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# Eco-CaMnO<sub>x</sub>: A Greener Generation of Eco-catalysts for Eco-friendly Oxidation Processes

Camille Bihanic, Sébastien Diliberto, Franck Pelissier, Eddy Petit, Clotilde Boulanger, and Claude Grison\*



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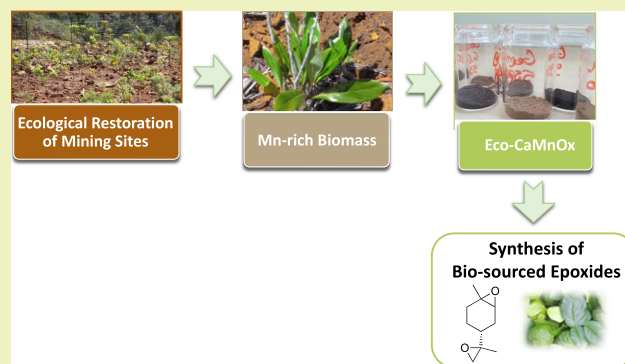
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**ABSTRACT:** Owing to the alarming problems of depletion of mineral resources and ever-growing pollution by metallic elements, biosourced catalysts were prepared from Mn-accumulating plant species from a large-scale program of ecological rehabilitation of mining sites. This new generation of catalysts, “Eco-CaMnO<sub>x</sub>” catalysts, were obtained directly from a controlled thermal treatment of four species of *Grevillea* genus, a Mn-rich biomass, and without any further chemical treatment. Eco-CaMnO<sub>x</sub> catalysts were characterized by microwave plasma-atomic emission spectrometer, X-ray powder diffraction spectroscopy, high-resolution transmission electron microscopy, and scanning transmission electron microscopy-energy-dispersive X-ray spectroscopy. These analyses revealed a natural richness in two unusual and valuable mixed calcium–manganese oxides: Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and CaMnO<sub>3</sub>. The high efficiency of Eco-CaMnO<sub>x</sub> catalysts was demonstrated via the epoxidation of various biosourced terpenes and lipids, using the mixture H<sub>2</sub>O<sub>2</sub>/NaHCO<sub>3</sub> as a green co-oxidant. This study demonstrated not only the high potential of Eco-CaMnO<sub>x</sub> catalysts as alternatives to oxidative reagents prohibited by REACH regulation but also the efficient synthesis of biosourced epoxides, which can be used as monomers for the preparation of biodegradable polymers. Finally, the original composition of Eco-CaMnO<sub>x</sub> catalysts led to distinctive catalytic behaviors compared to previously studied Eco-Mn and Pyr-Mn, allowing the preparation of sensitive epoxides such as linalool epoxide.

**KEYWORDS:** rehabilitation of mining sites; phytoextraction, biosourced Mn catalyst, Ca–Mn cluster, sustainable oxidation, eco-catalysis



## INTRODUCTION

Along with the increase of the world's population, which keeps demanding a higher standard of living, the claim for mineral resources is also rising. While several concerns have been raised over the elemental sustainability, the depletion of “trace metallic elements” (or “TEs”) is intensifying.<sup>1</sup> Growing exploitation of mineral resources is one of the main causes for the serious dissemination of TEs throughout the environment. TEs are among the most harmful pollutants. As they are not biodegradable, their wide dispersion into different ecosystems has raised concerns over their potential risks on human health and the environment.<sup>2</sup>

New Caledonia provides a demonstrative case of this situation. The New Caledonian lagoon is the largest in the world, being classified as one of the UNESCO World Heritage Sites. New Caledonia is one of the highest biodiversity “hotspots” in the world.<sup>3</sup> This high biodiversity results from the unusual composition of its soil, which is rich in heavy metals, particularly in nickel. However, nickel in soils also implies intensive mining activities.<sup>4</sup> Nickel mines are opencast. Excavations to access deep nickel lodes require the removal of topsoil, upper soil horizons, and vegetation. The removal of the

plant cover leads to the destruction of biodiversity, which promotes soil erosion.<sup>5,6</sup> The leaching of bare soils drags the sediments away into the streams near mining sites and then into the lagoon, threatening the New Caledonian coral reef.<sup>7,8</sup> This erosion also leads to dramatic events in the neighborhood, such as landslides.

The rehabilitation of mining sites is becoming a major priority. Over the last decade, our laboratory has led a large-scale program of ecological restoration of mining sites by the reintroduction of a vegetal cover, based on the rich endemic biodiversity of New Caledonia. Depending on the location of the mining site, pioneer species adapted to local constraints were selected. Among these species, many have the capacity to concentrate heavy metals from the soils into their aerial parts.<sup>9–11</sup> Manganese accumulators are the most widespread and the most adapted to the restoration of mining sites. In

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Figure 1. From the ecological restoration of New Caledonian mining sites to ecocatalysis.

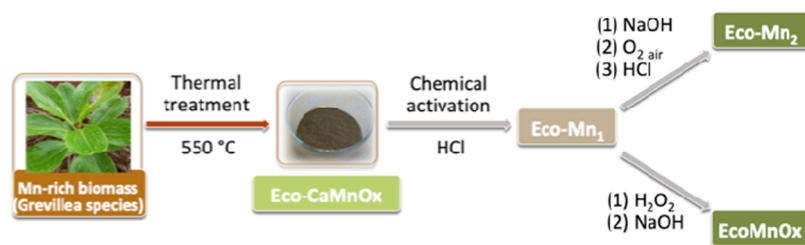


Figure 2. Steps for preparation of the previously studied Eco-Mn catalysts and of the new Eco-CaMnO<sub>x</sub> from Mn-accumulating plant species.

particular, species of the genus *Grevillea* (Proteaceae) are considered as the leading species for restoration, representing about 58% of the species reintroduced by our group (Figure 1).<sup>12,13</sup>

As such ecological programs could represent an economic cost for mining operators, our group has combined restoration with economic outlets. Taking advantage of the adaptive capacity of these particular plants to accumulate heavy metals, it is possible to directly turn metal-rich leaves into green and efficient catalysts used in organic chemistry. This original valorization of biomass has opened a new perspective in sustainable chemistry: “eco-catalysis” (Figure 1).<sup>14,15</sup> The catalysts coming from biomass, named eco-catalysts (Eco-M), associate the phytoextracted metal with many physiological elements essential for plant metabolism. These polymetallic systems create original chemical species and generate synergetic catalytic effects between their components. A wide range of eco-catalysts has been prepared and used in many revisited mechanisms of chemistry, such as green oxidation,<sup>16–19</sup> green reduction,<sup>20,21</sup> Lewis acid catalysis,<sup>22–28</sup> and cross-coupling reactions.<sup>15,29–31</sup>

Concerning manganese, two generations of Eco-Mn catalysts were prepared from Mn-accumulating plant species belonging to the genus *Grevillea* (Figure 2). In each case, the first step was the preparation of an intermediate Eco-Mn<sub>1</sub>. It was based on a controlled thermal treatment of Mn-rich biomass, followed by a chemical activation by HCl.<sup>16</sup> From Eco-Mn<sub>1</sub>, two oxidative eco-catalysts were formed by a sequential addition of either NaOH/O<sub>2</sub>/HCl (Eco-Mn<sub>2</sub>)<sup>16</sup> or H<sub>2</sub>O<sub>2</sub>/NaOH (Eco-MnO<sub>x</sub>).<sup>17</sup>

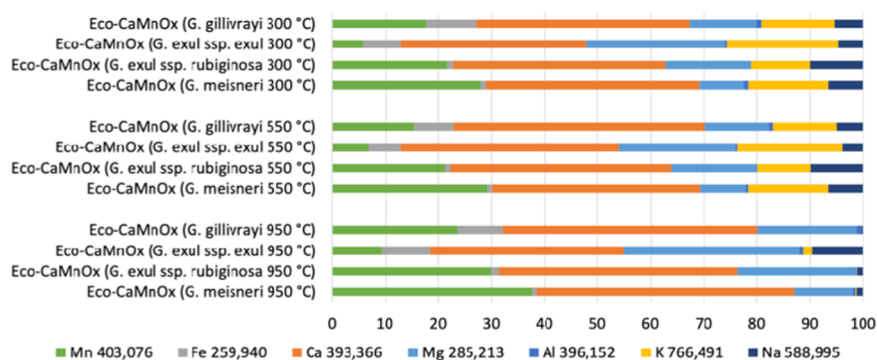
Eco-Mn revealed an original polymetallic composition resulting in marked Brønsted and Lewis acidities and displayed superior catalytic performances than conventional Mn catalysts. For example, Eco-Mn<sub>1</sub> was successfully employed in the aminoreduction of ketones<sup>20</sup> and constitutes the first example of reduction promoted by a Mn-based catalyst. Eco-Mn<sub>2</sub> and Eco-MnO<sub>x</sub> led to a practical and elegant solution to

the long-standing challenge of oxidative cleavage of 1,2-diols into aldehyde or ketones.<sup>17,18</sup> Supported Eco-Mn<sub>1</sub> provided also a huge potential as green catalysts for valuable epoxidation.<sup>18</sup> Finally, Eco-Mn<sub>1</sub> acted as “Janus catalysts” by promoting tandem sequences of multicomponent type oxidations (synthesis of substituted pyridines) and cyclizations (synthesis of *p*-cymene).<sup>16</sup> Comparison of their properties to that of commercial salts highlighted the superior catalytic activities of Eco-Mn.

Recently we reported an extensive structural study of Eco-Mn<sub>1</sub>, characterized by inductive coupled plasma-mass spectroscopy, X-ray powder diffraction spectroscopy (XRPD), and X-ray absorption spectroscopy (XANES and EXAFS), completed with density functional theory calculations.<sup>32</sup> In a systematic analysis, we also analyzed the thermal residues, from New Caledonian Mn-accumulating plant species of *Grevillea* generated before the chemical activation, by XRPD (Figure 2). We detected a polymetallic oxide (a mixed manganese–calcium oxide, Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub>) instead of polymetallic chlorides as for Eco-Mn<sub>1</sub> and Eco-Mn<sub>2</sub>.

While rare examples have described the use of mixed Mn–Ca oxide nanoparticles as oxidants,<sup>33,34</sup> no description was found for the use of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> in organic synthesis. However, mixed Mn–Ca oxides display biomimetic oxidative properties of the natural cofactor CaMn<sub>4</sub>O<sub>5</sub> of Photosystem II. Indeed, CaMn<sub>4</sub>O<sub>5</sub> performs the oxidation of water during the photosynthesis process,<sup>35</sup> and the complex Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> presents similar oxidative activities in the electrochemical oxidation of water.<sup>36–38</sup>

The above facts prompted us to further structurally characterize these new potential oxidative eco-catalysts, which we named Eco-CaMnO<sub>x</sub>. We investigated the mineral composition of Eco-CaMnO<sub>x</sub> by microwave plasma-atomic emission spectrometer (MP-AES) and their crystalline composition by XRPD. The morphology of Eco-CaMnO<sub>x</sub> was analyzed by high-resolution transmission electron microscopy (HRTEM), and the structural distribution of



**Figure 3.** Histogram representing the relative weight percentages of elements in Eco-CaMnO<sub>x</sub> catalysts, prepared from different plant species of Grevillea and thermal treatments, determined by MP-AES analyses.

137 mineral species was mapped by scanning transmission electron  
138 microscopy-energy-dispersive X-ray spectroscopy (STEM-  
139 EDX).

140 The oxidative potential of Eco-CaMnO<sub>x</sub> catalysts was then  
141 investigated in the epoxidation of terpenes with new challenges  
142 that would meet the principles of green chemistry: (1)  
143 developing a “waste-free” process to prepare catalysts, by  
144 suppressing the acidic and basic activation steps; (2)  
145 generating catalysts with high catalytic oxidative performances;  
146 and (3) providing an eco-friendlier synthesis of biosourced  
147 epoxides.

## 148 ■ EXPERIMENTAL SECTION

149 **Chemicals.** All materials and reagents were purchased from Sigma-  
150 Aldrich and were used without further purification.

151 **Preparation of Eco-CaMnO<sub>x</sub> Catalysts.** Eco-CaMnO<sub>x</sub> were  
152 prepared from harvested leaves of New Caledonian manganese-  
153 accumulating plants: *Grevillea exul* ssp. *exul*, *Grevillea exul* ssp.  
154 *rubiginosa*, *Grevillea gillivrayi*, and *Grevillea meisneri*. Plant leaves were  
155 coming from the litter of the plants. Harvests are made respecting  
156 legal authorizations. Harvested biomass was air-dried at room  
157 temperature (rt) and grinded. The obtained powder was thermally  
158 treated in an oven under air flow at 300, 550, or 950 °C for 6 h.

159 **Preparation of Synthetic Catalysts.** Synthetic ashes were  
160 obtained by mixing all together well-chosen commercial metallic  
161 salts, so that the relative percentage of metallic elements in the  
162 starting mixture was exactly the same as in the leaves of *Grevillea exul*  
163 ssp. *rubiginosa*. The salt mixture was then thermally treated at 550 °C  
164 following the same procedure as used for Eco-CaMnO<sub>x</sub>. The chosen  
165 salts were the following: manganese malate trihydrate (MnC<sub>4</sub>H<sub>4</sub>O<sub>5</sub>·  
166 3H<sub>2</sub>O), calcium oxalate (CaC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O), iron phosphate (FePO<sub>4</sub>·  
167 2H<sub>2</sub>O), magnesium phosphate (Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O), sodium chloride  
168 (NaCl), potassium chloride (KCl), and aluminum oxalate (Al<sub>2</sub>C<sub>6</sub>O<sub>12</sub>·  
169 xH<sub>2</sub>O).

170 Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> was synthesized by grinding CaCO<sub>3</sub> (4 mmol, 400 mg)  
171 and MnCO<sub>3</sub> (6 mmol, 690 mg) in a mortar until the obtained powder  
172 was homogeneous. The powder was then thermally treated in an oven  
173 under air flow at 800 °C for 18 h.

174 **Epoxidation of Alkenes.** In a typical procedure, the alkene (1.6  
175 mmol, 1 equiv), the catalyst (8 μmol, 0.005 equiv Mn), and NaHCO<sub>3</sub>  
176 (8 mmol, 5 equiv) were stirred in a mixture of acetone (20 mL) and  
177 water (20 mL) at room temperature for 10 min. H<sub>2</sub>O<sub>2</sub> (30% w/w in  
178 H<sub>2</sub>O, 8 mmol, 5 equiv) was added dropwise during 2 h in the mixture  
179 while stirring. After 2 h, the catalyst was filtered off and the reaction  
180 mixture was extracted with ethyl acetate. The organic phases were  
181 gathered and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was then removed by  
182 evaporation.

## ■ RESULTS AND DISCUSSION

183

**Preparation and Characterization of Eco-CaMnO<sub>x</sub> Catalysts.** *Preparation of Eco-CaMnO<sub>x</sub> Catalysts.* Eco-  
184 CaMnO<sub>x</sub> catalysts were prepared from Mn-rich biomass. Eco-  
185 CaMnO<sub>x</sub> catalysts were prepared from Mn-rich biomass. Eco-  
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In this study, two parameters were studied to investigate  
193 their influence on Eco-CaMnO<sub>x</sub> catalytic properties: the plant  
194 species, from which the catalysts were prepared, and the  
195 temperature of the thermal treatment. The dried leaves, from  
196 each of the four species of the Grevillea genus, were thermally  
197 treated in an oven, under air flow, at 300, 550, or 950 °C for 6  
198 h, to destroy the organic matter. Indeed, these temperatures  
199 were chosen according to the literature, as different manganese  
200 oxides could be formed depending on the corresponding  
201 heating temperature: MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, or Mn<sub>3</sub>O<sub>4</sub>.<sup>39,40</sup> Eco-  
202 CaMnO<sub>x</sub> catalysts were then characterized by MP-AES, XRPD,  
203 HRTEM, and STEM-EDX mapping.  
204

*MP-AES Analysis of Eco-CaMnO<sub>x</sub> Catalysts.* Metallic  
205 composition of intact Mn-accumulating plant leaves and of  
206 Eco-CaMnO<sub>x</sub> catalysts, resulting from different plant species  
207 and thermal treatments, was studied by MP-AES analyses.  
208 Analyses were performed in triplicate for each sample to  
209 determine the standard deviation of the measurement (Table  
210 S1).  
211

The results showed that Mn was the major transition metal  
212 in all eco-catalysts (1 to 16.1 wt %), except for Eco-CaMnO<sub>x</sub>  
213 (*G. exul* ssp. *exul* 300 °C) (Figure 3). As Ca, Mg, Na, K, and  
214 Fe are essential mineral components of plants, they were found  
215 in Eco-CaMnO<sub>x</sub> catalysts, Ca being the major mineral element  
216 for every eco-catalyst. Interestingly, the composition of Eco-  
217 CaMnO<sub>x</sub> catalysts derived from different plants of the same  
218 species was quite similar, as shown by low RSD (Table S1).  
219 This reproducibility of composition within species could be  
220 explained by the harvest timing.<sup>13</sup> Indeed, leaves were  
221 harvested when they became a vegetal litter: they have the  
222 highest Mn concentration for each species. As a result of the  
223 accumulating specificity of each plant species, the chemical  
224 composition appeared different between Eco-CaMnO<sub>x</sub> cata-  
225 lysts.  
226

Within a species the heating temperature at 550 and 950 °C  
227 did not have much influence on the chemical composition. But  
228 at 300 °C the elements were less concentrated. This might be  
229



**Table 1. Crystalline Species Identified in Eco-CaMnO<sub>x</sub> Catalysts and in Synthetic Ash Control**

|   | CaCO <sub>3</sub> | CaSO <sub>4</sub> | KCl | Ca <sub>2</sub> Mn <sub>3</sub> O <sub>8</sub> | CaMnO <sub>3</sub> | Mn <sub>2</sub> O <sub>3</sub> | K <sub>2</sub> SO <sub>4</sub> | K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub> |
|---|-------------------|-------------------|-----|--|--------------------|--------------------------------|--------------------------------|--|
| Eco-CaMnO <sub>x</sub> ( <i>G. gillivrayi</i> 300 °C) <sup>a</sup>            | x                 |                   |     |  |                    |                                |                                |  |
| Eco-CaMnO <sub>x</sub> ( <i>G. gillivrayi</i> 550 °C)                         | x                 |                   | x   | x  |                    |                                |                                | x  |
| Eco-CaMnO <sub>x</sub> ( <i>G. gillivrayi</i> 950 °C)                         |                   | x                 |     |  | x                  | x                              |                                |  |
| Eco-CaMnO <sub>x</sub> ( <i>G. exul</i> ssp. <i>exul</i> 550 °C) <sup>a</sup> | x                 |                   | x   |  |                    |                                | x                              |  |
| Eco-CaMnO <sub>x</sub> ( <i>G. exul</i> ssp. <i>rubiginosa</i> 550 °C)        | x                 |                   | x   | x  |                    |                                |                                | x  |
| Eco-CaMnO <sub>x</sub> ( <i>G. meisneri</i> 550 °C)                           | x                 |                   | x   | x  |                    |                                |                                | x  |
| synthetic ash control (550 °C)  |                   |                   | x   |  |                    | x                              |                                |  |

<sup>a</sup>Mn was not present in a crystalline form.

230 due to a partial degradation of the organic matter at 300 °C  
231 and a total degradation above 550 °C.

232 For further characterizations and experimentations, *G.*  
233 *gillivrayi* was chosen as the model species because the Eco-  
234 CaMnO<sub>x</sub> catalysts from *G. gillivrayi* present an average  
235 composition of minerals among the other species.

236 *XRPD Analysis of Eco-CaMnO<sub>x</sub> Catalysts.* XRPD was  
237 performed to deliver insights on the crystalline species present  
238 in Eco-CaMnO<sub>x</sub> catalysts and to compare with a reconstituted  
239 control of synthetic ashes. The synthetic ash control was  
240 obtained by mixing commercial metallic salts chosen so that  
241 the relative percentage of metallic elements in the starting  
242 mixture was exactly the same as in the leaves of *G. exul* ssp.

243 *rubiginosa*, and was followed by a thermal treatment at 550 °C.  
244 The identified crystalline phases are summarized in Table 1.  
245 Mn was not present in a crystalline form in the eco-catalysts  
246 prepared at 300 °C.

247 Interestingly, for the other temperatures, Mn was present as  
248 mixed calcium–manganese oxides. Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> was identified in  
249 all Eco-CaMnO<sub>x</sub> prepared at 550 °C, except for *G. exul* ssp.  
250 *exul* in which crystalline species of manganese was not  
251 observed. The absence of crystalline manganese species in *G.*  
252 *exul* ssp. *exul* could be linked to a low ratio of Mn/Ca (Table  
253 S1) preventing the crystallization process. CaMnO<sub>3</sub> was  
254 identified in all Eco-CaMnO<sub>x</sub> prepared at 950 °C. CaMnO<sub>3</sub>  
255 could result from the degradation of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> at high  
256 temperature, which was consistent with the calcination  
257 temperatures used by Han et al. to prepare these two  
258 complexes.<sup>41</sup>

259 No crystalline mixed manganese–calcium oxide was  
260 observed in the synthetic ash control. It suggested that a  
261 crystallization mechanism is specific to plant-derived eco-  
262 catalysts and that it cannot be reproduced in a simple mixture  
263 of ashes. This difference in crystallization pathways illustrates  
264 the vegetal footprint of Eco-CaMnO<sub>x</sub>, which is in accordance  
265 with what we reported for Eco-Mn<sub>1</sub>.<sup>32</sup>

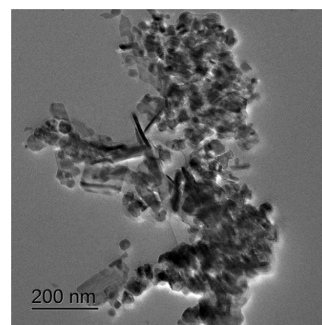
266 The structure of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> has been reported as infinite  
267 sheets of Mn<sub>3</sub>O<sub>8</sub><sup>4-</sup> held together by calcium ions. Mn ions are  
268 octahedrally coordinated by oxygen atoms and occupy three-  
269 fourths of the octahedral layer sites. The other one-fourth is  
270 vacant.<sup>37,42</sup> The negative charge is further compensated by the  
271 presence of Ca ions in trigonal prismatic sites located above  
272 and below layer vacancies.<sup>38</sup>

273 CaMnO<sub>3</sub> has a perovskite structure based on corner-shared  
274 MnO<sub>6</sub>-octahedra. Mn ions, present in the oxidation state IV,  
275 are located at the center of the octahedron, while each Ca ion  
276 occupies the interoctahedral sites.<sup>38,41</sup>

277 The layered structure of Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> shares similarities with  
278 the cofactor CaMn<sub>4</sub>O<sub>5</sub>, the oxygen-evolving complex present in  
279 Photosystem II, which performs the photo-oxidation of water  
280 during photosynthesis. The incorporation of calcium into

manganese oxides greatly improves water oxidation capaci-  
ties.<sup>43,44</sup> Research on a series of manganese–calcium oxides  
showed that Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and CaMnO<sub>3</sub> were efficient catalysts  
for the oxygen evolution reaction and oxygen reduction  
reaction. Indeed, manganese ions in Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and CaMnO<sub>3</sub>  
are in the oxidation state IV and they may present interesting  
oxidative properties similar to MnO<sub>2</sub>.

*HRTEM Analysis of Eco-CaMnO<sub>x</sub> Catalysts (*G. gillivrayi*,  
550 °C).* HRTEM images of Eco-CaMnO<sub>x</sub> (*G. gillivrayi*, 550  
°C) revealed different particles with various shapes (Figure 4).

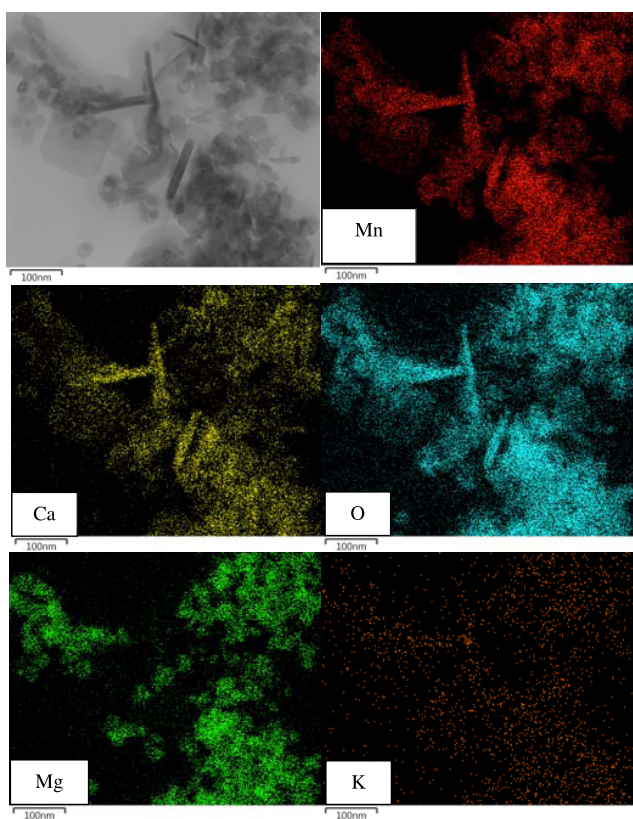


**Figure 4.** HRTEM image of Eco-CaMnO<sub>x</sub> catalysts (*G. gillivrayi* 550 °C).

Small round particles of about 10–50 nm in diameter, lamellar  
particles of about 10 nm width over 100 nm length, as well as  
thin layer-shape particles seemed blended together into a  
matrix.

*STEM-EDX Mapping of Eco-CaMnO<sub>x</sub> (*G. gillivrayi*, 550 °C).*  
The STEM-EDX analysis was used to establish the chemical  
composition mapping of Eco-CaMnO<sub>x</sub> catalysts (*G. gillivrayi*,  
550 °C) (Figure 5). Manganese, calcium, magnesium, and  
potassium were expectedly present, as shown by MP-AES  
analyses. The polymetallic structure of Eco-CaMnO<sub>x</sub> catalysts  
was supported by the aggregation of manganese, oxygen, and  
all of the other elements in the round particles, the layer-shape  
particles, and the matrix. However, it should be noticed that  
the lamellar particles were exclusively composed of manganese,  
oxygen, and calcium. The association of these only three  
elements in a single well-defined shape of particles confirmed  
the presence of the Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> complex, and that this complex  
is organized in lamellar sheets.

Extensive structural analyses of the different Eco-CaMnO<sub>x</sub>  
catalysts showed the presence of two unusual and valuable  
mixed calcium–manganese complexes: Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and  
CaMnO<sub>3</sub>. The oxidative potential of the Eco-CaMnO<sub>x</sub>  
catalysts was studied in the epoxidation of alkenes and  
especially terpenes, as biosourced substrates.



**Figure 5.** STEM-EDX mapping of Eco-CaMnO<sub>x</sub> catalysts (*G. gillivrayi*, 550 °C).

315 **Use of Eco-CaMnO<sub>x</sub> Catalysts in Synthesis.** The  
 316 standard methods used in fine chemical industries can access  
 317 epoxidation of substitute alkenes by the use of stoichiometric  
 318 amounts of organic peroxides or percarboxylic acids, such as  
 319 *meta*-chloroperoxybenzoic acid.<sup>45</sup> Other methods include the  
 320 use of dimethyldioxirane (also known as Murray's reagent),  
 321 formed in situ from the reaction between acetone and oxone,<sup>46</sup>  
 322 or electrophilic halide source in the presence of a base.<sup>47</sup>  
 323 Owing to safety concerns and/or the issue of large production  
 324 of wastes by these processes, there is a strong need to develop  
 325 new safer and eco-friendlier methods.

326 Hydrogen peroxide is considered as an ideal alternative  
 327 oxidant on both environmental and economic grounds.<sup>48</sup> Not  
 328 only is it relatively cheap, easily available, and stable at the  
 329 usual concentration (typically <60 wt %), but it is also a clean  
 330 oxidizing reagent, as it only forms water as a byproduct.  
 331 However, it requires an activation to catalyze the oxygen-  
 332 transfer process. Many catalytic systems using H<sub>2</sub>O<sub>2</sub> as the  
 333 oxidant for epoxidation of alkenes were based on transition-  
 334 metal catalysts.<sup>49–51</sup> However, the use of economically and  
 335 environmentally unsustainable metals, such as rhenium,<sup>52–55</sup>  
 336 vanadium,<sup>56,57</sup> molybdenum,<sup>58–60</sup> or tungsten,<sup>61–64</sup> prompted  
 337 the research toward inexpensive, abundant, and innocuous  
 338 transition metals. In particular, iron or manganese revealed to  
 339 be one of the more promising elements thanks to their  
 340 relatively low toxicity and their abundance in Earth's crust.<sup>65,66</sup>

341 Porphyrin–Mn have been extensively investigated as a mimic  
 342 of cytochrome P450,<sup>67–70</sup> but suffer from difficulties in  
 343 synthesis and purification. As they offer synthetic advantages  
 344 over porphyrin systems, considerable attention was given to  
 345 Salen–Mn,<sup>71,72</sup> in particular to the Jacobsen asymmetric

epoxidation reaction.<sup>73–75</sup> However, the homogeneous nature  
 of such metalloporphyrin and Schiff base complexes leads not  
 only to deactivation due to oxidative degradation of the  
 ligand<sup>76</sup> but also to environmental costs concerning their  
 nonrecyclability. To rectify both problems, heterogenization of  
 these Mn-based catalysts was demonstrated, by grafting on a  
 solid support or immobilization into porous solids, such as  
 silica, polymers, nanoparticles, and zeolites.<sup>77–80</sup> For example,  
 heterogeneous Ti silicates are nowadays used at an industrial  
 scale with H<sub>2</sub>O<sub>2</sub> for conducting epoxidation reactions with very  
 high catalytic and environmental performances.<sup>81</sup>

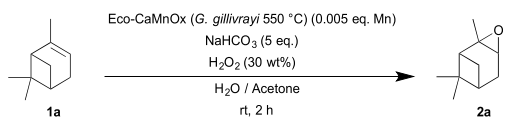
In our previous works, we showed that montmorillonite-  
 supported Eco-Mn<sub>1</sub> catalyzed the epoxidation of styrene. Eco-  
 Mn<sub>1</sub> contained only 0.31 mol % of manganese, a much lower  
 content of manganese than that reported in previously  
 described Mn-derived heterogeneous catalysts.<sup>82,83</sup> Compar-  
 ison of Eco-Mn<sub>1</sub> properties to those of heterogeneous catalysts  
 made by incorporation of commercial MnCl<sub>2</sub>·4H<sub>2</sub>O and FeCl<sub>3</sub>·  
 6H<sub>2</sub>O highlighted the superior catalytic activity of polymetallic  
 species present in Eco-Mn<sub>1</sub>. These promising results prompted  
 us to investigate the utilization of Eco-CaMnO<sub>x</sub> as an  
 epoxidizing agent and to study the possible cooperative  
 catalytic effect between Ca and Mn.

**Optimization of the Conditions for the Epoxidation of  $\alpha$ -  
 pinene.** The epoxidation of  $\alpha$ -pinene was chosen as a probe  
 reaction to optimize the reaction conditions.  $\alpha$ -pinene is a  
 monoterpene mostly found in pine trees, an abundant natural  
 resource. The pinene oxide represents an inexpensive  
 biosourced starting material for the synthesis of flavors,  
 fragrances, and agrochemical and therapeutic substances.<sup>84–86</sup>  
 However,  $\alpha$ -pinene oxide is a sensitive and reactive substrate,  
 which rearranges easily in acid conditions.<sup>87,88</sup> The rearrange-  
 ment of  $\alpha$ -pinene oxide leads to the formation of a wide range  
 of products, which depends largely on the acid–base  
 properties of the catalytic system. Over 200 compounds were  
 reported when the isomerization–reaction temperature was  
 above 100 °C.<sup>87</sup> It is well described that Lewis acid sites favor  
 the formation of campholenic aldehyde, pinocarveol, and iso-  
 pinocampnone, whereas Brønsted acid sites result in the  
 formation of *trans*-carveol, *trans*-sobrerol, and *p*-cymene.<sup>89–91</sup>  
 For instance, one of the most desired products resulting from  
 the  $\alpha$ -pinene oxide is campholenic aldehyde because it is an  
 intermediate for the manufacture of sandalwood fragrances.  
 The epoxidation of  $\alpha$ -pinene into  $\alpha$ -pinene oxide remains a  
 challenge because of its isomerization into many different  
 byproducts.

In a typical procedure,  $\alpha$ -pinene, Eco-CaMnO<sub>x</sub> (*G. gillivrayi*  
 550 °C), and NaHCO<sub>3</sub> were stirred in a mixture of  
 acetone:water (1:1) at room temperature for 10 min. H<sub>2</sub>O<sub>2</sub>  
 (30% w/w in H<sub>2</sub>O) was added dropwise during 2 h in the  
 mixture while stirring. After 2 h, the catalyst was filtered off and  
 the reaction mixture was extracted with ethyl acetate. The  
 organic layers were gathered and dried with Na<sub>2</sub>SO<sub>4</sub>. The  
 solvent was then removed by evaporation and the reaction  
 products analyzed by gas chromatography–mass spectrometry  
 (GC–MS)/flame ionization detector (FID).

**Effect of H<sub>2</sub>O<sub>2</sub> Amount.** The effect of the quantity of H<sub>2</sub>O<sub>2</sub>  
 added into the reaction mixture was studied, as an excessive  
 amount of H<sub>2</sub>O<sub>2</sub> could lead to a decrease in epoxide selectivity  
 by overoxidation.<sup>92</sup> The conversion, yield, and selectivity  
 followed the same trend (Table 2). Increasing the quantity of  
 H<sub>2</sub>O<sub>2</sub> increased the conversion, yield, and selectivity before  
 reaching a threshold. Almost total conversion of  $\alpha$ -pinene **1a**

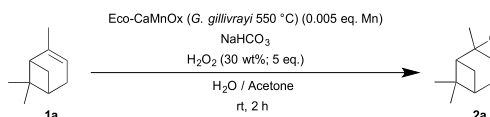
**Table 2. Effect of the Amount of H<sub>2</sub>O<sub>2</sub> and of the Adding Time on the Epoxidation of  $\alpha$ -pinene<sup>a</sup>**



| entry | H <sub>2</sub> O <sub>2</sub> (equiv) | addition time (min) | conversion (%) <sup>b</sup> | yield (%) <sup>b</sup> | selectivity (%) <sup>b,c</sup> |
|-------|---------------------------------------|---------------------|-----------------------------|------------------------|--------------------------------|
| 1     | 0                                     | 120                 | 0                           | 0                      | 0                              |
| 2     | 1                                     | 120                 | 62                          | 21                     | 34                             |
| 3     | 3                                     | 120                 | 80                          | 44                     | 55                             |
| 4     | 4                                     | 120                 | 77                          | 47                     | 61                             |
| 5     | 5                                     | 120                 | 98                          | 64                     | 65                             |
| 6     | 10                                    | 120                 | 99                          | 62                     | 63                             |
| 7     | 10                                    | 60                  | 98                          | 65                     | 66                             |
| 8     | 10                                    | 30                  | 63                          | 41                     | 65                             |

<sup>a</sup>Reaction conditions:  $\alpha$ -pinene (1.6 mmol, 1 equiv), catalyst (8  $\mu$ mol, 0.005 equiv Mn), NaHCO<sub>3</sub> (8 mmol, 5 equiv), H<sub>2</sub>O<sub>2</sub> (30 wt %), and H<sub>2</sub>O (20 mL): acetone (20 mL), rt, 2 h. <sup>b</sup>Conversion, yield, and selectivity were established by FID using biphenyl as internal standard. <sup>c</sup>Selectivity was calculated as the ratio of yield over conversion.

**Table 3. Effect of the Amount of NaHCO<sub>3</sub> on the Epoxidation of  $\alpha$ -pinene<sup>a</sup>**



| entry | NaHCO <sub>3</sub> (equiv) | conversion (%) <sup>b</sup> | yield (%) <sup>b</sup> | selectivity (%) <sup>b,c</sup> |
|-------|----------------------------|-----------------------------|------------------------|--------------------------------|
| 1     | 0                          | 0                           | 0                      | 0                              |
| 2     | 0.5                        | 36                          | 2                      | 6                              |
| 3     | 1                          | 47                          | 7                      | 15                             |
| 4     | 3                          | 82                          | 38                     | 46                             |
| 5     | 5                          | 98                          | 64                     | 65                             |

<sup>a</sup>Reaction conditions:  $\alpha$ -pinene (1.6 mmol, 1 equiv), catalyst (8  $\mu$ mol, 0.005 equiv Mn), NaHCO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> (30 wt%; 8 mmol, 5 equiv), and H<sub>2</sub>O (20 mL): acetone (20 mL), rt, 2 h. <sup>b</sup>Conversion, yield, and selectivity were established by FID using biphenyl as internal standard. <sup>c</sup>Selectivity was calculated as the ratio of yield over conversion.

and a yield of 64% in epoxide **2a** were reached with 5 equiv of H<sub>2</sub>O<sub>2</sub> (Table 2, entry 5). The addition time of H<sub>2</sub>O<sub>2</sub> in the reaction mixture was also investigated. Although the selectivity in epoxide remained similar by decreasing the addition time, the conversion dropped from 98% in 1–2 h (Table 2, entries 6, 7) to 63% in 30 min (Table 2, entry 8). These results supported the importance of a slow addition of H<sub>2</sub>O<sub>2</sub> in oxidative reactions. Indeed, it was reported that a gradual addition of H<sub>2</sub>O<sub>2</sub> decreased its self-decomposition.<sup>93,94</sup>

The selectivity in  $\alpha$ -pinene oxide gave some information about Eco-CaMnO<sub>x</sub>. The oxygenated byproducts observed, such as campholenic aldehyde, carveol, and iso-pinocamphone, could be explained by the easy opening and rearrangement of the epoxide by Lewis acid sites. This could reveal the presence of many metallic species in our catalysts, like Fe, Ca, and Mg, which could confer Lewis acid properties to Eco-CaMnO<sub>x</sub> catalysts. As it was reported that  $\alpha$ -pinene oxide could also rearrange spontaneously in acid or neutral aqueous phase media,<sup>90</sup> the epoxide was directly engaged in the reaction and without any catalyst, to test its stability. In the presence of Eco-CaMnO<sub>x</sub> catalysts a conversion of 45% was observed, whereas it was fully recovered without any catalyst. This result indicated that the epoxide was stable in our conditions, even in the presence of water, and that its rearrangement only occurred in the presence of Eco-CaMnO<sub>x</sub>. This supports the presence of Lewis acid sites in Eco-CaMnO<sub>x</sub>. Allylic oxidation is often a competitive process of epoxidation in the oxidation of cyclic olefins.<sup>95,96</sup> As both processes could occur simultaneously, it could explain the formation of verbenone, identified among the different byproducts.

For the following reactions, 5 equiv of H<sub>2</sub>O<sub>2</sub> was employed as it represented the smallest amount affording total conversion and high yield in epoxide. The addition time was kept at 2 h.

**Effect of NaHCO<sub>3</sub> Amount.** The effect of the quantity of NaHCO<sub>3</sub> added into the reaction mixture was investigated (Table 3). No conversion of  $\alpha$ -pinene was observed in the absence of sodium hydrogen carbonate (Table 3, entry 1). This result supported the essential presence of sodium hydrogen carbonate allowing the epoxidation. It is assumed

that NaHCO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> could produce in situ peroxy mono-carbonate ions (HCO<sub>4</sub><sup>-</sup>),<sup>97,98</sup> which would react with the Mn-eco-catalyst to form the active epoxidizing reagent. Indeed, a neutral or slightly basic pH (range from 7 to 9) is optimal for this bicarbonate-activated peroxide system, which corresponds to the pH values of the aqueous phase that ranged from 8.2 to 8.8 in our system.

An attempt to reduce NaHCO<sub>3</sub> quantity resulted in decreasing conversion, yield, and selectivity in epoxide. Therefore, 5 equiv of NaHCO<sub>3</sub> seemed to be the lowest quantity giving high conversion and yield (Table 3, entry 5).

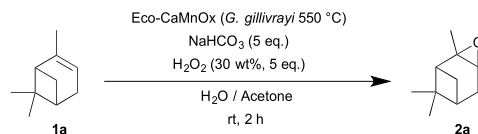
**Effect of Catalyst Loading.** The effect of the quantity of Eco-CaMnO<sub>x</sub> catalysts was then studied using  $\alpha$ -pinene as the substrate (Table 4). A low quantity of manganese gave high conversion rates. Almost total conversion and 64% yield were obtained with only 0.005 equiv in manganese (Table 4, entry 4). This result is remarkable compared to standard manganese-based catalysts, which usually require to be used in excess.<sup>99</sup> As a control, the reaction was carried out in the absence of Eco-CaMnO<sub>x</sub> catalysts. The reaction could not occur in the corresponding reaction time, in 2 h (Table 4, entry 1).

The oxidative capacity of Eco-CaMnO<sub>x</sub> was also compared to synthetic catalysts (Table 4, entries 7–9). The synthetic Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> catalyst was prepared following the procedure described by Najafpour et al.,<sup>38</sup> and commercial manganese dioxide was activated.

As expected, conversion of  $\alpha$ -pinene catalyzed by calcium oxide was negligible (Table 4, entry 9). Calcium oxide species alone cannot catalyze the epoxidation of  $\alpha$ -pinene, since calcium is not electroactive. However, conversion was increased by the addition of calcium to manganese oxide species; yields of 15 and 32% were obtained with commercial activated MnO<sub>2</sub> and synthetic Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> catalysts, respectively (Table 4, entries 7 and 8). A comparison of these three experiments shows that calcium enhances the reactivity of manganese, suggesting a synergistic effect of mixed calcium–manganese oxides toward epoxidation. These findings suggest that the addition of calcium does not change the oxidation potential of manganese, but might change the dispersion and/or exposition of manganese, enhancing its reactivity as suggested by the works of Han et al. on mixed calcium–manganese oxides.<sup>41</sup>



**Table 4. Effect of the Catalyst Loading on the Epoxidation of  $\alpha$ -pinene<sup>a</sup>**

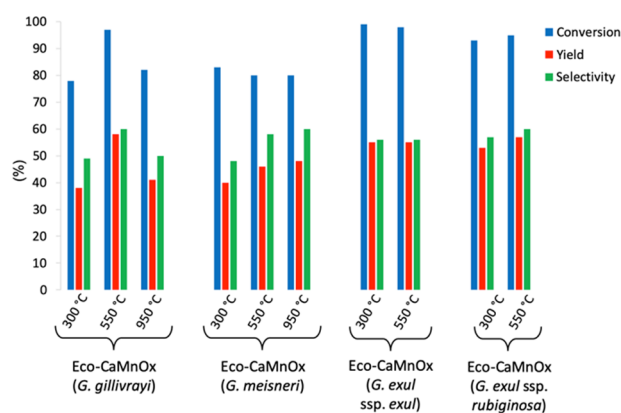


| entry | catalyst                                       | equiv Mn     | conversion (%) <sup>b</sup> | yield (%) <sup>b</sup> | selectivity (%) <sup>b,c</sup> | TON <sup>f</sup> | TOF <sup>g</sup> (h <sup>-1</sup> ) |
|-------|--|--------------|-----------------------------|------------------------|--------------------------------|------------------|-------------------------------------|
| 1     | Eco-CaMnO <sub>x</sub>                         | 0            | 0                           | 0                      | 0                              | 0                | 0                                   |
| 2     | Eco-CaMnO <sub>x</sub>                         | 0.001        | 89                          | 49                     | 55                             | 490              | 245                                 |
| 3     | Eco-CaMnO <sub>x</sub>                         | 0.0025       | 97                          | 48                     | 49                             | 192              | 96                                  |
| 4     | Eco-CaMnO <sub>x</sub>                         | 0.005        | 97                          | 62                     | 64                             | 124              | 62                                  |
| 5     | Eco-CaMnO <sub>x</sub>                         | 0.01         | 94                          | 55                     | 59                             | 55               | 28                                  |
| 6     | Eco-CaMnO <sub>x</sub>                         | 0.1          | 91                          | 61                     | 67                             | 6                | 3                                   |
| 7     | Ca <sub>2</sub> Mn <sub>3</sub> O <sub>8</sub> | 0.005        | 51                          | 32                     | 63                             | 64               | 32                                  |
| 8     | activated MnO <sub>2</sub>                     | 0.005        | 55                          | 15                     | 27                             | 30               | 15                                  |
| 9     | CaO  | <sup>d</sup> | <sup>e</sup>                | 0                      | 0                              |                  |                                     |

<sup>a</sup>Reaction conditions:  $\alpha$ -pinene (1.6 mmol, 1 equiv), the catalyst, NaHCO<sub>3</sub> (8 mmol, 5 equiv), H<sub>2</sub>O<sub>2</sub> (30 wt %; 8 mmol, 5 equiv), and H<sub>2</sub>O (20 mL): acetone (20 mL), rt, 2 h. <sup>b</sup>Conversion, yield, and selectivity were established by FID using biphenyl as the internal standard. <sup>c</sup>Selectivity was calculated as the ratio of yield over conversion. <sup>d</sup>0.02 equiv Ca was used, corresponding to the quantity of Ca engaged by 0.005 equiv Mn with Eco-CaMnO<sub>x</sub>. <sup>e</sup>Traces of verbenol, carveol, and campholenic aldehyde were detected by GC-MS. <sup>f</sup>TON = number of mol of the product formed per mol of catalyst. <sup>g</sup>TOF = number of mol of the product formed per mol of catalyst and per unit of time.

491 Interestingly, Eco-CaMnO<sub>x</sub> catalysts gave a twice-higher  
492 yield compared to synthetic Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> (Table 4, entries 4 and  
493 7). The enhanced reactivity of our catalyst might be due to a  
494 different structural organization of manganese linked to its  
495 vegetal footprint and/or due to the presence of traces of other  
496 electroactive metal species.

497 *Effect of the Plant Species and the Temperature of the*  
498 *Thermal Treatment Used to Prepare Eco-CaMnO<sub>x</sub>.* The  
499 different Eco-CaMnO<sub>x</sub> catalysts prepared from the four species  
500 of *Grevillea* were tested in the epoxidation of  $\alpha$ -pinene by  
501 using the optimized reaction conditions. The influence of the  
502 heating temperature during the thermal treatment of biomass  
503 was also investigated (Figure 6). For each plant species, each  
504 corresponding Eco-CaMnO<sub>x</sub> catalyst showed a potent catalytic  
505 activity. These results guarantee that every manganese-  
506 accumulating plant species used in rehabilitation could be  
507 valorized afterward by this process.



**Figure 6.** Effect of the plant species and of the temperature of the thermal treatment used to prepare Eco-CaMnO<sub>x</sub> on the epoxidation of  $\alpha$ -pinene. Reaction conditions:  $\alpha$ -pinene (1.6 mmol, 1 equiv), catalyst (8 mmol, 0.005 equiv Mn), NaHCO<sub>3</sub> (8 mmol, 5 equiv), H<sub>2</sub>O<sub>2</sub> (30 wt %; 8 mmol, 5 equiv), and H<sub>2</sub>O (20 mL): acetone (20 mL), rt, 2 h. Conversion, yield, and selectivity were established by FID using biphenyl as internal standard. Selectivity was calculated as the ratio of yield over conversion.

508 Within a species, the temperature of the thermal treatment  
509 did not seem to have much influence on the Eco-CaMnO<sub>x</sub>  
510 activities. Surprisingly, no loss of activity was observed for the  
511 eco-catalysts formed at 300 °C despite the residual organic  
512 matter. The Eco-CaMnO<sub>x</sub> catalysts of *G. gillivrayi* and *G.*  
513 *meisneri* prepared at 950 °C revealed similar activities as the  
514 corresponding Eco-CaMnO<sub>x</sub> catalysts prepared at lower  
515 temperatures (300 and 550 °C). The best catalyst in terms  
516 of activity and energy required for its preparation remained the  
517 one prepared at 550 °C.

518 The reaction conditions to perform the epoxidation of  $\alpha$ -  
519 pinene were optimized to reach a good compromise of the  
520 high efficiency of the reaction with sustainable and eco-  
521 responsible use of chemical products and solvents. In these  
522 conditions, almost total conversion was accessed with 65%  
523 selectivity in pinene oxide. Longer reaction times were tested,  
524 but it only resulted in a decrease in selectivity, the conversion  
525 remaining total. This result was in accordance with the high  
526 reactivity of pinene oxide and thus its conversion into isomeric  
527 products.<sup>100,101</sup>

528 Our system can be advantageously compared to other  
529 bicarbonate-activated peroxide systems based on Mn catalysts.  
530 For instance, Lane et al. obtained 89% yield but only in the  
531 presence of additives.<sup>82</sup> Qi et al. reached 40% selectivity using  
532 Mn<sup>2+</sup>-exchanged zeolites.<sup>92</sup>

533 *Substrate Scope for the Epoxidation of Terpenes and*  
534 *Lipids by Eco-CaMnO<sub>x</sub> Catalysts.* The epoxidation of diverse  
535 terpenes and lipids was carried out to evaluate the scope of our  
536 process (Table 5).

537 High conversions and yields were obtained with a large  
538 variety of terpenes, from cyclic to terminal substrates, which  
539 confirmed the efficiency of the method. In some cases, a longer  
540 reaction time was needed to reach higher conversions.

541 The chemoselectivity of Eco-CaMnO<sub>x</sub> catalysts was  
542 illustrated through the selective epoxidation of terpenes  
543 (Table 5, entries 2–8) bearing various functional groups,  
544 such as alcohol, ester, or enone, that remained unmodified.  
545 The epoxidation of monoterpenes like terpineol, isopulegol,  
546 and citronellyl acetate (Table 4, entries 2, 3 and 5) gave total  
547 conversion and selectivity. The epoxidation of (*R*)-(+)-limo-  
548 nene, linalool, geranyl acetate,  $\alpha$ -ionone, and  $\beta$ -ionone gave










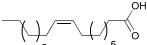
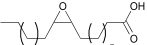
Table 5. Substrate Scope for the Epoxidation of Natural Substrates by Eocatalysts (Eco-CaMnO<sub>x</sub><sup>a</sup>, Eco-Mn<sub>1</sub><sup>18,e</sup> and Pyr-Mn<sup>108,f</sup>)

$$\text{R}_1\text{C}(\text{R}_2)=\text{C}(\text{R}_3)\text{R}_4 \xrightarrow[\text{H}_2\text{O} / \text{Acetone, RT}]{\text{Eco-CaMnOx (G. gillivrayi 550 }^\circ\text{C) (0.005 eq. Mn), NaHCO}_3 \text{ (5 eq.), H}_2\text{O}_2 \text{ (30 wt\%; 5 eq.)}}$$

$$\text{R}_1\text{C}(\text{R}_2)\text{C}(\text{R}_3)\text{R}_4\text{O}$$

| Entry | Substrate 1 | Eocatalyst solvent   | Product 2 | Reaction time (h) | Conversion (%) <sup>b</sup> | Yield (%) <sup>b</sup>   | Selectivity (%) <sup>b,c</sup>   |
|-------|-------------|--|-----------|-------------------|-----------------------------|--|--|
| 1     |             | Eco-CaMnOx<br>H <sub>2</sub> O/Acetone                       |           | 2                 | 93                          | <b>2b</b> <sub>1</sub> : 15<br><b>2b</b> <sub>2</sub> : 78                               | <b>2b</b> <sub>1</sub> : 16<br><b>2b</b> <sub>2</sub> : 84                               |
|       |             | Eco-Mn <sub>1</sub> <sup>18,e</sup><br>H <sub>2</sub> O/ DMF |           | 4                 | 50                          | <b>2b</b> <sub>1</sub> : 43<br><b>2b</b> <sub>2</sub> : 7                                | <b>2b</b> <sub>1</sub> : 86<br><b>2b</b> <sub>2</sub> : 14                               |
|       |             | Pyr-Mn <sup>108,f</sup><br>H <sub>2</sub> O/Acetone          |           | 2                 | 99                          | <b>2b</b> <sub>1</sub> : 1<br><b>2b</b> <sub>2</sub> : 98                                | <b>2b</b> <sub>1</sub> : 1<br><b>2b</b> <sub>2</sub> : 99                                |
|       |             |  |           |                   |                             |  |  |
| 2     |             | Eco-CaMnOx<br>H <sub>2</sub> O/Acetone                       |           | 2                 | > 99                        | > 99   | 100  |
| 3     |             | Eco-CaMnOx<br>H <sub>2</sub> O/Acetone                       |           | 4                 | > 99                        | > 99   | 100  |
| 4     |             | Eco-CaMnOx<br>H <sub>2</sub> O/Acetone                       |           | 4                 | > 99                        | <b>2e</b> <sub>1</sub> : 64<br><b>2e</b> <sub>2</sub> : 34<br><b>2e</b> <sub>3</sub> : 2 | <b>2e</b> <sub>1</sub> : 64<br><b>2e</b> <sub>2</sub> : 34<br><b>2e</b> <sub>3</sub> : 2 |
|       |             | Eco-Mn <sub>1</sub> <sup>18,e</sup><br>H <sub>2</sub> O/ DMF |           | 4                 | 65                          | <b>2e</b> <sub>3</sub> : 63  | <b>2e</b> <sub>3</sub> : 97  |
|       |             | Pyr-Mn <sup>108,f</sup><br>H <sub>2</sub> O/Acetone          |           | 2                 | > 99                        | <b>2e</b> <sub>4</sub> : 89  | <b>2e</b> <sub>4</sub> : 88  |
| 5     |             | Eco-CaMnOx<br>H <sub>2</sub> O/Acetone                       |           | 4                 | 99                          | 99   | 100  |

Table 5. continued

| Entry | Substrate 1   | Biocatalyst solvent                 | Product 2   | Reaction time (h) | Conversion (%) <sup>b</sup> | Yield (%) <sup>b</sup> | Selectivity (%) <sup>b,c</sup> |
|-------|---|-------------------------------------|---|-------------------|-----------------------------|------------------------|--------------------------------|
| 6     |  | Eco-CaMnO <sub>x</sub>              |  +  | 4                 | > 99                        | 2g <sub>1</sub> : 50   | 2g <sub>1</sub> : 50           |
|       |   | H <sub>2</sub> O/Acetone            |   |                   |                             | 2g <sub>2</sub> : 50   | 2g <sub>2</sub> : 50           |
| 7     |  | Eco-CaMnO <sub>x</sub>              |  +  | 4                 | 81                          | 2h <sub>1</sub> : 71   | 2h <sub>1</sub> : 88           |
|       |   | H <sub>2</sub> O/Acetone            |   |                   |                             | 2h <sub>2</sub> : 10   | 2h <sub>2</sub> : 12           |
| 8     |  | Eco-CaMnO <sub>x</sub>              |  +  | 2                 | > 99                        | 2i <sub>1</sub> : 70   | 2i <sub>1</sub> : 70           |
|       |   | H <sub>2</sub> O/Acetone            |   |                   |                             | 2i <sub>2</sub> : 30   | 2i <sub>2</sub> : 30           |
| 9     |  | Eco-CaMnO <sub>x</sub> <sup>d</sup> |    | 4                 | 66                          | 66                     | 100                            |
|       |   | H <sub>2</sub> O/Acetone            |   |                   |                             |                        |                                |
|       |   | Eco-Mn <sub>1</sub> <sup>18,f</sup> |   |                   |                             |                        |                                |
|       |   | H <sub>2</sub> O/ DMF               |   |                   |                             |                        |                                |
|       |   | Pyr-Mn <sup>108,f</sup>             |   | 2                 | 99                          | 82                     | 80                             |
|       |   | H <sub>2</sub> O/Acetone            |   |                   |                             |                        |                                |

<sup>a</sup>Reaction conditions: substrate (1.6 mmol, 1 equiv), catalyst (8 μmol, 0.005 equiv Mn), NaHCO<sub>3</sub> (8 mmol, 5 equiv), H<sub>2</sub>O<sub>2</sub> (30 wt %; 8 mmol, 5 equiv), and H<sub>2</sub>O (20 mL): acetone (20 mL), rt. <sup>b</sup>Conversion, yield, and selectivity were established by FID, using biphenyl as internal standard, and then confirmed by <sup>1</sup>H NMR from the isolated product. <sup>c</sup>Selectivity was calculated as the ratio of yield over conversion. <sup>d</sup>Catalyst: 0.5 equiv Mn. <sup>e</sup>Terpene (0.25 mmol, 1 equiv), supported catalyst (0.0031 equiv Mn), NaHCO<sub>3</sub> (0.05 mmol, 5 equiv), H<sub>2</sub>O<sub>2</sub> (30 wt %; 0.8 mmol, 3.2 equiv), and H<sub>2</sub>O/dimethylformamide (DMF) (2 mL), 0 °C, 4 h. <sup>f</sup>Terpene (0.18 mmol, 1 equiv), catalyst (0.00006 equiv Mn), NaHCO<sub>3</sub> (0.88 mmol, 5 equiv), H<sub>2</sub>O<sub>2</sub> (30 wt %; 1.75 mmol, 9.7 equiv), and H<sub>2</sub>O/acetone (2.6 mL), 30 °C, 2 h.

549 mono- (Table 5, entries 7 and 8) or diepoxides (Table 5,  
550 entries 1, 4, and 6) when the double bonds were electron-rich.  
551 In the case of limonene, 84% of selectivity of diepoxides was  
552 observed with very high conversion in 2 h (Table 4, entry 1).  
553 In comparison, Eco-Mn<sub>1</sub> led to 86% of monoepoxides, with  
554 only 50% of conversion.<sup>18</sup> This result highlighted the high  
555 reactivity of Eco-CaMnO<sub>x</sub>, which was close to Pyr-Mn. Both  
556 mono- and diepoxides are of high interest in the field of  
557 biosourced polymers as they both could be used as monomers  
558 for the synthesis of polycarbonates, polyethers, polyesters, or  
559 poly(hydro)urethanes.<sup>102–106</sup> Thus, they could represent  
560 substitutes for polymers synthesized from bisphenol A or  
561 epichlorhydrin, two toxic molecules classified as CMR.

562 In 4 h, the epoxidation of geranyl acetate gave a  
563 stoichiometric mixture of mono- and diepoxides (Table 5,  
564 entry 6). In consequence, the ester moiety did not deactivate  
565 Eco-CaMnO<sub>x</sub> in spite of its basic Lewis properties. The same  
566 reaction with 10 equiv of H<sub>2</sub>O<sub>2</sub> favored the formation of the  
567 diepoxide, reaching 79% of selectivity. It was thus possible to  
568 control the ratio monoepoxides/diepoxides by tuning the  
569 amount of H<sub>2</sub>O<sub>2</sub>.

570 Unlike Eco-Mn and conventional catalysts, the epoxidation  
571 of linalool led mainly to the monoepoxide, with 64% of  
572 selectivity (Table 5, entry 4). This result is unusual as the

resulting epoxide is highly reactive and acid-sensitive. It easily  
573 rearranges by cyclization into hydroxyfuranes or hydroxypyra-  
574 nes.<sup>107</sup> In this case, only 2% of hydroxyfuranes was observed.  
575 This indicated that our catalyst was not acidic, avoiding the  
576 intramolecular reaction. However, the rearrangement of the  
577 epoxide into the hydroxyfuran was easily observed when  
578 CDCl<sub>3</sub> was used for NMR assessments. As an example, only  
579 the hydroxyfuran was obtained with a 63% yield with the  
580 previous Eco-Mn,<sup>18</sup> whereas Pyr-Mn yielded hydroxypyran.<sup>108</sup>  
581 Therefore, Eco-CaMnO<sub>x</sub> allowed the preparation of very  
582 sensitive epoxides. The higher chemoselectivity of Eco-  
583 CaMnO<sub>x</sub> is the direct consequence of its preparation by a  
584 sole thermal treatment. This result is of interest, as linalool  
585 epoxide is an important molecule in the communication of  
586 pollinating insects.<sup>109</sup> Thirty-four percent of diepoxides were  
587 also obtained. This proved the strong oxidizing properties of  
588 Eco-CaMnO<sub>x</sub> as it succeeded in epoxidizing a terminal double  
589 bond.  
590

The monoepoxide was the only one identified with α- and β-  
591 ionones. The only other byproduct formed during the reaction  
592 on both ionones was the product of allylic oxidation, with 12  
593 and 30% of selectivity, respectively (Table 5, entries 7, 8).  
594

The other particularly noteworthy example was the  
595 epoxidation of oleic acid (Table 5, entry 9). Indeed, epoxides  
596

Table 6. Recycling Studies of Eco-CaMnO<sub>x</sub> Catalysts

| entry | run  | conversion (%) | yield (%) | selectivity (%) | post-run Mn content (wt % (±sd)) | post-run Ca content (wt % (±sd)) |
|-------|------|----------------|-----------|-----------------|----------------------------------|----------------------------------|
| 1     | no 1 | >99            | >99       | 100             | 11.22 (0.40)                     | 16.02 (0.61)                     |
| 2     | no 2 | >99            | >99       | 100             | 11.82 (2.20)                     | 16.78 (0.79)                     |
| 3     | no 3 | 79             | 79        | 100             | 8.93 (1.80)                      | 13.63 (0.76)                     |
| 4     | no 4 | 73             | 73        | 100             | 10.80 (0.81)                     | 14.78 (0.86)                     |

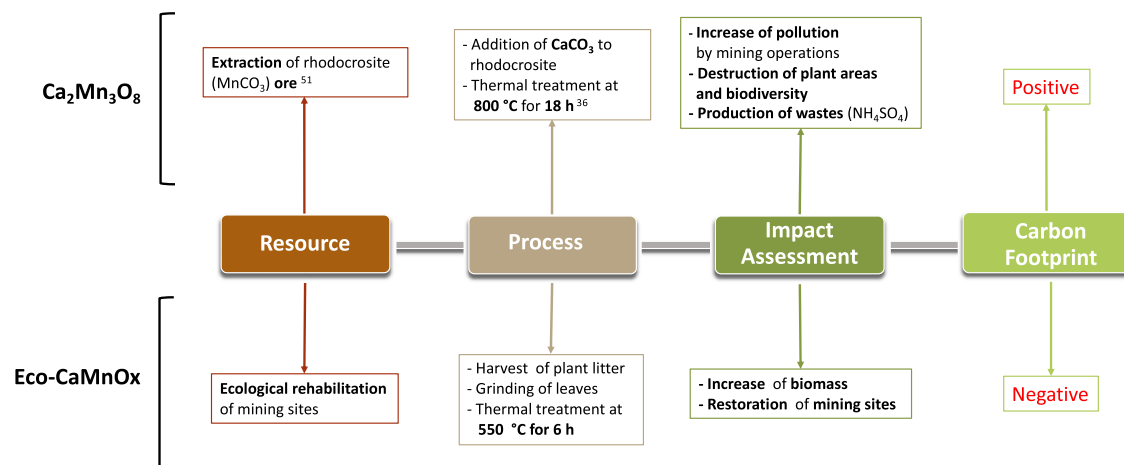


Figure 7. Qualitative environmental impact assessment of the catalyst preparation.

597 of fatty acids from vegetal oils are very interesting as platform  
 598 molecules for organic chemistry, but also as biodegradable  
 599 lubricants, plasticizers, and stabilizers of polymers.<sup>110–112</sup>  
 600 Sixty-six percent of conversion with a total selectivity in  
 601 epoxide was reached in 4 h with Eco-CaMnO<sub>x</sub> (0.5 equiv Mn),  
 602 while Eco-Mn was not able to catalyze this reaction. Pyr-Mn  
 603 seemed more efficient than Eco-CaMnO<sub>x</sub> but required twice as  
 604 much H<sub>2</sub>O<sub>2</sub>.

605 In addition to the higher reactivity of Eco-CaMnO<sub>x</sub>  
 606 compared to Eco-Mn, the experimental conditions were also  
 607 improved; epoxidations were conducted with acetone/H<sub>2</sub>O  
 608 instead of DMF. In a context of growing environmental  
 609 consciousness, it is motivating to be able to propose novel  
 610 catalysts, which combine efficiency, use of renewable resources,  
 611 and eco-friendly processes.

612 *Recycling and Leaching Studies of Eco-CaMnO<sub>x</sub> Cata-*  
 613 *lysts.* Recycling of Eco-CaMnO<sub>x</sub> catalysts was investigated by  
 614 conducting the epoxidation of isopulegol (Table 6). Eco-  
 615 CaMnO<sub>x</sub> catalysts were recycled by separation after  
 616 centrifugation of the crude, washing, drying, and reuse for an  
 617 identical experiment. Up to four successive reactions were  
 618 conducted. Conversion and yield remained quantitative for the  
 619 second run (Table 6, entries 1, 2), while a slight decrease was  
 620 observed after the third run (Table 6, entries 3, 4), suggesting a  
 621 small loss of activity of Eco-CaMnO<sub>x</sub> catalysts.

622 The small loss of activity was investigated by analyzing the  
 623 composition and structure of Eco-CaMnO<sub>x</sub> catalysts after each  
 624 run. No significant change of Mn and Ca contents was  
 625 observed by MP-AES (Table S2), and the structure  
 626 characterized by XRPD remained the same. Both results

indicated the high stability of Eco-CaMnO<sub>x</sub> catalysts, even in  
 the oxidizing conditions of the reaction.

629 Considering that the composition and structure of Eco-  
 630 CaMnO<sub>x</sub> remained similar after four runs, leaching of Eco-  
 631 CaMnO<sub>x</sub> was unlikely to occur but was still verified. Using  
 632 isopulegol as substrate, a specific experiment was conducted as  
 633 described by Sheldon et al.<sup>113</sup> After 30 min of reaction, Eco-  
 634 CaMnO<sub>x</sub> was removed from the reaction mixture by filtration;  
 635 conversion of isopulegol was analyzed after this time at 35%.  
 636 The reaction mixture was stirred for another 4 h without Eco-  
 637 CaMnO<sub>x</sub>; conversion of isopulegol remained at 35%,  
 638 indicating that the reaction did not occur after removing  
 639 Eco-CaMnO<sub>x</sub>. As expected, the elemental composition of the  
 640 reaction mixture was analyzed by MP-AES and no trace of  
 641 metal was detected. These two results showed that the Eco-  
 642 CaMnO<sub>x</sub> catalyst was a heterogeneous catalyst, in which  
 643 leaching of Mn can be excluded in the reported conditions.

## CONCLUSIONS

645 In this study, a new generation of ecocatalysts was easily  
 646 prepared from Mn-accumulating plant species, which are used  
 647 in ecological restoration. A controlled thermal treatment of  
 648 Mn-rich biomass led directly to green oxidative catalysts, Eco-  
 649 CaMnO<sub>x</sub>, thus avoiding any further chemical activation.  
 650 Characterization by MP-AES, XRPD, HRTEM, and STEM-  
 651 EDX revealed an original polymetallic system. Unusual mixed  
 652 manganese–calcium oxides, Ca<sub>2</sub>Mn<sub>3</sub>O<sub>8</sub> and CaMnO<sub>3</sub>, were  
 653 identified. All Eco-CaMnO<sub>x</sub> catalysts prepared from different  
 654 plant species demonstrated an excellent catalytic potential in  
 655 the epoxidation of terpenes and lipids, with only 0.005 equiv



656 Mn, in short reaction times, at room temperature, using green  
657 solvents and without any ligand or activation phase. Eco-  
658  $\text{CaMnO}_x$  catalysts afforded much higher conversions and  
659 yields than conventional activated manganese dioxide or  
660 synthetic  $\text{Ca}_2\text{Mn}_3\text{O}_8$ . Not only did these results demonstrate  
661 the vegetal footprint of Eco- $\text{CaMnO}_x$  catalysts but also they  
662 proved that these catalysts could represent potential substitutes  
663 to oxidative reagents inconsistent with the requirements of  
664 REACH regulation. A wide range of mono- and diepoxides  
665 were efficiently synthesized from terpenes, many of them  
666 coming from abundant natural resources. Eco- $\text{CaMnO}_x$  opens  
667 a new perspective for the valorization of Mn-rich biomass  
668 through the preparation of biosourced monomers for new-  
669 biodegradable polymers.<sup>105,106,114</sup> This new generation of  
670 ecocatalysts exhibits environmental and scientific benefits,  
671 suggesting a promising life-cycle analysis (Figure 7). It can  
672 drive a new approach of green chemistry with ecological,  
673 economic, and social advantages.

## 674 ■ ASSOCIATED CONTENT


### 675 ⓘ Supporting Information

676 The Supporting Information is available free of charge at  
677 <https://pubs.acs.org/doi/10.1021/acssuschemeng.9b05444>.

678 General methods for the characterization of Eco-  
679  $\text{CaMnO}_x$  and the analysis of the reaction products,  
680 MP-AES analyses of Mn-accumulating plant leaves and  
681 Eco- $\text{CaMnO}_x$  NMR analyses, scale-up of the epoxi-  
682 dation of alkene, the study of the leaching of Eco-  
683  $\text{CaMnO}_x$  recycling of Eco- $\text{CaMnO}_x$  (PDF)


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