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1 **MgAl and ZnAl layered double hydroxides modified with molybdate and tungstate anions as**  
2 **catalysts for oxidation of cyclohexane**

3  
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13  
14 **Abstract**

15 Catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone with H<sub>2</sub>O<sub>2</sub> was performed at a  
16 mild temperature of 40 °C and atmospheric pressure, using ZnAl or MgAl layered double hydroxides  
17 (LDHs) **modified** with tungstate and molybdate anions as catalysts in heterogeneous medium. The  
18 catalysts were prepared by direct anion exchange reactions of tungstate and molybdate on LDHs  
19 intercalated with chloride/carbonate anions. All the solids showed catalytic activity in the  
20 cyclohexane oxidation, with slight selectivity for the ketone product. The catalytic efficiency was  
21 sensitive to the M<sup>2+</sup> present in the composition of the LDH as well as to the anions. ZnAl-modified  
22 with WO<sub>4</sub> was more active and more selective for ketone than the MgAl-modified WO<sub>4</sub> or any  
23 molybdate-based LDH catalysts.

24  
25 **Keywords:** molybdate, tungstate, cyclohexane oxidation, layered double hydroxides - LDHs,  
26 heterogeneous catalysis

27  
28  
29 **Introduction**

30  
31 Selective oxidation of alkanes is a difficult reaction to perform, considering both kinetic and  
32 thermodynamic aspects [1,2]. Therefore, the oxo-functionalization process of these compounds,  
33 especially linear alkanes in their terminal position, has been intensely investigated, since the  
34 compounds resulting from this reaction have high value and are used in many areas of the chemical  
35 industry. For example, cyclohexane oxidation is one of the conventional methods to produce adipic

36 acid (AA), which is primarily used for the manufacture of nylon-6,6 polymer, in turn for production of  
37 polyurethanes as reactants to form plasticizers, lubricant components, polyester polyols, ε-  
38 caprolactam, etc. Yearly global AA production is more than 3.5 million metric tons, with demand  
39 growth of 5% annually [3,4]. The abundance of alkanes derived from oil and the range of possible  
40 compounds resulting from their chemical transformations means that their oxo-functionalization is  
41 still widely investigated in catalytic processes. Hence, their use extends far beyond fuels [3–7].

42 Different catalytic approaches employing chemical compounds and enzymes have been  
43 investigated for development of efficient and selective alkane oxo-functionalization reactions.  
44 Related to enzymes, most metalloenzymes active for alkane oxo-functionalization use copper or iron  
45 as metal catalytic species, such as monooxygenase systems operating under mild physiological  
46 conditions. Inspired by these biological systems, different metal ion complexes, mainly  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  
47  $\text{Mn}^{3+}$ , and  $\text{Co}^{3+}$ , have been investigated as biomimetic catalysts for oxo-functionalization of linear and  
48 cyclic alkanes [8–12]. Despite the promising results reported using, for example, metalloporphyrins  
49 [13–17], alkane oxo-functionalization remains a major catalytic challenge when aiming to scale up  
50 the results. Thus, the development of new technological processes to take advantage of these  
51 molecules is needed.

52 In addition to the cited metal compounds, tungsten and molybdenum compounds are have  
53 also been investigated as catalysts for this class of oxidation reactions, e.g., oxidation of alkanes,  
54 phenols, and olefins; alkene epoxidation; allylic acetoxylation to form glycerol from allylic alcohols;  
55 and asymmetric dihydroxylation of glutaraldehyde from cyclopentene [18–21]. These two metals are  
56 frequently used in different forms, like polyoxometalates (POM) [22–33], anions [34,35], complexes  
57 [36–40], in association with gold, platinum or copper nanoparticles [41–45], etc.

58 Regarding tungsten compounds, several  $\text{WO}_3$  and tungstate-based catalysts have been found  
59 active for cyclohexene oxidation [41,46–50]. Sato et al. demonstrated the efficiency of  $\text{Na}_2\text{WO}_4$  as a  
60 catalyst to convert cyclohexene to AA using 30%  $\text{H}_2\text{O}_2$  in a biphasic system [46]. Also, Vafaezadeh et  
61 al. demonstrated that silica-functionalized ammonium tungstate is a versatile oxidation catalyst for  
62 direct cyclohexene conversion into AA using  $\text{H}_2\text{O}_2$ [50]. Mai et al. [41] prepared a photothermal solid  
63 catalyst by loading Au nanoparticles (Au NPs) into  $\text{WO}_3$  nanosheets ( $\text{WO}_3$  NSs) to improve  
64 cyclohexane conversion and ketone-alcohol (KA) oil selectivity under solar light irradiation. High  
65 conversion of 9.0% and a high selectivity of 99.0% were observed, attributed to the improved light  
66 absorption, the effective charge separation, and the synergistic effect of photocatalysis and thermal  
67 catalysis.

68 Molybdenum species have also been investigated as catalysts for cycloalkane and  
69 cycloalkene oxidation reactions [32,33,51–55]. For instance, Conte et al. [32] prepared a  
70 molybdenum blue nanoring  $\text{Mo}^{5+}\text{-O-Mo}^{6+}$  (POM) and investigated it as a catalyst for solvent-free

71 cyclohexane oxidation to alcohol and ketone with O<sub>2</sub> gas. They observed a ketone/alcohol ratio (K/A)  
72 of 0.8 with 6% cycloalkane conversion to the products after 17 h of reaction. The strong catalytic  
73 activity was attributed mainly to the presence of Mo<sup>5+</sup> species in the POM composition. Using MoO<sub>3</sub>-  
74 containing MCM-41 mesoporous silica catalyst, Rana and Viswanathan [52] investigated the catalytic  
75 oxidation of cyclohexane into acetone, which led to a K/A ratio of 0.16 with up to 87.59%  
76 cyclohexanone selectivity while using 30 wt% H<sub>2</sub>O<sub>2</sub>. They attributed this result to the activity of  
77 tetrahedral MoO<sub>4</sub> sites in the solid structure. Also, using molybdenum and tungsten  
78 polyoxometalates supported on activated carbon fibers, Alcañiz-Monge et al. [33] investigated the  
79 influence of their respective peroxometallic intermediaries, formed *in situ* using hydrogen peroxide  
80 in acetonitrile, on the conversion of cyclohexane into adipic acid. They reported that compared to  
81 [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> catalytic species, the use of [PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>-based heteropoly salts offered many advantages  
82 due to their stronger oxidizing power, presenting higher catalytic activity and higher selectivity to AA  
83 synthesis. Lastly, using the inexpensive catalyst ammonium molybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>), Buonomenna  
84 and co-workers [55] reported the one-step cyclohexane oxidation to adipic acid using a microporous  
85 polymer membrane to compartmentalize the organic phase containing the substrate and the  
86 aqueous phase with the catalyst, hydrogen peroxide and succinic acid, to obtain selective oxidation  
87 of cyclohexane to adipic acid (90%).

88 Layered double hydroxides (LDHs) are a class of inorganic solids that can easily support  
89 polyoxometalate anions and can be designed as potential catalysts for oxidation reactions. LDHs  
90 consist of positively charged layers neutralized with exchangeable anions. The positive charges arise  
91 from the composition of LDHs based on metallic cations in different oxidation states (2+ and 3+) and  
92 M<sup>2+</sup>:M<sup>3+</sup> molar ratios. These positively charged layers are counterbalanced by hydrated or non-  
93 hydrated anions, located in the interlayer space and at the layer surface of the LDH. Due to the great  
94 flexibility of chemical composition of both the layers and the interlayer domains, which can  
95 accommodate different anions, this class of materials has been widely used for a variety of  
96 applications, among them catalysis [13, 15, 16, 56,57].

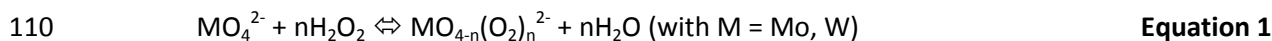
97 The catalytic properties of LDHs intercalated with tungstate and molybdate have been  
98 explored for various organic reactions such as olefin epoxidation [58,59], transesterification [60],  
99 H<sub>2</sub>O<sub>2</sub>-activated oxidation [61–64], alcohol dehydration [65] and oximation reaction [66]. Most of the  
100 Mo and W catalytic oxo species that have been immobilized in LDH matrices for oxidation reactions  
101 are tetrahedral anions (MoO<sub>4</sub><sup>2-</sup> or WO<sub>4</sub><sup>2-</sup>).

102 Concerning the oxygen species used for the catalytic oxidation reactions, in recent years the  
103 importance of hydrogen peroxide as an oxidizing agent has grown, because H<sub>2</sub>O<sub>2</sub> is an  
104 environmentally friendly reactant, besides being cheaper and safer in comparison to other organic

105 peroxides, with a high effective-oxygen content (47%) [67], producing water as the resulting  
106 byproduct [2,6,67–70].

107 Tungstate and molybdate activation by H<sub>2</sub>O<sub>2</sub> lead to the formation of active peroxy species  
108 MO<sub>2</sub>(OO)<sub>2</sub><sup>2-</sup> according to **Equation 1**:

109



111

112 In appropriate pH conditions, tungstate or molybdate [71] can also promote the H<sub>2</sub>O<sub>2</sub>  
113 disproportionation into a <sup>1</sup>O<sub>2</sub> singlet (**Equation 2**):

114



116

117 LDHs modified with W and Mo polyoxometallates (Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup>, W<sub>7</sub>O<sub>24</sub><sup>6-</sup>) have also been  
118 successfully evaluated as catalysts of alkene oxidation [62,63,72] and olefin epoxidation [58].

119 Intercalation of oxo- and polyoxotungstate and molybdate in LDHs is favored by their high  
120 negative charge density, even though some limitations arise due to the high affinity of LDHs toward  
121 competitive anions such as carbonate. Indeed, despite being known as anion exchangers, LDHs have  
122 an interaction affinity that depends on the chemical nature of the anions to be exchanged. The  
123 decreasing order of affinity can be exemplified as CO<sub>3</sub><sup>2-</sup> > SO<sub>4</sub><sup>2-</sup> > OH<sup>-</sup> > F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > I<sup>-</sup> [57].

124 In view of the known order of ionic affinity, LDHs have a higher affinity for carbonate ions  
125 (CO<sub>3</sub><sup>2-</sup>) than for other ions, so it is more difficult to exchange these ions for others. However, for this  
126 class of material to be used as a platform capable of exchanging different ions with different  
127 functionalities, e.g., anions with catalytic properties, it is first necessary to deintercalate the  
128 carbonate ions without changing the crystallinity and/or size homogeneity of the layered particles  
129 [56,57,73,74].

130 Among the available methods to achieve this goal, the process based on controlled  
131 acidification of the reaction medium using a buffer solution of acetic acid/acetate in the excess  
132 presence of the anions, e.g., chloride ions, is suitable to promote the carbonate ion (CO<sub>3</sub><sup>2-</sup>) exchange  
133 [73]. Based on this method, when the reaction medium is acidified, there is an increase in the  
134 amount of H<sup>+</sup> available in the solution, and these protons can react with the carbonate ions present  
135 in LDH, leading to the formation of hydrogen carbonate ions, which can again be protonated, leading  
136 to the formation of water and CO<sub>2</sub> which can finally be removed from the LDH.

137 Consequently, chloride Cl<sup>-</sup> ions present in excess in the reaction medium are intercalated in  
138 the interlayer space. Since the chloride ion is a monovalent anion, the tendency to exchange this

139 anion for another of interest related to the carbonate anion is facilitated, especially if it has a greater  
140 number of charges.

141 In this work, we prepared and characterized new LDH-based catalysts, namely MAI-LDHs (M  
142 = Zn<sup>2+</sup> or Mg<sup>2+</sup>), exchanged with anionic molybdate or tungstate species, and compared their catalytic  
143 performances in the cyclohexane oxidation reaction with H<sub>2</sub>O<sub>2</sub> to obtain cyclohexanone (K) and  
144 cyclohexanol (A) as main products (KA mixture).

145

## 146 **Experimental**

147

### 148 **Synthesis of the catalysts**

149

#### 150 *Preparation of the LDH precursors*

151 MgAl-LDH (denoted MA) and ZnAl-LDH (denoted ZA) were prepared by co-precipitation of a  
152 solution of 200 mL containing 0.75 mol of MgCl<sub>2</sub> (for MA) or ZnCl<sub>2</sub> (for ZA) and 0.25 mol of AlCl<sub>3</sub>·9H<sub>2</sub>O,  
153 with M<sup>2+</sup>:Al<sup>3+</sup> molar ratio of 3:1, according to a previously reported method [75]. The addition of the  
154 solution was performed under dynamic N<sub>2</sub> flow, constant magnetic stirring at room temperature and  
155 constant pH of 10.5, maintained by the addition of 2 mol L<sup>-1</sup> NaOH solution for 6 hours. After the  
156 addition was completed, the dispersion was aged at 80 °C for 14 hours under dynamic N<sub>2</sub> flow and  
157 constant magnetic stirring. The white solid was separated by centrifugation, washed 3 times with  
158 deionized water and kept in dispersion for further use.

159

#### 160 *Preparation of the chloride-containing LDH*

161 To prepare the LDH of ZnAl and MgAl intercalated solely with chloride (denoted by ZA-Cl or  
162 MA-Cl respectively), the carbonate intercalated ions were removed using the method described by Iyi  
163 et al. [73] under N<sub>2</sub> atmosphere and using decarbonated water. Then 100 mL of the ZA or MA  
164 dispersion was mixed with 100 mL of 2.5 mol L<sup>-1</sup> NaCl solution and 100 mL of 0.1 mol L<sup>-1</sup> buffer acetic  
165 acid/acetate solution. The dispersion pH was kept around 5.2 - 5.5 under magnetic stirring overnight  
166 at room temperature. The dispersion was centrifuged and the separated solid (ZA-Cl or MA-Cl) was  
167 washed with deionized and decarbonated water 3 times and kept in dispersion for further use.

168

#### 169 *Preparation of the LDH modified with molybdate and tungstate anions*

170 Molybdate and tungstate exchanged ZA-Cl or MA-Cl (denoted as ZA-W, ZA-Mo, MA-W or MA-  
171 Mo) were obtained by direct surface ion-exchange reactions of ZA-Cl or MA-Cl with Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O or  
172 Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O [69]. To prepare the LDH-W samples, ZA-Cl or MA-Cl (5 g) was dispersed in 50 mL of  
173 decarbonated water previously purged with N<sub>2</sub> and the pH was adjusted to 9.5 by the addition of 0.1

174 mol L<sup>-1</sup> NaOH solution. The dispersion was magnetically stirred at room temperature under N<sub>2</sub> flow  
175 and then a decarbonated water solution of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (100 mL, 0.1 mol L<sup>-1</sup>) was slowly added  
176 during 3 hours.

177 To complete the reaction, the mixture was maintained at 80 °C under dynamic N<sub>2</sub> flow for 16  
178 h. The resulting products were filtered, washed thoroughly with deionized and decarbonated water,  
179 and dried for 14 h at 50 °C. A similar procedure was used to prepare ZA-Mo and MA-Mo using  
180 Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O decarbonated water solution (0.1 mol L<sup>-1</sup>).

181

## 182 **Oxidation of cyclohexane**

183 ZA-W, ZA-Mo, MA-W and MA-Mo were investigated as catalysts for cyclohexane oxidation  
184 using hydrogen peroxide [69]. In the procedure for cyclohexane oxidation, the catalytic experiments  
185 were carried out at atmospheric pressure in a glass vial batch reactor (10 mL), equipped with a  
186 magnetic stirrer in dark conditions using a cyclohexane:H<sub>2</sub>O<sub>2</sub> molar ratio of 1:5. In a typical run, about  
187 50 mg of the catalyst (ZA-W, ZA-Mo, MA-W, MA-Mo) was dispersed with 5.0 mL of acetonitrile  
188 solvent in a vial reactor under stirring and cyclohexane (1 mmol) and 35% H<sub>2</sub>O<sub>2</sub> aqueous solution (5  
189 mmol) was added. The reaction medium was magnetically stirred for 3 h at 40 °C. The catalysts were  
190 separated by centrifugation (4000 RPM) and washed with 3 portions of 1.0 mL of acetonitrile. The  
191 supernatant and the washing solutions were transferred to the same 10 mL volumetric flask and  
192 analyzed with an Agilent 6850 gas chromatograph (flame ionization detector) equipped with a 30 m  
193 long DB-WAX capillary column with 0.25 mm internal diameter (J&W Scientific), using n-octanol as  
194 internal standard. Control experiments (blanks) were carried out by mixing the reactants (substrate  
195 and H<sub>2</sub>O<sub>2</sub>) without any catalyst and also in the presence of **i**) tungstate- or molybdate-free LDH (ZA-Cl  
196 or MA-Cl) or **ii**) sodium tungstate or sodium molybdate salts. The H<sub>2</sub>O<sub>2</sub> concentration was measured  
197 by standard iodometric titration. In addition to these general reaction conditions, reactions were also  
198 carried out at different reaction times and amounts of catalysts to achieve optimized conditions to  
199 maximize the desired products. The modified reaction conditions were reaction time (3 h, 8 h, 16 h,  
200 and 23 h), and amount of catalyst (50 mg and 15 mg). The reactions were performed in duplicate or  
201 triplicate and the conversion percentage yield of cyclohexane to the alcohol cyclohexanol (A) and  
202 ketone cyclohexane (K) products obtained (Table 3) was based on the amount of cyclohexane  
203 (substrate) added, with an estimated error between 3 and 10%.

204

## 205 **Materials characterization**

206

207 Fourier-transform infrared spectroscopy (FTIR) measurements were carried out using a Thermo  
208 Nicolet 5700 spectrometer, employing KBr pellets at a mass ratio of 1:100 (sample :KBr) with resolution  
209 of  $4\text{ cm}^{-1}$  and accumulation of 64 scans.

210 The Raman spectra were recorded from  $150$  to  $1500\text{ cm}^{-1}$  at room temperature using a  
211 confocal micro-Raman spectrometer (Jobin Yvon T64000) with an excitation wavelength of  $514.5\text{ nm}$   
212 (argon-ion laser-line). Spectra were acquired with resolution of  $1\text{ cm}^{-1}$  with a charge coupled device  
213 (CCD) multichannel detector cooled by liquid  $\text{N}_2$  coupled to an Olympus confocal microscope. Zeta  
214 potential data were acquired with a Nanosizer ZS from Malvern Instruments equipped with a  $633\text{ nm}$   
215 He-Ne laser with non-invasive back scattering (NIBS) configuration ( $173^\circ$ ). For analysis, solids were  
216 dispersed in deionized water at a concentration of  $0.01\%$  (w/w).

217 For the X-ray diffraction (XRD) analysis, the solids were placed on glass sample holders and  
218 the measurements were performed in reflection mode using a Shimadzu XRD-6000 diffractometer  
219 operating at  $30\text{ kV}$  and  $40\text{ mA}$  ( $\text{Cu K}\alpha$  radiation  $\lambda = 1.5418\text{ \AA}$ ) with Bragg-Brentano  $\theta$ - $2\theta$  geometry  
220 with a scan rate of  $1^\circ\cdot\text{min}^{-1}$ .

221 Transmission electron microscopy (TEM) and selected area electron diffraction (SAED)  
222 measurements were performed with a JEOL JEM-1200 microscope operating at  $110\text{ kV}$ . The samples  
223 were dispersed in propanone and deposited on FCF300-CU grids (300 mesh) covered with  
224 formvar/carbon film.

225 Scanning electron microscopic images (SEM) and energy dispersive spectra (EDS) were  
226 obtained with a Tescan VEGA3 LMU device, using tension of  $10\text{ KV}$ . The samples were deposited on  
227 aluminum stubs and the EDS spectra were collected with an SDD detector with  $80\text{ mm}^2$  in the range  
228 of  $0$  to  $10\text{ KeV}$ . Then the samples were gold-sputtered to obtain the SEM images.

229 The UV-Vis spectra of the solid samples were obtained using a Varian Cary 100 BIO Uv-visible  
230 spectrophotometer by placing the samples in a Teflon sample holder and measuring the absorbance  
231 in the  $200$  to  $800\text{ nm}$  range.

232 The textural properties were determined with a NOVA 1000 analyzer (Quantachrome) after  
233 degasifying the samples under vacuum for  $6$  hours ( $\text{ZnAl}$  samples were maintained at  $150\text{ }^\circ\text{C}$  during  
234 this period and those of  $\text{MgAl}$  at  $90\text{ }^\circ\text{C}$ ). The adsorption/desorption isotherms for  $\text{N}_2$  were obtained in  
235 a relative pressure range from  $0.05$  to  $0.99$ , and the specific surface area was calculated using the  
236 multi-point Brunauer-Emmet-Teller method (B.E.T.), with a relative pressure range from  $0.05$  to  $0.3$ .

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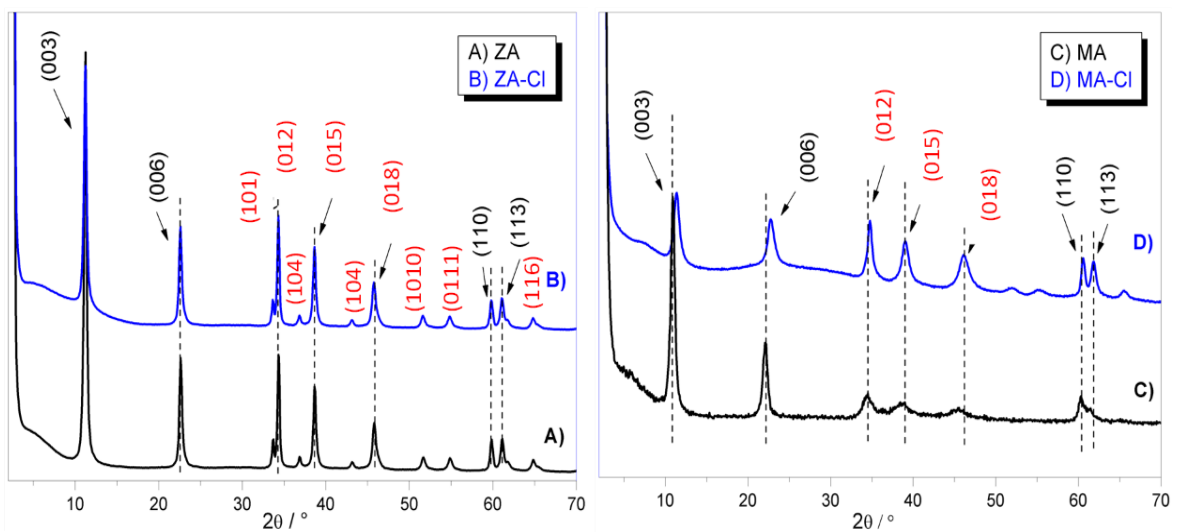
239 **Results and discussion**

240



241 Due to the strong ionic affinity of carbonate for LDH layers, to obtain LDH solids with surface  
 242 modified by tungstate and molybdate anions, two-step synthesis was performed involving first the  
 243 coprecipitation of ZnAl and MgAl LDH containing chloride (ZA and MA respectively) followed by a  
 244 harsh acidic treatment to fully exchange the undesirable carbonate anions of the precipitated solids  
 245 (ZA-Cl and MA-Cl respectively) [56,57,73].

246 Figure 1 shows the X-ray powder diffraction patterns of the LDH precursors (ZA and MA) (Fig.  
 247 1A, C) in addition to the chloride LDH prepared after the decarbonation treatment (ZA-Cl and MA-Cl)  
 248 (Fig. 1B, D).  
 249



250  
 251

252 **Figure 1.** X-ray powder diffraction patterns of synthesized LDH solids before (A for solid **ZA** and C for  
 253 solid **MA**) and after (B for solid **ZA-Cl** and D for solid **MA-Cl**) the carbonate deintercalation process.

254

255 All four samples displayed (Fig. 1) diffraction patterns typical of LDH structures (hexagonal  
 256 lattice with rhombohedral R-3m symmetry), with well defined (hkl) diffraction peaks. The basal  
 257 harmonic diffraction peak series occurred at low angles (003, 006), corresponding to the diffraction  
 258 by atomic planes parallel to the layers, while the (110) diffraction peak in the 60° region indicates the  
 259 metal-metal distance and allows calculating the cell parameter ( $a = 2d_{110}$ ) [76]. Analysis of the ZnAl-  
 260 LDH diffraction patterns (Fig. 1A, B) revealed practically no difference between the diffraction  
 261 profiles before (Fig. 1A) and after the carbonate removal (Fig. 1B). The basal distances calculated  
 262 using Bragg's equation, of both LDH ZA and ZA-Cl, were similar ( $d = 7.8 \text{ \AA}$ ). These distances  
 263 correspond to LDH gallery expansion due to  $\text{Cl}^-$  anion ( $r_i = 181 \text{ pm}$ ) intercalation, as reported  
 264 for chloride LDH [57,77,78]. Indeed, both ZA and ZA-Cl LDH phases contain low carbonate  
 265 anion contents as confirm by FTIR analysis (Fig. 3). Obviously, precipitation condition under

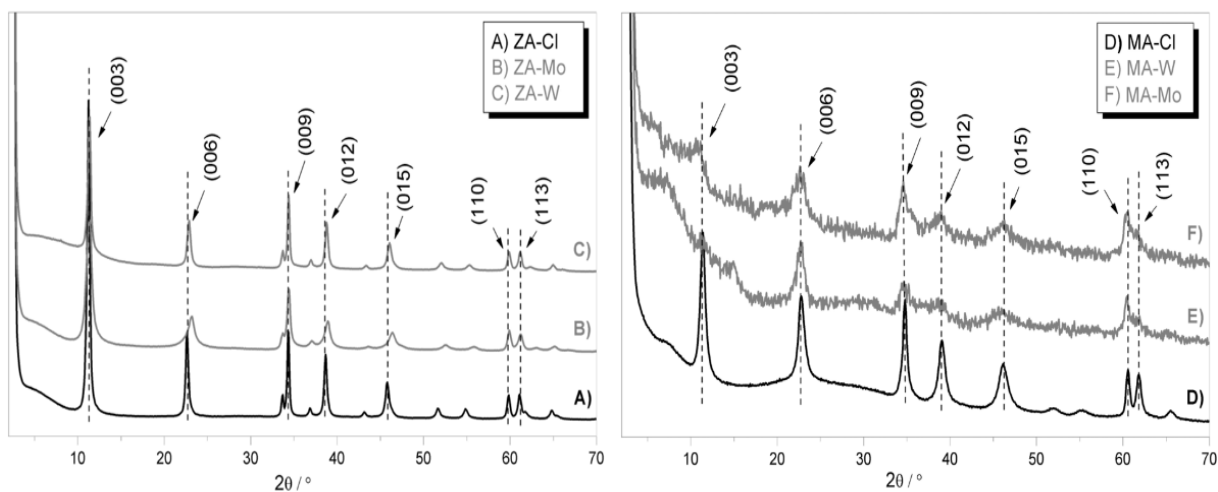
266 drastic N<sub>2</sub> gas flow, already prevented the formation of undesired LDH-CO<sub>3</sub> as the major  
267 phase, and further decarbonation process (step 2) did not improve much CO<sub>3</sub><sup>2-</sup>  
268 decontamination. Based on XRD data and FTIR, it is difficult to infer with certainty whether part of  
269 carbonate anions were co-intercalated with Cl<sup>-</sup> anion rather than totally adsorbed at the surface.

270 MA-Cl LDH displayed lower crystallinity (broader full width at half maximum (FWHM) of hkl  
271 diffraction lines) than ZnA-Cl LDH (Fig. 1C, D), as often observed. The carbonate removal process  
272 leads to XRD patterns with increased diffraction line widths (Fig. 1D), particularly visible for the  
273 (110)/(113) doublet, suggesting a decrease of both crystallinity and ordered domain size. Regarding  
274 the (003) and (006) peaks positions, slight shifts toward higher 2θ values were observed after the  
275 carbonate deintercalation/exchange process, indicating a decrease of the basal distance from 8.0 Å  
276 for MA to 7.7 Å for MA-Cl (Fig. 1D). This can be explained by the removal of co-intercalated CO<sub>3</sub><sup>2-</sup>  
277 anions that leads to a pure MA-Cl phase with the typical interlayer distance of 7.7 Å.

278 Samples prepared by anion exchange of molybdate (Fig. 2B, F) and tungstate (Fig. 2C, E) anions  
279 displayed XRD patterns with similar diffraction line series, suggesting these reactions occurred  
280 retaining the LDH structure. No basal distance change was observed after the molybdate and  
281 tungstate exchange reaction, suggesting that intercalations were not obtained (Fig. 2A, B, C). The  
282 basal distances of 7.8 Å were compatible with the presence of either carbonate or chloride ions  
283 intercalated between the layers. Moreover, after MoO<sub>4</sub><sup>2-</sup> and WO<sub>4</sub><sup>2-</sup> exchange, the LDH XRD patterns  
284 (Fig. 2E, F) showed a drastic decrease in intensity of the basal peaks, especially for the MA samples,  
285 indicating that crystallinity seemed to be mainly impacted by this process. This is typical of a loss of  
286 layer stacking order.

287 The question of whether molybdate and tungstate were adsorbed at the surface of the layers  
288 or intercalated between the LDH layers remains. Many publications [64,65,79] dealing with the  
289 intercalation of MoO<sub>4</sub><sup>2-</sup> and WO<sub>4</sub><sup>2-</sup> in LDHs under reaction conditions similar to those used in this  
290 work (basic pH and thermal activation) have reported basal distances around 7.9 Å. However, MoO<sub>4</sub><sup>2-</sup>  
291 and WO<sub>4</sub><sup>2-</sup> entities with respectively metal-O distance W-O = 1.78-1.79 Å and Mo-O = 1.75-1.78 Å,  
292 displayed thermochemical radii greater than SO<sub>4</sub><sup>2-</sup> anion radius (S-O distances 1.47-1.49 Å) and  
293 should lead, after intercalation in LDH, to a greater structural expansion of dehydrated sulfate (8.9 Å)  
294 [80,81]. Even though well crystalized, LDH-MoO<sub>4</sub><sup>2-</sup> and LDH-WO<sub>4</sub><sup>2-</sup> have not yet been synthesized.  
295 Only a few publications have mentioned an increase of basal distance after molybdate and tungstate  
296 intercalation. Mohapatra et al. [82] mentioned values of 8.59 Å and 9.11 Å for Zn<sub>3</sub>Y- WO<sub>4</sub><sup>2-</sup> and Zn<sub>3</sub>Y-  
297 MoO<sub>4</sub><sup>2-</sup> respectively. Similar basal spacing was obtained for Zn<sub>2</sub>Cr-WO<sub>4</sub> (9.15 Å) [83]. These structural  
298 data are consistent with oxometallate anions and water molecules that are densely packed in the

299 LDH galleries. Hence, accessibility to catalytic intercalated species with such a non-porous compact  
300 structure is questionable in terms of kinetic and efficiency reactivity or economic cost.  
301



302  
303 **Figure 2.** Powder X-ray diffraction patterns of LDHs before (A and D) and after tungstate (C and E)  
304 and molybdate (B and F) reactions. Here this figure is confusing. Left, blue is molybdate, with is  
305 tungstate. The same for red colored patterns. Better to keep the same colors. To be in accordance  
306 with fig. 3, just change fig. 2, left side.

307  
308 The semi-quantitative chemical compositions of the various materials were obtained from  
309 EDS analysis. First of all, the atomic composition determined by EDS for MA-W, MA-Mo, ZA-W and  
310 ZA-Mo LDH samples (Table 1) corresponded to high content values of molybdate and tungstate  
311 anions loaded in LDHs. The experimental  $Mg^{2+}/Al^{3+}$  molar ratio of MA samples (2.84 – 2.88) were  
312 close to the one (3.0) initially fixed in the preparation procedure. Subsequent coprecipitation,  
313 decarbonation and oxometallate reactions did not modify the  $Mg^{2+}/Al^{3+}$  chemical composition of  
314 the layers. Differently, the ZA solids displayed  $Zn^{2+}/Al^{3+}$  molar ratio (1.86 - 1.93) near 2.1 instead of  
315 the 3.1 imposed during coprecipitation. Obviously, under coprecipitation ZnA, LDHs reached the  
316 most stable composition of  $Zn_2A$ , with the best ordered structure, as shown by the XRD patterns.  
317 Similarly, after the exchange reactions with  $MoO_4^{2-}$  and  $WO_4^{2-}$  on ZA-Cl and MA-Cl, the LDHs retained  
318 the  $M^{2+}/M^{3+}$  ratio of their precursors. From the data of Table 1, it is clear that molybdate and  
319 tungstate were not fully exchanged in LDH even though chloride anions were removed (except for  
320 ZA-W). The maximum percentage of anion exchange capacity (AEC) was reached for ZA-Mo (68%).  
321 Competition of even traces of carbonate prevents the preparation of pure LDH- $MoO_4$  and LDH- $WO_4$   
322 phases. Obviously, diffusion of oxometallate in the LDH bulk is probably structurally restricted,  
323 favoring the intercalation of  $CO_3^{2-}$  anions in the interlayer spaces, while molybdate and tungstate

324 covered the platelet-like particles' surface. Nevertheless, the contents of catalytic species on the  
 325 surface were high, between  $9.65 \times 10^{-4}$  and  $1.10 \times 10^{-3}$  mol g<sup>-1</sup>.

326

327 **Table 1.** M<sup>2+</sup>/M<sup>3+</sup>/anion atomic ratio calculated based on EDS results.

LDH	Zn <sup>2+</sup> /Al <sup>3+</sup> or Mg <sup>2+</sup> /Al <sup>3+</sup>	MoO <sub>4</sub> <sup>2-</sup> or WO <sub>4</sub> <sup>2-</sup> /Al <sup>3+</sup> (% of AEC) <sup>#</sup>	Cl <sup>-</sup> /Al <sup>3+</sup>	CO <sub>3</sub> <sup>2-</sup> /Al <sup>3+</sup> *	Σ anions/Al <sup>3+</sup>	Calculated loading values (mol·g <sup>-1</sup> )
ZA-Cl	1.86	0.00	0.64	0.18	1	-
ZA-Mo	1.93	0.34(68%)	0.00	0.16	1	$1.13 \times 10^{-3}$
ZA-W	1.91	0.27 (54%)	0.16	0.15	1	$9.45 \times 10^{-4}$
MA-Cl	2.84	0.00	0.78	0.11	1	-
MA-Mo	2.87	0.28 (56%)	0.00	0.22	1	$9.65 \times 10^{-4}$
MA-W	2.88	0.12 (24%)	0.00	0.38	1	$1.10 \times 10^{-3}$

328 \*CO<sub>3</sub><sup>2-</sup> was obtained from calculation based on electroneutrality of the overall LDH structure. <sup>#</sup>Anion  
 329 exchange capacity (AEC). Novamente ZA e MA, não seria ZA-Cl e MA-Cl? Está confuso no texto todo.

330

331 TGA analyses (Fig. SI-1) confirmed the change in composition after oxometallate loading and  
 332 the effect of the oxyanions on the thermal decomposition profile. Carbonate decomposition is  
 333 associated with the thermal events around 410 – 420 °C, but it may last up to 900 °C when CO<sub>3</sub><sup>2-</sup>  
 334 anions are trapped in the collapsed layered double oxide structure (MA and ZA), which was clearly  
 335 and surprisingly not the case for LDHs loaded with molybdate and tungstate. As evaluated from the  
 336 mass loss of the intermediate thermal event (410 – 420 °C), MgAl LDH had higher carbonate contents  
 337 than ZnAl LDH (Table1). This can be explained by the higher basicity of the MgAl LDH compared to  
 338 ZnAl.

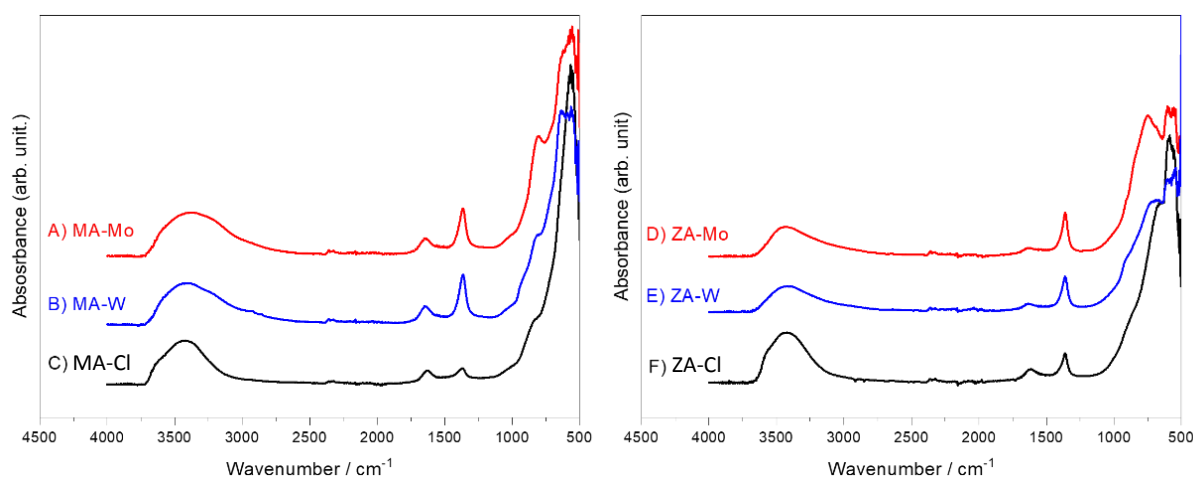
339 FTIR and Raman spectra confirmed that both oxometallate MO<sub>4</sub><sup>2-</sup> (M= Mo, W) and carbonate  
 340 CO<sub>3</sub><sup>2-</sup> anions coexist in the ZA and MA LDH structures. The ν<sub>3</sub> asymmetric and ν<sub>1</sub> symmetric stretching  
 341 vibration modes at around 1365 and 1060 cm<sup>-1</sup>, respectively, of the intercalated carbonate are  
 342 observed in all FTIR spectra (Fig. 3) [84]. The intensity of these bands slightly increased after  
 343 oxometallate exchange. The ν<sub>1</sub> mode at 1065 cm<sup>-1</sup> was also active in the Raman spectra, but the low  
 344 intensity of the corresponding bands confirmed the small content (Fig. 4). Also, the infrared spectrum  
 345 of ZA-Cl clearly evidenced that if carbonate anions were present, either intercalated or adsorbed at  
 346 the surface, the fraction was minor (Fig. 3).

347 The low energy absorption domains were characteristic of the LDH layers [85] with M-OH  
 348 vibration modes at 735 and 675 cm<sup>-1</sup> for MA species [86,87] and at 660 and 591 cm<sup>-1</sup> for ZA species  
 349 [88,89]. Lattice vibrations (O-M-O and MO<sub>6</sub> vibrations) appeared as two bands in the Raman spectra,  
 350 at 489 and 548 cm<sup>-1</sup> for ZnAl LDH and 471 and 553 for cm<sup>-1</sup> MgAl LDH.

351  $\text{MoO}_4^{2-}$  and  $\text{WO}_4^{2-}$  containing LDH displayed typical oxometallate tetrahedral vibration  
352 modes. For the molybdate modified LDHs,  $\nu_3$  asymmetric Mo-O bond stretching modes were  
353 observed at 806 and 831  $\text{cm}^{-1}$  respectively for MA-Mo and ZA-Mo, while the  $\nu_1$  Mo-O symmetric  
354 stretching band was only visible for ZA-Mo.  $\nu_4$  asymmetric bending modes, expected around 550 and  
355 510  $\text{cm}^{-1}$ , were superimposed with the LDH lattice vibrations [5,90–92].

356 MA-W and ZA-W showed typical bands related to  $\nu_1$  symmetric W-O stretching modes at 924  
357 (MA-W) and 914  $\text{cm}^{-1}$  (ZA-W) [92], and the W-O  $\nu_3$  stretching modes at 630  $\text{cm}^{-1}$  of MA-W, while at  
358 738 and 674  $\text{cm}^{-1}$  they referred to ZA-W. The bands attributed to  $\nu_4$  asymmetric bending modes are  
359 expected under 425  $\text{cm}^{-1}$  for W-O and therefore were not observed in the utilized spectral range  
360 [92,93].

361



362

363 **Figure 3.** FTIR vibrational spectra of the prepared solids: A, B and C for MA-Mo, MA-W and MA-Cl;  
364 and D, E and F for ZA-Mo, ZA-W and ZA-Cl, respectively.

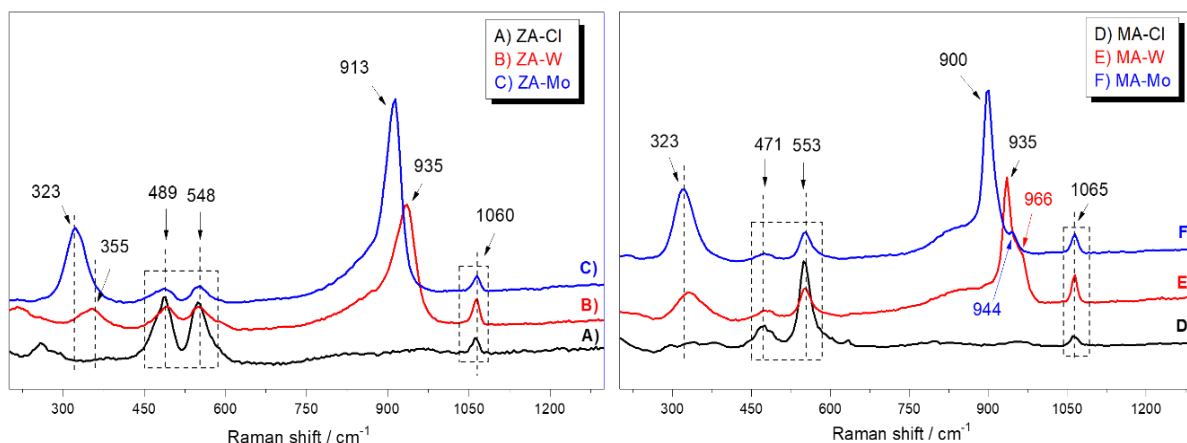
365

366 For tetrahedral (Td)  $\text{MO}_4$  species, the four vibration modes ( $\nu_1(\text{A}_1)$ ,  $\nu_2(\text{E})$ ,  $\nu_3(\text{F}_2)$ ,  $\nu_4(\text{F}_2)$ ) were  
367 all Raman active. The Raman spectra of LDH- $\text{MoO}_4$  (Fig. 4C, F) showed an intense band in the region  
368 of 900-913  $\text{cm}^{-1}$  (900 and 913  $\text{cm}^{-1}$  for MA-Mo and ZA-Mo respectively). We attributed this band to  
369 the  $\nu_1$  symmetric stretching mode of Td  $\text{MoO}_4$ . Furthermore, there was a lower intensity band in the  
370 region of 323  $\text{cm}^{-1}$ , which could correspond to either the  $\nu_2(\text{E})$  or  $\nu_4(\text{F}_2)$  angular deformations. These  
371 results were similar to data reported in the literature (897 and 317  $\text{cm}^{-1}$ ) [94]. In the MA-Mo  
372 spectrum, a shoulder band appeared at 944  $\text{cm}^{-1}$ , which could be attributed to the presence of  
373 heptamolybdate ( $\text{Mo}_7\text{O}_{24}^{6-}$ ) species, suggesting that this solid is composed by a mixture between  
374 molybdate and heptamolybdate ions [68,95].

375

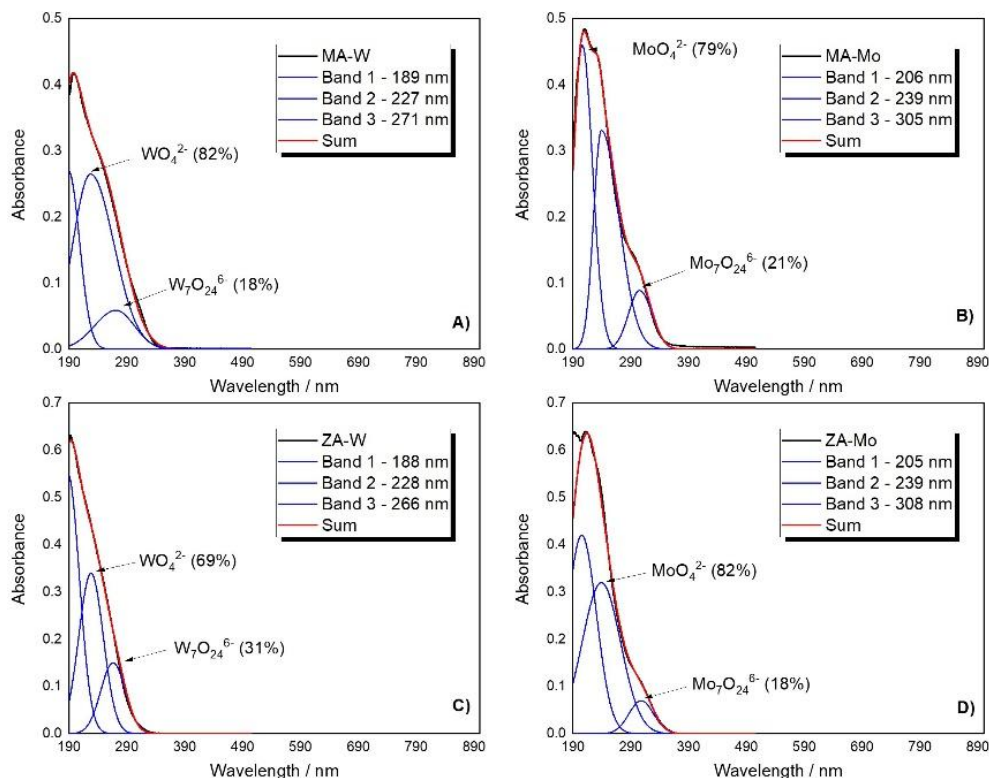
376 The Raman spectra of  $\text{WO}_4^{2-}$  containing LDH (Fig. 4B for ZA-W and Fig. 4E for MA-W) were  
377 very similar to those of LDH- $\text{MoO}_4^{2-}$ , with  $\nu_1$  and  $\nu_3$  modes appearing at 935  $\text{cm}^{-1}$  and 355  $\text{cm}^{-1}$ . The

377 broad shoulder at  $830\text{ cm}^{-1}$  probably arose from the splitting of the  $\nu_3(\text{F}_2)$  vibration due to reduction  
 378 of symmetry from the cubic point Td symmetry to lower symmetry when  $\text{WO}_4^{2-}$  attached to the LDH  
 379 surface [96]. Such broad bands were also observed for  $\text{MoO}_4$  loaded samples. Like the bands of the  
 380  $\text{WO}_4^{2-}$  anions, there was also a shoulder in the region of  $966\text{ cm}^{-1}$ , which can be attributed to the  
 381 presence of heptatungstate ( $\text{W}_7\text{O}_{24}^{6-}$ ) ions, suggesting that the solid MA-W can also be composed of a  
 382 mixture of tungstate and heptatungstate ions [97].  
 383



384  
 385 **Figure 4.** Raman vibrational spectra of the prepared solids before the ion exchange process (A: solid  
 386 ZA-Cl and D: solid MA-Cl); and after the exchange of chloride ions by molybdate or tungstate ions (B:  
 387 solid ZA-W, C: solid ZA-Mo, E: solid MA-W and F: solid MA-Mo).  
 388

389 While exchange reactions were performed at basic pH (9.5) to ensure adsorption of  
 390 tetrahedral  $\text{MO}_4^{2-}$  species, the LDH surface can have a slightly less acidic environment, which shifts  
 391 the speciation equilibrium to partial formation of polyoxometalate species, namely heptamolybdate  
 392 ( $\text{Mo}_7\text{O}_{24}^{6-}$ ) and heptatungstate ( $\text{W}_7\text{O}_{24}^{6-}$ ), as observed in the Raman spectra for MA-Mo and MA-W.  
 393 To better identify the nature and the proportion of the immobilized oxometallate species on the  
 394 solids MA and ZA, diffuse reflectance UV-Vis spectra were acquired to quantify the oxometallate  
 395 species' proportion (Fig. 5).



396

397 **Figure 5.** Experimental UV-Vis electronic spectra of solids MA-W (A), MA-Mo (B), ZA-W (C) and ZA-Mo  
 398 (D) (black line) and their respective deconvolution substances (blue and red lines) with regard to the  
 399 main species tungstate ( $\text{WO}_4^{2-}$ ), heptatungstate ( $\text{W}_7\text{O}_{24}^{6-}$ ), molybdate ( $\text{MoO}_4^{2-}$ ) and heptamolybdate  
 400 ( $\text{Mo}_7\text{O}_{24}^{6-}$ ).

401

402

403 The experimental spectra were deconvoluted in Gaussian curves while the ratio between the  
 404 anionic species' typical bands was estimated in percentage, considering the areas of the bands  
 405 resulting from the deconvolution process. Data are reported in Table 2. For comparison, the loading  
 406 value of the tungstate or molybdate species (mol) in the mass of the solid MA or ZA (mol/g) were  
 407 also estimated.

408

409 **Table 2.** Estimated loading of oxometallate species in the LDHs samples according to UV-Vis spectra  
 410 and EDS patterns (mol  $\text{g}^{-1}$  of tungstate or molybdate species).

Sample	LDH	$\text{MoO}_4^{2-}/\text{WO}_4^{2-}$		$\text{Mo}_7\text{O}_{24}^{6-}/\text{W}_7\text{O}_{24}^{6-}$		Loading by EDS
	$\lambda_{\text{max}}$ (nm)	$\lambda_{\text{max}}$ (nm)	Area (%)	$\lambda_{\text{max}}$ (nm)	Area (%)	
MA-W	189	227	82	271	18	$1.10 \times 10^{-3}$
MA-Mo	206	239	79	305	21	$9.65 \times 10^{-4}$
ZA-W	188	228	69	266	31	$9.45 \times 10^{-4}$
ZA-Mo	205	239	82	308	18	$1.13 \times 10^{-3}$

411

412 Three main bands were identified for all solids (Fig. 5). The bands at lower wavelength can be  
413 attributed to the LDH (MA or ZA) absorption from blank experiments. The two bands at 227 - 239 nm  
414 and 266 – 308 nm are associated, respectively, with  $\text{MO}_4^{2-}$  and  $\text{M}_7\text{O}_{24}^{6-}$  species according to the  
415 literature [69,98]. These absorption bands correspond to O ligand to 4d or 5d orbitals of,  
416 respectively,  $\text{Mo}^{6+}$  and  $\text{W}^{6+}$  cations. From deconvolution, it can be inferred there was a greater  
417 amount of tungstate (82% and 69%) and molybdate anions (79% and 82%) in comparison to  
418 heptametallate (18 – 31%).

419 This result corroborates the result obtained by Raman vibrational spectroscopy for MA-W  
420 and MA-Mo, where the presence of  $\text{M}_7\text{O}_{24}^{6-}$  species was associated to the shoulders at 966 and 944  
421  $\text{cm}^{-1}$  (Fig. 4-F). Unexpectedly,  $\text{W}_7\text{O}_{24}^{6-}$  and  $\text{Mo}_7\text{O}_{24}^{6-}$  loaded on ZA were not revealed by Raman  
422 spectroscopy (Fig. 4).

423 In view of the results obtained by the characterization techniques, it is possible to infer that  
424 different anionic species indeed were immobilized in the synthesized solids, namely molybdate and  
425 heptamolybdate or tungstate and heptatungstate. In addition, it appears there were different  
426 proportions of these anionic species in the corresponding solids.

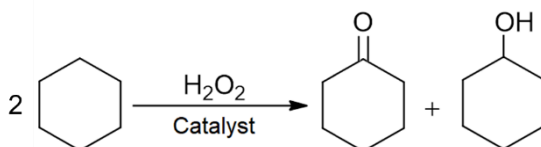
427

428

#### 429 **Cyclohexane oxidation**

430

431 The LDH-molybdate and LDH-tungstate catalytic activity was evaluated for the oxidation  
432 reaction of the cyclohexane to cyclohexanone and cyclohexanol (K+A mixture), as the main products,  
433 using hydrogen peroxide as oxidant agent in acetonitrile as solvent, according to Fig. 6.



434

435 **Figure 6.** Schematic representation of the catalytic cyclohexane oxidation by hydrogen peroxide,  
436 producing the main K+A mixture products (ketone+alcohol).

437

438 A reasonably low temperature of 40 °C and excess of solvent acetonitrile (dilute medium)  
439 was used to avoid the decomposition of hydrogen peroxide. Nevertheless, it was observed in some  
440 cases (discussed later) [69,98]. The catalytic results are presented in Table 3. The control reactions,  
441 performed under conditions free of a molybdate and tungstate catalysts, involving only reagents or



442 reagents with LDH-Cl, showed a very low conversion percentage of cyclohexane either into  
443 cyclohexanone ketone (K) or cyclohexanol alcohol (A) (below 0.20% of ketone+alcohol yield).

444 From Table 3, the conversion of cyclohexane to both ketone (K) and alcohol (A) products, in  
445 general increased when using tungstate and molybdate containing LDH in comparison with the  
446 control reactions (Table SI-1), suggesting that the W and Mo species have a catalytic contribution to  
447 the activation of the oxidizing agent. The conversion results also showed that the catalytic reaction  
448 efficiency is dependent on the composition of both the LDH layers ( $Zn^{2+}$  or  $Mg^{2+}$ ) and the  
449 oxometallate anions (W or Mo). Despite these reactions, all the catalysts showed selectivity to the  
450 ketone products, in general around 60% or higher, consequently better than results presented for  
451 other catalysts based on W or Mo (Table SI-2). The best conversion values were observed for ZA-W,  
452 the solid combining LDH layers with  $Zn^{2+}$  and immobilized tungstate species (W). Comparison of  
453 catalyst efficiency showed that, for the same catalytic reaction conditions (3 h reaction time and  
454 same catalyst amount), the order of conversion yield (%) followed the decreasing series: ZA-W > MA-  
455 W > MA-Mo  $\approx$  ZA-Mo (entries 1-4, Table 3).

456 ZA-W showed a total conversion percentage yield from cyclohexane to ketone and alcohol  
457 products of about 31 times more than ZA-Mo (Table 3, entry 4 - 1.06% in comparison with entry 3 -  
458 0.040%). In fact, some experimental observations during the catalytic reactions shed light on the  
459 different catalytic results observed for these two solids.

460 We observed that at the exact moment of adding the 35%  $H_2O_2$  solution in the reaction  
461 medium using the catalyst ZA-Mo, the solid color changed from white to dark red-orange with the  
462 concomitant beginning of intense  $O_2$  evolution in the reaction medium. After reaction for 1.5 hours,  
463 the  $O_2$  bubbling ceased, and the white color of the catalytic solid returned. The similar solid color  
464 change was also expected for the solid containing tungstate species (ZA-W), but it was not  
465 perceptible, probably due to the lower concentration of the anionic W species in this ZA (or MA)  
466 support (loading), as presented in Table 2. However, unlike the ZA-Mo solid, the ZA-W solid showed  
467 no apparent oxygen evolution when mixed with  $H_2O_2$ .

468

470 **Table 3.** Conversion of cyclohexane to cyclohexanol alcohol (A) and cyclohexanone ketone (K) by H<sub>2</sub>O<sub>2</sub> in the catalytic oxidation reaction<sup>1</sup>.

Entry	Cyclohexane (mmol)	H <sub>2</sub> O <sub>2</sub> (mmol)	Catalyst (mass/mg)	Reaction time (h)	Yield conversion (%)		Total yield% (%K+%A) <sup>2</sup>	Selectivity of Ketone (%) <sup>3</sup>	Loading (mol g <sup>-1</sup> )	Species estimated by Raman and UV-Vis analyses	MO <sub>4</sub> <sup>2-</sup> (Mol) <sup>4</sup>	M <sub>7</sub> O <sub>24</sub> <sup>6-</sup> (Mol) <sup>4</sup>
					Ketone (K)	Alcohol (A)						
1	1.0	5.0	MA-Mo (50)	3	0.037	0.025	0.062	60	9.65x10 <sup>-4</sup>	MoO <sub>4</sub> <sup>2-</sup> (79%) Mo <sub>7</sub> O <sub>24</sub> <sup>6-</sup> (21%)	7.6x10 <sup>-4</sup>	2.9x10 <sup>-5</sup>
2	1.0	5.0	MA-W (50)	3	0.14	0.13	0.27	48	1.10x10 <sup>-3</sup>	WO <sub>4</sub> <sup>2-</sup> (82%) W <sub>7</sub> O <sub>24</sub> <sup>6-</sup> (18%)	9.0x10 <sup>-4</sup>	2.8x10 <sup>-5</sup>
3	1.0	5.0	ZA-Mo (50)	3	0.024	0.016	0.040	60	1.13x10 <sup>-3</sup>	MoO <sub>4</sub> <sup>2-</sup> (82%) Mo <sub>7</sub> O <sub>24</sub> <sup>6-</sup> (18%)	9.3x10 <sup>-4</sup>	2.9x10 <sup>-5</sup>
4	1.0	5.0	ZA-W (50)	3	0.67	0.41	1.07	63	9.45x10 <sup>-4</sup>	WO <sub>4</sub> <sup>2-</sup> (69%) W <sub>7</sub> O <sub>24</sub> <sup>6-</sup> (31%)	6.6x10 <sup>-4</sup>	4.1x10 <sup>-5</sup>
5	1.0	5.0	ZA-W (50)	6	1.75	0.89	2.64	66	9.45x10 <sup>-4</sup>	WO <sub>4</sub> <sup>2-</sup> (69%) W <sub>7</sub> O <sub>24</sub> <sup>6-</sup> (31%)	6.5x10 <sup>-4</sup>	4.2x10 <sup>-5</sup>
6	1.0	5.0	ZA-W (50)	8	1.83	1.35	3.18	57	9.45x10 <sup>-4</sup>	WO <sub>4</sub> <sup>2-</sup> (69%) W <sub>7</sub> O <sub>24</sub> <sup>6-</sup> (31%)	6.5x10 <sup>-4</sup>	4.2x10 <sup>-5</sup>
7	1.0	5.0	ZA-W (50)	16	1.97	0.99	2.95	66	9.45x10 <sup>-4</sup>	WO <sub>4</sub> <sup>2-</sup> (69%) W <sub>7</sub> O <sub>24</sub> <sup>6-</sup> (31%)	6.5x10 <sup>-4</sup>	4.2x10 <sup>-5</sup>
8	0.3	1.0	ZA-W (15)	16	2.44	1.5	3.94	62	9.45x10 <sup>-4</sup>	WO <sub>4</sub> <sup>2-</sup> (69%) W <sub>7</sub> O <sub>24</sub> <sup>6-</sup> (31%)	6.5x10 <sup>-4</sup>	4.2x10 <sup>-5</sup>
9	0.3	1.0	ZA-W (15)	23	2.32	1.5	3.86	60	9.45x10 <sup>-4</sup>	WO <sub>4</sub> <sup>2-</sup> (69%) W <sub>7</sub> O <sub>24</sub> <sup>6-</sup> (31%)	6.5x10 <sup>-4</sup>	4.2x10 <sup>-5</sup>
10	1.0	5.0	ZA-W (50) <sup>5</sup>						9.45x10 <sup>-4</sup>			
			1 reuse	3	0.52	0.31	0.83	62				
11	1.0	5.0	2 reuse	3	0.43	0.37	0.80	62				
12	1.0	5.0	3 reuse	3	0.43	0.36	0.79	54				
13	1.0	5.0	4 reuse	3	0.41	0.34	0.75	55				

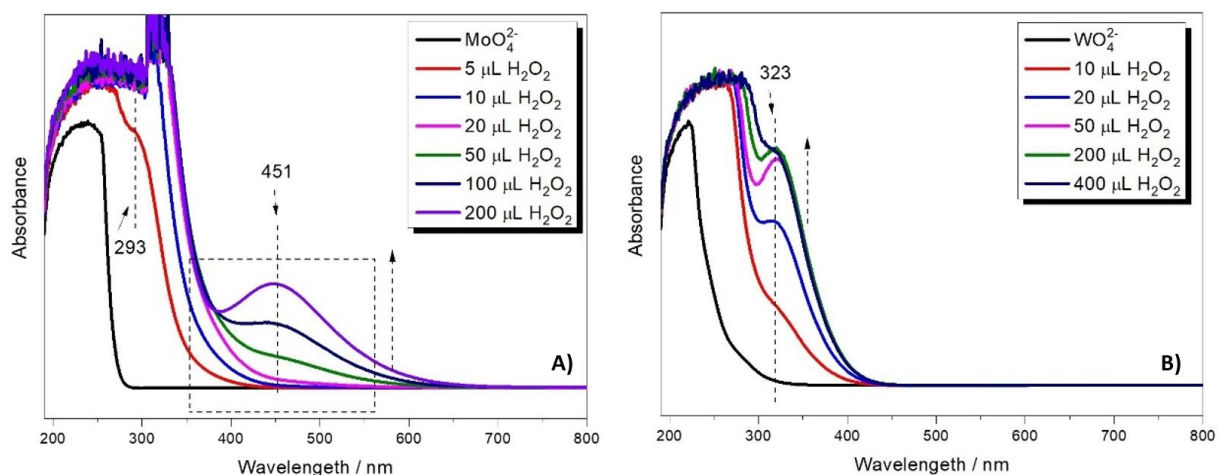
471 <sup>1</sup>General catalytic oxidation reaction conditions: dilute hydrogen peroxide (aqueous solution, 35%), at 40 °C, in the presence of acetonitrile as the solvent, with H<sub>2</sub>O<sub>2</sub>/substrate molar ratio =  
472 5:1. Conversion percentage values based on the initial cyclohexane quantity. <sup>2</sup> Total yield of cyclohexane conversion to K+A = [mols of cyclohexane reacted]/[initial mols of cyclohexane  
473 used]x 100 and <sup>3</sup> Ketone product selectivity: [total mol of ketone formed/total mol of cyclohexane converted] x100 [99]. The % conversion values were calculated in at least twice. The error  
474 of the results was in the range of 3 to 10%. <sup>4</sup>The mol quantity of all species was calculated based on the loading values (Table 2) and the deconvolution percentage data (Fig. 5). <sup>5</sup>The reuse  
475 experiments were performed in reaction conditions similar to those used for the reaction entry 4.

477 Monitoring of H<sub>2</sub>O<sub>2</sub> by UV-Vis spectroscopy (Fig. SI-2) allowed comparing the reactivity of ZA-  
478 W and ZA-Mo catalysts. Fig. SI-2A shows the electronic spectrum of H<sub>2</sub>O<sub>2</sub> (5 mmol) in 3 mL of  
479 acetonitrile at a similar concentration (35%) used in the catalytic reaction. The broad band located in  
480 the region from 190 nm to 340 nm (maximum at 250 nm) was attributed to the n → σ\* electronic  
481 transition of the H<sub>2</sub>O<sub>2</sub> molecules. The electronic spectra (Fig. SI-2B) of the supernatant of catalytic  
482 reaction using ZA-W catalyst were recorded at different reaction times. We observed that H<sub>2</sub>O<sub>2</sub> was  
483 still available in the reaction medium (band with stronger intensity) even after 3 hours of reaction  
484 time, suggesting that even after this time, sufficient H<sub>2</sub>O<sub>2</sub> was still present to promote the conversion  
485 of cyclohexane to its oxidation products. However, when using ZA-Mo as catalyst, H<sub>2</sub>O<sub>2</sub> was fully  
486 consumed after 1.5 hours (Fig. SI-2C) and the cyclohexane conversion stopped. H<sub>2</sub>O<sub>2</sub> was probably  
487 disproportionate in the medium, explaining the intense evolution of oxygen observed in the catalytic  
488 reactions promoted by the solid ZA-Mo, unlike the solid ZA-W.

489 In addition to the intense evolution of oxygen, we also observed an intense dark orange color  
490 in the solid ZA-Mo, as previously mentioned. This finding suggests that the color change observed in  
491 this ZA-Mo solid may have been directly related to the presence of H<sub>2</sub>O<sub>2</sub> in the medium and to the  
492 interaction between the oxidant H<sub>2</sub>O<sub>2</sub> and the anionic Mo species immobilized in LDH.

493 To better identify the molybdenum and tungsten species resulting from the presence of H<sub>2</sub>O<sub>2</sub>  
494 in the medium, UV-Vis spectra of Na<sub>2</sub>MoO<sub>4</sub> or Na<sub>2</sub>WO<sub>4</sub> aqueous solutions (0.1 mol L<sup>-1</sup>) were recorded  
495 at increasing additions of H<sub>2</sub>O<sub>2</sub> amounts. The pH of these solutions was previously adjusted to 8.0  
496 using a 0.1 mol L<sup>-1</sup> NaOH solution (Figure 7).

497



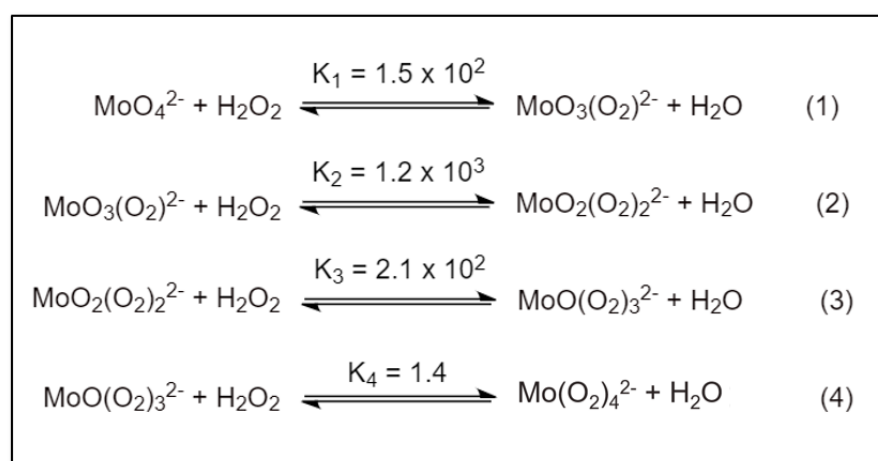
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499

500 **Figure 7.** UV-Vis spectra of aqueous solutions of A) Na<sub>2</sub>MoO<sub>4</sub> and B) Na<sub>2</sub>WO<sub>4</sub> with progressive  
501 addition of 35% H<sub>2</sub>O<sub>2</sub> solution.

502

503 For the aqueous solution of Na<sub>2</sub>MoO<sub>4</sub> (Fig. 7B), we observed that before the addition of H<sub>2</sub>O<sub>2</sub>  
 504 the solution was colorless. As the amount of H<sub>2</sub>O<sub>2</sub> increased, along with the H<sub>2</sub>O<sub>2</sub> adsorption band  
 505 (250 nm), a new band appeared in the region of 293 nm, whose intensity increased with rising  
 506 amount of H<sub>2</sub>O<sub>2</sub>. According to Van Laar et al. [100] and Nardello et al. [71], as the H<sub>2</sub>O<sub>2</sub>/Mo<sup>6+</sup> ratio  
 507 increases, different oxoperoxo-molybdenum species are formed, and the appearance of a band in  
 508 the region of 293 nm can be attributed to the formation of a di-peroxomolybdate species  
 509 (MoO<sub>2</sub>(O<sub>2</sub>)<sub>2</sub><sup>2-</sup>), with a slightly yellowish color (Scheme 1, species 2). After successive addition of H<sub>2</sub>O<sub>2</sub>,  
 510 this species was converted into tetra-peroxomolybdate (Mo(O<sub>2</sub>)<sub>4</sub><sup>2-</sup>), with red-brown color, and a new  
 511 band in the region of 450 nm was observed (Scheme 1, species 4) [71,101]. Van Laar [100] also  
 512 observed that the simultaneous presence of the di- and tetra-peroxomolybdate species in solution  
 513 indicated that the tri-peroxomolybdate species may also be present as an intermediate species, as  
 514 indicated by a shoulder in the region of 330 nm (Scheme 1 species 3). This band at 330 nm  
 515 contributes to the total broad absorption band (Fig. 7A). According to these authors [100,102], when  
 516 the Mo<sup>6+</sup> ions interact with H<sub>2</sub>O<sub>2</sub>, the formed species is responsible for catalyzing the H<sub>2</sub>O<sub>2</sub>  
 517 disproportionation and the different peroxo-species formed are intermediate species in this process,  
 518 explaining the intense oxygen evolution observed. Interestingly, all peroxomolybdate species  
 519 displayed the same negative charge (2-). Consequently, conversion of molybdate loaded on the LDH  
 520 surface into peroxomolybdate did not affect the overall neutrality of the LDH structure, which  
 521 remained stable under the catalytic reaction conditions.  
 522



523  
 524 **Scheme 1.** Representative speciation scheme of peroxomolybdate with increasing H<sub>2</sub>O<sub>2</sub>/Mo molar  
 525 ratio [101].  
 526

527 The electronic spectrum observed (Fig.7B) for the Na<sub>2</sub>WO<sub>4</sub> solution had a band in the region  
 528 of 250 nm, and after the successive addition of hydrogen peroxide solution, a shoulder around 323

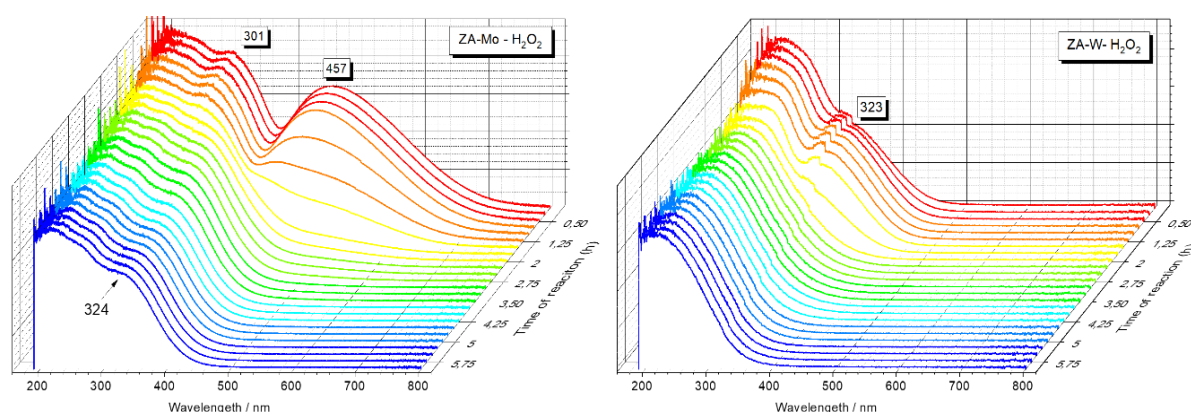
529 nm was observed, whose intensity increased with rising amount of H<sub>2</sub>O<sub>2</sub>. There was no evidence of  
530 the formation of any other band, as was observed in the case of the Na<sub>2</sub>MoO<sub>4</sub> solution.

531 Sels et al. [103] observed that the interaction of H<sub>2</sub>O<sub>2</sub> with tungstate ions led to the direct  
532 formation of tetra-peroxotungstate as a single species, identified by an absorption band around 330  
533 nm. Like the peroxomolybdate, this species is also responsible for catalyzing the disproportionation  
534 of H<sub>2</sub>O<sub>2</sub>, but with slower H<sub>2</sub>O<sub>2</sub> disproportionation kinetics. Indeed, as already discussed for Fig. Si-2,  
535 H<sub>2</sub>O<sub>2</sub> was still available after 3 hours of reaction catalyzed by ZA-W, increasing the efficiency of  
536 cyclohexane oxidation.

537 Therefore, these results confirm that in the presence of H<sub>2</sub>O<sub>2</sub>, molybdate and tungstate ions  
538 led to the formation of peroxy-species, which were responsible for catalyzing the disproportionation  
539 reaction of H<sub>2</sub>O<sub>2</sub> from the reaction medium, with disproportionate kinetics depending on the nature  
540 of the metal ions (W<sup>6+</sup> or Mo<sup>6+</sup>).

541 To gain insight about the oxidation mechanism, the intermediate molybdate (ZA-Mo) and  
542 tungstate (ZA-W) catalytic species formation were characterized by *in situ* UV-Vis analysis in the  
543 presence of H<sub>2</sub>O<sub>2</sub> (35%) during a period of 6 hours for ZA-Mo and 6.1 hours for ZA-W. (Fig. 8).

544



545

546

547 **Figure 8.** UV-Vis spectra recorded of the supernatant of the catalytic oxidation reaction of  
548 cyclohexane with hydrogen peroxide catalyzed by ZA-Mo and ZA-W at different times (Z) using the  
549 same reaction conditions described in Table 3.

550

551

552 For the reaction catalyzed by ZA-Mo, peroxomolybdate species appeared at the beginning of  
553 the reaction, when H<sub>2</sub>O<sub>2</sub> was added. The dispersion immediately became orange. The UV-Vis spectra  
554 showed two absorption bands, at 301 nm and 457 nm, indicating the simultaneous formation of  
555 diperoxo-molybdate (MoO<sub>2</sub>(O<sub>2</sub>)<sub>2</sub><sup>2-</sup>) (band at 301 nm) and tetra-peroxomolybdate (Mo(O<sub>2</sub>)<sub>4</sub><sup>2-</sup>) (band at

556 457 nm), similar to that observed for sodium molybdate solutions mixed with H<sub>2</sub>O<sub>2</sub> (Fig. 7B). The  
557 band at 457 nm disappeared after 2 h and a new band at 324 nm (as a shoulder) was observed and  
558 remained for another 4 hours of monitoring (6 hours all told), suggesting the formation of the tri-  
559 peroxomolybdate species resulting from the decomposition of tetra-peroxomolybdate species. In  
560 fact, because this shoulder at 324 nm was part of a larger and more extended band, probably there  
561 was a mixture of species such as molybdates and other peroxomolybdates.

562 For ZA-W (Fig. 8), only the presence of a large shoulder at 323 nm was observed at the initial  
563 moments of the reaction, which can be attributed to the formation of mixtures of species including  
564 di- and tetra-peroxotungstate anions. After about 2 h of reaction time, this shoulder disappeared,  
565 but the spectral profile remained unchanged up to 6 h, suggesting the presence of a mixture of  
566 species, including the tungstate anion WO<sub>4</sub><sup>2-</sup> initially present in the solid.

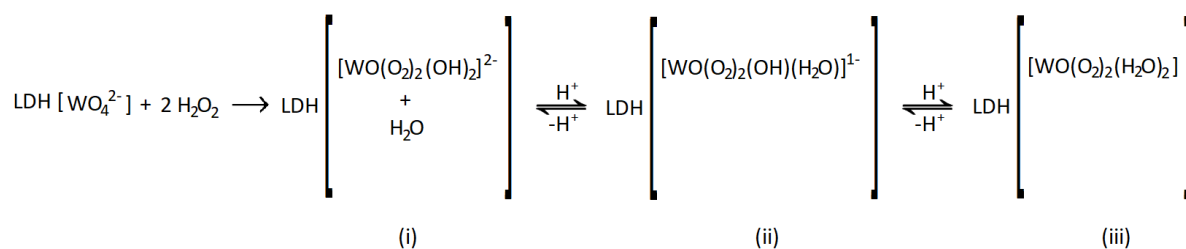
567 Based on these *in situ* data, we can suggest that the presence of H<sub>2</sub>O<sub>2</sub> caused the formation  
568 of multiple peroxo species, including di-, tri-, and tetra-peroxomolybdate or peroxotungstate  
569 catalytic species, attached at the LDH layers' surface. Many studies have reported that the di-peroxo  
570 species (MoO<sub>2</sub>(O<sub>2</sub>)<sub>2</sub><sup>2-</sup>) is the most active species in catalytic reactions combining hydrogen peroxide  
571 and either molybdate or tungstate compounds, in solution or immobilized on different supports. Di-  
572 peroxometalate species (Mo or W) obtained by the reaction of hydrogen peroxide and solids  
573 resulting in the immobilization of MoO<sub>4</sub><sup>2-</sup> or WO<sub>4</sub><sup>2-</sup> species on LDHs was reported by Maciucă et al.  
574 [69,98] to be an intermediate catalytic species involved in the oxidation reaction of  
575 tetrahydrothiophene to sulfolane. Vafaezadeh et al. also reported that a diperoxo-molybdate  
576 species was observed as an intermediate catalytic species involved in the cyclohexene oxidation  
577 reaction when a tungstate species immobilized on functionalized silica was used as solid catalyst [50].

578 The tungstate and molybdate immobilization on the hydroxylated LDH layers' surface did not  
579 appear to present a limitation for the formation of intermediate active species and the catalytic  
580 oxidation. In particular, the adsorbed molybdate (ZA-Mo) caused greater disproportionation of H<sub>2</sub>O<sub>2</sub>  
581 and evolution of O<sub>2</sub>, which contributed to an unproductive decomposition of H<sub>2</sub>O<sub>2</sub> [67], hence  
582 leading to less conversion of the cyclohexane into cyclohexanone and cyclohexanol products  
583 compared to ZA-W.

584 Table 3 also shows that for the same W or Mo catalytic species, better conversion yields were  
585 observed for the ZnAl LDH immobilization matrix (Table 3, entry 3 versus 4) than for the MgAl  
586 support (entry 1 versus 2). A possible explanation is the difference of basicity of the LDH structure,  
587 with the MgAl LDH being more basic than the ZnAl LDH due to the difference of electronegativity  
588 between Mg and Zn, as shown by catalytic evaluation using aldol condensation [104–107]. The  
589 basicity of the support could then affect the speciation of the oxometallate species [68]. It has been  
590 widely reported that the peroxo catalytic active species formed by the reaction of WO<sub>4</sub><sup>2-</sup> (or MoO<sub>4</sub><sup>2-</sup>)

591 and hydrogen peroxide in catalytic oxidation reactions is strongly dependent on the acidity of the  
 592 reaction medium [6,50,67,68], as shown by Scheme 2.

593



594

595 **Scheme 2.** Schematic representation of the plausible di-peroxocatalytic species obtained by the  
 596 reaction of tungstate species immobilized on LDH solid with magnesium/aluminum (MA) or  
 597 zinc/aluminum (ZA) composition [67].

598

599 It has been reported that the species obtained (i) by the reaction of tungstate and 2 mol of  
 600 hydrogen peroxide (Scheme 2) is dependent on the acidity of the reaction medium and can be in  
 601 equilibrium with both species (ii) and (iii). Species (ii) and (iii) are reported to be more active in the  
 602 catalytic oxidation reaction [50,67]. Noyori et al. [67] also reported that species (ii) is predominant,  
 603 mainly in the pH range of 0.4 to 3.0.

604 The remarkable difference in the catalytic results observed for the solid ZA-W (Table 3, entry  
 605 4) compared to solid MA-W (Table 3, entry 2), of about 4.0 times the total yield (%) of ketone +  
 606 alcohol products, with more pronounced selectivity to ketone for the reaction catalyzed by ZA-W  
 607 (63% selectivity to ketone, entry 4 compared to 48%, entry 2), suggested that the acidity of the solid  
 608 support with zinc LDH can favor more active species  $[\text{WO}(\text{O}_2)_2(\text{OH})(\text{H}_2\text{O})]^{-1}$  (Scheme 2, ii). A  
 609 qualitative evaluation of the pH of ZA-W and MA-W dispersions in acetonitrile solvent showed that  
 610 the pH values were more acid for the ZA-W suspension than for the MA-W suspension, suggesting  
 611 that pH could be the key parameter affecting the observed catalytic results.

612 Changes in the pH of the reaction medium can also explain the differences in the observed  
 613 catalytic results between reactions 7 and 8 (Table 3), where a 1.33-fold increase in the total  
 614 conversion yield (K+A) (with similar selectivity for the ketone product) from entry 7 to 8 was  
 615 observed. Indeed, the decrease in cyclohexane/  $\text{H}_2\text{O}_2$  molar ratio from 1:5 (entry 7) to 0.3:1 (entry 8)  
 616 and in catalyst mass from 50 mg (entry 7) to 15 mg (entry 8) led to a decrease of pH value to 8.0  
 617 (entry 8). This resulted in a more favorable pH condition for the stabilization of catalytically active  
 618 species  $[\text{WO}(\text{O}_2)_2(\text{OH})(\text{H}_2\text{O})]^{-1}$  (Scheme 2, ii) and  $[\text{WO}(\text{O}_2)_2(\text{H}_2\text{O})_2]$  (Scheme 2, iii).

619 Vafaezadeh et al. [50] observed that when the monoprotonated peroxotungstate species (ii)  
 620 (Scheme 2) decreased, there was a reduction in the conversion of cyclohexene to oxidation products,

621 and this fact was attributed to the increase of the reaction from 0.89 to 1.08, caused by increasing  
622 the molar ratio of cyclohexene/H<sub>2</sub>O<sub>2</sub> from 1:4 to 1:6. Unfortunately, it is difficult to determine the  
623 reaction pH in organic media under the experimental conditions used, and the apparent pH values of  
624 the reaction solutions 7 and 8 were not determined.

625 In addition, the effect of reaction time on the cyclohexane conversion yield in the reactions  
626 catalysed by ZA-W and the selectivity for the related products were studied. The effect of reaction  
627 time is reported in entries 4 to 9 (Table 3). We clearly observed that increasing the reaction time  
628 (from 3 to 23 h), regardless of the mass of catalyst used or molar ratio of cyclohexane/H<sub>2</sub>O<sub>2</sub>, caused  
629 the total yield of cyclohexane conversion into (ketone+alcohol) to increase. For the first 6 hours, the  
630 conversion yield (similar conditions, entries 4 to 7) increased nearly linearly (+ 0.41% h<sup>-1</sup>) before  
631 stabilizing at a value of about 3.8-3.9%. This general trend was confirmed under different  
632 cyclohexane/H<sub>2</sub>O<sub>2</sub> and catalyst mass conditions (entries 8 and 9). Moreover, the selectivity to the  
633 ketone product remained almost constant between 60 and 66%, independent of the various reaction  
634 conditions (reaction time, reagent composition, catalyst mass). These results suggest stability of the  
635 product over long reaction times, as reported by Jing Dai et al. [6]. Rezaei et al. [99] observed an  
636 optimum conversion time of 4 h for the oxidation reaction of cyclohexane by hydrogen peroxide to  
637 ketone and alcohol (conversion value of 6.59%) catalyzed by vanadyl pyrophosphate supported on  
638 mesoporous silica. When the reaction time was increased to 16 h, decreases of conversion yield and  
639 byproduct formation, including 1,3-cyclohexanediol, 1,4-cyclohexanedione and 4-  
640 hydroxycyclohexanone, were observed.

641 It is well known that metalloporphyrins (MP) are efficient catalysts for cyclohexane oxidation  
642 under mild experimental condition (room temperature and 30 minutes reaction time). Depending on  
643 the structure of the porphyrin ligand and the metal ions of the MP complex, using different oxidant  
644 species (H<sub>2</sub>O<sub>2</sub>, peracids, iodosylbenzene, O<sub>2</sub>, etc.), promising yields of alcohol (majority product) and  
645 ketone have been consistently observed [13–15,108–111].

646 Nan et al. reported the catalytic results of cyclohexane and other alkanes and alkenes  
647 oxidized by 30% H<sub>2</sub>O<sub>2</sub> using iron(III) porphyrin [Fe(TPFPP)X] (where X<sup>1-</sup> = axial anionic ligand of the  
648 Fe<sup>3+</sup>-complex), finding it to be a very efficient metalloporphyrin catalyst for epoxidation and  
649 hydroxylation of different organic substrates in a biomimetic model of cytochrome P-450 [112].  
650 Depending on the value of X<sup>1-</sup>, they observed very good results of alcohol and ketone. For example,  
651 the best results were alcohol yield of 30% and ketone yield of 1% (using Fe(TPFPP)NO<sub>3</sub> as catalyst  
652 (1x10<sup>-3</sup> mmol), H<sub>2</sub>O<sub>2</sub> (0.02 mmol/0.5 mL CH<sub>3</sub>CN), cyclohexane (1 mmol) in a solvent mixture of  
653 CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> (3:1), for 1 h of reaction under stirring). However, when the yields reported based on  
654 the amount of H<sub>2</sub>O<sub>2</sub> used were converted into percentage of conversion of the substrate to both  
655 products (as used in this work to describe the catalytic results of the solids ZA-W and the others – see

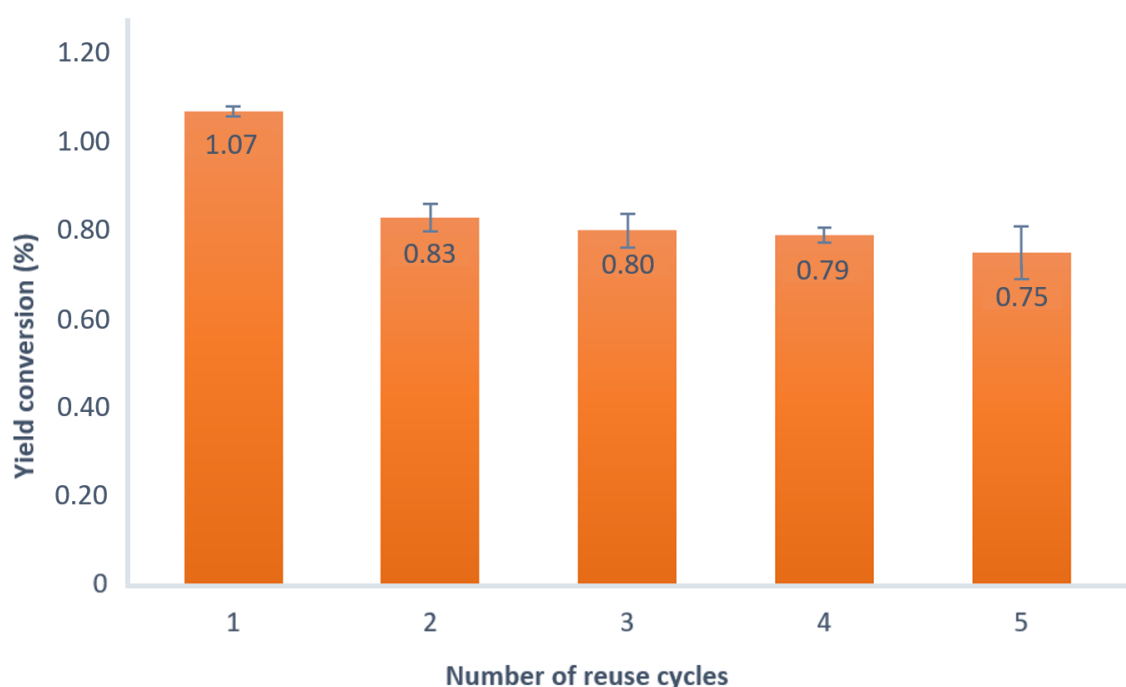


656 footnote of Table 3) the catalytic results were 0.060% conversion to alcohol and 0.002% to ketone,  
657 with total conversion yield of 0.062%, similar to the total yield observed for the catalyst MA-Mo  
658 (Table 3, entry 1). This was far from the best result of the catalyst studied here, ZA-W, which in non-  
659 optimized condition (Table 3, entry 4) presented a total yield 1.07%, about 17 times higher than the  
660 result when using iron porphyrin.

661 Despite the pronounced selectivity of the iron porphyrin to the alcohol product and the ZA-W  
662 to the ketone product, the results presented in Table 3 demonstrated that the solids studied in this  
663 work are comparable to the metalloporphyrin catalyst for the cyclohexane oxidation under the  
664 investigated experimental conditions using H<sub>2</sub>O<sub>2</sub> as oxidant.

665 Finally, catalyst recycling experiments were carried out by reusing the ZA-W, 4 times. The  
666 recycling results are shown in Table 3, entries 10 to 13 and Figure 9. The recycling conditions were  
667 the same as those in the first use of the catalyst (Table 3, entry 4). The conversion of cyclohexane to  
668 ketone+alcohol products and selectivity to ketone did present a decrease of 22% in yield between  
669 the first and second reactions, which could be attributed to the loss of outermost tungstate anions  
670 decorating the solid. However, from the third to the fifth reaction, there's less than 10% of decrease  
671 in yield, suggesting that what remains of the catalytic species is quite stable in the LDH and the solid  
672 is suitable for heterogeneous processes.

673



674

675 **Figure 9.** Cyclohexane yield conversion versus number of reuses.

676

677 **Conclusion**

678 Researchers are seeking to develop new materials able to catalyze organic synthesis  
679 according to the tenets of green chemistry, i.e., economy of atoms, reaction stages and energy; and  
680 less harm to the environment through sustainable and recyclable processes. Among the targeted  
681 reactions, oxidation of alkane is still a hot topic that is widely investigated, particularly the selective  
682 production of ketones and alcohols from alkanes using H<sub>2</sub>O<sub>2</sub>, a cheap and environmentally friendly  
683 reagent. Mono-molybdate and mono-tungstate are known for their catalytic reactivity towards the  
684 oxidation of alkanes by H<sub>2</sub>O<sub>2</sub> in homogeneous media.

685 This study highlights the potential of layered double hydroxides as supports for mono-  
686 molybdate and mono-tungstate for the catalytic oxidation of cyclohexane to cyclohexanone and  
687 cyclohexanol. Due to their unique anion exchange properties, we were able to immobilize high  
688 amounts of mono-molybdate (MoO<sub>4</sub><sup>2-</sup>) and mono-tungstate (WO<sub>4</sub><sup>2-</sup>) on the LDH matrices ZnAl (resp.  
689 1.13x10<sup>-3</sup> and 9.45x10<sup>-4</sup> mol g<sup>-1</sup>) and MgAl HDL (resp. 9.65x10<sup>-4</sup> and 1.10x10<sup>-3</sup> mol g<sup>-1</sup>). During the  
690 intercalation step, the LDH structure was preserved, with the oxometallates being mainly distributed  
691 on the platelet surfaces.

692 The prepared HDL/oxometallate showed outstanding catalytic activity towards the oxidation  
693 of cyclohexane by H<sub>2</sub>O<sub>2</sub>, leading to the conversion to cyclohexanone and cyclohexanol. The maximum  
694 conversion yield obtained reached 3.94% (ZA-W). Improvement was possible by increasing the  
695 catalytic conditions (quantity of catalysts, temperature). The selectivity towards ketone reached a  
696 value of 66% (ZA-W). Probably due to a lower basicity of the ZA LDH and a moderate reactivity of  
697 WO<sub>4</sub><sup>2-</sup> compared to the MoO<sub>4</sub><sup>2-</sup> species, the ZA-W supported catalyst was the most efficient catalyst  
698 for the conversion of cyclohexane into related ketone and alcohol.

699 Peroxomolybdate and peroxotungstate intermediates were identified by UV-Vis spectroscopy,  
700 demonstrating that their immobilization on LDH supports favored the formation of these reactive  
701 catalytic species. Nevertheless, the high reactivity of MoO<sub>4</sub><sup>2-</sup> caused the disproportionation of H<sub>2</sub>O<sub>2</sub>  
702 and the abundant evolution of molecular oxygen, which inactivated the oxidant and limited the  
703 oxidation of cyclohexane. In the case of the ZA-W phases, the most stable diperoxotungstate species  
704 was an efficient catalyst. In addition, the recycling of the ZA-W catalyst over 5 cycles showed  
705 maintenance of the conversion rate up to 75%.

706 In conclusion, the solid catalyst developed in this work based on LDH support provides  
707 structural and thermal stability and they are recyclable. The solid catalysts are also very versatile, as  
708 the tungstate and molybdate ions are known to be applied in a range of different reactions. Last but  
709 not the least, the material developed in this work achieved good yield in mild reaction conditions,  
710 not needing excessive heating or elevated pressures.

711

712

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