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Eco-CaMnO_x: 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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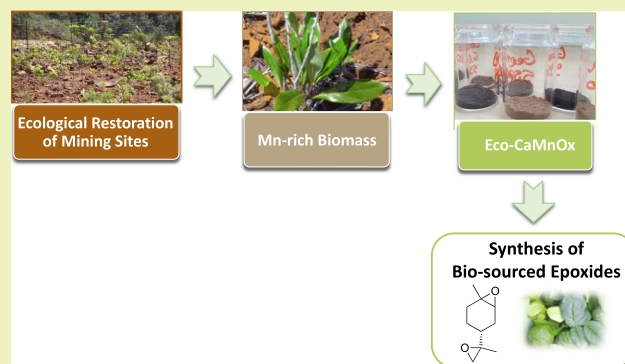
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Supporting Information

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_x” 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_x 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: Ca₂Mn₃O₈ and CaMnO₃. The high efficiency of Eco-CaMnO_x catalysts was demonstrated via the epoxidation of various biosourced terpenes and lipids, using the mixture H₂O₂/NaHCO₃ as a green co-oxidant. This study demonstrated not only the high potential of Eco-CaMnO_x 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_x 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.¹ 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.²

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.³ 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.⁴ 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.^{5,6} 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.^{7,8} 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.^{9–11} 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.

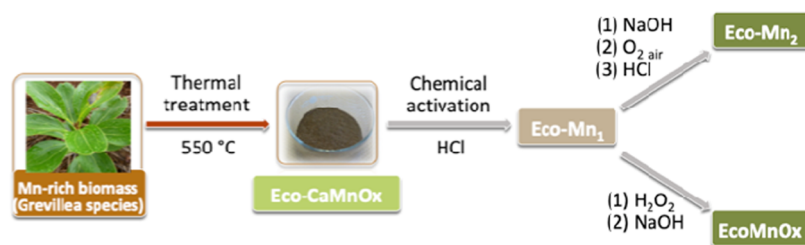


Figure 2. Steps for preparation of the previously studied Eco-Mn catalysts and of the new Eco-CaMnO_x from Mn-accumulating plant species.

63 particular, species of the genus *Grevillea* (Proteaceae) are
 64 considered as the leading species for restoration, representing
 65 about 58% of the species reintroduced by our group (Figure
 66 1).^{12,13}

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

84 Concerning manganese, two generations of Eco-Mn catalysts
 85 were prepared from Mn-accumulating plant species belonging
 86 to the genus *Grevillea* (Figure 2). In each case, the first step
 87 was the preparation of an intermediate Eco-Mn₁. It was based
 88 on a controlled thermal treatment of Mn-rich biomass,
 89 followed by a chemical activation by HCl.¹⁶ From Eco-Mn₁,
 90 two oxidative eco-catalysts were formed by a sequential
 91 addition of either NaOH/O₂/HCl (Eco-Mn₂)¹⁶ or H₂O₂/
 92 NaOH (Eco-MnO_x).¹⁷

93 Eco-Mn revealed an original polymetallic composition
 94 resulting in marked Brønsted and Lewis acidities and displayed
 95 superior catalytic performances than conventional Mn
 96 catalysts. For example, Eco-Mn₁ was successfully employed
 97 in the aminoreduction of ketones²⁰ and constitutes the first
 98 example of reduction promoted by a Mn-based catalyst. Eco-
 99 Mn₂ and Eco-MnO_x led to a practical and elegant solution to

the long-standing challenge of oxidative cleavage of 1,2-diols
 into aldehyde or ketones.^{17,18} Supported Eco-Mn₁ provided
 also a huge potential as green catalysts for valuable
 epoxidation.¹⁸ Finally, Eco-Mn₁ acted as “Janus catalysts” by
 promoting tandem sequences of multicomponent type
 oxidations (synthesis of substituted pyridines) and cyclizations
 (synthesis of *p*-cymene).¹⁶ 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-
 Mn₁, characterized by inductive coupled plasma-mass spec-
 troscopy, X-ray powder diffraction spectroscopy (XRPD), and
 X-ray absorption spectroscopy (XANES and EXAFS),
 completed with density functional theory calculations.³² 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, Ca₂Mn₃O₈) instead of polymetallic chlorides as
 for Eco-Mn₁ and Eco-Mn₂.

While rare examples have described the use of mixed Mn-
 Ca oxide nanoparticles as oxidants,^{33,34} no description was
 found for the use of Ca₂Mn₃O₈ in organic synthesis. However,
 mixed Mn-Ca oxides display biomimetic oxidative properties
 of the natural cofactor CaMn₄O₅ of Photosystem II. Indeed,
 CaMn₄O₅ performs the oxidation of water during the
 photosynthesis process,³⁵ and the complex Ca₂Mn₃O₈ presents
 similar oxidative activities in the electrochemical oxidation of
 water.^{36–38}

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

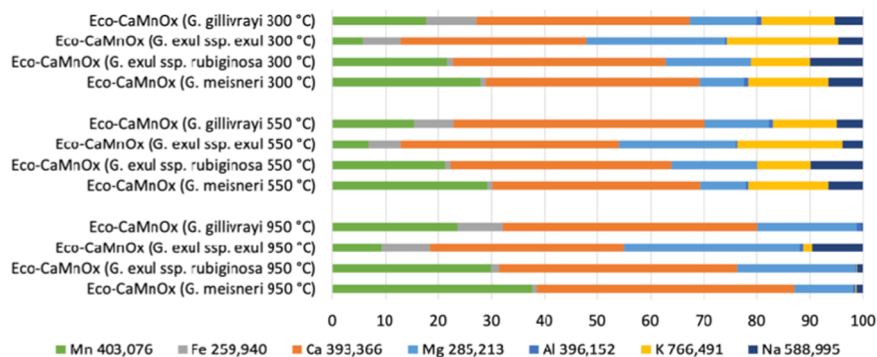


Figure 3. Histogram representing the relative weight percentages of elements in Eco-CaMnO_x catalysts, prepared from different plant species of Grevillea and thermal treatments, determined by MP-AES analyses.

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_x 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_x Catalysts.** Eco-CaMnO_x 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_x. The chosen
 165 salts were the following: manganese malate trihydrate (MnC₄H₄O₅·
 166 3H₂O), calcium oxalate (CaC₂O₄·2H₂O), iron phosphate (FePO₄·
 167 2H₂O), magnesium phosphate (Mg₃(PO₄)₂·xH₂O), sodium chloride
 168 (NaCl), potassium chloride (KCl), and aluminum oxalate (Al₂C₆O₁₂·
 169 xH₂O).

170 Ca₂Mn₃O₈ was synthesized by grinding CaCO₃ (4 mmol, 400 mg)
 171 and MnCO₃ (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 NaHCO₃
 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. H₂O₂ (30% w/w in
 178 H₂O, 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 Na₂SO₄. The solvent was then removed by
 182 evaporation.

183 ■ RESULTS AND DISCUSSION

Preparation and Characterization of Eco-CaMnO_x Catalysts. Preparation of Eco-CaMnO_x Catalysts. Eco-
 CaMnO_x catalysts were prepared from Mn-rich biomass. Four species of the Grevillea genus are mainly used to
 rehabilitate mining sites across both provinces in New Caledonia: *G. gillivrayi*, *G. meisneri*, *G. exul* ssp. *exul*, and *G.*
exul ssp. *rubiginosa*. Plant leaves were harvested by hand from the plant litter, on the mining sites, which are currently
 rehabilitated by our group.

In this study, two parameters were studied to investigate their influence on Eco-CaMnO_x catalytic properties: the plant
 species, from which the catalysts were prepared, and the temperature of the thermal treatment. The dried leaves, from
 each of the four species of the Grevillea genus, were thermally treated in an oven, under air flow, at 300, 550, or 950 °C for 6
 h, to destroy the organic matter. Indeed, these temperatures were chosen according to the literature, as different manganese
 oxides could be formed depending on the corresponding heating temperature: MnO₂, Mn₂O₃, or Mn₃O₄.^{39,40} Eco-
 CaMnO_x catalysts were then characterized by MP-AES, XRPD, HRTEM, and STEM-EDX mapping.

MP-AES Analysis of Eco-CaMnO_x Catalysts. Metallic composition of intact Mn-accumulating plant leaves and of
 Eco-CaMnO_x catalysts, resulting from different plant species and thermal treatments, was studied by MP-AES analyses.
 Analyses were performed in triplicate for each sample to determine the standard deviation of the measurement (Table
 S1).

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

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

Table 1. Crystalline Species Identified in Eco-CaMnO_x Catalysts and in Synthetic Ash Control

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

^aMn 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_x catalysts from *G. gillivrayi* present an average
235 composition of minerals among the other species.

236 *XRPD Analysis of Eco-CaMnO_x Catalysts.* XRPD was
237 performed to deliver insights on the crystalline species present
238 in Eco-CaMnO_x 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. Ca₂Mn₃O₈ was identified in
249 all Eco-CaMnO_x 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. CaMnO₃ was
254 identified in all Eco-CaMnO_x prepared at 950 °C. CaMnO₃
255 could result from the degradation of Ca₂Mn₃O₈ at high
256 temperature, which was consistent with the calcination
257 temperatures used by Han et al. to prepare these two
258 complexes.⁴¹

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_x, which is in accordance
265 with what we reported for Eco-Mn₁.³²

266 The structure of Ca₂Mn₃O₈ has been reported as infinite
267 sheets of Mn₃O₈⁴⁻ 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.^{37,42} The negative charge is further compensated by the
271 presence of Ca ions in trigonal prismatic sites located above
272 and below layer vacancies.³⁸

273 CaMnO₃ has a perovskite structure based on corner-shared
274 MnO₆-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.^{38,41}

277 The layered structure of Ca₂Mn₃O₈ shares similarities with
278 the cofactor CaMn₄O₅, 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.^{43,44} Research on a series of manganese–calcium oxides
showed that Ca₂Mn₃O₈ and CaMnO₃ were efficient catalysts
for the oxygen evolution reaction and oxygen reduction
reaction. Indeed, manganese ions in Ca₂Mn₃O₈ and CaMnO₃
are in the oxidation state IV and they may present interesting
oxidative properties similar to MnO₂.

*HRTEM Analysis of Eco-CaMnO_x Catalysts (*G. gillivrayi*,
550 °C).* HRTEM images of Eco-CaMnO_x (*G. gillivrayi*, 550
°C) revealed different particles with various shapes (Figure 4).

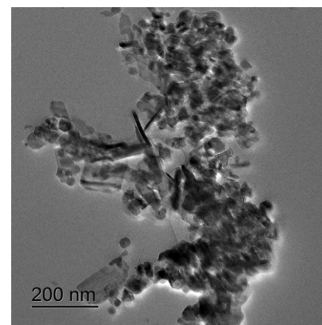


Figure 4. HRTEM image of Eco-CaMnO_x catalysts (*G. gillivrayi* 550 °C).

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_x (*G. gillivrayi*, 550 °C).*
The STEM-EDX analysis was used to establish the chemical
composition mapping of Eco-CaMnO_x 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_x 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 Ca₂Mn₃O₈ complex, and that this complex
is organized in lamellar sheets.

Extensive structural analyses of the different Eco-CaMnO_x
catalysts showed the presence of two unusual and valuable
mixed calcium–manganese complexes: Ca₂Mn₃O₈ and
CaMnO₃. The oxidative potential of the Eco-CaMnO_x
catalysts was studied in the epoxidation of alkenes and
especially terpenes, as biosourced substrates.

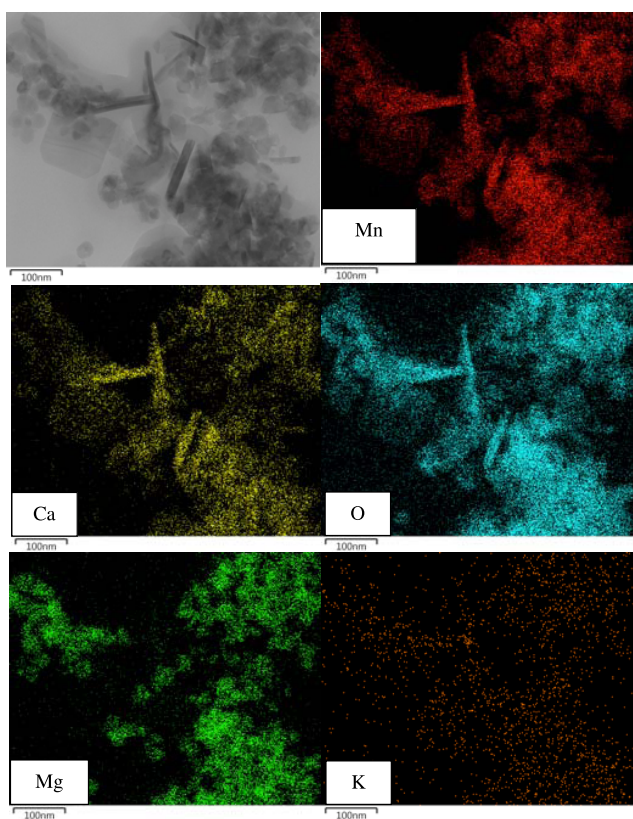


Figure 5. STEM-EDX mapping of Eco-CaMnO_x catalysts (*G. gillivrayi*, 550 °C).

epoxidation reaction.^{73–75} However, the homogeneous nature of such metalloporphyrin and Schiff base complexes leads not only to deactivation due to oxidative degradation of the ligand⁷⁶ 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.^{77–80} For example, heterogeneous Ti silicates are nowadays used at an industrial scale with H₂O₂ for conducting epoxidation reactions with very high catalytic and environmental performances.⁸¹

In our previous works, we showed that montmorillonite-supported Eco-Mn₁ catalyzed the epoxidation of styrene. Eco-Mn₁ contained only 0.31 mol % of manganese, a much lower content of manganese than that reported in previously described Mn-derived heterogeneous catalysts.^{82,83} Comparison of Eco-Mn₁ properties to those of heterogeneous catalysts made by incorporation of commercial MnCl₂·4H₂O and FeCl₃·6H₂O highlighted the superior catalytic activity of polymetallic species present in Eco-Mn₁. These promising results prompted us to investigate the utilization of Eco-CaMnO_x as an epoxidizing agent and to study the possible cooperative catalytic effect between Ca and Mn.

Optimization of the Conditions for the Epoxidation of α -pinene. The epoxidation of α -pinene was chosen as a probe reaction to optimize the reaction conditions. α -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. However, α -pinene oxide is a sensitive and reactive substrate, which rearranges easily in acid conditions. The rearrangement of α -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. It is well described that Lewis acid sites favor the formation of campholenic aldehyde, pinocarveol, and isopinocampheol, whereas Brønsted acid sites result in the formation of *trans*-carveol, *trans*-sobrerol, and *p*-cymene. For instance, one of the most desired products resulting from the α -pinene oxide is campholenic aldehyde because it is an intermediate for the manufacture of sandalwood fragrances. The epoxidation of α -pinene into α -pinene oxide remains a challenge because of its isomerization into many different byproducts.

In a typical procedure, α -pinene, Eco-CaMnO_x (*G. gillivrayi* 550 °C), and NaHCO₃ were stirred in a mixture of acetone:water (1:1) at room temperature for 10 min. H₂O₂ (30% w/w in H₂O) 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 Na₂SO₄. The solvent was then removed by evaporation and the reaction products analyzed by gas chromatography–mass spectrometry (GC–MS)/flame ionization detector (FID).

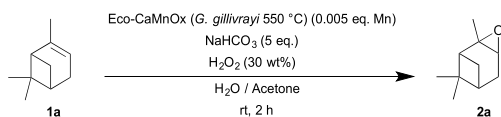
Effect of H₂O₂ Amount. The effect of the quantity of H₂O₂ added into the reaction mixture was studied, as an excessive amount of H₂O₂ could lead to a decrease in epoxide selectivity by overoxidation.⁹² The conversion, yield, and selectivity followed the same trend (Table 2). Increasing the quantity of H₂O₂ increased the conversion, yield, and selectivity before 407 reaching a threshold. Almost total conversion of α -pinene **1a** 408

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

Hydrogen peroxide is considered as an ideal alternative oxidant on both environmental and economic grounds.⁴⁸ Not only is it relatively cheap, easily available, and stable at the usual concentration (typically <60 wt %), but it is also a clean oxidizing reagent, as it only forms water as a byproduct. However, it requires an activation to catalyze the oxygen-transfer process. Many catalytic systems using H₂O₂ as the oxidant for epoxidation of alkenes were based on transition-metal catalysts.^{49–51} However, the use of economically and environmentally unsustainable metals, such as rhenium,^{52–55} vanadium,^{56,57} molybdenum,^{58–60} or tungsten,^{61–64} prompted the research toward inexpensive, abundant, and innocuous transition metals. In particular, iron or manganese revealed to be one of the more promising elements thanks to their relatively low toxicity and their abundance in Earth’s crust.^{65,66}

Porphyrin–Mn have been extensively investigated as a mimic of cytochrome P450,^{67–70} but suffer from difficulties in synthesis and purification. As they offer synthetic advantages over porphyrin systems, considerable attention was given to Salen–Mn,^{71,72} in particular to the Jacobsen asymmetric

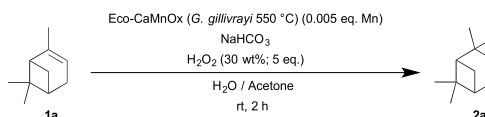
Table 2. Effect of the Amount of H₂O₂ and of the Adding Time on the Epoxidation of α -pinene^a



| entry | H ₂ O ₂ (equiv) | addition time (min) | conversion (%) ^b | yield (%) ^b | selectivity (%) ^{b,c} |
|-------|---------------------------------------|---------------------|-----------------------------|------------------------|--------------------------------|
| 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 |

^aReaction conditions: α -pinene (1.6 mmol, 1 equiv), catalyst (8 μ mol, 0.005 equiv Mn), NaHCO₃ (8 mmol, 5 equiv), H₂O₂ (30 wt %), and H₂O (20 mL): acetone (20 mL), rt, 2 h. ^bConversion, yield, and selectivity were established by FID using biphenyl as internal standard. ^cSelectivity was calculated as the ratio of yield over conversion.

Table 3. Effect of the Amount of NaHCO₃ on the Epoxidation of α -pinene^a



| entry | NaHCO ₃ (equiv) | conversion (%) ^b | yield (%) ^b | selectivity (%) ^{b,c} |
|-------|----------------------------|-----------------------------|------------------------|--------------------------------|
| 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 |

^aReaction conditions: α -pinene (1.6 mmol, 1 equiv), catalyst (8 μ mol, 0.005 equiv Mn), NaHCO₃, H₂O₂ (30 wt%; 8 mmol, 5 equiv), and H₂O (20 mL): acetone (20 mL), rt, 2 h. ^bConversion, yield, and selectivity were established by FID using biphenyl as internal standard. ^cSelectivity was calculated as the ratio of yield over conversion.

and a yield of 64% in epoxide **2a** were reached with 5 equiv of H₂O₂ (Table 2, entry 5). The addition time of H₂O₂ 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 H₂O₂ in oxidative reactions. Indeed, it was reported that a gradual addition of H₂O₂ decreased its self-decomposition.^{93,94}

The selectivity in α -pinene oxide gave some information about Eco-CaMnO_x. 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_x catalysts. As it was reported that α -pinene oxide could also rearrange spontaneously in acid or neutral aqueous phase media,⁹⁰ the epoxide was directly engaged in the reaction and without any catalyst, to test its stability. In the presence of Eco-CaMnO_x 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_x. This supports the presence of Lewis acid sites in Eco-CaMnO_x. Allylic oxidation is often a competitive process of epoxidation in the oxidation of cyclic olefins.^{95,96} 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 H₂O₂ 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 NaHCO₃ Amount. The effect of the quantity of NaHCO₃ added into the reaction mixture was investigated (Table 3). No conversion of α -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 NaHCO₃ and H₂O₂ could produce in situ peroxy mono-carbonate ions (HCO₄⁻),^{97,98} 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 NaHCO₃ quantity resulted in decreasing conversion, yield, and selectivity in epoxide. Therefore, 5 equiv of NaHCO₃ seemed to be the lowest quantity giving high conversion and yield (Table 3, entry 5).

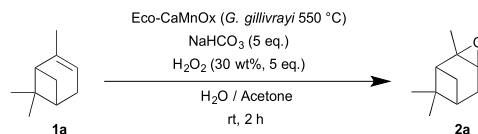
Effect of Catalyst Loading. The effect of the quantity of Eco-CaMnO_x catalysts was then studied using α -pinene as the substrate (Table 4). A low quantity of manganese gave high conversion rates. Almost total conversion and 64% yield were obtained with only 0.005 equiv in manganese (Table 4, entry 4). This result is remarkable compared to standard manganese-based catalysts, which usually require to be used in excess.

As a control, the reaction was carried out in the absence of Eco-CaMnO_x catalysts. The reaction could not occur in the corresponding reaction time, in 2 h (Table 4, entry 1).

The oxidative capacity of Eco-CaMnO_x was also compared to synthetic catalysts (Table 4, entries 7–9). The synthetic Ca₂Mn₃O₈ catalyst was prepared following the procedure described by Najafpour et al.,³⁸ and commercial manganese dioxide was activated.

As expected, conversion of α -pinene catalyzed by calcium oxide was negligible (Table 4, entry 9). Calcium oxide species alone cannot catalyze the epoxidation of α -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 MnO₂ and synthetic Ca₂Mn₃O₈ 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.⁴¹

Table 4. Effect of the Catalyst Loading on the Epoxidation of α -pinene^a



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

^aReaction conditions: α -pinene (1.6 mmol, 1 equiv), the catalyst, NaHCO₃ (8 mmol, 5 equiv), H₂O₂ (30 wt %; 8 mmol, 5 equiv), and H₂O (20 mL): acetone (20 mL), rt, 2 h. ^bConversion, yield, and selectivity were established by FID using biphenyl as the internal standard. ^cSelectivity was calculated as the ratio of yield over conversion. ^d0.02 equiv Ca was used, corresponding to the quantity of Ca engaged by 0.005 equiv Mn with Eco-CaMnO_x. ^eTraces of verbenol, carveol, and campholenic aldehyde were detected by GC-MS. ^fTON = number of mol of the product formed per mol of catalyst. ^gTOF = number of mol of the product formed per mol of catalyst and per unit of time.

491 Interestingly, Eco-CaMnO_x catalysts gave a twice-higher
492 yield compared to synthetic Ca₂Mn₃O₈ (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_x.* The
499 different Eco-CaMnO_x catalysts prepared from the four species
500 of *Grevillea* were tested in the epoxidation of α -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_x 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.

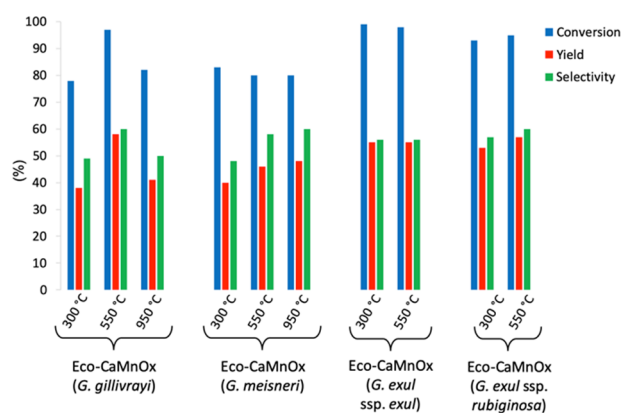


Figure 6. Effect of the plant species and of the temperature of the thermal treatment used to prepare Eco-CaMnO_x on the epoxidation of α -pinene. Reaction conditions: α -pinene (1.6 mmol, 1 equiv), catalyst (8 mmol, 0.005 equiv Mn), NaHCO₃ (8 mmol, 5 equiv), H₂O₂ (30 wt %; 8 mmol, 5 equiv), and H₂O (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_x
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_x catalysts of *G. gillivrayi* and *G.*
513 *meisneri* prepared at 950 °C revealed similar activities as the
514 corresponding Eco-CaMnO_x 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 α -
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.^{100,101}

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.⁸² Qi et al. reached 40% selectivity using
532 Mn²⁺-exchanged zeolites.⁹²

533 *Substrate Scope for the Epoxidation of Terpenes and*
534 *Lipids by Eco-CaMnO_x 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.


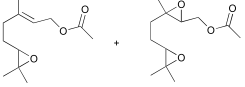

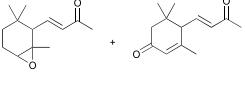

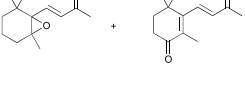
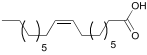
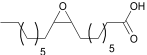
541 The chemoselectivity of Eco-CaMnO_x catalysts was
542 illustrated through the selective epoxidation of terpenes
543 (Table 5, entries 2–8) bearing various functional groups,
544 such as alcohol, ester, or enone, that remained unmodified.
545 The epoxidation of monoterpenes like terpineol, isopulegol,
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, α -ionone, and β -ionone gave

Table 5. Substrate Scope for the Epoxidation of Natural Substrates by Eocatalysts (Eco-CaMnO_x^a, Eco-Mn₁^{18,e} and Pyr-Mn^{108,f})

Reaction scheme showing the epoxidation of an alkene (1) to an epoxide (2) using Eco-CaMnO_x (G. gillivrayi 550 °C) (0.005 eq. Mn), NaHCO₃ (5 eq.), H₂O₂ (30 wt%; 5 eq.), H₂O / Acetone, RT.

| Entry | Substrate 1 | Eocatalyst solvent | Product 2 | Reaction time (h) | Conversion (%) ^b | Yield (%) ^b | Selectivity (%) ^{b,c} | | | |
|-------------------------|--------------------------|-------------------------------------|-----------------------|----------------------------|-----------------------------|----------------------------|--------------------------------|----|----------------------------|----------------------------|
| 1 | | Eco-CaMnOx | | 2 | 93 | 2b₁ : 15 | 2b₁ : 16 | | | |
| | | H ₂ O/Acetone | | | | 2b₂ : 78 | 2b₂ : 84 | | | |
| | | Eco-Mn ₁ ^{18,e} | | | | | 4 | 50 | 2b₁ : 43 | 2b₁ : 86 |
| | | H ₂ O/ DMF | | | | 2b₂ : 7 | | | 2b₂ : 14 | |
| Pyr-Mn ^{108,f} | H ₂ O/Acetone | 2 | 99 | 2b₁ : 1 | 2b₁ : 1 | | | | | |
| | | | | 2b₂ : 98 | 2b₂ : 99 | | | | | |
| 2 | | Eco-CaMnOx | | 2 | > 99 | > 99 | 100 | | | |
| | 1c | H ₂ O/Acetone | 2c | | | | | | | |
| 3 | | Eco-CaMnOx | | 4 | > 99 | > 99 | 100 | | | |
| | 1d | H ₂ O/Acetone | 2d | | | | | | | |
| 4 | | Eco-CaMnOx | | 4 | > 99 | 2e₁ : 64 | 2e₁ : 64 | | | |
| | | H ₂ O/Acetone | | | | 2e₂ : 34 | 2e₂ : 34 | | | |
| | | | | | | 2e₃ : 2 | 2e₃ : 2 | | | |
| | 1e | Eco-Mn ₁ ^{18,e} | | 4 | 65 | 2e₃ : 63 | 2e₃ : 97 | | | |
| | | H ₂ O/ DMF | 2e₃ | | | | | | | |
| | | Pyr-Mn ^{108,f} | | 2 | > 99 | 2e₄ : 89 | 2e₄ : 88 | | | |
| | | H ₂ O/Acetone | 2e₄ | | | | | | | |
| 5 | | Eco-CaMnOx | | 4 | 99 | 99 | 100 | | | |
| | 1f | H ₂ O/Acetone | 2f | | | | | | | |

Table 5. continued

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

^aReaction conditions: substrate (1.6 mmol, 1 equiv), catalyst (8 μmol, 0.005 equiv Mn), NaHCO₃ (8 mmol, 5 equiv), H₂O₂ (30 wt %; 8 mmol, 5 equiv), and H₂O (20 mL): acetone (20 mL), rt. ^bConversion, yield, and selectivity were established by FID, using biphenyl as internal standard, and then confirmed by ¹H NMR from the isolated product. ^cSelectivity was calculated as the ratio of yield over conversion. ^dCatalyst: 0.5 equiv Mn. ^eTerpene (0.25 mmol, 1 equiv), supported catalyst (0.0031 equiv Mn), NaHCO₃ (0.05 mmol, 5 equiv), H₂O₂ (30 wt %; 0.8 mmol, 3.2 equiv), and H₂O/dimethylformamide (DMF) (2 mL), 0 °C, 4 h. ^fTerpene (0.18 mmol, 1 equiv), catalyst (0.00006 equiv Mn), NaHCO₃ (0.88 mmol, 5 equiv), H₂O₂ (30 wt %; 1.75 mmol, 9.7 equiv), and H₂O/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-Mn₁ led to 86% of monoepoxides, with
554 only 50% of conversion.¹⁸ This result highlighted the high
555 reactivity of Eco-CaMnO_x, 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.^{102–106} 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_x in spite of its basic Lewis properties. The same
566 reaction with 10 equiv of H₂O₂ 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 H₂O₂.

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.¹⁰⁷ 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 CDCl₃ was used for NMR assessments. As an example, only
579 the hydroxyfuran was obtained with a 63% yield with the
580 previous Eco-Mn,¹⁸ whereas Pyr-Mn yielded hydroxypyran.¹⁰⁸
581 Therefore, Eco-CaMnO_x allowed the preparation of very
582 sensitive epoxides. The higher chemoselectivity of Eco-
583 CaMnO_x 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.¹⁰⁹ Thirty-four percent of diepoxides were
587 also obtained. This proved the strong oxidizing properties of
588 Eco-CaMnO_x 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_x 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) |

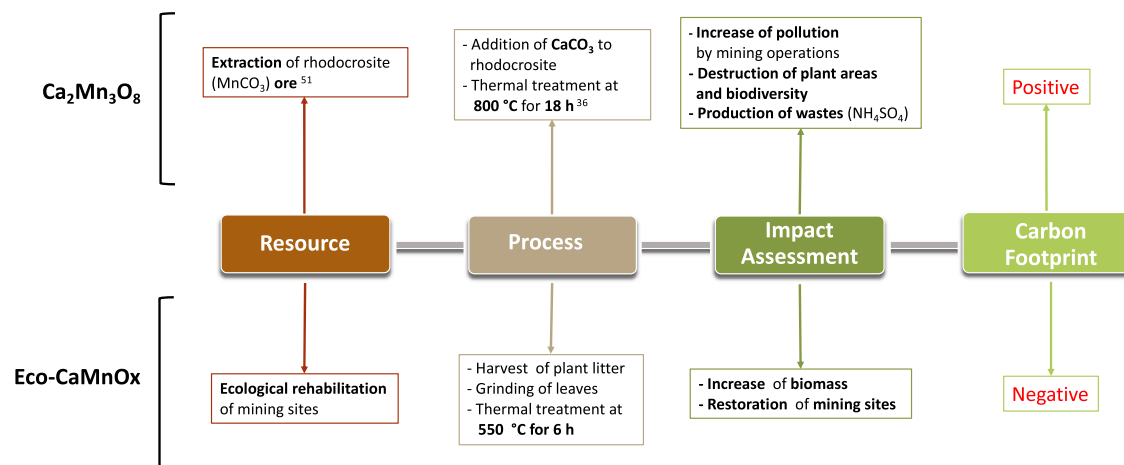


Figure 7. Qualitative environmental impact assessment of the catalyst preparation.

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.^{110–112}
 600 Sixty-six percent of conversion with a total selectivity in
 601 epoxide was reached in 4 h with Eco-CaMnO_x (0.5 equiv Mn),
 602 while Eco-Mn was not able to catalyze this reaction. Pyr-Mn
 603 seemed more efficient than Eco-CaMnO_x but required twice as
 604 much H₂O₂.

605 In addition to the higher reactivity of Eco-CaMnO_x
 606 compared to Eco-Mn, the experimental conditions were also
 607 improved; epoxidations were conducted with acetone/H₂O
 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_x Cata-*
 613 *lysts.* Recycling of Eco-CaMnO_x catalysts was investigated by
 614 conducting the epoxidation of isopulegol (Table 6). Eco-
 615 CaMnO_x 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_x catalysts.

622 The small loss of activity was investigated by analyzing the
 623 composition and structure of Eco-CaMnO_x 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_x catalysts, even in
 the oxidizing conditions of the reaction.

629 Considering that the composition and structure of Eco-
 630 CaMnO_x remained similar after four runs, leaching of Eco-
 631 CaMnO_x 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.¹¹³ After 30 min of reaction, Eco-
 634 CaMnO_x 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_x; conversion of isopulegol remained at 35%,
 638 indicating that the reaction did not occur after removing
 639 Eco-CaMnO_x. 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_x 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_x, 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, Ca₂Mn₃O₈ and CaMnO₃, were
 653 identified. All Eco-CaMnO_x 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 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- 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- 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.^{105,106,114} 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 CaMnO_x and the analysis of the reaction products,
680 MP-AES analyses of Mn-accumulating plant leaves and
681 Eco- CaMnO_x NMR analyses, scale-up of the epoxi-
682 dation of alkene, the study of the leaching of Eco-
683 CaMnO_x recycling of Eco- CaMnO_x (PDF)


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707 Notes

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