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Camille Bihanic, Sebastien Diliberto, Franck Pelissier, Eddy Petit, Clotilde Boulanger, et al.. Eco-CaMnOx: A Greener Generation of Eco-catalysts for Eco-friendly Oxidation Processes. ACS Sustainable Chemistry & Engineering, 2020, 8 (10), pp.4044 - 4057. 10.1021/acssuschemeng.9b05444 . hal-03083124

HAL Id: hal-03083124

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Cite This: <https://dx.doi.org/10.1021/acssuschemeng.9b05444>

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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_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

Received: September 13, 2019

Revised: January 14, 2020

Published: January 24, 2020

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.

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).^{12,13}

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).^{14,15} 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,^{16–19} green reduction,^{20,21} Lewis acid catalysis,^{22–28} and cross-coupling reactions.^{15,29–31}

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-Mn₁. It was based on a controlled thermal treatment of Mn-rich biomass, followed by a chemical activation by HCl.¹⁶ From Eco-Mn₁, two oxidative eco-catalysts were formed by a sequential addition of either NaOH/O₂/HCl (Eco-Mn₂)¹⁶ or H₂O₂/NaOH (Eco-MnO_x).¹⁷

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-Mn₁ was successfully employed in the aminoreduction of ketones²⁰ and constitutes the first example of reduction promoted by a Mn-based catalyst. Eco-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 spectroscopy, 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

184 **Preparation and Characterization of Eco-CaMnO_x Catalysts.** Preparation of Eco-CaMnO_x Catalysts. Eco-
185 CaMnO_x catalysts were prepared from Mn-rich biomass. Eco-
186 Four species of the *Grevillea* genus are mainly used to
187 rehabilitate mining sites across both provinces in New
188 Caledonia: *G. gillivrayi*, *G. meisneri*, *G. exul* ssp. *exul*, and *G.*
189 *exul* ssp. *rubiginosa*. Plant leaves were harvested by hand from
190 the plant litter, on the mining sites, which are currently
191 rehabilitated by our group.
192

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

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

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

227 Within a species the heating temperature at 550 and 950 °C
228 did not have much influence on the chemical composition. But
229 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.

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

For further characterizations and experimentations, *G. gillivrayi* was chosen as the model species because the Eco-CaMnO_x catalysts from *G. gillivrayi* present an average composition of minerals among the other species.

XRPD Analysis of Eco-CaMnO_x Catalysts. XRPD was performed to deliver insights on the crystalline species present in Eco-CaMnO_x catalysts and to compare with a reconstituted control of synthetic ashes. The synthetic ash control was obtained by mixing commercial metallic salts chosen so that the relative percentage of metallic elements in the starting mixture was exactly the same as in the leaves of *G. exul* ssp. *rubiginosa*, and was followed by a thermal treatment at 550 °C. The identified crystalline phases are summarized in Table 1. Mn was not present in a crystalline form in the eco-catalysts prepared at 300 °C.

Interestingly, for the other temperatures, Mn was present as mixed calcium–manganese oxides. Ca₂Mn₃O₈ was identified in all Eco-CaMnO_x prepared at 550 °C, except for *G. exul* ssp. *exul* in which crystalline species of manganese was not observed. The absence of crystalline manganese species in *G. exul* ssp. *exul* could be linked to a low ratio of Mn/Ca (Table S1) preventing the crystallization process. CaMnO₃ was identified in all Eco-CaMnO_x prepared at 950 °C. CaMnO₃ could result from the degradation of Ca₂Mn₃O₈ at high temperature, which was consistent with the calcination temperatures used by Han et al. to prepare these two complexes.⁴¹

No crystalline mixed manganese–calcium oxide was observed in the synthetic ash control. It suggested that a crystallization mechanism is specific to plant-derived eco-catalysts and that it cannot be reproduced in a simple mixture of ashes. This difference in crystallization pathways illustrates the vegetal footprint of Eco-CaMnO_x, which is in accordance with what we reported for Eco-Mn₁.³²

The structure of Ca₂Mn₃O₈ has been reported as infinite sheets of Mn₃O₈^{4−} held together by calcium ions. Mn ions are octahedrally coordinated by oxygen atoms and occupy three-fourths of the octahedral layer sites. The other one-fourth is vacant.^{37,42} The negative charge is further compensated by the presence of Ca ions in trigonal prismatic sites located above and below layer vacancies.³⁸

CaMnO₃ has a perovskite structure based on corner-shared MnO₆-octahedra. Mn ions, present in the oxidation state IV, are located at the center of the octahedron, while each Ca ion occupies the interoctahedral sites.^{38,41}

The layered structure of Ca₂Mn₃O₈ shares similarities with the cofactor CaMn₄O₅, the oxygen-evolving complex present in Photosystem II, which performs the photo-oxidation of water during photosynthesis. The incorporation of calcium into

manganese oxides greatly improves water oxidation capacities.^{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.^{84–86} However, α -pinene oxide is a sensitive and reactive substrate, which rearranges easily in acid conditions.^{87,88} 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.⁸⁷ It is well described that Lewis acid sites favor the formation of campholenic aldehyde, pinocarveol, and isopinocampnone, whereas Brønsted acid sites result in the formation of *trans*-carveol, *trans*-sobrerol, and *p*-cymene.^{89–91} 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 reaching a threshold. Almost total conversion of α -pinene **1a**

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 synthetical 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.

that NaHCO₃ and H₂O₂ could produce in situ peroxymono- 449 carbonate ions (HCO₄⁻),^{97,98} which would react with the Mn- 450 eco-catalyst to form the active epoxidizing reagent. Indeed, a 451 neutral or slightly basic pH (range from 7 to 9) is optimal for 452 this bicarbonate-activated peroxide system, which corresponds 453 to the pH values of the aqueous phase that ranged from 8.2 to 454 8.8 in our system. 455

An attempt to reduce NaHCO₃ quantity resulted in 456 decreasing conversion, yield, and selectivity in epoxide. 457 Therefore, 5 equiv of NaHCO₃ seemed to be the lowest 458 quantity giving high conversion and yield (Table 3, entry 5). 459

Effect of Catalyst Loading. The effect of the quantity of 460 Eco-CaMnO_x catalysts was then studied using α -pinene as the 461 substrate (Table 4). A low quantity of manganese gave high 462 conversion rates. Almost total conversion and 64% yield were 463 obtained with only 0.005 equiv in manganese (Table 4, entry 464 4). This result is remarkable compared to standard manganese- 465 based catalysts, which usually require to be used in excess.⁹⁹ 466

As a control, the reaction was carried out in the absence of 467 Eco-CaMnO_x catalysts. The reaction could not occur in the 468 corresponding reaction time, in 2 h (Table 4, entry 1). 469

The oxidative capacity of Eco-CaMnO_x was also compared 470 to synthetic catalysts (Table 4, entries 7–9). The synthetic 471 Ca₂Mn₃O₈ catalyst was prepared following the procedure 472 described by Najafpour et al.,³⁸ and commercial manganese 473 dioxide was activated. 474

As expected, conversion of α -pinene catalyzed by calcium 475 oxide was negligible (Table 4, entry 9). Calcium oxide species 476 alone cannot catalyze the epoxidation of α -pinene, since 477 calcium is not electroactive. However, conversion was 478 increased by the addition of calcium to manganese oxide 479 species; yields of 15 and 32% were obtained with commercial 480 activated MnO₂ and synthetic Ca₂Mn₃O₈ catalysts, respectively 481 (Table 4, entries 7 and 8). A comparison of these three 482 experiments shows that calcium enhances the reactivity of 483 manganese, suggesting a synergistic effect of mixed calcium– 484 manganese oxides toward epoxidation. These findings suggest 485 that the addition of calcium does not change the oxidation 486 potential of manganese, but might change the dispersion and/ 487 or exposition of manganese, enhancing its reactivity as 488 suggested by the works of Han et al. on mixed calcium– 489 manganese oxides.⁴¹ 490

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	7 ^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.

Interestingly, Eco-CaMnO_x catalysts gave a twice-higher yield compared to synthetic Ca₂Mn₃O₈ (Table 4, entries 4 and 7). The enhanced reactivity of our catalyst might be due to a different structural organization of manganese linked to its vegetal footprint and/or due to the presence of traces of other electroactive metal species.

Effect of the Plant Species and the Temperature of the Thermal Treatment Used to Prepare Eco-CaMnO_x. The different Eco-CaMnO_x catalysts prepared from the four species of *Grevillea* were tested in the epoxidation of α -pinene by using the optimized reaction conditions. The influence of the heating temperature during the thermal treatment of biomass was also investigated (Figure 6). For each plant species, each corresponding Eco-CaMnO_x catalyst showed a potent catalytic activity. These results guarantee that every manganese-accumulating plant species used in rehabilitation could be 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.

Within a species, the temperature of the thermal treatment did not seem to have much influence on the Eco-CaMnO_x activities. Surprisingly, no loss of activity was observed for the eco-catalysts formed at 300 °C despite the residual organic matter. The Eco-CaMnO_x catalysts of *G. gillivrayi* and *G. meisneri* prepared at 950 °C revealed similar activities as the corresponding Eco-CaMnO_x catalysts prepared at lower temperatures (300 and 550 °C). The best catalyst in terms of activity and energy required for its preparation remained the one prepared at 550 °C.

The reaction conditions to perform the epoxidation of α -pinene were optimized to reach a good compromise of the high efficiency of the reaction with sustainable and eco-responsible use of chemical products and solvents. In these conditions, almost total conversion was accessed with 65% selectivity in pinene oxide. Longer reaction times were tested, but it only resulted in a decrease in selectivity, the conversion remaining total. This result was in accordance with the high reactivity of pinene oxide and thus its conversion into isomeric products.^{100,101}

Our system can be advantageously compared to other bicarbonate-activated peroxide systems based on Mn catalysts. For instance, Lane et al. obtained 89% yield but only in the presence of additives.⁸² Qi et al. reached 40% selectivity using Mn²⁺-exchanged zeolites.⁹²

Substrate Scope for the Epoxidation of Terpenes and Lipids by Eco-CaMnO_x Catalysts. The epoxidation of diverse terpenes and lipids was carried out to evaluate the scope of our process (Table 5).

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

The chemoselectivity of Eco-CaMnO_x catalysts was illustrated through the selective epoxidation of terpenes (Table 5, entries 2–8) bearing various functional groups, such as alcohol, ester, or enone, that remained unmodified. The epoxidation of monoterpenes like terpineol, isopulegol, and citronellyl acetate (Table 4, entries 2, 3 and 5) gave total conversion and selectivity. The epoxidation of (R)-(+)-limonene, linalool, geranyl acetate, α -ionone, and β -ionone gave 548

Table 5. Substrate Scope for the Epoxidation of Natural Substrates by Ecocatalysts (Eco-CaMnO_x^a, Eco-Mn_I¹⁸ and Pyr-Mn¹²⁰)

$ \begin{array}{c} \text{R}_1 \quad \text{R}_3 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{R}_2 \quad \text{R}_4 \end{array} \xrightarrow[\text{H}_2\text{O} / \text{Acetone}]{\begin{array}{c} \text{Eco-CaMnO}_x \text{ (G. gillivrayi 550 }^\circ\text{C) (0.005 eq. Mn)} \\ \text{NaHCO}_3 \text{ (5 eq.)} \\ \text{H}_2\text{O}_2 \text{ (30 wt\%; 5 eq.)} \\ \text{RT} \end{array}} \begin{array}{c} \text{R}_1 \quad \text{R}_3 \\ \diagdown \quad \diagup \\ \text{C} - \text{C} - \text{O} \\ \diagup \quad \diagdown \\ \text{R}_2 \quad \text{R}_4 \end{array} $							
Entry	Substrate 1	Ecocatalyst solvent	Product 2	Reaction time (h)	Conversion (%) ^b	Yield (%) ^b	Selectivity (%) ^{b,c}
1	1b	Eco-CaMnO _x H ₂ O/Acetone	2b₁	2	93	2b₁ : 15	2b₁ : 16
		Eco-Mn _I ^{18,e} H ₂ O/ DMF		4	50	2b₁ : 43	2b₁ : 86
						2b₂ : 7	2b₂ : 14
		Pyr-Mn ^{108,f} H ₂ O/Acetone		2	99	2b₁ : 1	2b₁ : 1
						2b₂ : 98	2b₂ : 99
2	1c	Eco-CaMnO _x H ₂ O/Acetone	2c	2	> 99	> 99	100
3	1d	Eco-CaMnO _x H ₂ O/Acetone	2d	4	> 99	> 99	100
4	1e	Eco-CaMnO _x H ₂ O/Acetone	2e₁	4	> 99	2e₁ : 64	2e₁ : 64
			2e₂			2e₂ : 34	2e₂ : 34
			2e₃			2e₃ : 2	2e₃ : 2
		Eco-Mn _I ^{18,e} H ₂ O/ DMF	2e₃	4	65	2e₃ : 63	2e₃ : 97
		Pyr-Mn ^{108,f} H ₂ O/Acetone	2e₄	2	> 99	2e₄ : 89	2e₄ : 88
5	1f	Eco-CaMnO _x H ₂ O/Acetone	2f	4	99	99	100

Table 5. continued

Entry	Substrate 1	Ecocatalyst solvent	Product 2	Reaction time (h)	Conver- sion (%) ^b	Yield (%) ^b	Selectivity (%) ^{b,c}
6		Eco- CaMnOx H ₂ O/Acetone		4	> 99	2g ₁ : 50 2g ₂ : 50	2g ₁ : 50 2g ₂ : 50
7		Eco- CaMnOx H ₂ O/Acetone		4	81	2h ₁ : 71 2h ₂ : 10	2h ₁ : 88 2h ₂ : 12
8		Eco- CaMnOx H ₂ O/Acetone		2	> 99	2i ₁ : 70 2i ₂ : 30	2i ₁ : 70 2i ₂ : 30
9		Eco- CaMnOx ^d H ₂ O/Acetone		4	66	66	100
		Eco-Mn ₁ ^{18,f} H ₂ O/ DMF		4	0	0	0
		Pyr-Mn ^{108,f} H ₂ O/Acetone		2	99	82	80

^aReaction conditions: substrate (1.6 mmol, 1 equiv), catalyst (8 μ mol, 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.

mono- (Table 5, entries 7 and 8) or diepoxides (Table 5, entries 1, 4, and 6) when the double bonds were electron-rich. In the case of limonene, 84% of selectivity of diepoxides was observed with very high conversion in 2 h (Table 4, entry 1). In comparison, Eco-Mn₁ led to 86% of monoepoxides, with only 50% of conversion.¹⁸ This result highlighted the high reactivity of Eco-CaMnO_x, which was close to Pyr-Mn. Both mono- and diepoxides are of high interest in the field of biosourced polymers as they both could be used as monomers for the synthesis of polycarbonates, polyethers, polyesters, or poly(hydro)urethanes.^{102–106} Thus, they could represent substitutes for polymers synthesized from bisphenol A or epichlorhydrin, two toxic molecules classified as CMR.

In 4 h, the epoxidation of geranyl acetate gave a stoichiometric mixture of mono- and diepoxides (Table 5, entry 6). In consequence, the ester moiety did not deactivate Eco-CaMnO_x in spite of its basic Lewis properties. The same reaction with 10 equiv of H₂O₂ favored the formation of the diepoxide, reaching 79% of selectivity. It was thus possible to control the ratio monoepoxides/diepoxides by tuning the amount of H₂O₂.

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

resulting epoxide is highly reactive and acid-sensitive. It easily rearranges by cyclization into hydroxyfuranes or hydroxypyranes.¹⁰⁷ In this case, only 2% of hydroxyfuranes was observed. This indicated that our catalyst was not acidic, avoiding the intramolecular reaction. However, the rearrangement of the epoxide into the hydroxyfuran was easily observed when CDCl₃ was used for NMR assessments. As an example, only the hydroxyfuran was obtained with a 63% yield with the previous Eco-Mn,¹⁸ whereas Pyr-Mn yielded hydroxypyran.¹⁰⁸ Therefore, Eco-CaMnO_x allowed the preparation of very sensitive epoxides. The higher chemoselectivity of Eco-CaMnO_x is the direct consequence of its preparation by a sole thermal treatment. This result is of interest, as linalool epoxide is an important molecule in the communication of pollinating insects.¹⁰⁹ Thirty-four percent of diepoxides were also obtained. This proved the strong oxidizing properties of Eco-CaMnO_x as it succeeded in epoxidizing a terminal double bond.

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

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

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.

of fatty acids from vegetal oils are very interesting as platform molecules for organic chemistry, but also as biodegradable lubricants, plasticizers, and stabilizers of polymers.^{110–112} Sixty-six percent of conversion with a total selectivity in epoxide was reached in 4 h with Eco-CaMnO_x (0.5 equiv Mn), while Eco-Mn was not able to catalyze this reaction. Pyr-Mn seemed more efficient than Eco-CaMnO_x but required twice as much H₂O₂.

In addition to the higher reactivity of Eco-CaMnO_x compared to Eco-Mn, the experimental conditions were also improved; epoxidations were conducted with acetone/H₂O instead of DMF. In a context of growing environmental consciousness, it is motivating to be able to propose novel catalysts, which combine efficiency, use of renewable resources, and eco-friendly processes.

Recycling and Leaching Studies of Eco-CaMnO_x Catalysts. Recycling of Eco-CaMnO_x catalysts was investigated by conducting the epoxidation of isopulegol (Table 6). Eco-CaMnO_x catalysts were recycled by separation after centrifugation of the crude, washing, drying, and reuse for an identical experiment. Up to four successive reactions were conducted. Conversion and yield remained quantitative for the second run (Table 6, entries 1, 2), while a slight decrease was observed after the third run (Table 6, entries 3, 4), suggesting a small loss of activity of Eco-CaMnO_x catalysts.

The small loss of activity was investigated by analyzing the composition and structure of Eco-CaMnO_x catalysts after each run. No significant change of Mn and Ca contents was observed by MP-AES (Table S2), and the structure 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.

Considering that the composition and structure of Eco-CaMnO_x remained similar after four runs, leaching of Eco-CaMnO_x was unlikely to occur but was still verified. Using isopulegol as substrate, a specific experiment was conducted as described by Sheldon et al.¹¹³ After 30 min of reaction, Eco-CaMnO_x was removed from the reaction mixture by filtration; conversion of isopulegol was analyzed after this time at 35%. The reaction mixture was stirred for another 4 h without Eco-CaMnO_x; conversion of isopulegol remained at 35%, indicating that the reaction did not occur after removing Eco-CaMnO_x. As expected, the elemental composition of the reaction mixture was analyzed by MP-AES and no trace of metal was detected. These two results showed that the Eco-CaMnO_x catalyst was a heterogeneous catalyst, in which leaching of Mn can be excluded in the reported conditions.

CONCLUSIONS

In this study, a new generation of ecocatalysts was easily prepared from Mn-accumulating plant species, which are used in ecological restoration. A controlled thermal treatment of Mn-rich biomass led directly to green oxidative catalysts, Eco-CaMnO_x, thus avoiding any further chemical activation. Characterization by MP-AES, XRPD, HRTEM, and STEM-EDX revealed an original polymetallic system. Unusual mixed manganese–calcium oxides, Ca₂Mn₃O₈ and CaMnO₃, were identified. All Eco-CaMnO_x catalysts prepared from different plant species demonstrated an excellent catalytic potential in the epoxidation of terpenes and lipids, with only 0.005 equiv

Mn, in short reaction times, at room temperature, using green solvents and without any ligand or activation phase. Eco-CaMnO_x catalysts afforded much higher conversions and yields than conventional activated manganese dioxide or synthetic Ca₂Mn₃O₈. Not only did these results demonstrate the vegetal footprint of Eco-CaMnO_x catalysts but also they proved that these catalysts could represent potential substitutes to oxidative reagents inconsistent with the requirements of REACH regulation. A wide range of mono- and diepoxides were efficiently synthesized from terpenes, many of them coming from abundant natural resources. Eco-CaMnO_x opens a new perspective for the valorization of Mn-rich biomass through the preparation of biosourced monomers for new biodegradable polymers.^{105,106,114} This new generation of ecocatalysts exhibits environmental and scientific benefits, suggesting a promising life-cycle analysis (Figure 7). It can drive a new approach of green chemistry with ecological, economic, and social advantages.

ASSOCIATED CONTENT

Supporting Information

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

General methods for the characterization of Eco-CaMnO_x and the analysis of the reaction products, MP-AES analyses of Mn-accumulating plant leaves and Eco-CaMnO_x NMR analyses, scale-up of the epoxidation of alkene, the study of the leaching of Eco-CaMnO_x, recycling of Eco-CaMnO_x (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank the French National Center for Scientific Research (CNRS) for financial support. Both North and South provinces of New Caledonia are acknowl-

edged for permissions to harvest New Caledonian Mn-hyperaccumulating plants. In the same way, KNS, SLN, and Dr. Cyril Poullain are acknowledged for the cultivation and harvest of plants in New Caledonia. Erwan Oliviero, from Plateforme Microscopie Electronique et Analytique of University of Montpellier, has our thanks for HRTEM and SEM-EDX analyses. Sci-GuidEdit is acknowledged for writing assistance and proofreading the article.

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