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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
4 Carolina Machado Terzi^{1,2}, Everton Henrique dos Santos^{1,3}, Charles Carvalho^{1,3}, Vanessa Prevot³,
5 Fernando Wypych², Claude Forano^{3*}, Shirley Nakagaki^{1*}

6
7 ¹Laboratório de Bioinorgânica e Catálise, ²Laboratório de Química de Materiais Avançados -
8 ^{1,2}Departamento de Química, Centro Politécnico, Universidade Federal do Paraná (UFPR) 81531990,
9 Curitiba/PR, Brazil, ³Université Clermont Auvergne, CNRS, INP Clermont, ICCF, F-63000 Clermont-
10 Ferrand, France

11
12 *Corresponding authors: shirleyn@ufpr and claude.forano@uca.fr

13
14 **Abstract**

15 Catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone with H₂O₂ 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 M²⁺ present in the composition of the LDH as well as to the anions. ZnAl-modified
22 with WO₄ was more active and more selective for ketone than the MgAl-modified WO₄ 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, e-
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 Cu^{2+} , Fe^{3+} ,
47 Mn^{3+} , and 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 WO_3 and tungstate-based catalysts have been found
59 active for cyclohexene oxidation [41,46–50]. Sato et al. demonstrated the efficiency of Na_2WO_4 as a
60 catalyst to convert cyclohexene to AA using 30% H_2O_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 H_2O_2 [50]. Mai et al. [41] prepared a photothermal solid
63 catalyst by loading Au nanoparticles (Au NPs) into WO_3 nanosheets (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 O₂ 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 Mo⁵⁺ species in the POM composition. Using MoO₃-
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% H₂O₂. They attributed this result to the activity of
77 tetrahedral MoO₄ 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 [PW₁₂O₄₀]³⁻ catalytic species, the use of [PMo₁₂O₄₀]³⁻-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 ((NH₄)₆Mo₇O₂₄), 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 M²⁺:M³⁺ 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].

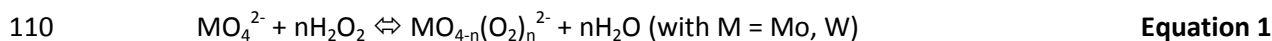
97 The catalytic properties of LDHs intercalated with tungstate and molybdate have been
98 explored for various organic reactions such as olefin epoxidation [58,59], transesterification [60],
99 H₂O₂-activated oxidation [61–64], alcohol dehydration [65] and oximation reaction [66]. Most of the
100 Mo and W catalytic oxo species that have been immobilized in LDH matrices for oxidation reactions
101 are tetrahedral anions (MoO₄²⁻ or WO₄²⁻).

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 H₂O₂ 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 H₂O₂ lead to the formation of active peroxy species
108 MO₂(OO)₂²⁻ according to **Equation 1**:

109



111

112 In appropriate pH conditions, tungstate or molybdate [71] can also promote the H₂O₂
113 disproportionation into a ¹O₂ singlet (**Equation 2**):

114



116

117 LDHs modified with W and Mo polyoxometallates (Mo₇O₂₄⁶⁻, W₇O₂₄⁶⁻) 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 CO₃²⁻ > SO₄²⁻ > OH⁻ > F⁻ > Cl⁻ > Br⁻ > NO₃⁻ > I⁻ [57].

124 In view of the known order of ionic affinity, LDHs have a higher affinity for carbonate ions
125 (CO₃²⁻) 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 (CO₃²⁻) exchange
133 [73]. Based on this method, when the reaction medium is acidified, there is an increase in the
134 amount of H⁺ 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 CO₂ which can finally be removed from the LDH.

137 Consequently, chloride Cl⁻ 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^{2+} or Mg^{2+}), exchanged with anionic molybdate or tungstate species, and compared their catalytic
143 performances in the cyclohexane oxidation reaction with H_2O_2 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 $MgCl_2$ (for MA) or $ZnCl_2$ (for ZA) and 0.25 mol of $AlCl_3 \cdot 9H_2O$,
153 with $M^{2+}:Al^{3+}$ molar ratio of 3:1, according to a previously reported method [75]. The addition of the
154 solution was performed under dynamic N_2 flow, constant magnetic stirring at room temperature and
155 constant pH of 10.5, maintained by the addition of 2 mol L^{-1} NaOH solution for 6 hours. After the
156 addition was completed, the dispersion was aged at 80 °C for 14 hours under dynamic N_2 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_2 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^{-1} NaCl solution and 100 mL of 0.1 mol L^{-1} 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 $Na_2WO_4 \cdot 2H_2O$ or
172 $Na_2MoO_4 \cdot 2H_2O$ [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_2 and the pH was adjusted to 9.5 by the addition of 0.1

174 mol L⁻¹ NaOH solution. The dispersion was magnetically stirred at room temperature under N₂ flow
175 and then a decarbonated water solution of Na₂WO₄·2H₂O (100 mL, 0.1 mol L⁻¹) was slowly added
176 during 3 hours.

177 To complete the reaction, the mixture was maintained at 80 °C under dynamic N₂ 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 Na₂MoO₄·2H₂O decarbonated water solution (0.1 mol L⁻¹).

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:H₂O₂ 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% H₂O₂ 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 H₂O₂) 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 H₂O₂ 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 cm^{-1} and accumulation of 64 scans.

210 The Raman spectra were recorded from 150 to 1500 cm^{-1} at room temperature using a
211 confocal micro-Raman spectrometer (Jobin Yvon T64000) with an excitation wavelength of 514.5 nm
212 (argon-ion laser-line). Spectra were acquired with resolution of 1 cm^{-1} with a charge coupled device
213 (CCD) multichannel detector cooled by liquid 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 nm
215 He-Ne laser with non-invasive back scattering (NIBS) configuration (173°). 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 kV and 40 mA ($\text{Cu K}\alpha$ radiation $\lambda = 1.5418\text{ \AA}$) with Bragg-Brentano θ - 2θ 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 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 KV . The samples were deposited on
227 aluminum stubs and the EDS spectra were collected with an SDD detector with 80 mm^2 in the range
228 of 0 to 10 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 nm range.

232 The textural properties were determined with a NOVA 1000 analyzer (Quantachrome) after
233 degasifying the samples under vacuum for 6 hours (ZnAl samples were maintained at $150\text{ }^\circ\text{C}$ during
234 this period and those of MgAl at $90\text{ }^\circ\text{C}$). The adsorption/desorption isotherms for 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 .

237

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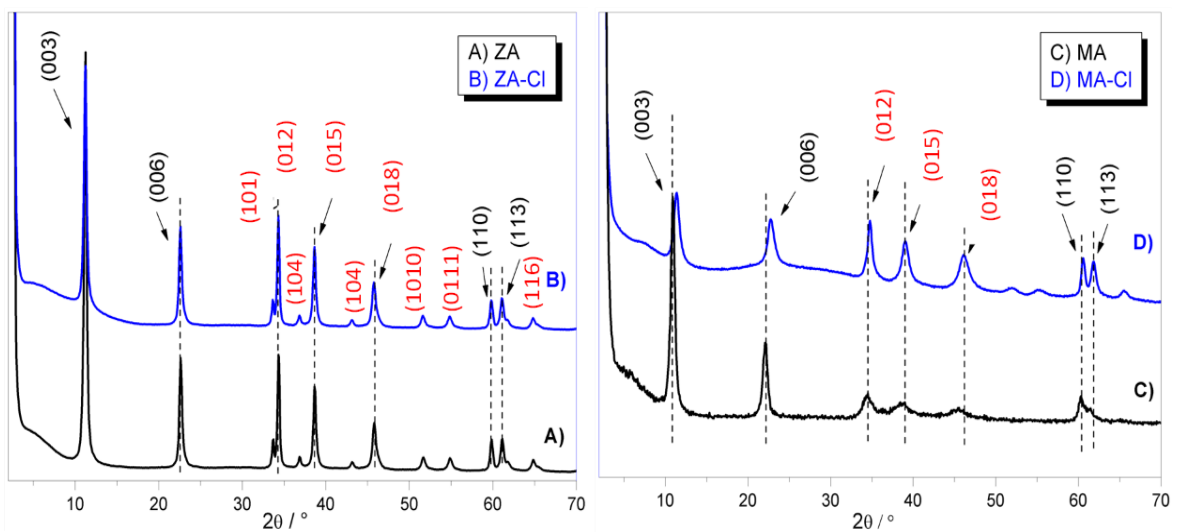
239 **Results and discussion**

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 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

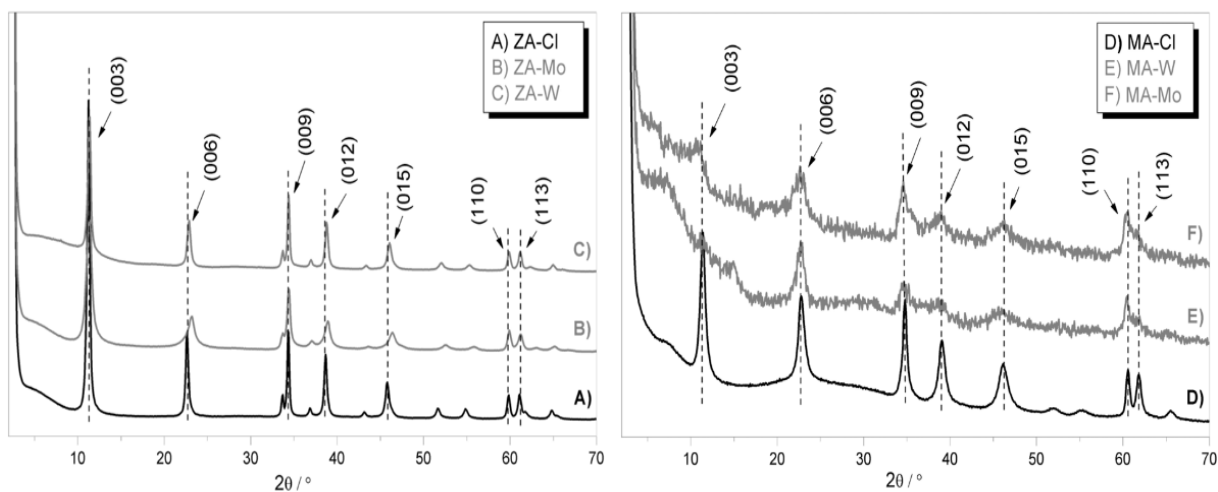
266 drastic N₂ gas flow, already prevented the formation of undesired LDH-CO₃ as the major
267 phase, and further decarbonation process (step 2) did not improve much CO₃²⁻
268 decontamination. Based on XRD data and FTIR, it is difficult to infer with certainty whether part of
269 carbonate anions were co-intercalated with Cl⁻ 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 CO₃²⁻
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 MoO₄²⁻ and WO₄²⁻ 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 MoO₄²⁻ and WO₄²⁻ 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, MoO₄²⁻
291 and WO₄²⁻ 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 SO₄²⁻ 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-MoO₄²⁻ and LDH-WO₄²⁻ 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 Zn₃Y- WO₄²⁻ and Zn₃Y-
297 MoO₄²⁻ respectively. Similar basal spacing was obtained for Zn₂Cr-WO₄ (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 9.65×10^{-4} and $1.10 \times 10^{-3} \text{ mol g}^{-1}$.

326

327 **Table 1.** M^{2+}/M^{3+} /anion atomic ratio calculated based on EDS results.

LDH	Zn^{2+}/Al^{3+} or Mg^{2+}/Al^{3+}	MoO_4^{2-} or WO_4^{2-}/Al^{3+} (% of AEC) [#]	Cl^-/Al^{3+}	CO_3^{2-}/Al^{3+} *	Σ anions/ Al^{3+}	Calculated loading values ($\text{mol} \cdot \text{g}^{-1}$)
ZA-Cl	1.86	0.00	0.64	0.18	1	-
ZA-Mo	1.93	0.34(68%)	0.00	0.16	1	1.13×10^{-3}
ZA-W	1.91	0.27 (54%)	0.16	0.15	1	9.45×10^{-4}
MA-Cl	2.84	0.00	0.78	0.11	1	-
MA-Mo	2.87	0.28 (56%)	0.00	0.22	1	9.65×10^{-4}
MA-W	2.88	0.12 (24%)	0.00	0.38	1	1.10×10^{-3}

328 * CO_3^{2-} was obtained from calculation based on electroneutrality of the overall LDH structure. [#]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_3^{2-}
 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.

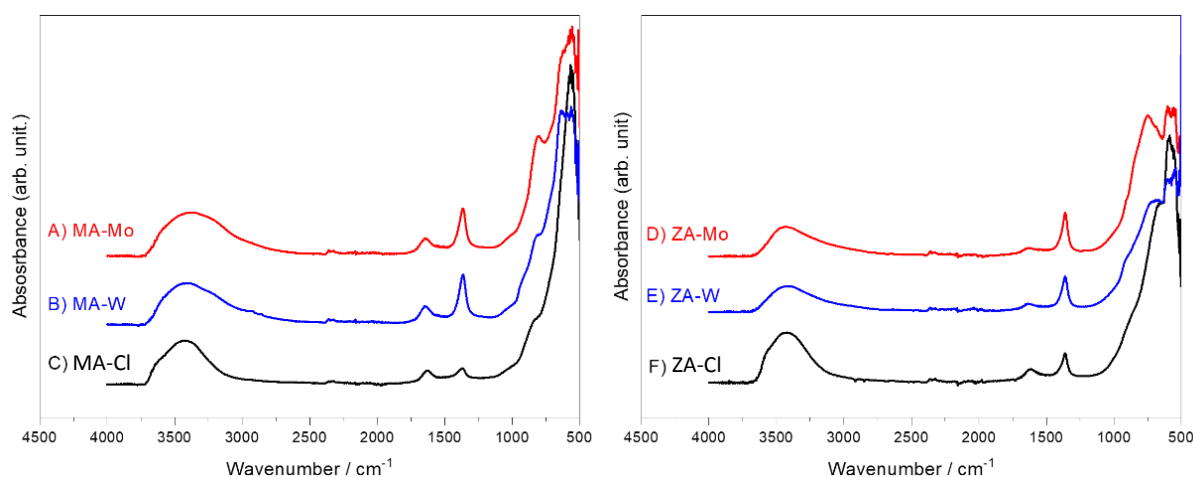
339 FTIR and Raman spectra confirmed that both oxometallate MO_4^{2-} (M= Mo, W) and carbonate
 340 CO_3^{2-} anions coexist in the ZA and MA LDH structures. The ν_3 asymmetric and ν_1 symmetric stretching
 341 vibration modes at around 1365 and 1060 cm^{-1} , respectively, of the intercalated carbonate are
 342 observed in all FTIR spectra (Fig. 3) [84]. The intensity of these bands slightly increased after
 343 oxometallate exchange. The ν_1 mode at 1065 cm^{-1} 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^{-1} for MA species [86,87] and at 660 and 591 cm^{-1} for ZA species
 349 [88,89]. Lattice vibrations (O-M-O and MO_6 vibrations) appeared as two bands in the Raman spectra,
 350 at 489 and 548 cm^{-1} for ZnAl LDH and 471 and 553 for cm^{-1} MgAl LDH.

351 MoO_4^{2-} and WO_4^{2-} containing LDH displayed typical oxometallate tetrahedral vibration
352 modes. For the molybdate modified LDHs, ν_3 asymmetric Mo-O bond stretching modes were
353 observed at 806 and 831 cm^{-1} respectively for MA-Mo and ZA-Mo, while the ν_1 Mo-O symmetric
354 stretching band was only visible for ZA-Mo. ν_4 asymmetric bending modes, expected around 550 and
355 510 cm^{-1} , were superimposed with the LDH lattice vibrations [5,90–92].

356 MA-W and ZA-W showed typical bands related to ν_1 symmetric W-O stretching modes at 924
357 (MA-W) and 914 cm^{-1} (ZA-W) [92], and the W-O ν_3 stretching modes at 630 cm^{-1} of MA-W, while at
358 738 and 674 cm^{-1} they referred to ZA-W. The bands attributed to ν_4 asymmetric bending modes are
359 expected under 425 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.

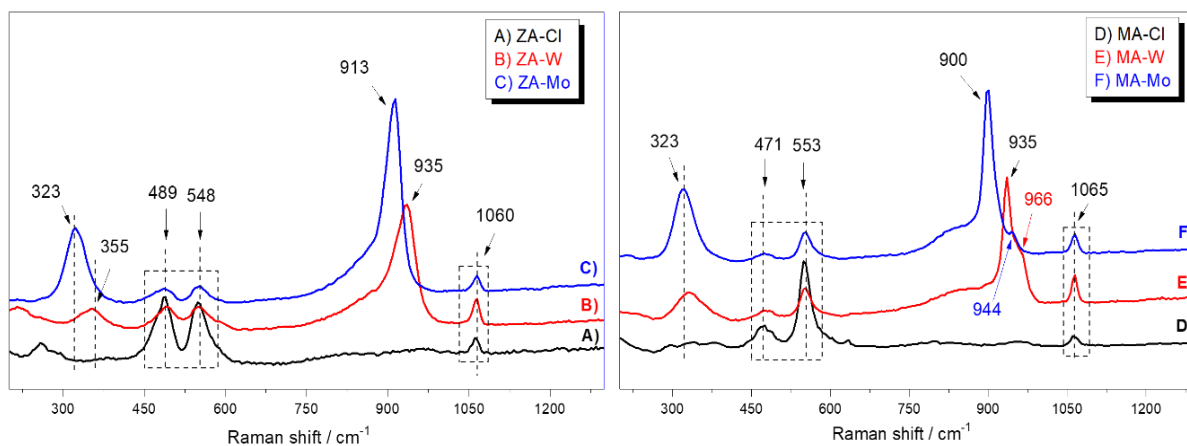
365

366 For tetrahedral (Td) 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- MoO_4 (Fig. 4C, F) showed an intense band in the region
368 of 900-913 cm^{-1} (900 and 913 cm^{-1} for MA-Mo and ZA-Mo respectively). We attributed this band to
369 the ν_1 symmetric stretching mode of Td MoO_4 . Furthermore, there was a lower intensity band in the
370 region of 323 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 cm^{-1}) [94]. In the MA-Mo
372 spectrum, a shoulder band appeared at 944 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

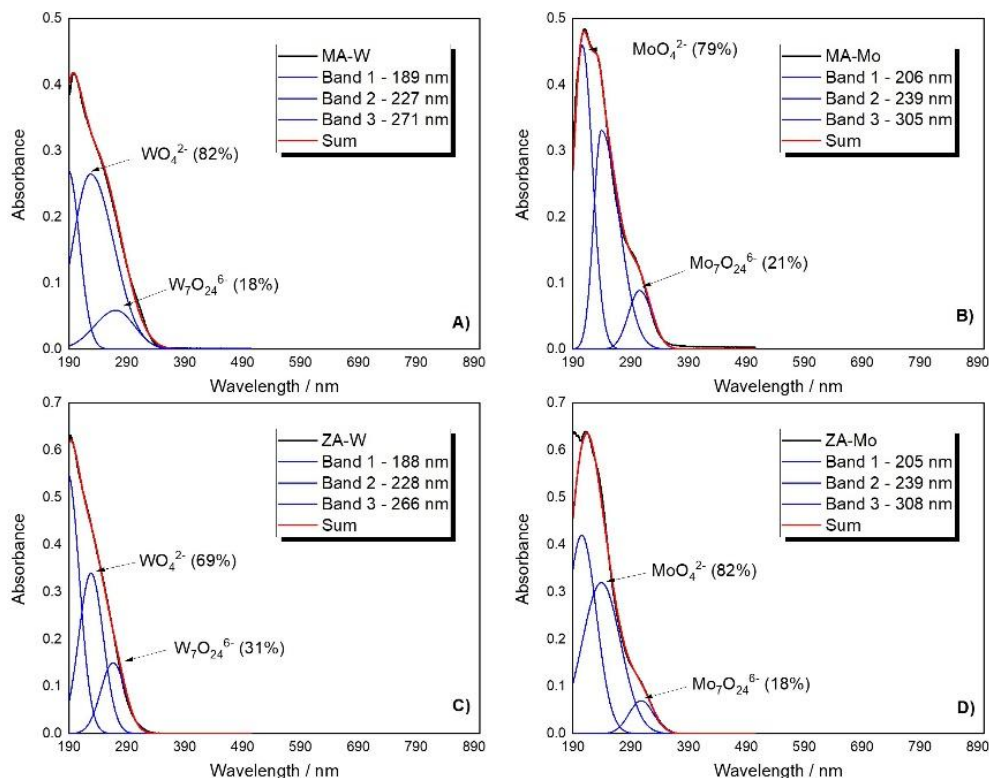
376 The Raman spectra of WO_4^{2-} containing LDH (Fig. 4B for ZA-W and Fig. 4E for MA-W) were
very similar to those of LDH- MoO_4^{2-} , with ν_1 and ν_3 modes appearing at 935 cm^{-1} and 355 cm^{-1} . The

377 broad shoulder at 830 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 WO_4^{2-} attached to the LDH
 379 surface [96]. Such broad bands were also observed for MoO_4 loaded samples. Like the bands of the
 380 WO_4^{2-} anions, there was also a shoulder in the region of 966 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 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 (WO_4^{2-}), heptatungstate ($\text{W}_7\text{O}_{24}^{6-}$), molybdate (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 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
	λ_{max} (nm)	λ_{max} (nm)	Area (%)	λ_{max} (nm)	Area (%)	
MA-W	189	227	82	271	18	1.10×10^{-3}
MA-Mo	206	239	79	305	21	9.65×10^{-4}
ZA-W	188	228	69	266	31	9.45×10^{-4}
ZA-Mo	205	239	82	308	18	1.13×10^{-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 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, Mo^{6+} and 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 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.

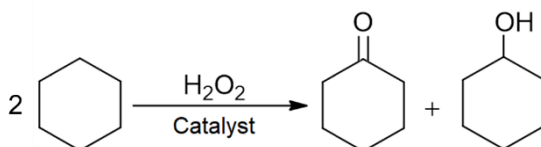
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428

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 H₂O₂ in the catalytic oxidation reaction¹.

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

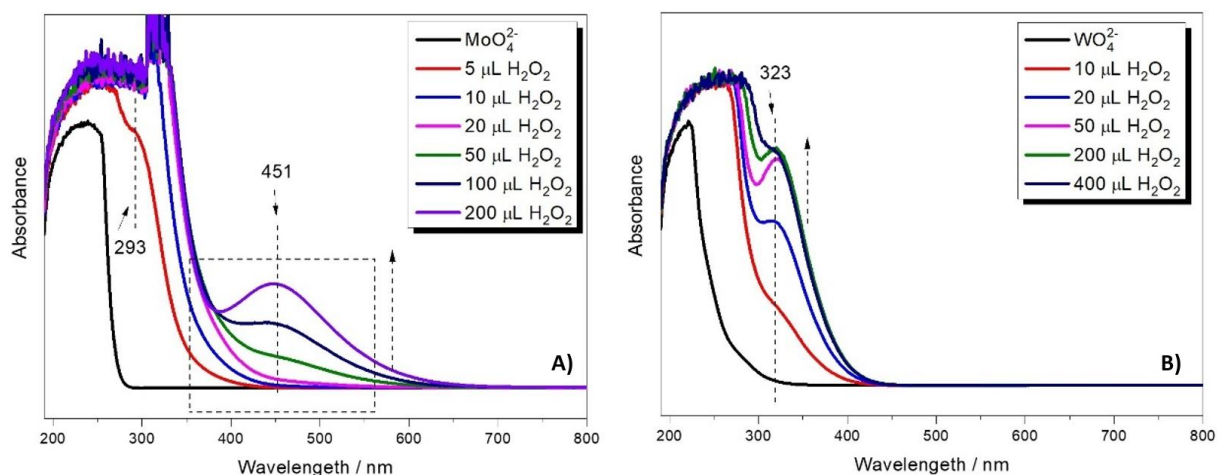
471 ¹General catalytic oxidation reaction conditions: dilute hydrogen peroxide (aqueous solution, 35%), at 40 °C, in the presence of acetonitrile as the solvent, with H₂O₂/substrate molar ratio =
472 5:1. Conversion percentage values based on the initial cyclohexane quantity. ² Total yield of cyclohexane conversion to K+A = [mols of cyclohexane reacted]/[initial mols of cyclohexane
473 used]x 100 and ³ 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%. ⁴The mol quantity of all species was calculated based on the loading values (Table 2) and the deconvolution percentage data (Fig. 5). ⁵The reuse
475 experiments were performed in reaction conditions similar to those used for the reaction entry 4.

477 Monitoring of H₂O₂ 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 H₂O₂ (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 H₂O₂ 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 H₂O₂ 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 H₂O₂ was still present to promote the conversion
485 of cyclohexane to its oxidation products. However, when using ZA-Mo as catalyst, H₂O₂ was fully
486 consumed after 1.5 hours (Fig. SI-2C) and the cyclohexane conversion stopped. H₂O₂ 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 H₂O₂ in the medium and to the
492 interaction between the oxidant H₂O₂ and the anionic Mo species immobilized in LDH.

493 To better identify the molybdenum and tungsten species resulting from the presence of H₂O₂
494 in the medium, UV-Vis spectra of Na₂MoO₄ or Na₂WO₄ aqueous solutions (0.1 mol L⁻¹) were recorded
495 at increasing additions of H₂O₂ amounts. The pH of these solutions was previously adjusted to 8.0
496 using a 0.1 mol L⁻¹ NaOH solution (Figure 7).

497



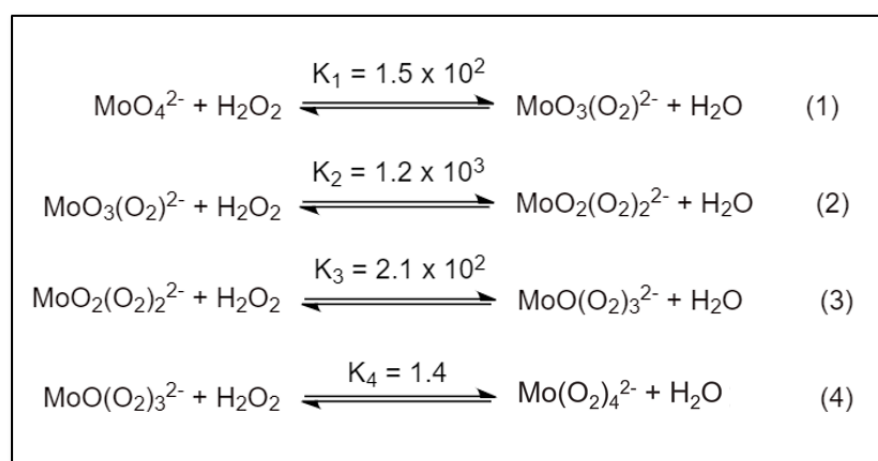
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499

500 **Figure 7.** UV-Vis spectra of aqueous solutions of A) Na₂MoO₄ and B) Na₂WO₄ with progressive
501 addition of 35% H₂O₂ solution.

502

503 For the aqueous solution of Na₂MoO₄ (Fig. 7B), we observed that before the addition of H₂O₂
 504 the solution was colorless. As the amount of H₂O₂ increased, along with the H₂O₂ adsorption band
 505 (250 nm), a new band appeared in the region of 293 nm, whose intensity increased with rising
 506 amount of H₂O₂. According to Van Laar et al. [100] and Nardello et al. [71], as the H₂O₂/Mo⁶⁺ 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 (MoO₂(O₂)₂²⁻), with a slightly yellowish color (Scheme 1, species 2). After successive addition of H₂O₂,
 510 this species was converted into tetra-peroxomolybdate (Mo(O₂)₄²⁻), 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 Mo⁶⁺ ions interact with H₂O₂, the formed species is responsible for catalyzing the H₂O₂
 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 H₂O₂/Mo molar
 525 ratio [101].
 526

527 The electronic spectrum observed (Fig.7B) for the Na₂WO₄ solution had a band in the region
 528 of 250 nm, and after the successive addition of hydrogen peroxide solution, a shoulder around 323

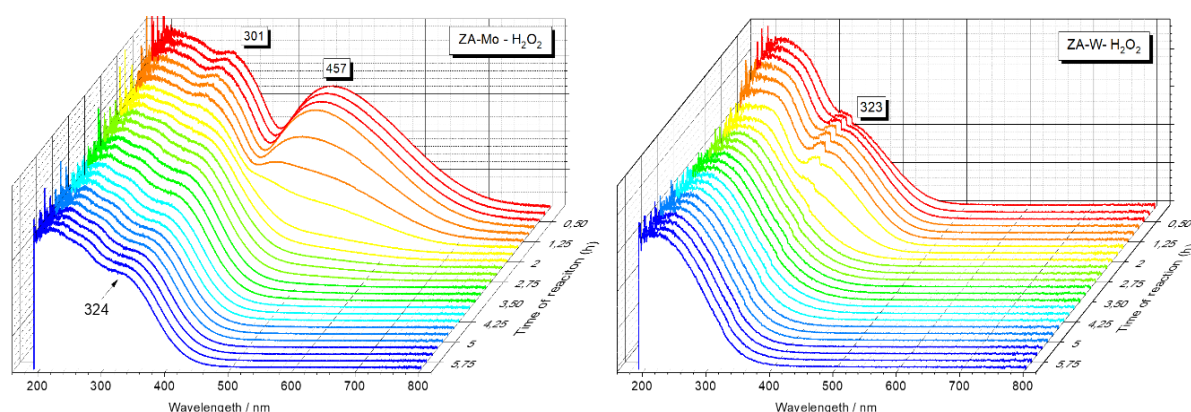
529 nm was observed, whose intensity increased with rising amount of H₂O₂. There was no evidence of
530 the formation of any other band, as was observed in the case of the Na₂MoO₄ solution.

531 Sels et al. [103] observed that the interaction of H₂O₂ 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 H₂O₂, but with slower H₂O₂ disproportionation kinetics. Indeed, as already discussed for Fig. Si-2,
535 H₂O₂ 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 H₂O₂, molybdate and tungstate ions
538 led to the formation of peroxy-species, which were responsible for catalyzing the disproportionation
539 reaction of H₂O₂ from the reaction medium, with disproportionate kinetics depending on the nature
540 of the metal ions (W⁶⁺ or Mo⁶⁺).

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 H₂O₂ (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 H₂O₂ 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 (MoO₂(O₂)₂²⁻) (band at 301 nm) and tetra-peroxomolybdate (Mo(O₂)₄²⁻) (band at

556 457 nm), similar to that observed for sodium molybdate solutions mixed with H₂O₂ (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 WO₄²⁻ initially present in the solid.

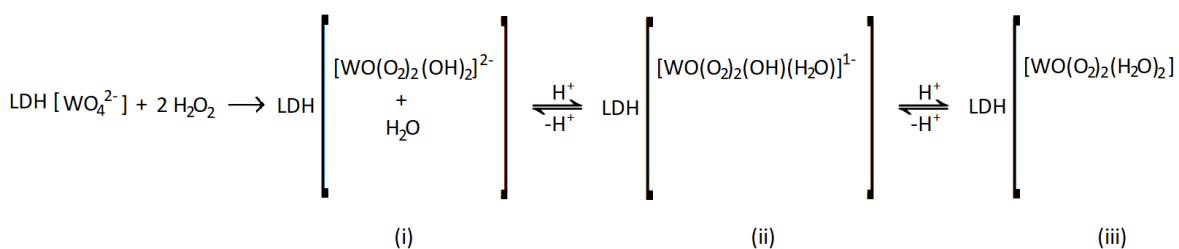
567 Based on these *in situ* data, we can suggest that the presence of H₂O₂ caused the formation
568 of multiple peroxo species, including di-, tri-, and tetra-peroxomolybdate or peroxotungstate
569 catalytic species, attached at the LDH layers' surface. Many studies have reported that the di-peroxo
570 species (MoO₂(O₂)₂²⁻) 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 MoO₄²⁻ or WO₄²⁻ 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 H₂O₂
581 and evolution of O₂, which contributed to an unproductive decomposition of H₂O₂ [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 WO₄²⁻ (or MoO₄²⁻)

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/ H_2O_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/H₂O₂ 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/H₂O₂, 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⁻¹) before
631 stabilizing at a value of about 3.8-3.9%. This general trend was confirmed under different
632 cyclohexane/H₂O₂ 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 (H₂O₂, peracids, iodosylbenzene, O₂, etc.), promising yields of alcohol (majority product) and
645 ketone have been consistently observed [13–15,108–111].

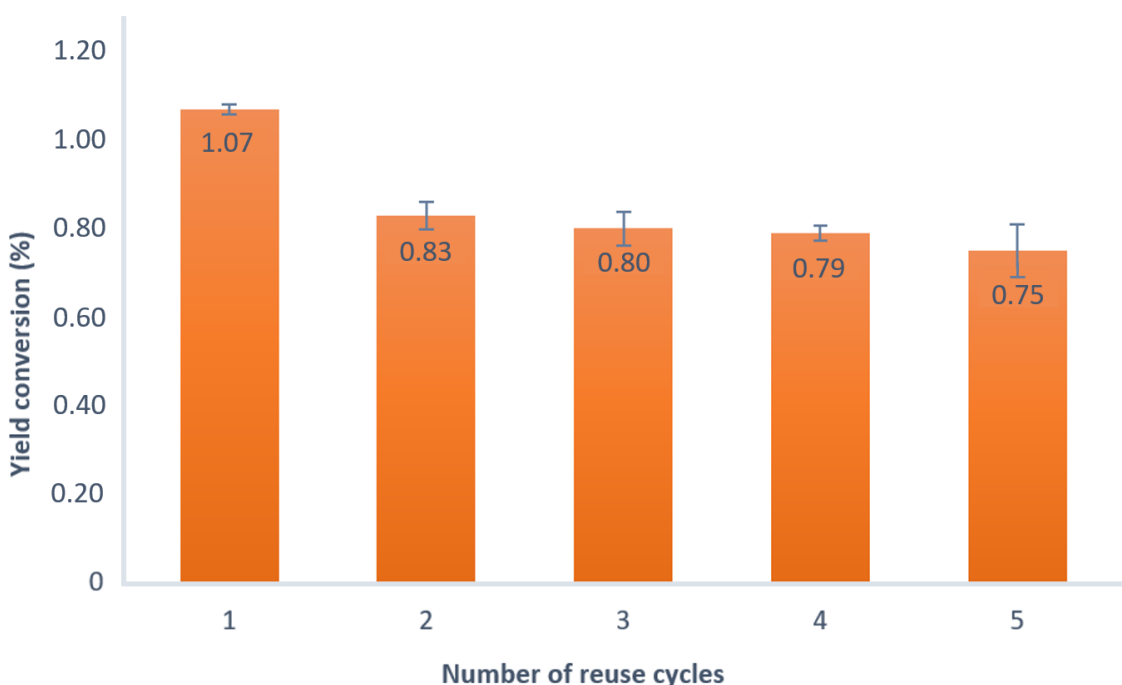
646 Nan et al. reported the catalytic results of cyclohexane and other alkanes and alkenes
647 oxidized by 30% H₂O₂ using iron(III) porphyrin [Fe(TPFPP)X] (where X¹⁻ = axial anionic ligand of the
648 Fe³⁺-complex), finding it to be a very efficient metalloporphyrin catalyst for epoxidation and
649 hydroxylation of different organic substrates in a biomimetic model of cytochrome P-450 [112].
650 Depending on the value of X¹⁻, 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)NO₃ as catalyst
652 (1x10⁻³ mmol), H₂O₂ (0.02 mmol/0.5 mL CH₃CN), cyclohexane (1 mmol) in a solvent mixture of
653 CH₃CN/CH₂Cl₂ (3:1), for 1 h of reaction under stirring). However, when the yields reported based on
654 the amount of H₂O₂ 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 H₂O₂ 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 H₂O₂, 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 H₂O₂ 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 (MoO₄²⁻) and mono-tungstate (WO₄²⁻) on the LDH matrices ZnAl (resp.
689 1.13x10⁻³ and 9.45x10⁻⁴ mol g⁻¹) and MgAl HDL (resp. 9.65x10⁻⁴ and 1.10x10⁻³ mol g⁻¹). 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 H₂O₂, 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 WO₄²⁻ compared to the MoO₄²⁻ 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 MoO₄²⁻ caused the disproportionation of H₂O₂
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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720 **References**

- 721 [1] J.M. Thomas, R. Raja, G. Sankar, R.G. Bell, Molecular-sieve catalysts for the selective oxidation
722 of linear alkanes by molecular oxygen, *Nature*. 398 (1999) 227–230.
723 <https://doi.org/10.1038/18417>.
- 724 [2] M. Bordeaux, A. Galarneau, J. Drone, Catalytic, Mild, and Selective Oxyfunctionalization of
725 Linear Alkanes: Current Challenges, *Angew. Chemie Int. Ed.* 51 (2012) 10712–10723.
726 <https://doi.org/10.1002/anie.201203280>.
- 727 [3] K.C. Hwang, A. Sagadevan, One-pot room-temperature conversion of cyclohexane to adipic
728 acid by ozone and UV light, *Science*. 346 (2014) 1495–1498.
729 <https://doi.org/10.1126/science.1259684>.
- 730 [4] Merchant Research and Consulting, Adipic Acid (ADPA), 2018 World Market Outlook and
731 Forecast up to 2027, Birmingham, UK, 2018.
- 732 [5] J. Luo, Y. Huang, B. Ding, P. Wang, X. Geng, J. Zhang, Y. Wei, Single-Atom Mn Active Site in a
733 Triol-Stabilized β -Anderson Manganohexamolybdate for Enhanced Catalytic Activity towards
734 Adipic Acid Production, *Catalysts*. 8 (2018) 121. <https://doi.org/10.3390/catal8030121>.
- 735 [6] J. Dai, W. Zhong, W. Yi, M. Liu, L. Mao, Q. Xu, D. Yin, Bifunctional H₂WO₄/TS-1 catalysts for
736 direct conversion of cyclohexane to adipic acid: Active sites and reaction steps, *Appl. Catal. B*
737 *Environ.* 192 (2016) 325–341. <https://doi.org/10.1016/j.apcatb.2016.04.005>.
- 738 [7] ~~J. Zhang, J. Liu, X. Wang, J. Mai, W. Zhao, Z. Ding, Y. Fang, Construction of Z-scheme tungsten
739 trioxide nanosheets-nitrogen-doped carbon dots composites for the enhanced photothermal
740 synergistic catalytic oxidation of cyclohexane, *Appl. Catal. B Environ.* 259 (2019) 118063.
741 <https://doi.org/10.1016/j.apcatb.2019.118063>.~~
- 742 [8] O. Perraud, A.B. Sorokin, J.-P. Dutasta, A. Martinez, Oxidation of cycloalkanes by H₂O₂ using a
743 copper-hemicryptophane complex as a catalyst, *Chem. Commun.* 49 (2013) 1288.
744 <https://doi.org/10.1039/c2cc37829a>.
- 745 [9] G. Olivo, O. Cussó, M. Borrell, M. Costas, Oxidation of alkane and alkene moieties with
746 biologically inspired nonheme iron catalysts and hydrogen peroxide: from free radicals to
747 stereoselective transformations, *JBIC J. Biol. Inorg. Chem.* 22 (2017) 425–452.
748 <https://doi.org/10.1007/s00775-016-1434-z>.
- 749 [10] ~~M. V. Kirillova, T.A. Fernandes, V. André, A.M. Kirillov, Mild C–H functionalization of alkanes
750 catalyzed by bioinspired copper(II) cores, *Org. Biomol. Chem.* 17 (2019) 7706–7714.
751 <https://doi.org/10.1039/C9OB01442J>.~~
- 752 [11] F.A. Chavez, J.M. Rowland, M.M. Olmstead, P.K. Mascharak, Syntheses, Structures, and
753 Reactivities of Cobalt(III)–Alkylperoxo Complexes and Their Role in Stoichiometric and
754 Catalytic Oxidation of Hydrocarbons, *J. Am. Chem. Soc.* 120 (1998) 9015–9027.
755 <https://doi.org/10.1021/ja9814873>.
- 756 [12] L. Ma, Y. Pan, W.-L. Man, H.-K. Kwong, W.W.Y. Lam, G. Chen, K.-C. Lau, T.-C. Lau, Highly
757 Efficient Alkane Oxidation Catalyzed by [Mn V (N)(CN)₄]²⁻. Evidence for [Mn VII (N)(O)(CN)
758 4]²⁻ as an Active Intermediate, *J. Am. Chem. Soc.* 136 (2014) 7680–7687.
759 <https://doi.org/10.1021/ja5019546>.

- 760 [13] S. Nakagaki, K.A.D.F. Castro, G.M. Ucoski, M. Halma, V. Prévot, C. Forano, F. Wypych, Anionic
761 Iron(III) Porphyrin Immobilized on/into Exfoliated Macroporous Layered Double Hydroxides as
762 Catalyst for Oxidation Reactions, *J. Braz. Chem. Soc.* 25 (2014) 2329–2338.
763 <https://doi.org/10.5935/0103-5053.20140241>.
- 764 [14] J.T. Groves, T.E. Nemo, R.S. Myers, Hydroxylation and epoxidation catalyzed by iron-porphine
765 complexes. Oxygen transfer from iodosylbenzene, *J. Am. Chem. Soc.* 101 (1979) 1032–1033.
766 <https://doi.org/10.1021/ja00498a040>.
- 767 [15] K.C.M. Westrup, R.M. Silva Jr., K.M. Mantovani, L. Bach, J.F. Stival, P.G.P. Zamora, F. Wypych,
768 G.S. Machado, S. Nakagaki, Light-assisted cyclohexane oxidation catalysis by a manganese(III)
769 porphyrin immobilized onto zinc hydroxide salt and zinc oxide obtained by zinc hydroxide salt
770 hydrothermal decomposition, *Appl. Catal. A Gen.* 602 (2020) 117708.
771 <https://doi.org/10.1016/j.apcata.2020.117708>.
- 772 [16] K.M. Mantovani, J.F. Stival, F. Wypych, L. Bach, P.G. Peralta Zamora, M. Luiza Rocco, S.
773 Nakagaki, Unusual catalytic activity after simultaneous immobilization of two
774 metalloporphyrins on hydrozincite/nanocrystalline anatase, *J. Catal.* 352 (2017) 442–451.
775 <https://doi.org/10.1016/j.jcat.2017.06.015>.
- 776 [17] ~~C.-M. Che, J.-S. Huang, Metalloporphyrin-based oxidation systems: from biomimetic reactions
777 to application in organic synthesis, *Chem. Commun.* (2009) 3996–4015.
778 <https://doi.org/10.1039/b901221d>.~~
- 779 [18] C.L. Hill, R.D. Gall, The first combinatorially prepared and evaluated inorganic catalysts.
780 Polyoxometalates for the aerobic oxidation of the mustard analog tetrahydrothiophene (THT),
781 *J. Mol. Catal. A Chem.* 114 (1996) 103–111. [https://doi.org/10.1016/S1381-1169\(96\)00308-1](https://doi.org/10.1016/S1381-1169(96)00308-1).
- 782 [19] I. V. KOZHEVNIKOV, Heteropoly Acids and Related Compounds as Catalysts for Fine Chemical
783 Synthesis, *Catal. Rev.* 37 (1995) 311–352. <https://doi.org/10.1080/01614949508007097>.
- 784 [20] C.L. Hill, C.M. Prosser-McCartha, Homogeneous catalysis by transition metal oxygen anion
785 clusters, *Coord. Chem. Rev.* 143 (1995) 407–455. [https://doi.org/10.1016/0010-8545\(95\)01141-B](https://doi.org/10.1016/0010-8545(95)01141-B).
- 787 [21] B.M. Choudary, N.S. Chowdari, S. Madhi, M.L. Kantam, A Trifunctional Catalyst for One-Pot
788 Synthesis of Chiral Diols via Heck Coupling–N-Oxidation–Asymmetric Dihydroxylation:
789 Application for the Synthesis of Diltiazem and Taxol Side Chain, *J. Org. Chem.* 68 (2003) 1736–
790 1746. <https://doi.org/10.1021/jo026687i>.
- 791 [22] T. Kwon, G.A. Tsigdinos, T.J. Pinnavaia, Pillaring of layered double hydroxides (LDH's) by
792 polyoxometalate anions, *J. Am. Chem. Soc.* 110 (1988) 3653–3654.
793 <https://doi.org/10.1021/ja00219a048>.
- 794 [23] M.A. Drezdson, Synthesis of isopolymetalate-pillared hydrotalcite via organic-anion-pillared
795 precursors, *Inorg. Chem.* 27 (1988) 4628–4632. <https://doi.org/10.1021/ic00298a024>.
- 796 [24] ~~Mark A. Drezdson, Pillared hydrotalcites, 4774212, 1988.
797 <https://patents.justia.com/patent/4774212>.~~
- 798 [25] K. Chibwe, W. Jones, Synthesis of polyoxometalate pillared layered double hydroxides via
799 calcined precursors, *Chem. Mater.* 1 (1989) 489–490. <https://doi.org/10.1021/cm00005a006>.

- 800 [26] K. Chibwe, W. Jones, Intercalation of organic and inorganic anions into layered double
801 hydroxides, *J. Chem. Soc. Chem. Commun.* (1989) 926.
802 <https://doi.org/10.1039/c39890000926>.
- 803 [27] E. Narita, P. Kaviratna, T.J. Pinnavaia, Synthesis of Heteropolyoxometalate Pillared Layered
804 Double Hydroxides via Calcined Zinc-Aluminium Oxide Precursors, *Chem. Lett.* 20 (1991) 805–
805 808. <https://doi.org/10.1246/cl.1991.805>.
- 806 [28] E.D. Dimotakis, T.J. Pinnavaia, New route to layered double hydroxides intercalated by organic
807 anions: precursors to polyoxometalate-pillared derivatives, *Inorg. Chem.* 29 (1990) 2393–
808 2394. <https://doi.org/10.1021/ic00338a001>.
- 809 [29] ~~J. Wang, Y. Tian, R.C. Wang, A. Clearfield, Pillaring of layered double hydroxides with
810 polyoxometalates in aqueous solution without use of preswelling agents, *Chem. Mater.* 4
811 (1992) 1276–1282. <https://doi.org/10.1021/cm00024a030>.~~
- 812 [30] E. Narita, P.D. Kaviratna, T.J. Pinnavaia, Direct synthesis of a polyoxometalate-pillared layered
813 double hydroxide by coprecipitation, *J. Chem. Soc. Chem. Commun.* (1993) 60.
814 <https://doi.org/10.1039/c39930000060>.
- 815 [31] J. Luo, Y. Huang, B. Ding, P. Wang, X. Geng, J. Zhang, Y. Wei, Single-Atom Mn Active Site in a
816 Triol-Stabilized β -Anderson Manganohexamolybdate for Enhanced Catalytic Activity towards
817 Adipic Acid Production, *Catalysts* 8 (2018) 121–134. <https://doi.org/10.3390/catal8030121>.
- 818 [32] M. Conte, X. Liu, D.M. Murphy, S.H. Taylor, K. Whiston, G.J. Hutchings, Insights into the
819 Reaction Mechanism of Cyclohexane Oxidation Catalysed by Molybdenum Blue Nanorings,
820 *Catal. Letters*. 146 (2016) 126–135. <https://doi.org/10.1007/s10562-015-1660-y>.
- 821 [33] J. Alcañiz-Monge, G. Trautwein, A. Garcia-Garcia, Influence of peroxometallic intermediaries
822 present on polyoxometalates nanoparticles surface on the adipic acid synthesis, *J. Mol. Catal.*
823 *A Chem.* 394 (2014) 211–216. <https://doi.org/10.1016/j.molcata.2014.07.023>.
- 824 [34] T. Tatsumi, K. Yamamoto, H. Tajima, H. Tominaga, Shape Selective Epoxidation of Alkenes
825 Catalyzed by Polyoxometalate-Intercalated Hydrotalcite, *Chem. Lett.* 21 (1992) 815–818.
826 <https://doi.org/10.1246/cl.1992.815>.
- 827 [35] T. Tatsumi, K. Yamamoto, H. Tajima, H. Tominaga, *New Frontiers in Catalysis*, 1st ed., Elsevier,
828 Amsterdam, 1993.
- 829 [36] A.A. Gonzalez, K. Zhang, S.P. Nolan, R. Lopez de la Vega, S.L. Mukerjee, C.D. Hoff, G.J. Kubas,
830 Thermodynamic and kinetic studies of the complexes $W(CO)_3(PCy_3)_2L$ ($L = H_2, N_2, NCCH_3,$
831 $pyridine, P(OMe)_3, CO$), *Organometallics*. 7 (1988) 2429–2435.
832 <https://doi.org/10.1021/om00102a001>.
- 833 [37] S.-S. Sun, D.T. Tran, O.S. Odongo, A.J. Lees, Photophysical and Photochemical Properties of
834 $W(0)$ and $Re(I)$ Carbonyl Complexes Incorporating Ferrocenyl-Substituted Pyridine Ligands,
835 *Inorg. Chem.* 41 (2002) 132–135. <https://doi.org/10.1021/ic010713y>.
- 836 [38] A.S. Pronin, Y.M. Gayfulin, T.S. Sukhikh, A.N. Lavrov, V. V. Yanshole, Y. V. Mironov,
837 Heterometallic Re/Mo and Re/W cubane-type cluster complexes, *Inorg. Chem. Front.* 9 (2022)
838 186–194. <https://doi.org/10.1039/D1QI01230D>.
- 839 [39] W.-Q. Zhang, A.J. Atkin, I.J.S. Fairlamb, A.C. Whitwood, J.M. Lynam, Synthesis and Reactivity of

- 840 Molybdenum Complexes Containing Functionalized Alkynyl Ligands: A Photochemically
841 Activated CO-Releasing Molecule (PhotoCO-RM), *Organometallics*. 30 (2011) 4643–4654.
842 <https://doi.org/10.1021/om200495h>.
- 843 [40] Y. Tanabe, Y. Sekiguchi, H. Tanaka, A. Konomi, K. Yoshizawa, S. Kuriyama, Y. Nishibayashi,
844 Preparation and reactivity of molybdenum complexes bearing pyrrole-based PNP-type pincer
845 ligand, *Chem. Commun.* 56 (2020) 6933–6936. <https://doi.org/10.1039/D0CC02852E>.
- 846 [41] J. Mai, Y. Fang, J. Liu, J. Zhang, X. Cai, Y. Zheng, Simple synthesis of WO₃-Au composite and
847 their improved photothermal synergistic catalytic performance for cyclohexane oxidation,
848 *Mol. Catal.* 473 (2019) 110389–110395. <https://doi.org/10.1016/j.mcat.2019.04.018>.
- 849 [42] Y. Xiao, J. Liu, J. Mai, C. Pan, X. Cai, Y. Fang, High-performance silver nanoparticles coupled
850 with monolayer hydrated tungsten oxide nanosheets: The structural effects in photocatalytic
851 oxidation of cyclohexane, *J. Colloid Interface Sci.* 516 (2018) 172–181.
852 <https://doi.org/10.1016/j.jcis.2018.01.057>.
- 853 [43] J. Long, H. Liu, S. Wu, S. Liao, Y. Li, Selective Oxidation of Saturated Hydrocarbons Using Au–Pd
854 Alloy Nanoparticles Supported on Metal–Organic Frameworks, *ACS Catal.* 3 (2013) 647–654.
855 <https://doi.org/10.1021/cs300754k>.
- 856 [44] Y. Shiraishi, Y. Sugano, S. Ichikawa, T. Hirai, Visible light-induced partial oxidation of
857 cyclohexane on WO₃ loaded with Pt nanoparticles, *Catal. Sci. Technol.* 2 (2012) 400–405.
858 <https://doi.org/10.1039/C1CY00331C>.
- 859 [45] S.S. Acharyya, S. Ghosh, R. Bal, Nanoclusters of Cu(II) supported on nanocrystalline W(VI)
860 oxide: a potential catalyst for single-step conversion of cyclohexane to adipic acid, *Green
861 Chem.* 17 (2015) 3490–3499. <https://doi.org/10.1039/C5GC00379B>.
- 862 [46] K. Sato, M. Aoki, R. Noyori, A “Green” Route to Adipic Acid: Direct Oxidation of Cyclohexenes
863 with 30 Percent Hydrogen Peroxide, *Science* (80-.). 281 (1998) 1646–1647.
864 <https://doi.org/10.1126/science.281.5383.1646>.
- 865 [47] S. Ghosh, S.S. Acharyya, S. Adak, L.N.S. Konathala, T. Sasaki, R. Bal, Selective oxidation of
866 cyclohexene to adipic acid over silver supported tungsten oxide nanostructured catalysts,
867 *Green Chem.* 16 (2014) 2826–2834. <https://doi.org/10.1039/c4gc00130c>.
- 868 [48] M. Shang, T. Noël, Q. Wang, Y. Su, K. Miyabayashi, V. Hessel, S. Hasebe, 2- and 3-Stage
869 temperature ramping for the direct synthesis of adipic acid in micro-flow packed-bed
870 reactors, *Chem. Eng. J.* 260 (2015) 454–462. <https://doi.org/10.1016/j.cej.2014.08.061>.
- 871 [49] Y. Usui, K. Sato, A green method of adipic acid synthesis: organic solvent- and halide-free
872 oxidation of cycloalkanones with 30% hydrogen peroxide, *Green Chem.* 5 (2003) 373–375.
873 <https://doi.org/10.1039/b305847f>.
- 874 [50] M. Vafaezadeh, M. Mahmoodi Hashemi, Simple and green oxidation of cyclohexene to adipic
875 acid with an efficient and durable silica-functionalized ammonium tungstate catalyst, *Catal.
876 Commun.* 43 (2014) 169–172. <https://doi.org/10.1016/j.catcom.2013.10.001>.
- 877 [51] M. Sutradhar, A.P.C. Ribeiro, M.F.C. Guedes da Silva, A.M.F. Palavra, A.J.L. Pombeiro,
878 Application of molybdenum complexes for the oxidation of cyclohexane in acetonitrile, ionic
879 liquid and supercritical CO₂ media, a comparative study, *Mol. Catal.* 482 (2020) 100356–
880 100366. <https://doi.org/10.1016/j.mcat.2017.10.026>.

- 881 [52] R.K. Rana, B. Viswanathan, Mo incorporation in MCM-41 type zeolite, *Catal. Letters*. 52 (1998)
882 25–29. <https://doi.org/https://doi.org/10.1023/A:1019019403375>.
- 883 [53] N.J. Campbell, A.C. Dengel, C.J. Edwards, W.P. Griffith, Studies on transition metal peroxo
884 complexes. Part 8. The nature of peroxomolybdates and peroxotungstates in aqueous
885 solution, *J. Chem. Soc. Dalton Trans.* (1989) 1203–1208. <https://doi.org/10.1039/dt9890001203>.
- 886 [54] M. Amini, M.M. Haghdoost, M. Bagherzadeh, Oxido-peroxido molybdenum(VI) complexes in
887 catalytic and stoichiometric oxidations, *Coord. Chem. Rev.* 257 (2013) 1093–1121.
888 <https://doi.org/10.1016/j.ccr.2012.11.018>.
- 889 [55] M.G. Buonomenna, G. Golemme, M.P. De Santo, E. Drioli, Direct Oxidation of Cyclohexene
890 with Inert Polymeric Membrane Reactor, *Org. Process Res. Dev.* 14 (2010) 252–258.
891 <https://doi.org/10.1021/op900022t>.
- 892 [56] T. Hibino, Acid Treatment of Layered Double Hydroxides Containing Carbonate, *Eur. J. Inorg.
893 Chem.* 2014 (2014) 5311–5321. <https://doi.org/10.1002/ejic.201402372>.
- 894 [57] N. Iyi, T. Matsumoto, Y. Kaneko, K. Kitamura, Deintercalation of Carbonate Ions from a
895 Hydrotalcite-Like Compound: Enhanced Decarbonation Using Acid–Salt Mixed Solution, *Chem.
896 Mater.* 16 (2004) 2926–2932. <https://doi.org/10.1021/cm049579g>.
- 897 [58] P. LIU, H. WANG, Z. FENG, P. YING, C. LI, Direct immobilization of self-assembled
898 polyoxometalate catalyst in layered double hydroxide for heterogeneous epoxidation of
899 olefins, *J. Catal.* 256 (2008) 345–348. <https://doi.org/10.1016/j.jcat.2008.03.022>.
- 900 [59] P. Levecque, H. Poelman, P. Jacobs, D. De Vos, B. Sels, Regio- and stereoselective terpene
901 epoxidation using tungstate-exchanged takovites: a study of phase purity, takovite
902 composition and stable catalytic activity, *Phys. Chem. Chem. Phys.* 11 (2009) 2964–2975.
903 <https://doi.org/10.1039/b820336a>.
- 904 [60] K. Colombo, S. Maruyama, C. Yamamoto, F. Wypych, Intercalation of Molybdate Ions into
905 Ni/Zn Layered Double Hydroxide Salts: Synthesis, Characterization, and Preliminary Catalytic
906 Activity in Methyl Transesterification of Soybean Oil, *J. Braz. Chem. Soc.* 28 (2017) 1315–1322.
907 <https://doi.org/10.21577/0103-5053.20160298>.
- 908 [61] B.F. Sels, D.E. De Vos, P.A. Jacobs, Bromide-Assisted Oxidation of Substituted Phenols with
909 Hydrogen Peroxide to the Corresponding p-Quinol and p-Quinol Ethers over WO₄²⁻-
910 Exchanged Layered Double Hydroxides, *Angew. Chemie Int. Ed.* 44 (2005) 310–313.
911 <https://doi.org/10.1002/anie.200461555>.
- 912 [62] U.S. Agarwalla, Mo- and W-containing layered double hydroxides: Mild and selective
913 oxidation of alkenes with H₂O₂, *Indian J. Chem. - Sect. A.* 60 (2021) 656–662.
914 <http://op.niscair.res.in/index.php/IJCA/article/view/42530>.
- 915 [63] J. Wahlen, D.E. De Vos, B.F. Sels, V. Nardello, J.-M. Aubry, P.L. Alsters, P.A. Jacobs, Molybdate-
916 exchanged layered double hydroxides for the catalytic disproportionation of hydrogen
917 peroxide into singlet oxygen: Evaluation and improvements of 1O₂ generation by combined
918 chemiluminescence and trapping experiments, *Appl. Catal. A Gen.* 293 (2005) 120–128.
919 <https://doi.org/10.1016/j.apcata.2005.07.014>.
- 920 [64] C. Yuan, H. Liu, X. Gao, Magnetically Recoverable Heterogeneous Catalyst: Tungstate
921 Intercalated Mg–Al-Layered Double Hydroxides-Encapsulated Fe₃O₄ Nanoparticles for Highly

- 922 Efficient Selective Oxidation of Sulfides with H₂O₂, *Catal. Letters*. 144 (2014) 16–21.
923 <https://doi.org/10.1007/s10562-013-1129-9>.
- 924 [65] E. V. Korneeva, A.S. Ivanova, V.M. Bondareva, L.M. Plyasova, T.S. Glazneva, Structural,
925 textural, and acid–base properties of layered Mg–Al oxides modified with a tungstate or
926 phosphate and their activity and selectivity in gas-phase glycerol dehydration, *Kinet. Catal.* 56
927 (2015) 605–616. <https://doi.org/10.1134/S0023158415050109>.
- 928 [66] S. Zhao, J. Xu, M. Wei, Y.-F. Song, Synergistic catalysis by polyoxometalate-intercalated
929 layered double hydroxides: oximation of aromatic aldehydes with large enhancement of
930 selectivity, *Green Chem.* 13 (2011) 384. <https://doi.org/10.1039/c0gc00664e>.
- 931 [67] R. Noyori, M. Aoki, K. Sato, Green oxidation with aqueous hydrogen peroxide, *Chem.*
932 *Commun.* (2003) 1977–1986. <https://doi.org/10.1039/b303160h>.
- 933 [68] E. Gardner, T.J. Pinnavaia, On the nature of selective olefin oxidation catalysts derived from
934 molybdate- and tungstate-intercalated layered double hydroxides, *Appl. Catal. A Gen.* 167
935 (1998) 65–74. [https://doi.org/10.1016/S0926-860X\(97\)00299-8](https://doi.org/10.1016/S0926-860X(97)00299-8).
- 936 [69] A.-L. Maciucă, C.-E. Ciocan, E. Dumitriu, F. Fajula, V. Hulea, V., Mo- and W-containing layered
937 double hydroxides as effective catalysts for mild oxidation of thioethers and thiophenes with
938 H₂O₂, *Catal. Today*. 138 (2008) 33–37. <https://doi.org/10.1016/j.cattod.2008.04.031>.
- 939 [70] G.-J. ten Brink, I.W.C.E. Arends, R.A. Sheldon, Green, Catalytic Oxidation of Alcohols in Water,
940 *Science* (80-.). 287 (2000) 1636–1639. <https://doi.org/10.1126/science.287.5458.1636>.
- 941 [71] V. Nardello, J. Marko, G. Vermeersch, J.M. Aubry, 90Mo NMR and kinetic studies of
942 peroxomolybdic intermediates involved in the catalytic disproportionation of hydrogen
943 peroxide by molybdate ions, *Inorg. Chem.* 34 (1995) 4950–4957.
944 <https://doi.org/10.1021/ic00124a007>.
- 945 [72] B.F. Sels, D.E. De Vos, P.J. Grobet, F. Pierard, F. Kirsch-De Mesmaeker, P.A. Jacobs, Molybdate-
946 and Tungstate-Exchanged Layered Double Hydroxides as Catalysts for 1O₂ Formation:
947 Characterization of Reactive Oxygen Species and a Critical Evaluation of 1O₂ Detection
948 Methods, *J. Phys. Chem. B*. 103 (1999) 11114–11123. <https://doi.org/10.1021/jp992236z>.
- 949 [73] N. Iyi, H. Yamada, One-step Conversion of CO₃²⁻ LDH (Layered Double Hydroxide) into
950 Anion-exchangeable LDHs Using an Acetate-buffer/Salt Method, *Chem. Lett.* 39 (2010) 591–
951 593. <https://doi.org/10.1246/cl.2010.591>.
- 952 [74] N. Iyi, H. Yamada, Efficient decarbonation of carbonate-type layered double hydroxide
953 (CO₃²⁻-LDH) by ammonium salts in alcohol medium, *Appl. Clay Sci.* 65–66 (2012) 121–127.
954 <https://doi.org/10.1016/j.clay.2012.05.001>.
- 955 [75] S.S.C. Pushparaj, C. Forano, V. Prevot, A.S. Lipton, G.J. Rees, J. V. Hanna, U.G. Nielsen, How the
956 Method of Synthesis Governs the Local and Global Structure of Zinc Aluminum Layered
957 Double Hydroxides, *J. Phys. Chem. C*. 119 (2015) 27695–27707.
958 <https://doi.org/10.1021/acs.jpcc.5b09490>.
- 959 [76] S. Nakagaki, K. Mantovani, G.S. Machado, K.A.D.F. Castro, F. Wypych, G. Sippel Machado, K.
960 Dias de Freitas Castro, F. Wypych, Recent Advances in Solid Catalysts Obtained by
961 Metalloporphyrins Immobilization on Layered Anionic Exchangers: A Short Review and Some
962 New Catalytic Results, *Molecules*. 21 (2016) 291.

- 963 <https://doi.org/10.3390/molecules21030291>.
- 964 [77] E.S. Zhitova, S. V. Krivovichev, I. Pekov, H.C. Greenwell, Crystal chemistry of natural layered
965 double hydroxides. 5. Single-crystal structure refinement of hydrotalcite,
966 [Mg₆Al₂(OH)₁₆](CO₃)(H₂O)₄, Mineral. Mag. 83 (2019) 269–280.
967 <https://doi.org/10.1180/mgm.2018.145>.
- 968 [78] N. Iyi, K. Fujii, K. Okamoto, T. Sasaki, Factors influencing the hydration of layered double
969 hydroxides (LDHs) and the appearance of an intermediate second staging phase, Appl. Clay
970 Sci. 35 (2007) 218–227. <https://doi.org/10.1016/j.clay.2006.08.011>.
- 971 [79] L. Claes, R. Matthesen, I. Rombouts, I. Stassen, T. De Baerdemaeker, D. Depla, J.A. Delcour, B.
972 Lagrain, D.E. De Vos, Bio-Based Nitriles from the Heterogeneously Catalyzed Oxidative
973 Decarboxylation of Amino Acids, ChemSusChem. 8 (2015) 345–352.
974 <https://doi.org/10.1002/cssc.201402801>.
- 975 [80] M. Khitous, Z. Salem, D. Halliche, Effect of interlayer anions on chromium removal using Mg–
976 Al layered double hydroxides: Kinetic, equilibrium and thermodynamic studies, Chinese J.
977 Chem. Eng. 24 (2016) 433–445. <https://doi.org/10.1016/j.cjche.2015.11.018>.
- 978 [81] N. Thomas, Synthesis of 3R 1 and 1H Polytypes of Sulfate-Intercalated Layered Double
979 Hydroxides (LDHs) by Postintracrystalline Oxidation and Simultaneous Intercalation-Oxidation
980 of Thiosulfate, Cryst. Growth Des. 12 (2012) 1378–1382. <https://doi.org/10.1021/cg201452c>.
- 981 [82] L. Mohapatra, K. Parida, M. Satpathy, Molybdate/Tungstate Intercalated Oxo-Bridged Zn/Y
982 LDH for Solar Light Induced Photodegradation of Organic Pollutants, J. Phys. Chem. C. 116
983 (2012) 13063–13070. <https://doi.org/10.1021/jp300066g>.
- 984 [83] J. Zhu, H. Fan, J. Sun, S. Ai, Anion-exchange precipitation synthesis of α -Ag₂WO₄/Zn–Cr
985 layered double hydroxides composite with enhanced visible-light-driven photocatalytic
986 activity, Sep. Purif. Technol. 120 (2013) 134–140.
987 <https://doi.org/10.1016/j.seppur.2013.09.043>.
- 988 [84] L.B. Staal, S.S. Charan Pushparaj, C. Forano, V. Prevot, D.B. Ravnsbæk, M. Bjerring, U.G.
989 Nielsen, Competitive reactions during synthesis of zinc aluminum layered double hydroxides
990 by thermal hydrolysis of urea, J. Mater. Chem. A. 5 (2017) 21795–21806.
991 <https://doi.org/10.1039/C7TA05761J>.
- 992 [85] J.T. Klopogge, L. Hickey, R.L. Frost, FT-Raman and FT-IR spectroscopic study of synthetic
993 Mg/Zn/Al-hydrotalcites, J. Raman Spectrosc. 35 (2004) 967–974.
994 <https://doi.org/10.1002/jrs.1244>.
- 995 [86] N. Touisni, F. Charmantray, V. Helaine, C. Forano, L. Hecquet, C. Mousty, Optimized
996 immobilization of transketolase from E. coli in MgAl-layered double hydroxides, Colloid
997 Surface B 112 (2013) 452–459. <https://doi.org/10.1016/j.colsurfb.2013.07.023>.
- 998 [87] K. Charradi, C. Forano, V. Prevot, D. Madern, A. Ben Haj Amara, C. Mousty, Characterization of
999 Hemoglobin Immobilized in MgAl-Layered Double Hydroxides by the Coprecipitation Method,
1000 Langmuir. 26 (2010) 9997–10004. <https://doi.org/10.1021/la1001286>.
- 1001 [88] Y. Feng, D. Li, Y. Wang, D.G. Evans, X. Duan, Synthesis and characterization of a UV absorbent-
1002 intercalated Zn–Al layered double hydroxide, Polym. Degrad. Stab. 91 (2006) 789–794.
1003 <https://doi.org/10.1016/j.polymdegradstab.2005.06.006>.

- 1004 [89] J. Liu, J. Song, H. Xiao, L. Zhang, Y. Qin, D. Liu, W. Hou, N. Du, Synthesis and thermal properties
1005 of ZnAl layered double hydroxide by urea hydrolysis, *Powder Technol.* 253 (2014) 41–45.
1006 <https://doi.org/10.1016/j.powtec.2013.11.007>.
- 1007 [90] M. Zouaoui, I. Jendoubi, M.F. Zid, N.F. Bourguiba, Synthesis, crystal structure and physico-
1008 chemical investigations of a new lyonsite molybdate $\text{Na}_{0.24}\text{Ti}_{1.44}(\text{MoO}_4)_3$, *J. Solid State*
1009 *Chem.* 300 (2021) 122221–122231. <https://doi.org/10.1016/j.jssc.2021.122221>.
- 1010 [91] A. Mohmoud, S. Rakass, H. Oudghiri Hassani, F. Kooli, M. Abboudi, S. Ben Aoun, Iron
1011 Molybdate $\text{Fe}_2(\text{MoO}_4)_3$ Nanoparticles: Efficient Sorbent for Methylene Blue Dye Removal
1012 from Aqueous Solutions, *Molecules.* 25 (2020) 5100–5118.
1013 <https://doi.org/10.3390/molecules25215100>.
- 1014 [92] R.A. Nyquist, R.O. Kagel, *Handbook of Infrared and Raman Spectra of Inorganic Compounds*
1015 *and Organic Salts: Infrared spectra of inorganic compounds (3800 – 45 cm⁻¹)*, Academic Press,
1016 New York and London, 1971.
- 1017 [93] M. Vafaezadeh, M.M. Hashemi, M. Shakourian-Fard, Design of silica supported task-specific
1018 ionic liquid catalyst system for oxidation of cyclohexene to adipic acid with 30% H_2O_2 , *Catal.*
1019 *Commun.* 26 (2012) 54–57. <https://doi.org/10.1016/j.catcom.2012.04.031>.
- 1020 [94] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part B:*
1021 *Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, 2008.
1022 <https://doi.org/10.1002/9780470405888>.
- 1023 [95] G. Busca, Differentiation of mono-oxo and polyoxo and of monomeric and polymeric
1024 vanadate, molybdate and tungstate species in metal oxide catalysts by IR and Raman
1025 spectroscopy, *J. Raman Spectrosc.* 33 (2002) 348–358. <https://doi.org/10.1002/jrs.867>.
- 1026 [96] T.. Basiev, A.. Sobol, Y.. Voronko, P.. Zverev, Spontaneous Raman spectroscopy of tungstate
1027 and molybdate crystals for Raman lasers, *Opt. Mater. (Amst).* 15 (2000) 205–216.
1028 [https://doi.org/10.1016/S0925-3467\(00\)00037-9](https://doi.org/10.1016/S0925-3467(00)00037-9).
- 1029 [97] J. Twu, P.K. Dutta, Raman spectroscopic studies of intercalated molybdate ions in layered
1030 metal hydroxides, *Chem. Mater.* 4 (1992) 398–401. <https://doi.org/10.1021/cm00020a031>.
- 1031 [98] A.-L. Maciucă, E. Dumitriu, F. Fajula, V. Hulea, Mild oxidation of tetrahydrothiophene to
1032 sulfolane over V-, Mo- and W-containing layered double hydroxides, *Appl. Catal. A Gen.* 338
1033 (2008) 1–8. <https://doi.org/10.1016/j.apcata.2007.12.023>.
- 1034 [99] M. Rezaei, A. Najafi Chermahini, H.A. Dabbagh, Green and selective oxidation of cyclohexane
1035 over vanadium pyrophosphate supported on mesoporous KIT-6, *Chem. Eng. J.* 314 (2017)
1036 515–525. <https://doi.org/10.1016/j.cej.2016.12.009>.
- 1037 [100] F.M.P.. van Laar, D.. De Vos, F. Pierard, A. Kirsch-De Mesmaeker, L. Fiermans, P.. Jacobs,
1038 Generation of Singlet Molecular Oxygen from H_2O_2 with Molybdate-Exchanged Layered
1039 Double Hydroxides: Effects of Catalyst Composition and Reaction Conditions, *J. Catal.* 197
1040 (2001) 139–150. <https://doi.org/10.1006/jcat.2000.3070>.
- 1041 [101] L.J. Csányi, I. Horváth, Z.M. Galbács, Peroxide derivatives of molybdenum(VI) in neutral and
1042 alkaline media, *Transit. Met. Chem.* 14 (1989) 90–94. <https://doi.org/10.1007/BF01040598>.
- 1043 [102] R. Wang, W. Jiao, B. Gao, Efficient biomimetic aerobic oxidation of phenylethane catalyzed by

- 1044 P(4VP-co-St)/SiO₂-supported metalloporphyrins, *Appl. Surf. Sci.* 255 (2009) 7766–7772.
1045 <https://doi.org/10.1016/j.apsusc.2009.04.166>.
- 1046 [103] B. Sels, D. De Vos, M. Buntinx, F. Pierard, A. Kirsch-De Mesmaeker, P. Jacobs, Layered double
1047 hydroxides exchanged with tungstate as biomimetic catalysts for mild oxidative bromination,
1048 *Nature*. 400 (1999) 855–857. <https://doi.org/10.1038/23674>.
- 1049 [104] W.Y. Hernández, F. Aliç, A. Verberckmoes, P. Van Der Voort, Tuning the acidic–basic
1050 properties by Zn-substitution in Mg–Al hydrotalcites as optimal catalysts for the aldol
1051 condensation reaction, *J. Mater. Sci.* 52 (2017) 628–642. <https://doi.org/10.1007/s10853-016-0360-3>.
1052
- 1053 [105] M. Sánchez-Cantú, L. Pérez-Díaz, E. Rubio-Rosas, V. Abril-Sandoval, J. Merino-Aguirre, F.
1054 Reyes-Cruz, L. Orea, MgZnAl hydrotalcite-like compounds preparation by a green method:
1055 effect of zinc content, *Chem. Pap.* 68 (2014) 638–649. <https://doi.org/10.2478/s11696-013-0491-9>.
1056
- 1057 [106] M.C.I. Bezen, C. Breitung, J.A. Lercher, On the acid–base properties of Zn–Mg–Al mixed
1058 oxides, *Appl. Catal. A Gen.* 399 (2011) 93–99. <https://doi.org/10.1016/j.apcata.2011.03.053>.
- 1059 [107] T.M. Rossi, J.C. Campos, M.M.V.M. Souza, CO₂ capture by Mg–Al and Zn–Al hydrotalcite-like
1060 compounds, *Adsorption*. 22 (2016) 151–158. <https://doi.org/10.1007/s10450-015-9732-2>.
- 1061 [108] M. Halma, F. Wypych, S.M. Drechsel, S. Nakagaki, Synthesis, characterization and catalytic
1062 behavior of iron porphyrins immobilized in layered double hydroxides, *J. Porphyr.
1063 Phthalocyanines*. 6 (2002) 502–513. <https://doi.org/10.1142/s1088424602000634>.
- 1064 [109] G.S. Machado, G.G.C. Arízaga, F. Wypych, S. Nakagaki, Immobilization of anionic
1065 metalloporphyrins on zinc hydroxide nitrate and study of an unusual catalytic activity, *J. Catal.*
1066 274 (2010) 130–141. <https://doi.org/10.1016/j.jcat.2010.06.012>.
- 1067 [110] J.R. Lindsay Smith, Y. Iamamoto, F.S. Vinhado, Oxidation of alkanes by iodosylbenzene (PhIO)
1068 catalysed by supported Mn(III) porphyrins: Activity and mechanism, *J. Mol. Catal. A Chem.* 252
1069 (2006) 23–30. <https://doi.org/10.1016/j.molcata.2006.01.064>.
- 1070 [111] K.A.D.F. Castro, S. Silva, P.M.R. Pereira, M.M.Q. Simões, M. da G.P.M.S. Neves, J.A.S.
1071 Cavaleiro, F. Wypych, J.P.C. Tomé, S. Nakagaki, Galactodendritic Porphyrinic Conjugates as
1072 New Biomimetic Catalysts for Oxidation Reactions, *Inorg. Chem.* 54 (2015) 4382–4393.
1073 <https://doi.org/10.1021/acs.inorgchem.5b00196>.
- 1074 [112] W. Nam, M.H. Lim, S.-Y. Oh, J.H. Lee, H.J. Lee, S.K. Woo, C. Kim, W. Shin, Remarkable Anionic
1075 Axial Ligand Effects of Iron(III) Porphyrin Complexes on the Catalytic Oxygenations of
1076 Hydrocarbons by H₂O₂ and the Formation of Oxoiron(IV) Porphyrin Intermediates by m-
1077 Chloroperoxybenzoic Acid, *Angew. Chemie.* 39 (2000) 3646–3649.
1078 [https://doi.org/10.1002/1521-3773\(20001016\)39:20<3646::AID-ANIE3646>3.0.CO;2-Q](https://doi.org/10.1002/1521-3773(20001016)39:20<3646::AID-ANIE3646>3.0.CO;2-Q).
- 1079
- 1080