (40 mL, 325 moles) and low amount of catalyst (2 mg, 0.001 mmol as Cu) working at 120 °C under O₂ atmosphere (1 atm) was performed. Under these extremely low catalyst content conditions, conversions around 60 % were reached without observing noticeable decrease of activity (Figure S7). Importantly, the selectivity towards the corresponding benzylic hydroperoxide, alcohol and ketone was still higher than 90 %.

Additionally, information with respect to the role of leached Cu and the oxidation mechanism was obtained by hot filtration tests. In these experiments, the reaction is initiated in the presence of CuLa-MOF and, then, the solid removed while the reaction mixture is still hot close to the reaction temperature. The clear liquid solution in the absence of solid particles is allowed to continue the reaction while observing that in the absence of solid catalyst, indane oxidation progresses from about 38 % till 72 %. Figure 5 shows a comparison of the temporal profile of indane conversion in the presence of CuLa-MOF and in the hot filtration experiment. The results of the hot filtration test cannot be fully explained by the low percentage of Cu leached from the solid to the liquid phase as the control experiment, using this small concentration of soluble Cu(OAc)₂, reveals. Based on precedent data from literature, in which removal of the solid acting as radical initiator, does not alter the temporal profile for benzylic oxidations, it is here proposed that the hydroperoxide present in the reaction mixture, and being generated from the beginning of the reaction, in combination with small amounts of copper ions, is responsible for the progress of the oxidation reaction in the absence of solid CuLa-MOF. [26,27,40,41]

This proposal assumes the operation of a radical chain mechanism in which indanyl radicals react with molecular oxygen



Figure 5. Time-conversion plot for the aerobic oxidation of indane using CuLa-MOF (\blacksquare), after filtering the catalyst at ~40 % conversion in the absence (o) and in the presence of TEMPO added at this conversion (Δ). Reaction conditions: Catalyst (20 mg), indane (20 mmol), 120 °C, O₂ atmosphere (1 atm).

forming a peroxyl radical that in the propagation steps forms hydroperoxy and another indanyl radical.^[26,27] To support this proposal, i.e. the involvement of carbon centered radicals in the oxidation, a well-known radical scavenger, TEMPO, was added in a hot filtration experiment.

Figure 5 also shows the influence of addition of TEMPO on the time conversion plot on a hot filtration experiment. As observed, the presence of TEMPO inhibits almost completely the oxidation of indane after removal of the solidcatalyst, indicating that the most likely reaction intermediates of the process have carbon centered radical character.

The catalytic activity of CuLa-MOF was compared to that of Cu(OAc)₂ as homogeneous Cu^{II} catalyst, using the same Cu^{II} content as the CuLa-MOF solid (Figure 6). It was observed that the required amounts of Cu(Oac)₂ were dissolved in indane. Although the exact coordination of dissolved Cu(Oac)₂ is surely different than that of CuLa-MOF or its leachate, it provides a useful information about the catalytic activity of solubilized Cu^{II} compounds in indane. To address the issue about the possible role of La^{III} as catalyst, either in nodal positions or upon leaching, a control experiment in which lanthanum carbonate was used as homogeneous catalyst for indane oxidation was performed. The reaction was followed for twenty-four hours, without observing any conversion. This experimental fact supports the lack of catalytic activity of La^{III} to promote hydrocarbon oxidation. A commercial Cu-MOF, namely Cu₃(BTC)₂, was also included in the comparison. It was determined that the homogeneous system resulting from dissolved Cu(Oac)₂ promoted the aerobic oxidation of indane faster than CuLa-MOF under similar conditions. The activity of CuLa-MOF and Cu₃(BTC)₂ was on the other hand similar at initial times, although at longer reaction times CuLa-MOF outperforms Cu₃(BTC)₂ as catalyst (Figure 6a). Also, hydroperoxide/-ol/-one selectivity using CuLa-MOF catalyst was higher than that of Cu₃(BTC)₂ and coincident at moderate conversions, and also higher than that of Cu(Oac)₂ (Figure 6b). This catalytic behavior can be interpreted considering that the solubility of Cu(Oac)₂ allows better accessibility to Cu^{II} sites than when this transition metal is forming part of the structure of the solid catalyst. The product selectivity on the other hand is influenced by the nature of the reaction surface in where oxidation is taking place.^[26]

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Figure 6. Time-conversion (a) and selectivity-conversion (b) plot for the aerobic oxidation of indane in the presence of the heterogeneous solid catalysts CuLa-MOF (\blacksquare) and Cu₃(BTC)₂ (o) or the homogeneous Cu(AcO)₂ salt (Δ). Reaction conditions: Catalyst (20 mg or 0.011 mmol of Cu), substrate (20 mmol), 120 °C, O₂ atmosphere (1 atm).

The influence of the oxygen pressure on the benzylic oxidation of indane was determined by performing the reaction under inert atmosphere or in the presence of air or oxygen. It was observed that indane conversion increases significantly with oxygen pressure (Figure S8). Under inert atmosphere, no oxidation took place. However, if after having started the reaction under Ar for 24 h and observing no conversion, the atmosphere is suddenly changed from Ar to O₂, then evolution of oxidized products is observed, at a similar rate as in the case in which the reaction is started under oxygen.

To learn more about the reaction mechanism and, particularly, the nature of the reactive oxygen species that could be involved in the process, two reactions were carried out, where dimethylsulfoxide (DMSO) or p-benzoquinone was present. DMSO is a selective quencher of HO radicals, while p-benzoquinone is selective for the quenching of O_2^{-} and HOO⁻ radicals.^[26,42] The obtained results are shown in Figure 7 in which temporal profiles of a reaction in the absence of any guencher is also included for comparison. Figure 7 shows that the presence of *p*-benzoquinone completely inhibits indane oxidation, while the presence of DMSO has a marginal influence on the time conversion plot. This marginal influence could be due to polarity changes of the medium by DMSO including oxygen solubility. However, the complete inhibition of the oxidation by p-benzoquinone strongly suggests the involvement of superoxide or hydroperoxyl radical as the active oxygen species responsible for the benzylic oxidation.

Other quenchers that were also used to get additional information on the oxidation process were benzoic acid and DMF (Figure S9). The rationale behind the use these compounds as quenchers was to poison free coordination positions around metal ions to avoid interaction of these metal ions with oxygen or substrates.^[43, 44] A generally accepted paradigm in catalysis by MOFs is that active sites should be metal ions occupying nodal positions in MOF structures having free coordination positions.^[37, 44, 45] These coordination positions will activate substrates and reagents, but if a ligand is present in the reaction mixture it can compete favorably with substrates and reagents, the ligand should lead to an apparent deactivation of the catalyst. In precedents in the literature it has been found that carboxylic acids having similar coordination strength as typical MOF linkers can be poisons for oxidation of benzylic alcohols.^[16]

Similarly, it is well known that removal of dimethylformamide (DMF) frequently used as solvent in MOF synthesis is a necessary activation step for most catalytic reactions.^[19, 44] Based on this previous knowledge we wanted to determine if the presence of



Figure 7. Time conversion (a) and selectivity (b) plot for the aerobic oxidation of indane using CuLaPDC as catalyst (**■**) in the presence of DMSO (Δ) or *p*-benzoquinone (\circ) as radical quencher. Reaction conditions: Catalyst (20 mg or 0.011 mmol of Cu), substrate (20 mmol), DMSO or *p*-benzoquinone (20 mol % respect indane), 120 °C, O₂ atmosphere (1 atm).

these two compounds having strong affinity for metal ions would inhibit oxidation. As it can be seen in Figure S8, this was the case and the activity of CuLa-MOF for indane oxidation becomes considerably diminished when any of these two ligand molecules are present. According with these facts, we propose that the reaction mechanism should involve a step on oxygen activation by the metal ions of the MOF that requires some interaction between molecular oxygen and the metal centers.^[26] As previously reported, Cu^{II} ions have the ability to interact with molecular O₂ leading to the formation of Cu^{II} superoxo species able to activate C-H bonds, such as those encountered in the benzylic substrates employed in the present work. [41, 46] The scope of CuLa-MOF as catalyst for benzylic oxidations was expanded by studying a series of alkyl aromatic compounds (Figures S9-S12). The results are summarized in Table 2 and Figure S14. Table 1 shows that all the alkyl aromatics undergo the expected benzylic oxidation with a rate (Figure S14) that increases for tertiary benzylic positions (cumene) and with the presence of two benzylic groups (indane) with respect to secondary benzylic groups (sec-butyl-, isobutyl- and n-butylbenzenes), in accordance with the relative stability of the corresponding benzylic radicals.

Table 2. Aerobic oxidation of aromatic benzylic hydrocarbons using
CuLa-MOF as catalyst.a

	Conversion (%)	Main reaction products	Selectivity (%)
n-Butylbenzene	~ 30	1-Phenyl-1-	~ 30
		butylhydroperoxid	~35
		е	~35
		1-phenyl-1-butanol	
		Butyrophenone	
Isobutylbenzene	~ 60	(1-Hydroperoxy-2-	24
		methylpropyl)benz	
		ene	~68
		Phenylisopropyl	~8
		ketone	
		Benzoic acid	
Cumene	100	Acetophenone	~ 86
		Cumyl	~ 7
		hydroperoxide	
sec-Butylbenzene	84	Acetophenone	~ 45
		Propiophenone	~ 47

[a] Reaction conditions: Catalyst (20 mg), substrate (20 mmol), O2 atmosphere (1 atm), 120 $^{\circ}$ C and reaction time depending of the substrate to achieve the indicated conversion (Figures S9 to S12).

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Table 3. Aerobic oxidation of cycloalkenes using CuLa-MOF as catalyst.								
	Conversion	Selectivity ^a						
	(%)	(%)						
		Epoxide	Alcohol	Ketone	HPOX. ^d			
Cyclooctene ^b	96	99.5	-	-	< 0.5			
Cyclooctene ^c	80	98.2	-	-	1.8			
Cycloheptene ^c	94	45.2	-	54.8	< 1			
Cyclohexene ^c	77	~ 1.0	30.6	68.0	< 1			

^a The oxidation to the corresponding alcohol, ketone or hydroperoxide takes place in the allylic position of the cycloakene.

 $^{\rm b}$ Reaction conditions: Catalyst (20 mg, 0.05 mol %), substrate (20 mmol), O_2 (1 atm), 120 $^{\rm o}C$, reaction time 48 h.

 $^{\rm c}$ Reaction conditions: Catalyst (20 mg, 0.05 molt %), substrate (20 mmol), O₂ (5 atm), 120 °C and reaction time depending of the substrate to achieve the indicated conversion (Figures S14-S16).

^{d.} HPOX = Hydroperoxide.

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The negative influence of the steric hindrance around the benzylic positions on the reaction rate observed for secbutylbenzene or isobutylbenzene with respect to cumene and nbutylbenzene suggests that the substrate has to adsorb on the solid catalyst surface to form the radicals. Besides benzylic oxidation and as already indicated above, the activity of CuLa-MOF was also tested for the aerobic epoxidation of cycloalkenes. The results are summarized in Table 3. It was observed that in the presence of oxygen at atmospheric pressure, CuLa-MOF promotes the epoxidation of cyclooctene by oxygen with almost complete selectivity at high conversion.

CuLa-MOF could be reused three times for the aerobic epoxidation of cyclooctene, observing some decrease of the catalytic activity in the second cycle, while the activity of CuLa-MOF is maintained for the third and fourth cycle, as indicated by the time conversion plot of the epoxidation, and the final yield at the end of the reaction (Figure 8).



Figure 8. (a) Time-conversion plots for the aerobic oxidation of cyclooctene for the fresh (\blacksquare), 2nd use (\bullet), 3th use (\blacktriangle) and 4th use (Δ) of CuLa-MOF catalyst. Temporal evolution of cyclooctene oxide selectivity (\circ) for the first use and hot filtration test when using fresh CuLa-MOF (\square); (b) Time-conversion plot for the aerobic oxidation of cyclooctene using the homogeneous Cu(OAc)₂ salt as homogeneous catalysts. Reaction conditions: Catalyst (20 mg or 0.011 mmol), substrate (20 mmol), oxygen atmosphere (1 atm), 120 °C.



Scheme 1. Proposed reaction mechanism for the aerobic oxidation of cyloalkenes using molecular oxygen and CuLa-MOF as catalyst.

Comparison of the catalytic activity of CuLa-MOF for this process shows that this MOF is significantly more active than commercial $Cu_3(BTC)_2$, although soluble $Cu(OAc)_2$ exhibits higher activity than CuLa-MOF. Again, this relative activity is not unprecedented since soluble homogeneous catalysts exhibit higher intrinsic activity than similar centers incorporated in an insoluble material.

However, the heterogeneous conditions allow easy recovery of the catalyst by filtration or decantation, a recovery that is not possible for homogeneous catalysts. A notable observation that contrasts with the previous experiments of benzylic oxidations was that hot filtration of CuLa-MOF stops completely epoxidation of cyclooctene.

The behavior of cyclooctene contrasts with that of cycloheptene and cyclohexene. In agreement with the literature,^[15] the allylic oxidation was almost the exclusive process observed for cyclohexene, while cycloheptene exhibits an intermediate behavior between cyclooctene and cyclohexene. In this case, both allylic oxidation and epoxidation takes place with similar selectivity. Although the influence of the size of the ring on the outcome of the reaction has been observed previously and reported in the literature, using NHPI adsorbed on Fe-BTC, no convincing explanation has been given.^[15] It seems that geometry and conformation of the hydroperoxides and C=C double bonds in cycloalkenes should change as a function of the ring size, and these conformations and geometries favor epoxide for larger rings versus allylic oxidation in medium size rings. The involvement of the corresponding hydroperoxide in C=C epoxidation is supported by the detection of this intermediate during the course of the reaction, particularly at short reaction times. Scheme 1 summarizes the proposed reaction mechanism for the aerobic epoxidation of cyclooctene using CuLa-MOF, based on previous reports in the literature.[15,24,46].

Conclusions

CuLa-MOF exhibits similar catalytic activity for benzylic aerobic oxidation and epoxidation of cycloalkenes, but greater than that of Cu₃(BTC)₂, which is a benchmark Cu^{II} MOF catalyst largely used in the literature.^[14,47]. Besides, the selectivity of the CuLa-MOF is similar to that of Cu(OAc)₂, which was used as homogeneous catalyst. The catalyst is reusable with some minor decrease from the first to the second catalytic cycle. The reaction mechanism seems to follow the expected radical chain autooxidation for benzylic

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hydrocarbons, and epoxidation by a hydroperoxide intermediate for [12] cycloalkenes.

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Novel Copper(II)-Lanthanum(III) Metal Organic Framework as Selective Catalyst for the Aerobic Oxidation of Benzylic Hydrocarbons and Cycloalkenes.

Patricio Cancino,^{a,b} Andrés Vega,^{b,c} Andrea Santiago-Portillo,^d Sergio Navalon,^d Mercedes Alvaro,^d Pedro Aguirre,^a Evgenia Spodine,^{*a,b} and Hermenegildo García,^{*d}



 $\{[Cu_{0.5}La_2(HPDC)(PDC)_2(SO_4)(H_2O)_2] \cdot H_2O\}_n$