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Cu^{II}- and Co^{II}-Based MOFs: {[La$_2$Cu$_3$(μ-H$_2$O)(ODA)$_6$(H$_2$O)$_3$]·3H$_2$O}$_n$ and {[La$_2$Co$_3$(ODA)$_6$(H$_2$O)$_6$]·12H$_2$O}$_n$. The Relevance of Physicochemical Properties on the Catalytic Aerobic Oxidation of Cyclohexene

Luis Santibáñez [1,2], **Néstor Escalona** [3,4,5], **Julia Torres** [6], **Carlos Kremer** [6], **Patricio Cancino** [1,*] and **Evgenia Spodine** [1,2,*]

1   Faculty of Science Chemistry and Pharmaceuticals, University of Chile, 8380544 Santiago, Chile; santibanezcamposl@gmail.com
2   Center for the Development of Nanoscience and Nanotechnology, CEDENNA, 9160000 Santiago, Chile
3   Faculty of Chemistry and Pharmacy, Pontifical Catholic University of Chile, 7810000 Santiago, Chile; neescalona@ing.puc.cl
4   Department of Chemical Engineering and Bioprocesses, Ingeniery school, Pontifical Catholic University of Chile, 7810000 Santiago, Chile
5   Millenium Nuclei on Catalytic Processes towards Sustainable Chemistry (CSC), 7810000 Santiago, Chile
6   Departament Estrella Campos, Facultay of Chemistry, University of the Republic, 11800 Montevideo, Uruguay; jtorres@fq.edu.uy (J.T.); ckremer@fq.edu.uy (C.K.)
*   Correspondence: pcancino@ciq.uchile.cl (P.C.); espodine@uchile.cl (E.S.); Tel.: +56-2-2978-2862 (P.C. & E.S.)

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Abstract: The aerobic oxidation of cyclohexene was done using the heterometallic metal organic frameworks (MOFs) {[La$_2$Cu$_3$(μ-H$_2$O)(ODA)$_6$(H$_2$O)$_3$]·3H$_2$O}$_n$ (LaCuODA)) (**1**) and {[La$_2$Co$_3$(ODA)$_6$(H$_2$O)$_6$]·12H$_2$O}$_n$ (LaCoODA) (**2**) as catalysts, in solvent free conditions (ODA, oxydiacetic acid). After 24 h of reaction, the catalytic system showed that LaCoODA had a better catalytic performance than that of LaCuODA (conversion 85% and 67%). The structures of both catalysts were very similar, showing channels running along the *c* axis. The physicochemical properties of both MOFs were determined to understand the catalytic performance. The Langmuir surface area of LaCoODA was shown to be greater than that of LaCuODA, while the acid strength and acid sites were greater for LaCuODA. On the other hand, the redox potential of the active sites was related to Co^{II}/Co^{III} in LaCoODA and Cu^{II}/Cu^{I} in LaCuODA. Therefore, it is concluded that the Langmuir surface area and the redox potentials were more important than the acid strength and acid sites of the studied MOFs, in terms of the referred catalytic performance. Finally, the reaction conditions were also shown to play an important role in the catalytic performance of the studied systems. Especially, the type of oxidant and the way to supply it to the reaction medium influenced the catalytic results.

Keywords: metal organic framework; heterogeneous catalyst; aerobic oxidation; cyclohexene

1. Introduction

The oxidation of cyclic olefins is a reaction that has become of interest for many industries, such as the agrochemical, pharmaceutical, and perfumery industries, as well as the manufacture of adhesives [1–4], because the products of this reaction such as epoxides, alcohol, ketones, and aldehydes are used in commodities. However, it has become necessary to find alternative routes of production

for these compounds, in order to decrease the carbon footprint and the generation of environmentally harmful sub-products [5].

Catalysis is an important tool in many industrial processes when it comes to reducing the energy cost, as well as the reaction time and the sub-product generation, enhancing the selectivity. In this sense, homogeneous and supported catalysts are classically used in the oxidation of cycloalkenes [6,7]. However, they present well known problems such as the inability to separate and recover the homogeneous catalyst, and on the other hand, the leaching of the catalyst from the support, preventing its reusability. Heterogeneous catalysts, particularly inorganic polymers, present a good alternative, as these are insoluble and stable under the usual cycloalkene oxidation conditions. The corresponding catalytic activity of inorganic polymers can be found in the literature in several reviews [8–14]. These inorganic polymers are based on metallic cores coordinated with organic linkers, with the metal centres being the catalytically active species. Transition metal ions are a good choice when designing these systems as their cost is low and their abundance is high. In this context, cobalt (II) containing molecular sieves show activity in the epoxidation with molecular oxygen of styrene at 100 °C, presenting a conversion of 45% with a selectivity of 62% to the desired epoxide [15]. The same research group reported a family of cobalt (II) exchanged zeolite X catalysts, which permitted, for the studied catalytic systems, an almost complete conversion of styrene [16].

Copper (I) species have been used as a catalyst in the aerobic oxidation of different amines to imines, with a conversion ranging in most cases from 85% to 95% using CuCl [17]. A different biomimetic Cu (I) species, $[Cu(CH_3CN)_4]PF_6$, was reported for the aerobic oxidation of secondary alcohols, yielding over a 90% conversion in most experiments [18]. A Cu(II) compound, used as a catalyst for an aerobic oxidation was $Cu_2(OH)PO_4$, and this catalyst produced a 30% conversion for styrene and 47% for cyclohexene [19]. Two catalysts, based on Cu(II) using N-benzylethanolamine or triisopropanolamine as ligands, were also used in the oxidation of cycloalkanes assisted by H_2O_2; a conversion of 23% was achieved for cycloheptane [20].

However, owing to the lower catalytic activity of some of these systems, as compared with that of the homogeneous ones, it is sometimes necessary to add co-oxidants such as TEMPO [21], isobutyraldehyde [22], TBHP [23,24], or H_2O_2 [25]. For example, $Cu_3(BTC)_2$ (BTC, 1,3,5-benzenetricarboxylate) is a Cu(II) complex assisted by TEMPO, used as a catalyst for the oxidation of benzylic alcohols, yielding 89% of conversion [5]. However, these co-catalysts sometimes produce harmful by-products, such as tert-butanol, in the case of TBHP. Therefore, aerobic oxidation using only molecular oxygen as the oxidizing agent becomes an ideal goal to achieve.

Metal organic frameworks (MOFs) can be modified by changing either the metal ions or the organic linkers, thus modifying the catalytic properties or the capability of adsorbing gases. Monometallic MOFs based on copper (II) [26,27], cobalt (II) [28,29], vanadium (IV) [30,31], or iron (III) ions [32–34] have been used in heterogeneous catalytic systems. The use of MOFs as catalysts in the aerobic oxidation of olefins has been reported by Fu et al. [35]. These researchers used catalysts based on copper (II) and cobalt (II) with 2,5-dihydroxyterephthalic acid (DOBDC), $[M_2(DOBDC) (H_2O)_2]\cdot 8H_2O$ (M= Cu^{II} or Co^{II}), and molecular oxygen to oxidize cyclohexene at 80 °C. Under these conditions and after 15 h, the reaction only produced 14.6% conversion for the copper catalyst and 10.5% for the cobalt catalyst. Tuci et al. found better results using a different cobalt (II) catalyst, $[Co(L-RR)(H_2O)]\cdot H_2O$ (L-RR = (R,R)-thiazolidine-2,4-dicarboxylate), at 70 °C. However, molecular oxygen pressure was increased from 1 to 5 bar. A conversion of 37% with a selectivity of 49% to 2-cyclohexen-1-one was achieved [36].

Heterometallic MOFs also present activity for the oxidation of different substrates. For example, copper (II)-based MOFs with adsorbed palladium or gold nanoparticles have been used in the oxidation of benzylic alcohols [37,38], and a bimetallic catalyst of Pd–Au nanoparticles supported on an aluminium (III) MOF was used in the aerobic oxidative reaction of carbonylation of amines [39]. However, as mentioned, these systems use supported catalysts, which may not be optimal.

Our group has worked with heterogeneous Cu^{II}- 4f MOF catalysts, tuning the organic linkers [40], the *4f* lanthanide ion [41], and using different substrates for the aerobic oxidation reaction [42]. We now report the study of the effect of changing the *3d* transition metal ion of two MOFs used as catalysts in a solvent-free system, with molecular oxygen as an oxidant in the oxidation of cyclohexene, without the use of a co-catalyst. Cobalt (II) and copper (II) were chosen as the *3d* redox transition metal ions, while the *4f* ion was lanthanum (III). The studied catalysts were $\{[La_2Cu_3(\mu\text{-}H_2O)(ODA)_6(H_2O)_3]\cdot3H_2O\}_n$ (LaCuODA) (**1**) and $\{[La_2Co_3(ODA)_6(H_2O)_6]\cdot12H_2O\}_n$ (LaCoODA) (**2**) (H_2ODA = oxydiacetic acid).

2. Results

2.1. Characterization

2.1.1. Structural Description

Crystal structures were obtained as described in [43,44], and will be briefly described in order to understand the catalytic results. X-ray structural analyses of LaCuODA (**1**) and LaCoODA (**2**) reveal that both belong to the hexagonal crystal system, with space group *P*-62c for **1** and *P*6/mcc for **2**. The skeleton of the structures is similar in both porous MOFs. The La^{III} is coordinated by three tridentate ODA ligands, thus nine oxygen atoms define the coordination sphere of this metal centre. Each $[La(ODA)_3]^{3-}$ unit is connected to six M^{II} (M = Cu^{II}, Co^{II}) ions via single *syn-anti* μ-carboxylato-O-O' bridges. The M^{II} ions are surrounded by four oxygen atoms from $[La(ODA)_3]^{3-}$ units in (**1**) and (**2**). The difference in the coordination pattern of (**1**) and (**2**) is that Co^{II} ion in (**2**) is bound to two water molecules in the axial positions, forming a slightly distorted octahedron. On the other hand, Cu^{II} in (**1**) is bound to just one molecule of water, being penta-coordinated. In spite of this difference, the main structural feature of these MOFs is the formation of hexagonal channels along the crystallographic *c* axis (Figure 1). The maximum size of the channel can be estimated in 11.39 Å for (**1**) and 11.09 Å for (**2**). Crystallization water molecules are hosted in the channels. In the special case of (**1**), one of the crystallization water molecules per unit formula is in a fixed position forming a $\mu_2\text{-}H_2O$ bridge between La^{III} ions.
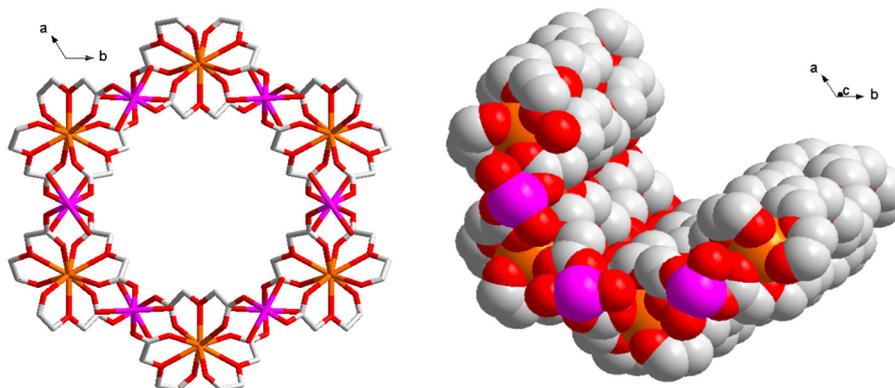
Figure 1. Left: partial view of complex (**2**) along the crystallographic *c* axis, showing the generated hexagonal channels. H atoms and crystallization water molecules are omitted for clarity. **Right**: cross-section of the channel showing the inner exposed surface. Color code: La, orange; Co, pink; O, red; C, light grey.

The determination of the acid strength for LaCoODA showed an initial potential of 24.5 mV after 4 h of stabilization with the first addition of N-butylamine, while LaCuODA presented a higher value of 93.7 mV. The ranges of initial potential defined for the strength of acid sites are as follows: potential > 100 mV, very strong acid site; 100 mV > potential > 0 mV, strong acid site; 0 mV > potential > −100 mV weak acid site; −100 mV > potential, very weak acid site. Thus, LaCuODA presents acid sites that can be defined as nearly strong, while LaCoODA presents weak acid sites. As for the number of acid sites,

LaCoODA has 0.295 miliequivalent of acid sites per gram and LaCuODA has 0.783 miliequivalent of acid sites per gram (Table 1).

Table 1. Determination of acid strength and number of acid sites for LaM(ODA).

Catalyst	Initial Potential (mV)	Number of Acid Sites (meq/g)
LaCuODA (**1**)	93.7	0.783
LaCoODA (**2**)	24.5	0.295

The Thermogravimetric (TGA) profile of both complexes was reported and analyzed previously [43,44]. Compound (**1**) presents two mass losses. The first one between 56 and 94 °C corresponds to all water molecules per formula unit. The second one appears around 240 °C and can be associated with the beginning of the decomposition of the structure. Thermal analyses of (**2**) show that the loss of water involved a well-defined two-step process. The first step corresponds to twelve molecules of crystallization water (below 50 °C). The second step (between 110 and 135 °C) includes the six water molecules coordinated to Co^{II}. The decomposition of the structure is evident above 260 °C.

Table 2 shows the pore diameter and estimated surface area of the catalysts obtained by the BET and Langmuir models from the CO_2 adsorption isotherm at 273 K. The LaCoODA has a BET surface area of 762 m^2/g, which is greater than that of LaCuODA (514 m^2/g); a similar trend was obtained from the Langmuir area values. On the other hand, the pore size is the same for both catalysts, and it is consistent with the pore size described by the crystallographic data (11.39 (**1**) and 11.09 (**2**) Å). These results permit to classify the catalysts in the range of microporous materials.

Table 2. Textural properties from CO_2 adsorption measures.

Catalyst	BET Area (m^2/g)	Langmuir Area (m^2/g)	Pore Size (nm)
LaCuODA (**1**)	514	555	1.031
LaCoODA (**2**)	762	783	1.031

2.1.2. Catalytic Results

LaCuODA and LaCoODA were used as catalysts for the aerobic oxidation of cyclohexene, in the absence of additional organic solvent or co-oxidant. The obtained results are summarized in Table 3, while the obtained products are shown in Scheme 1.

Table 3. Catalytic results after 24 h of the aerobic oxidation of cyclohexene at 75 °C using LaMODA (M=Co^{II}, Cu^{II}).

Catalyst	Conversion (%)	Selectivity (%)		
		Cyclohexene Oxide	2-Cyclohexen-1-ol	2-Cyclohexen-1-one
LaCuODA (**1**)	67	5	40	55
LaCoODA (**2**)	85	0	25	75

Reactions conditions: cyclohexene (50 mmol) and (0.01 mmol) of LaM(ODA) (M = Co^{II}, Cu^{II}), 1 bar of continuous oxygen flow. The mixture is stirred (960 rpm) at 75 °C for 24 h.
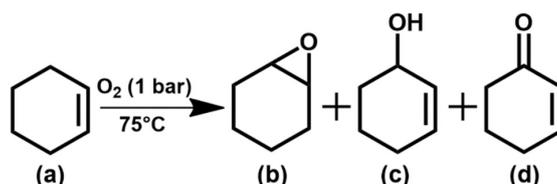
Scheme 1. Products derived from the catalytic oxidation of cyclohexene (**a**). Cyclohexene oxide (**b**); 2-cyclohexen-1-ol (**c**); 2-cyclohexen-1-one (**d**).

The conversion after 24 h of reaction shows that the MOF based on cobalt (II) has a better catalytic performance than that of the catalyst based on copper (II) (Table 2). The main product for both catalysts was 2-cyclohexen-1-one, with the selectivity for this product being 75% for LaCoODA and 55% for LaCuODA. Thus, the influence on both the conversion and selectivity of the reaction of the nature of the *3d* transition metal ion becomes evident.

3. Discussion

To understand these results, it is important to remark that the catalysts present a few differences, mentioned in the structural description of the environment and geometry of the *3d* metal ion, being **1** square pyramidal and **2** octahedral. The difference between them is the number of water molecules in the axial positions (one and two, respectively). Taking into account the data obtained in the TGA measurements, it was assumed that, under the reaction conditions, all water molecules were removed, and thus both compounds could be considered isostructural. The crystal structure shows channels along the *c axis* for both catalysts, with water molecules inside. The TGA analyses permit to infer that, for the used reaction conditions, these water molecules could leave the channels, making the channels partially free for the entry of the substrate and the oxidant. Besides, the CO_2 absorption measurements complement the crystallographic results, showing that the BET and Langmuir surface areas are bigger for LaCoODA as compared with LaCuODA. Thus, it is possible to suppose that the catalyst based on Co^{II} has a greater amount of active sites, favoring in this way the interaction between the catalyst and the substrate/oxidant. Moreover, even though both catalysts permit to obtain the same major product (2-cyclohexen-1-one), the distribution of the products is completely different. Table 3 shows that the cobalt (II) MOF with better catalyst performance also permits to obtain a higher selectivity for 2-cyclohexen-1-one.

However, the catalysts present additional differences that could permit to explain the obtained results. Both transition metal ions have different chemical properties, such as the redox potential or the Lewis acidity. These properties can modulate the reaction mechanism and the activation of the oxidant [45]. The implied redox properties during the oxidation reaction are different because, for LaCoODA, the Co^{II}/Co^{III} couple must be active, while for LaCuODA, the redox couple is Cu^{II}/Cu^{I}. For LaCoODA, the activation will occur with the oxidation of the cobalt(II) centres through a single electron transfer to molecular oxygen and the formation of the superoxide anion [35]. In the case of LaCuODA, we recently reported the generation of a $Cu-O_2$ adduct at the beginning of the catalytic cycle of the oxidation reaction [41]. In the formation of this adduct, the Lewis acidity plays an important role, with the interaction between the catalyst and the oxidant being an acid–base interaction. [45] When we compare the acid sites and the amount of these sites in the catalyst, it is possible to conclude that the LaCuODA has stronger acid sites than LaCoODA. Apparently, the greater surface area of LaCoODA and the redox properties of the cobalt (II) ion predominate over the acid properties of the copper (II) ion, thus LaCoODA has a better catalytic performance for the oxidation reaction of cyclohexene. It is possible to conclude that the combination of the structural and physicochemical properties of the studied catalytic systems is determinant for the catalytic behavior.

As LaCoODA showed the best performance, this catalyst was used for the optimization of some catalytic parameters. The first parameter to be studied was the thermal dependence of the conversion. Figure 2 (Table S1) shows a linear dependence between the conversion and the reaction temperature. As mentioned above, the increase of the conversion with temperature can be explained by assuming that the channels present in the catalyst start to release the encapsulated water molecules, and the presence of free space in the channels facilities the interaction between the metal centres and the oxidant/substrate.
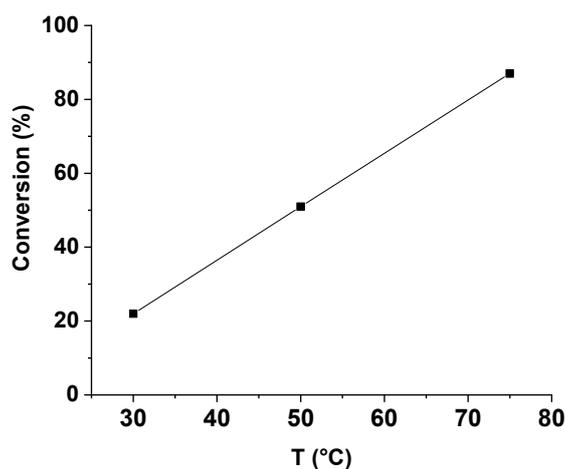
Figure 2. Thermal dependence of conversion, using LaCoODA as catalyst.

To test this assumption, we compared the catalytic performance of non-activated LaCoODA and thermally activated LaCoODA. Figure 3 (Table S2) summarizes the results, which shows that both the as prepared catalyst and the activated catalyst display a similar time dependence in their activity. As expected at short times of reaction, the oxidation process increases significantly as the reaction evolves, but it is possible to observe that, after 12 h, the activity starts to approach an asymptotic value, increasing only slightly for a sample of 24 h of reaction. The overlap of the curves indicates that the catalytic activity is similar within the experimental error for both the activated and non-activated catalyst. Apparently, the rehydration process of the catalyst is so fast that, practically, it is not possible to enhance the catalytic performance by thermal activation.
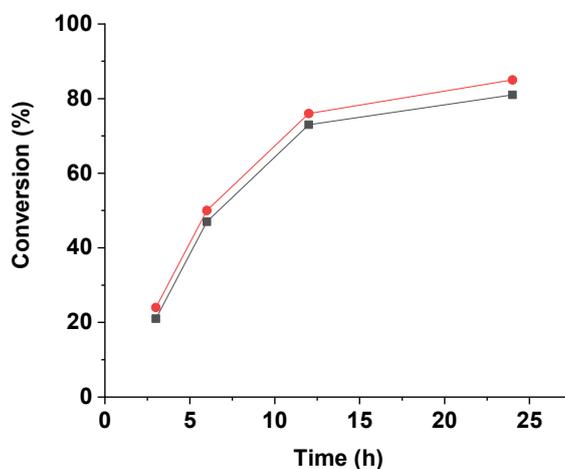
Figure 3. Time dependence of conversion using LaCoODA as catalyst. Non-activated (■); activated (●).

If we compare the results obtained with other previously reported works with similar catalysts, it is possible to find interesting aspects to discuss. For example, our group reported in 2017 [46] the catalytic performance of LaCuODA in the oxidation reaction of cyclohexene, using *tert*-butylhydroperoxide (TBHP) as an oxidant in DCE/water as a reaction medium. The achieved catalytic performance under the studied conditions in this work, that is, solvent free and O_2 as oxidant, was better in conversion and selectivity than using TBHP and the biphasic medium (Table 4). We propose that, considering that, in the DCE/water medium, the channels are fully occupied with water molecules, there must be many water molecules obstructing the interaction of the active metal centres of the catalyst and the substrate/oxidant.

Table 4. Catalytic results using LaCuODA after 24 h of oxidation of cyclohexene at 75 °C.

Oxidant	Conversion (%)	Selectivity (%)			Reference
		Cyclohexene Oxide	2-Cyclohexen-1-ol	2-Cyclohexen-1-one	
O_2	**67**	5	40	55	This work
TBHP *	48	5	31	56	[46]

* When using *tert*-butylhydroperoxide (TBHP) as oxidant, 1,2-cyclohexenediol was also detected as a minor reaction product (8%).

Table 5 shows the comparison between different catalytic results for Co^{II}-based MOF catalysts. All four catalysts have a distorted octahedral geometry around the cobalt(II) ion. However, one position of the octahedron is occupied by a water molecule for (**III**) and by two water molecules for **2**, **I**, and **II**. [35,36,43,44,47] Besides, all the compounds have channels with water molecules inside them, but the crystallographic diameter of the pores varies among them. Compounds **2**, **I** and **II** have a diameter *ca.* 11 Å, while compound **III** has only 5.7 Å. Despite the structural similarities of the pores of **2**, **I**, and **II**, the catalytic results reveal significant differences. Moreover, from the comparison using two sets of data (one set corresponds to 24 h of reaction, that is, catalysts **2** and **III**, and the second one to 10 and 12 hours of reaction corresponds to data for **2**, **I**, and **II**, shown in Table 5), it becomes evident that **2** has by far the best catalytic performance.

Table 5. Catalytic results of different Co^{II}-based metal organic frameworks (MOFs) using solvent free conditions.

Catalyst	Conversion (%)	Reaction Conditions			Reference
		Temperature	Time	O_2 Pressure	
		(°C)	(h)	(bar)	
$\{[La_2Co_3(ODA)_6(H_2O)_6]\cdot12H_2O\}_n$ (**2**)	**73**	75	12	1 (flow)	This work
$\{[La_2Co_3(ODA)_6(H_2O)_6]\cdot12H_2O\}_n$ (**2**)	84	75	24	1 (flow)	This work
$[Co_2(DOBDC)(H_2O)_2]\cdot8H_2O$ (**I**)	8.1	80	10	1 (balloon)	[35]
$[Co_2(DOBDC)(H_2O)_2]\cdot8H_2O$ (**II**)	50	80	10	1 (balloon)	[47]
$[Co(L\text{-}RR)(H_2O)\cdot H_2O]$ (**III**)	28	70	24	1 (charged)	[36]

Flow: continuous flow of oxygen at 1 bar of pressure. **Balloon:** oxygen atmosphere, using a balloon fully filled with oxygen. **Charged**: the reactor is pressurized with oxygen at 1 bar of pressure.

However, the catalytic systems present some differences that could permit to explain the obtained results. As the structures do not clarify these differences, maybe the reaction conditions can give some light on the obtained data. As the temperature is quite similar for all the reported systems, the oxygen pressure is an interesting parameter to analyze. Even though the oxygen pressure used is the same for all the catalytic systems, the way of supplying the oxidant to the reacting substrate is not the same. Thus, the amount of oxygen in the reactor varies depending on the source used. That is, the pressurized oxygen in the reaction vessel has an initial finite concentration [36], while a continuous oxygen flow maintains the concentration of the oxidant in the reaction vessel. On the other hand, the oxygen concentration provided by a balloon is variable [35,47].

Therefore, it is possible to conclude that oxygen concentration is determinant in the reaction mechanism. Depending on the amount of oxygen in the reaction medium, the chance to obtain the interaction between the active site and oxidant/substrate will be modified [42], and thus the onset of the chain reactions that will form the products.

4. Materials and Methods

4.1. Synthesis

Compounds (**1**) $\{[La_2Cu_3(\mu\text{-}H_2O)(ODA)_6(H_2O)_3]\cdot3H_2O\}_n$ (LaCuODA) and (**2**) $\{[La_2Co_3(ODA)_6(H_2O)_6]\cdot12H_2O\}_n$ (LaCoODA)) have been previously reported [43,44] and were prepared accordingly, with slight modifications of the synthetic route. Complex (**1**) was synthesized by direct reaction of stoichiometric amounts of $LaCl_3\cdot7H_2O$ (0.37 g, 1.0 mmol), $CuCl_2\cdot2H_2O$ (0.20 g, 1.5 mmol),

and oxydiacetic acid 0.40 g, 3.0 mmol). Reagents were dissolved in water (*ca.* 35 mL); pH was adjusted with diluted ammonia to 5–6. Light blue crystals of the complex appeared after 2–3 weeks. These were separated by filtration and washed twice with water. Complex (**2**) was prepared starting from La_2O_3 (98 mg, 0.3 mmol), $Co(COOCH_3)_2 \cdot 4H_2O$ (224 mg, 0.9 mmol), and oxydiacetic acid (322 mg, 2.4 mmol). Then, 30 mL water was added, and the mixture was placed in a Teflon-lined 45 mL stainless steel acid digestion vessel and heated at 120 °C for 45 h. The resulting solution was filtered, and the filtrate was allowed to stand at room temperature. After five days, a pale red polycrystalline solid appeared. It was filtered and washed twice with water.

The purity of the solids was checked by elemental analysis (C, H) and IR spectroscopy.

Calculated for $La_2Cu_3C_{24}H_{38}O_{37}$ (1), C, 20.8; H, 2.8. Found, C, 21.2; H, 2.9%.

Calculated for $La_2Co_3C_{24}H_{60}O_{48}$ (2): C, 18.3; H, 4.0. Found, C, 18.5; H, 4.2%.

IR spectra were almost identical for both complexes, and can be used as a quick control of the purity of the compounds. The shift of ν_{COO} (1724, 1419 cm^{-1}) of the free ligand to *ca.* 1600 and 1430 cm^{-1} is noticeable. Besides, upon complexation, ν_{COC} (1149 cm^{-1}) for the free ligand shifts to *ca.* 1120 cm^{-1} (see Supplementary Information Figure S1a,b).

4.2. Surface Area Determination

The specific surface area (S_{BET}) was measured by CO_2 sorption measurement at 273 K, using Micrometrics 3 Flex equipment. Prior to the measurements, the samples were outgassed at 250 °C for 2 h. The BET surface area was estimated from the adsorption branch of the isotherms in the range $0.05 \leq P/P \leq 0.15$. Additionally, the surface area was also estimated using the Langmuir equation. The average pore diameter was calculated using the DFT method, applied to the CO_2 adsorption isotherm (Figures S2 and S3).

4.3. Catalytic Reactions

In a 50 mL round bottom flask provided with a refrigerant, 50 mmol of cyclohexene and 0.01 mmol of $LaMODA$ (M = Co^{II} or Cu^{II}) were added, and the substrate to be oxidized was heated to the desired temperature. The system was connected to a 1 bar continuous oxygen flow, and the mixture was stirred at a constant speed (960 rpm). Studies of the thermal and reaction time dependence of the conversion were done with LaCo(ODA), measuring results at 30, 50, and 75 °C for 24 h and measuring results at 3, 6, 8, 12, and 24 h at 75 °C. Experiments were also done using the previously activated LaCoODA catalyst. The activation of the catalyst was performed by placing the solid in a vacuum oven at 80 °C for 2 h before its use in the catalytic reactions.

All the products were analyzed by gas chromatography, using a 5890 model SERIES II Hewlett Packard gas chromatograph equipped with a capillary non-polar Equity-1 column and an FID detector.

4.4. Determination of Acid Strength and Number of Acid Sites

The acid strength and the number of acid sites in the catalysts were determined with a potentiometric titration, as reported by Cid and Pecchi [48]. A suspension of 50.8 mg of LaCoODA (49.8 mg of LaCuODA) in 100 ml of acetonitrile was titrated with a 0.01 N solution of N-butylamine in acetonitrile, using an Ag/AgCl electrode immersed in the suspension. The first addition of 50 μL of titrant to the suspension was left stirring for 4 h, in order to stabilize the system. The first potentiometric measurement indicates the strength of the acid sites. After this first measurement was recorded, 50 μL/min of titrant was added until the potential of the system remained constant. The spent volume indicates the miliequivalents of acid sites per gram of solid. For the number of acid sites, a constant potential was achieved by the LaCoODA suspension after 0.015 miliequivalents of N-butylamine was added. In the case of the LaCuODA suspension, 0.039 miliequivalents of N-butylamine was added before a constant potential was achieved.

5. Conclusions

For the studied catalysts, the physicochemical properties controlled the catalytic performance of the reaction, with the surface area and redox properties being determinant to explain the better results of LaCoODA over LaCuODA. Therefore, it is concluded that the Langmuir surface area and the redox potentials were more important than the acid strength and acid sites of the studied MOFs, in terms of the referred catalytic performance.

The channels play an important role in the catalytic processes; the removal of the water molecules from the channels is fundamental to favor the interaction between the active sites and the oxidant/catalyst.

The type of oxidant and the way to supply it are relevant to understand the difference in the results that exists among similar compounds. The amount of oxidant available within the reaction is key to obtain better results.

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