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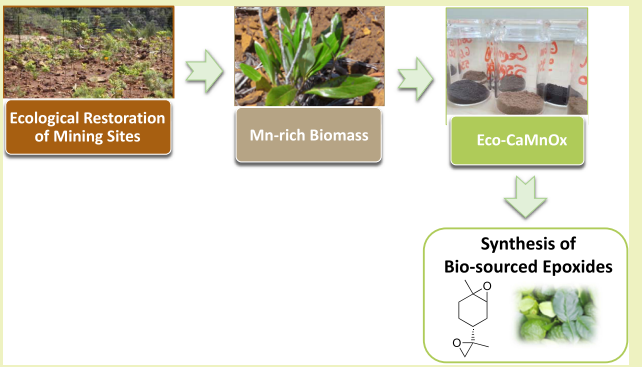
ABSTRACT: Owing to the alarming problems of depletion of mineral resources and ever-growing pollution by metallic elements, biosourced catalysts were prepared from Mn-accumulating plant species from a large-scale program of ecological rehabilitation of mining sites. This new generation of catalysts, "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: $Ca_2Mn_3O_8$ and $CaMnO_3$. The high efficiency of Eco-CaMnO$_x$ catalysts was demonstrated via the epoxidation of various biosourced terpenes and lipids, using the mixture H_2O_2/$NaHCO_3$ 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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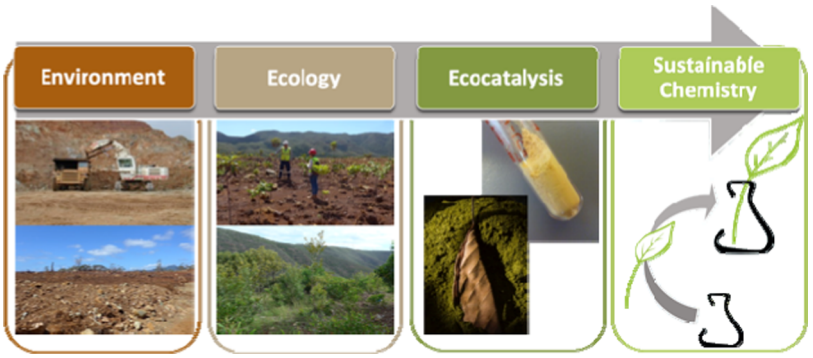


Figure 1. From the ecological restoration of New Caledonian mining sites to ecocatalysis.

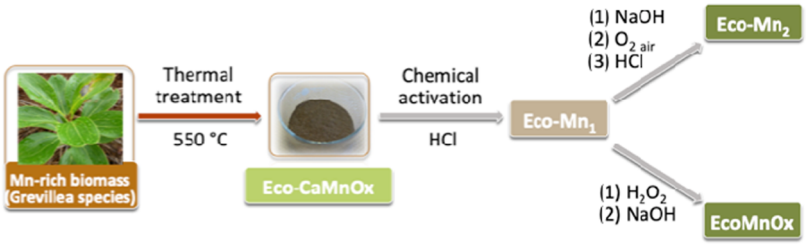


Figure 2. Steps for preparation of the previously studied Eco-Mn catalysts and of the new Eco-$CaMnO_x$ from Mn-accumulating plant species.

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 of Grevillea (Figure 2). In each case, the first step was the preparation of an intermediate Eco-Mn_1. It was based on a controlled thermal treatment of Mn-rich biomass, followed by a chemical activation by HCl.[16] From Eco-Mn_1, two oxidative eco-catalysts were formed by a sequential addition of either $NaOH/O_2/HCl$ (Eco-Mn_2)[16] or H_2O_2/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-Mn_1 was successfully employed in the aminoreduction of ketones[20] and constitutes the first example of reduction promoted by a Mn-based catalyst. Eco-Mn_2 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-Mn_1 provided also a huge potential as green catalysts for valuable epoxidation.[18] Finally, Eco-Mn_1 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-Mn_1, 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 XPRD (Figure 2). We detected a polymetallic oxide (a mixed manganese−calcium oxide, $Ca_2Mn_3O_8$) instead of polymetallic chlorides as for Eco-Mn_1 and Eco-Mn_2.

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 $Ca_2Mn_3O_8$ in organic synthesis. However, mixed Mn−Ca oxides display biomimetic oxidative properties of the natural cofactor $CaMn_4O_5$ of Photosystem II. Indeed, $CaMn_4O_5$ performs the oxidation of water during the photosynthesis process,[35] and the complex $Ca_2Mn_3O_8$ 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

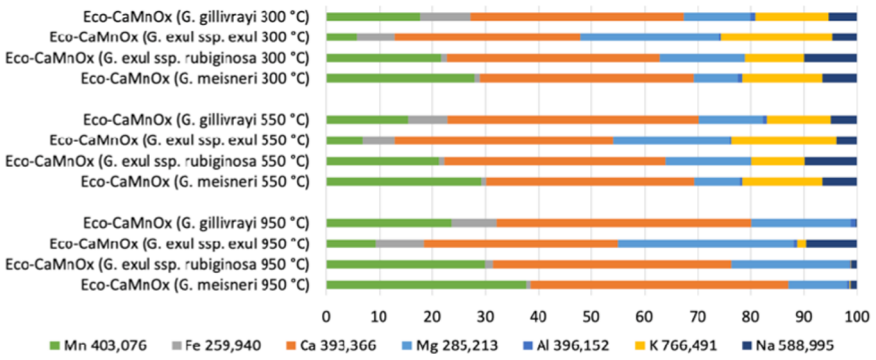


Figure 3. Histogram representing the relative weight percentages of elements in Eco-CaMnO$_x$ catalysts, prepared from different plant species of Grevillea and thermal treatments, determined by MP-AES analyses.

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

The oxidative potential of Eco-CaMnO$_x$ catalysts was then investigated in the epoxidation of terpenes with new challenges that would meet the principles of green chemistry: (1) developing a "waste-free" process to prepare catalysts, by suppressing the acidic and basic activation steps; (2) generating catalysts with high catalytic oxidative performances; and (3) providing an eco-friendlier synthesis of biosourced epoxides.

EXPERIMENTAL SECTION

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

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

Preparation of Synthetic Catalysts. Synthetic ashes were obtained by mixing all together well-chosen commercial metallic salts, so that the relative percentage of metallic elements in the starting mixture was exactly the same as in the leaves of *Grevillea exul* ssp. *rubiginosa*. The salt mixture was then thermally treated at 550 °C following the same procedure as used for Eco-CaMnO$_x$. The chosen salts were the following: manganese malate trihydrate ($MnC_4H_4O_5 \cdot 3H_2O$), calcium oxalate ($CaC_2O_4 \cdot 2H_2O$), iron phosphate ($FePO_4 \cdot 2H_2O$), magnesium phosphate ($Mg_3(PO_4)_2 \cdot xH_2O$), sodium chloride (NaCl), potassium chloride (KCl), and aluminum oxalate ($Al_2C_6O_{12} \cdot xH_2O$).

$Ca_2Mn_3O_8$ was synthesized by grinding $CaCO_3$ (4 mmol, 400 mg) and $MnCO_3$ (6 mmol, 690 mg) in a mortar until the obtained powder was homogeneous. The powder was then thermally treated in an oven under air flow at 800 °C for 18 h.

Epoxidation of Alkenes. In a typical procedure, the alkene (1.6 mmol, 1 equiv), the catalyst (8 μmol, 0.005 equiv Mn), and $NaHCO_3$ (8 mmol, 5 equiv) were stirred in a mixture of acetone (20 mL) and water (20 mL) at room temperature for 10 min. H_2O_2 (30% w/w in H_2O, 8 mmol, 5 equiv) 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 phases were gathered and dried with Na_2SO_4. The solvent was then removed by evaporation.

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: MnO_2, Mn_2O_3, or Mn_3O_4.[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$_x$ catalysts.

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	$Ca_2Mn_3O_8$	$CaMnO_3$	Mn_2O_3	K_2SO_4	$K_3Na(SO_4)_2$
Eco-$CaMnO_x$ (*G. gillivrayi* 300 °C)[a]	x							
Eco-$CaMnO_x$ (*G. gillivrayi* 550 °C)	x		x	x				x
Eco-$CaMnO_x$ (*G. gillivrayi* 950 °C)		x			x	x		
Eco-$CaMnO_x$ (*G. exul* ssp. *exul* 550 °C)[a]	x		x				x	
Eco-$CaMnO_x$ (*G. exul* ssp. *rubiginosa* 550 °C)	x		x	x				x
Eco-$CaMnO_x$ (*G. meisneri* 550 °C)	x		x	x				x
synthetic ash control (550 °C)			x			x		

[a]Mn 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. $Ca_2Mn_3O_8$ 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. $CaMnO_3$ was identified in all Eco-$CaMnO_x$ prepared at 950 °C. $CaMnO_3$ could result from the degradation of $Ca_2Mn_3O_8$ 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-Mn_1.[32]

The structure of $Ca_2Mn_3O_8$ has been reported as infinite sheets of $Mn_3O_8^{4-}$ 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]

$CaMnO_3$ has a perovskite structure based on corner-shared MnO_6-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 $Ca_2Mn_3O_8$ shares similarities with the cofactor $CaMn_4O_5$, 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 $Ca_2Mn_3O_8$ and $CaMnO_3$ were efficient catalysts for the oxygen evolution reaction and oxygen reduction reaction. Indeed, manganese ions in $Ca_2Mn_3O_8$ and $CaMnO_3$ are in the oxidation state IV and they may present interesting oxidative properties similar to MnO_2.

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).

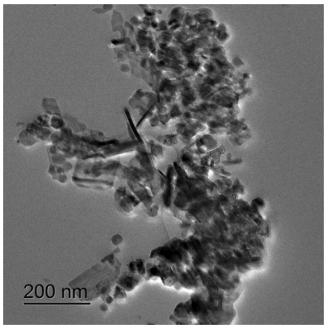


Figure 4. HRTEM image of Eco-$CaMnO_x$ catalysts (*G. gillivrayi* 550 °C).

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 $Ca_2Mn_3O_8$ 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: $Ca_2Mn_3O_8$ and $CaMnO_3$. The oxidative potential of the Eco-$CaMnO_x$ catalysts was studied in the epoxidation of alkenes and especially terpenes, as biosourced substrates.

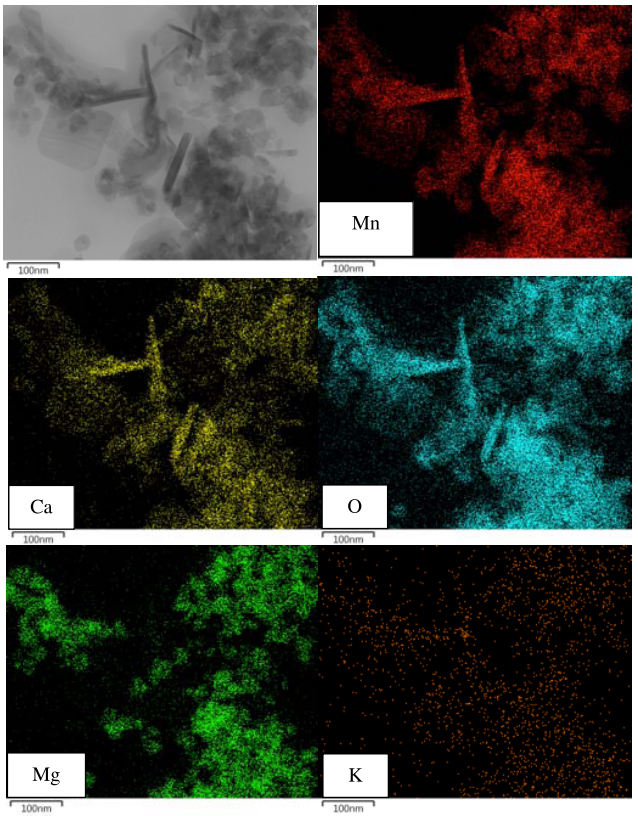


Figure 5. STEM-EDX mapping of Eco-CaMnO$_x$ catalysts (*G. gillivrayi*, 550 °C).

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 H_2O_2 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 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 ligand[76] 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 H_2O_2 for conducting epoxidation reactions with very high catalytic and environmental performances.[81]

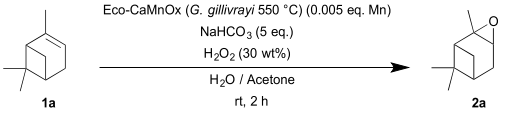
In our previous works, we showed that montmorillonite-supported Eco-Mn$_1$ catalyzed the epoxidation of styrene. Eco-Mn$_1$ contained only 0.31 mol % of manganese, a much lower content of manganese than that reported in previously described Mn-derived heterogeneous catalysts.[82,83] Comparison of Eco-Mn$_1$ properties to those of heterogeneous catalysts made by incorporation of commercial $MnCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ highlighted the superior catalytic activity of polymetallic species present in Eco-Mn$_1$. 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 isopinocamphone, 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 $NaHCO_3$ were stirred in a mixture of acetone:water (1:1) at room temperature for 10 min. H_2O_2 (30% w/w in H_2O) was added dropwise during 2 h in the mixture while stirring. After 2 h, the catalyst was filtered off and the reaction mixture was extracted with ethyl acetate. The organic layers were gathered and dried with Na_2SO_4. The solvent was then removed by evaporation and the reaction products analyzed by gas chromatography−mass spectrometry (GC−MS)/flame ionization detector (FID).

Effect of H_2O_2 Amount. The effect of the quantity of H_2O_2 added into the reaction mixture was studied, as an excessive amount of H_2O_2 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 H_2O_2 increased the conversion, yield, and selectivity before reaching a threshold. Almost total conversion of α-pinene **1a**

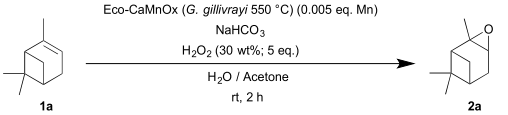
Table 2. Effect of the Amount of H_2O_2 and of the Adding Time on the Epoxidation of α-pinene[a]



entry	H_2O_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

[a]Reaction conditions: α-pinene (1.6 mmol, 1 equiv), catalyst (8 μmol, 0.005 equiv Mn), $NaHCO_3$ (8 mmol, 5 equiv), H_2O_2 (30 wt %), and H_2O (20 mL): acetone (20 mL), rt, 2 h. [b]Conversion, yield, and selectivity were established by FID using biphenyl as internal standard. [c]Selectivity was calculated as the ratio of yield over conversion.

Table 3. Effect of the Amount of $NaHCO_3$ 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

[a]Reaction conditions: α-pinene (1.6 mmol, 1 equiv), catalyst (8 μmol, 0.005 equiv Mn), $NaHCO_3$, H_2O_2 (30 wt %; 8 mmol, 5 equiv), and H_2O (20 mL): acetone (20 mL), rt, 2 h. [b]Conversion, yield, and selectivity were established by FID using biphenyl as internal standard. [c]Selectivity was calculated as the ratio of yield over conversion.

and a yield of 64% in epoxide **2a** were reached with 5 equiv of H_2O_2 (Table 2, entry 5). The addition time of H_2O_2 in the reaction mixture was also investigated. Although the selectivity in epoxide remained similar by decreasing the addition time, the conversion dropped from 98% in 1−2 h (Table 2, entries 6, 7) to 63% in 30 min (Table 2, entry 8). These results supported the importance of a slow addition of H_2O_2 in oxidative reactions. Indeed, it was reported that a gradual addition of H_2O_2 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 with 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 H_2O_2 was employed as it represented the smallest amount affording total conversion and high yield in epoxide. The addition time was kept at 2 h.

Effect of $NaHCO_3$ Amount. The effect of the quantity of $NaHCO_3$ 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 $NaHCO_3$ and H_2O_2 could produce in situ peroxymonocarbonate ions (HCO_4^-),[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 $NaHCO_3$ quantity resulted in decreasing conversion, yield, and selectivity in epoxide. Therefore, 5 equiv of $NaHCO_3$ seemed to be the lowest quantity giving high conversion and yield (Table 3, entry 5).

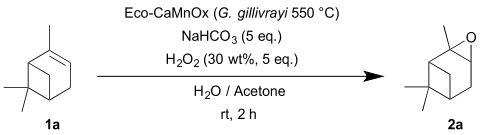
Effect of Catalyst Loading. The effect of the quantity of Eco-CaMnO_x catalysts was then studied using α-pinene as the substrate (Table 4). A low quantity of manganese gave high conversion rates. Almost total conversion and 64% yield were obtained with only 0.005 equiv in manganese (Table 4, entry 4).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

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 $Ca_2Mn_3O_8$ 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 MnO_2 and synthetic $Ca_2Mn_3O_8$ 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	$Ca_2Mn_3O_8$	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		

[a]Reaction conditions: α-pinene (1.6 mmol, 1 equiv), the catalyst, $NaHCO_3$ (8 mmol, 5 equiv), H_2O_2 (30 wt %; 8 mmol, 5 equiv), and H_2O (20 mL): acetone (20 mL), rt, 2 h. [b]Conversion, yield, and selectivity were established by FID using biphenyl as the internal standard. [c]Selectivity was calculated as the ratio of yield over conversion. [d]0.02 equiv Ca was used, corresponding to the quantity of Ca engaged by 0.005 equiv Mn with Eco-CaMnO$_x$. [e]Traces of verbenol, carveol, and campholenic aldehyde were detected by GC−MS. [f]TON = number of mol of the product formed per mol of catalyst. [g]TOF = 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 $Ca_2Mn_3O_8$ (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.

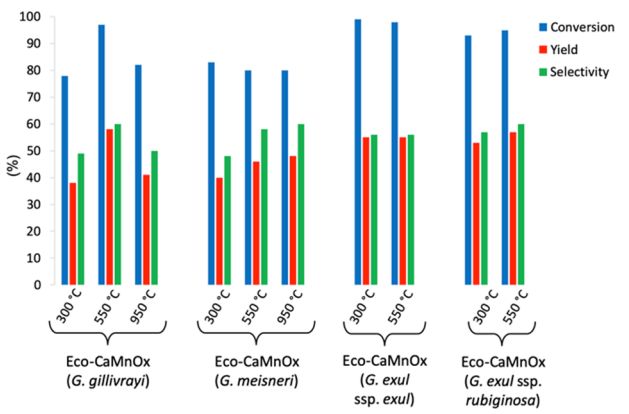


Figure 6. Effect of the plant species and of the temperature of the thermal treatment used to prepare Eco-CaMnO$_x$ on the epoxidation of α-pinene. Reaction conditions: α -pinene (1.6 mmol, 1 equiv), catalyst (8 mmol, 0.005 equiv Mn), $NaHCO_3$ (8 mmol, 5 equiv), H_2O_2 (30 wt %; 8 mmol, 5 equiv), and H_2O (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]

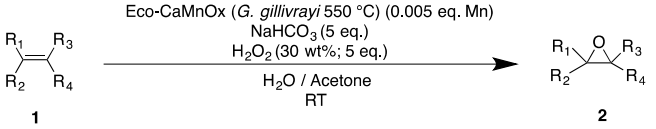
Our system can be advantageously compared to other bicarbonate-activated peroxide systems based on Mn catalysts. For instance, Lane et al. obtained 89% yield but only in the presence of additives.[82] Qi et al. reached 40% selectivity using Mn^{2+}-exchanged zeolites.[92]

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

Table 5. Substrate Scope for the Epoxidation of Natural Substrates by Ecocatalysts (Eco-CaMnO$_x$[a], Eco-Mn$_1$,[18] and Pyr-Mn[120])



1 2

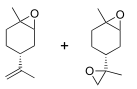
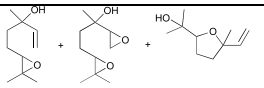
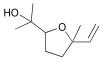
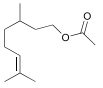
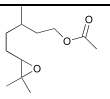
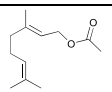
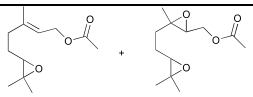
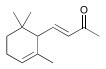
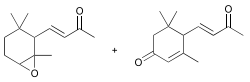
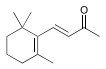
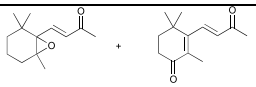
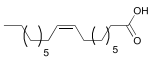
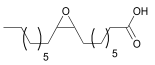
Entry	Substrate 1	Ecocatalyst solvent	Product 2	Reaction time (h)	Conversion (%)[b]	Yield (%)[b]	Selectivity (%)[b,c]
1	 **1b**	Eco-CaMnOx H$_2$O/Acetone	 **2b$_1$** **2b$_2$**	2	93	**2b$_1$**: 15 **2b$_2$**: 78	**2b$_1$**: 16 **2b$_2$**: 84
		Eco-Mn$_1$[18,e] H$_2$O/ DMF		4	50	**2b$_1$**: 43 **2b$_2$**: 7	**2b$_1$**: 86 **2b$_2$**: 14
		Pyr-Mn[108,f] H$_2$O/Acetone		2	99	**2b$_1$**: 1 **2b$_2$**: 98	**2b$_1$**: 1 **2b$_2$**: 99
2	 **1c**	Eco-CaMnOx H$_2$O/Acetone	 **2c**	2	> 99	> 99	100
3	 **1d**	Eco-CaMnOx H$_2$O/Acetone	 **2d**	4	> 99	> 99	100
4	 **1e**	Eco-CaMnOx H$_2$O/Acetone	 **2e$_1$** **2e$_2$** **2e$_3$**	4	> 99	**2e$_1$**: 64 **2e$_2$**: 34 **2e$_3$**: 2	**2e$_1$**: 64 **2e$_2$**: 34 **2e$_3$**: 2
		Eco-Mn$_1$[18,e] H$_2$O/ DMF	 **2e$_3$**	4	65	**2e$_3$**: 63	**2e$_3$**: 97
		Pyr-Mn[108,f] H$_2$O/Acetone	 **2e$_4$**	2	> 99	**2e$_4$**: 89	**2e$_4$**: 88
5	 **1f**	Eco-CaMnOx H$_2$O/Acetone	 **2f**	4	99	99	100

Table 5. continued

Entry	Substrate 1	Ecocatalyst solvent	Product 2	Reaction time (h)	Conversion (%)[b]	Yield (%)[b]	Selectivity (%)[b,c]
6	 **1g**	Eco-CaMnOx H_2O/Acetone	 **2g$_1$** **2g$_2$**	4	> 99	**2g$_1$**: 50 **2g$_2$**: 50	**2g$_1$**: 50 **2g$_2$**: 50
7	 **1h**	Eco-CaMnOx H_2O/Acetone	 **2h$_1$** **2h$_2$**	4	81	**2h$_1$**: 71 **2h$_2$**: 10	**2h$_1$**: 88 **2h$_2$**: 12
8	 **1i**	Eco-CaMnOx H_2O/Acetone	 **2i$_1$** **2i$_2$**	2	> 99	**2i$_1$**: 70 **2i$_2$**: 30	**2i$_1$**: 70 **2i$_2$**: 30
9	 **1j**	Eco-CaMnOx[d] H_2O/Acetone	 **2j**	4	66	66	100
		Eco-Mn$_1$[18,f] H_2O/ DMF		4	0	0	0
		Pyr-Mn[108,f] H_2O/Acetone		2	99	82	80

[a]Reaction conditions: substrate (1.6 mmol, 1 equiv), catalyst (8 μmol, 0.005 equiv Mn), $NaHCO_3$ (8 mmol, 5 equiv), H_2O_2 (30 wt %; 8 mmol, 5 equiv), and H_2O (20 mL): acetone (20 mL), rt. [b]Conversion, yield, and selectivity were established by FID, using biphenyl as internal standard, and then confirmed by ^{1}H NMR from the isolated product. [c]Selectivity was calculated as the ratio of yield over conversion. [d]Catalyst: 0.5 equiv Mn. [e]Terpene (0.25 mmol, 1 equiv), supported catalyst (0.0031 equiv Mn), $NaHCO_3$ (0.05 mmol, 5 equiv), H_2O_2 (30 wt %; 0.8 mmol, 3.2 equiv), and H_2O/dimethylformamide (DMF) (2 mL), 0 °C, 4 h. [f]Terpene (0.18 mmol, 1 equiv), catalyst (0.00006 equiv Mn), $NaHCO_3$ (0.88 mmol, 5 equiv), H_2O_2 (30 wt %; 1.75 mmol, 9.7 equiv), and H_2O/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-Mn$_1$ 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.

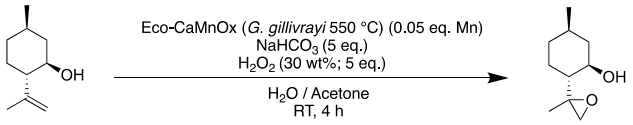
In 4 h, the epoxidation of geranyl acetate gave a stoichiometric mixture of mono- and diepoxides (Table 5, entry 6). In consequence, the ester moiety did not deactivate Eco-CaMnO$_x$ in spite of its basic Lewis properties. The same reaction with 10 equiv of H_2O_2 favored the formation of the diepoxide, reaching 79% of selectivity. It was thus possible to control the ratio monoepoxides/diepoxides by tuning the amount of H_2O_2.

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 hydroxyfurane was easily observed when $CDCl_3$ was used for NMR assessments. As an example, only the hydroxyfurane 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



1d **2d**

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)

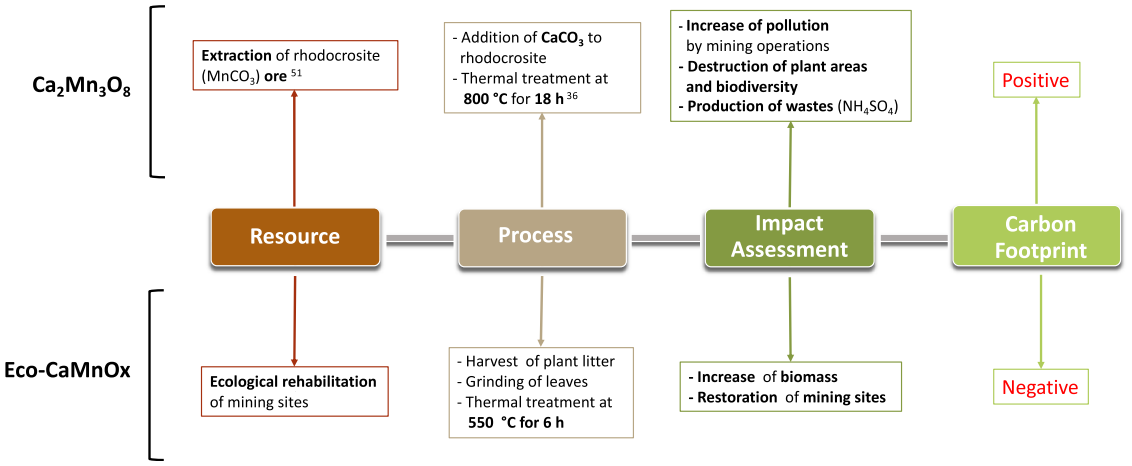


Figure 7. Qualitative environmental impact assessment of the catalyst preparation.

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 H_2O_2.

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/H_2O 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, $Ca_2Mn_3O_8$ and $CaMnO_3$, 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 $Ca_2Mn_3O_8$. 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

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■ REFERENCES

(1) Hunt, A. J.; Farmer, T. J.; Clark, J. H. Elemental Sustainability and the Importance of Scarce Element Recovery. In *RSC Green Chemistry*; Hunt, A., Ed.; Royal Society of Chemistry: Cambridge, 2013; Chapter 1, pp 1−28.

(2) *Ecology of Industrial Pollution*, 1st ed.; Batty, L. C.; Hallberg, K. B., Eds.; Cambridge University Press: Cambridge, NY, 2010.

(3) Myers, N. Threatened Biotas: "Hot Spots" in Tropical Forests. *Environmentalist* **1988**, *8*, 187−208.

(4) US Geological Survey & Orienteering S. *Mineral Commodity Summaries*; Government Printing Office, 2009; p 112.

(5) Robineau, B.; Berthault, L.; Christmann, P. Nouvelle-Calédonie, Terre de Nickel. *Geosicences* **2011**, 50−57.

(6) Jaffré, T.; Latham, M.; Schmid, M. Aspects de l'influence de l'extraction du minerai de nickel sur la végétation et les sols en Nouvelle-Calédonie. *Cah. O.R.S.T.O.M., Ser. Biol.* **1977**, *12*, 307−321.

(7) Losfeld, G.; L'Huillier, L.; Fogliani, B.; Jaffré, T.; Grison, C. Mining in New Caledonia: Environmental Stakes and Restoration Opportunities. *Environ. Sci. Pollut. Res.* **2015**, *22*, 5592−5607.

(8) Gunkel-Grillon, P.; Laporte-Magoni, C.; Lemestre, M.; Bazire, N. Toxic Chromium Release from Nickel Mining Sediments in Surface Waters, New Caledonia. *Environ. Chem. Lett.* **2014**, *12*, 511−516.

(9) Isnard, S.; L'huillier, L.; Rigault, F.; Jaffré, T. How Did the Ultramafic Soils Shape the Flora of the New Caledonian Hotspot? *Plant Soil* **2016**, *403*, 53−76.

(10) Pillon, Y.; Munzinger, J.; Amir, H.; Lebrun, M. Ultramafic Soils and Species Sorting in the Flora of New Caledonia. *J. Ecol.* **2010**, *98*, 1108−1116.

(11) Reeves, R. D. Tropical Hyperaccumulators of Metals and Their Potential for Phytoextraction. *Plant Soil* **2003**, *249*, 57−65.

(12) Losfeld, G.; Mathieu, R.; L'Huillier, L.; Fogliani, B.; Jaffré, T.; Grison, C. Phytoextraction from Mine Spoils: Insights from New Caledonia. *Environ. Sci. Pollut. Res.* **2015**, *22*, 5608−5619.

(13) Losfeld, G.; L'Huillier, L.; Fogliani, B.; Mc Coy, S.; Grison, C.; Jaffré, T. Leaf-Age and Soil-Plant Relationships: Key Factors for Reporting Trace-Elements Hyperaccumulation by Plants and Design Applications. *Environ. Sci. Pollut. Res.* **2015**, *22*, 5620−5632.

(14) Grison, C. Combining Phytoextraction and Ecocatalysis: A Novel Concept for Greener Chemistry, an Opportunity for Remediation. *Environ. Sci. Pollut. Res.* **2015**, *22*, 5589−5591.

(15) Deyris, P.-A.; Grison, C. Nature, Ecology and Chemistry: An Unusual Combination for a New Green Catalysis, Ecocatalysis. *Curr. Opin. Green Sustainable Chem.* **2018**, *10*, 6−10.

(16) Escande, V.; Renard, B.-L.; Grison, C. Lewis Acid Catalysis and Green Oxidations: Sequential Tandem Oxidation Processes Induced by Mn-Hyperaccumulating Plants. *Environ. Sci. Pollut. Res.* **2015**, *22*, 5633−5652.

(17) Escande, V.; Lam, C. H.; Grison, C.; Anastas, P. T. EcoMnOx, a Biosourced Catalyst for Selective Aerobic Oxidative Cleavage of Activated 1,2-Diols. *ACS Sustainable Chem. Eng.* **2017**, *5*, 3214−3222.

(18) Escande, V.; Petit, E.; Garoux, L.; Boulanger, C.; Grison, C. Switchable Alkene Epoxidation/Oxidative Cleavage with H_2O_2 /$NaHCO_3$: Efficient Heterogeneous Catalysis Derived from Bio-sourced Eco-Mn. *ACS Sustainable Chem. Eng.* **2015**, *3*, 2704−2715.

(19) Escande, V.; Lam, C. H.; Coish, P.; Anastas, P. T. Heterogeneous Sodium-Manganese Oxide Catalyzed Aerobic Oxidative Cleavage of 1,2-Diols. *Angew. Chem., Int. Ed.* **2017**, *56*, 9561−9565.

(20) Escande, V.; Velati, A.; Garel, C.; Renard, B.-L.; Petit, E.; Grison, C. Phytoextracted Mining Wastes for Ecocatalysis: Eco-Mn, an Efficient and Eco-Friendly Plant-Based Catalyst for Reductive Amination of Ketones. *Green Chem.* **2015**, *17*, 2188−2199.
(21) Escande, V.; Poullain, C.; Clavé, G.; Petit, E.; Masquelez, N.; Hesemann, P.; Grison, C. Bio-Based and Environmental Input for Transfer Hydrogenation Using EcoNi(0) Catalyst in Isopropanol. *Appl. Catal., B* **2017**, *210*, 495−503.
(22) Deyris, P.-A.; Adler, P.; Petit, E.; Legrand, Y.-M.; Grison, C. Woody Species: A New Bio-Based Material for Dual Ca/Mg Catalysis with Remarkable Lewis Acidity Properties. *Green Chem.* **2019**, *21*, 3133−3142.
(23) Deyris, P.-A.; Bert, V.; Diliberto, S.; Boulanger, C.; Petit, E.; Legrand, Y.-M.; Grison, C. Biosourced Polymetallic Catalysis: A Surprising and Efficient Means to Promote the Knoevenagel Condensation. *Front. Chem.* **2018**, *6*, 48.
(24) Escande, V.; Olszewski, T. K.; Grison, C. From Biodiversity to Catalytic Diversity: How to Control the Reaction Mechanism by the Nature of Metallophytes. *Environ. Sci. Pollut. Res.* **2015**, *22*, 5653−5666.
(25) Grison, C. M.; Velati, A.; Escande, V.; Grison, C. Metallophytes for Organic Synthesis: Towards New Bio-Based Selective Protection/Deprotection Procedures. *Environ. Sci. Pollut. Res.* **2015**, *22*, 5686−5698.
(26) Escande, V.; Velati, A.; Grison, C. Ecocatalysis for 2H-Chromenes Synthesis: An Integrated Approach for Phytomanagement of Polluted Ecosystems. *Environ. Sci. Pollut. Res* **2015**, *22*, 5677−5685.
(27) Escande, V.; Olszewski, T. K.; Petit, E.; Grison, C. Biosourced Polymetallic Catalysts: An Efficient Means To Synthesize Under-exploited Platform Molecules from Carbohydrates. *ChemSusChem* **2014**, *7*, 1915−1923.
(28) Escande, V.; Olszewski, T. K.; Grison, C. Preparation of Ecological Catalysts Derived from Zn Hyperaccumulating Plants and Their Catalytic Activity in Diels−Alder Reaction. *C. R. Chim.* **2014**, *17*, 731−737.
(29) Olszewski, T. K.; Adler, P.; Grison, C. Bio-Based Catalysts from Biomass Issued after Decontamination of Effluents Rich in Copper—An Innovative Approach towards Greener Copper-Based Catalysis. *Catalysts* **2019**, *9*, 214.
(30) Clavé, G.; Pelissier, F.; Campidelli, S.; Grison, C. Ecocatalyzed Suzuki Cross Coupling of Heteroaryl Compounds. *Green Chem.* **2017**, *19*, 4093−4103.
(31) Garel, C.; Renard, B.-L.; Escande, V.; Galtayries, A.; Hesemann, P.; Grison, C. CC Bond Formation Strategy through Ecocatalysis: Insights from Structural Studies and Synthetic Potential. *Appl. Catal., A* **2015**, *504*, 272−286.
(32) Garel, C.; Fonda, E.; Michalowicz, A.; Diliberto, S.; Boulanger, C.; Petit, E.; Legrand, Y. M.; Poullain, C.; Grison, C. Structure and Composition of First Biosourced Mn-Rich Catalysts with a Unique Vegetal Footprint. *Mater. Today Sustainability* **2019**, No. 100020.
(33) Amini, M.; Najafpour, M. M.; Nayeri, S.; Pashaei, B.; Bagherzadeh, M. Nano-Layered Manganese Oxides as Low-Cost, Easily Synthesized, Environmentally Friendly and Efficient Catalysts for Epoxidation of Olefins. *RSC Adv.* **2012**, *2*, 3654−3657.
(34) Amini, M.; Najafpour, M. M.; Zare, M.; Amini, E. Nanolayered Manganese-Calcium Oxide as an Efficient and Environmentally Friendly Catalyst for Alcohol Oxidation. *J. Mol. Catal. A: Chem.* **2014**, *394*, 303−308.
(35) Bricker, T. M.; Ghanotakis, D. F. Introduction to Oxygen Evolution and the Oxygen-Evolving Complex. In *Oxygenic Photosynthesis: The Light Reactions; Advances in Photosynthesis and Respiration*; Springer: Dordrecht, 1996; pp 113−136.
(36) Park, Y. J.; Doeff, M. M. Synthesis and Electrochemical Characterization of M2Mn3O8 (M = Ca, Cu) Compounds and Derivatives. *Solid State Ionics* **2006**, *177*, 893−900.
(37) Ramírez, A.; Bogdanoff, P.; Friedrich, D.; Fiechter, S. Synthesis of Ca2Mn3O8 Films and Their Electrochemical Studies for the Oxygen Evolution Reaction (OER) of Water. *Nano Energy* **2012**, *1*, 282−289.
(38) Najafpour, M. M.; Pashaei, B.; Nayeri, S. Calcium Manganese-(IV) Oxides: Biomimetic and Efficient Catalysts for Water Oxidation. *Dalton Trans.* **2012**, *41*, 4799−4805.
(39) Dent Glasser, L. S.; Smith, I. B. Oriented Transformations in the System MnO-O-H_2O. *Mineral. Mag. J. Mineral. Soc.* **1968**, *36*, 976−987.
(40) Büchel, K. H.; Moretto, H.-H.; Werner, D. Manganese Compounds and Manganese. In *Industrial Inorganic Chemistry*, 2nd ed.; John Wiley & Sons, 2000; pp 282−293.
(41) Han, X.; Zhang, T.; Du, J.; Cheng, F.; Chen, J. Porous Calcium−Manganese Oxide Microspheres for Electrocatalytic Oxygen Reduction with High Activity. *Chem. Sci.* **2012**, *4*, 368−376.
(42) Ansell, G. B.; Modrick, M. A.; Longo, J. M.; Poeppeimeler, K. R.; Horowitz, H. S. Structure of Calcium Manganese Oxide Ca2Mn3O8. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *38*, 1795−1797.
(43) Brudvig, G. W. Water Oxidation Chemistry of Photosystem II. *Philos. Trans. R. Soc., B* **2008**, *363*, 1211−1219.
(44) Najafpour, M. M.; Ghobadi, M. Z.; Haghighi, B.; Eaton-Rye, J. J.; Tomo, T.; Shen, J.-R.; Allakhverdiev, S. I. Nano-Sized Manganese-Calcium Cluster in Photosystem II. *Biochemistry* **2014**, *79*, 324−336.
(45) Sienel, G.; Rieth, R.; Rowbottom, K. T. Epoxides. In *Ullmann's Encyclopedia of Industrial Chemistry*; American Cancer Society, 2000.
(46) Adam, W.; Saha-Möller, C. R.; Zhao, C.-G. Dioxirane Epoxidation of Alkenes. In *Oxidation of Organic Compounds by Dioxiranes*; John Wiley & Sons, Ltd, 2014; pp 1−309.
(47) Bellucci, G.; Chiappe, C.; Moro, G. L.; Ingrosso, G. Facial Stereoselectivity of Two-Step Additions Initiated by Electrophilic Halogens to Methylenecyclohexanes. A Comparison with Epoxidation. *J. Org. Chem.* **1995**, *60*, 6214−6217.
(48) Noyori, R.; Aoki, M.; Sato, K. Green Oxidation with Aqueous Hydrogen Peroxide. *Chem. Commun.* **2003**, 1977−1986.
(49) Joergensen, K. A. Transition-Metal-Catalyzed Epoxidations. *Chem. Rev.* **1989**, *89*, 431−458.
(50) Grigoropoulou, G.; Clark, J. H.; Elings, J. A. Recent Developments on the Epoxidation of Alkenes Using Hydrogen Peroxide as an Oxidant. *Green Chem.* **2003**, *5*, 1−7.
(51) Lane, B. S.; Burgess, K. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev.* **2003**, *103*, 2457−2474.
(52) Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. Alkylrhenium Oxides as Homogeneous Epoxidation Catalysts: Activity, Selectivity, Stability, Deactivation. *J. Mol. Catal.* **1994**, *86*, 243−266.
(53) Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. Highly Efficient Epoxidation of Olefins Using Aqueous H2O2 and Catalytic Methyltrioxorhenium/Pyridine: Pyridine-Mediated Ligand Acceleration. *J. Am. Chem. Soc.* **1997**, *119*, 6189−6190.
(54) Owens, G. S.; Durazo, A.; Abu-Omar, M. M. Kinetics of MTO-Catalyzed Olefin Epoxidation in Ambient Temperature Ionic Liquids: UV/Vis and 2H NMR Study. *Chem. − Eur. J.* **2002**, *8*, 3053−3059.
(55) Yamazaki, S. An Effective Procedure for the Synthesis of Acid-Sensitive Epoxides: Use of 1-Methylimidazole as the Additive on Methyltrioxorhenium-Catalyzed Epoxidation of Alkenes with Hydrogen Peroxide. *Org. Biomol. Chem.* **2010**, *8*, 2377−2385.
(56) Conte, V.; Di Furia, F.; Licini, G. Liquid Phase Oxidation Reactions by Peroxides in the Presence of Vanadium Complexes. *Appl. Catal., A* **1997**, *157*, 335−361.
(57) Bortolini, O.; Di Furia, F.; Schrimin, P.; Modena, G. Metal Catalysis in Oxidation by Peroxides Part 8 [1] Further Insight on the Mechanism of Vanadium(V) Catalyzed Oxidation of Sulphides and Alkenes by Hydrogen Peroxide. *J. Mol. Catal.* **1980**, *7*, 59−74.
(58) Dinoi, C.; Ciclosi, M.; Manoury, E.; Maron, L.; Perrin, L.; Poli, R. Olefin Epoxidation by H2O2/MeCN Catalysed by Cyclopentadienyloxidotungsten(VI) and Molybdenum(VI) Complexes: Experiments and Computations. *Chem. − Eur. J.* **2010**, *16*, 9572−9584.
(59) Griffith, W. P.; Parkin, B. C.; White, A. J. P.; Williams, D. J. The Crystal Structures of [NMe4]2[(PhPO3){MoO(O2)2}2-{MoO-(O2)2(H2O)}] and [NBun4]2[W4O6(O2)6(OH2)(H2O)2] and

Their Use as Catalytic Oxidants. *J. Chem. Soc., Dalton Trans.* **1995**, 3131−3138.
(60) Gresley, N. M.; Griffith, W. P.; Laemmel, A. C.; Nogueira, H. I. S.; Parkin, B. C. Studies on Polyoxo and Polyperoxo-Metalates Part 511Part 4: Ref. [4].: Peroxide-Catalysed Oxidations with Hetero-polyperoxo-Tungstates and -Molybdates. *J. Mol. Catal. A: Chem.* **1997**, *117*, 185−198.
(61) Venturello, C.; Alneri, E.; Ricci, M. A New, Effective Catalytic System for Epoxidation of Olefins by Hydrogen Peroxide under Phase-Transfer Conditions. *J. Org. Chem.* **1983**, *48*, 3831−3833.
(62) Sato, K.; Aoki, M.; Ogawa, M.; Hashimoto, T.; Noyori, R. A Practical Method for Epoxidation of Terminal Olefins with 30% Hydrogen Peroxide under Halide-Free Conditions. *J. Org. Chem.* **1996**, *61*, 8310−8311.
(63) Villa de P, A. L.; Sels, B. F.; De Vos, D. E.; Jacobs, P. A. A Heterogeneous Tungsten Catalyst for Epoxidation of Terpenes and Tungsten-Catalyzed Synthesis of Acid-Sensitive Terpene Epoxides. *J. Org. Chem.* **1999**, *64*, 7267−7270.
(64) Kamata, K.; Sugahara, K.; Ishimoto, R.; Nojima, S.; Okazaki, M.; Matsumoto, T.; Mizuno, N. Highly Selective Epoxidation of Cycloaliphatic Alkenes with Aqueous Hydrogen Peroxide Catalyzed by [PO4WO(O2)24]3−/Imidazole. *ChemCatChem* **2014**, *6*, 2327−2332.
(65) Gerber, G. B.; Léonard, A.; Hantson, P. Carcinogenicity, Mutagenicity and Teratogenicity of Manganese Compounds. *Crit. Rev. Oncol. Hematol.* **2002**, *42*, 25−34.
(66) 24—Manganese, Technetium and Rhenium. In *Chemistry of the Elements*, 2nd ed.; Greenwood, N. N.; Earnshaw, A., Eds.; Butter-worth-Heinemann: Oxford, 1997; pp 1040−1069.
(67) Anelli, P. L.; Banfi, S.; Montanari, F.; Quici, S. Synergistic Effect of Lipophilic Carboxylic Acids and Heterocyclic Axial Ligands in Alkene Epoxidation by Hydrogen Peroxide Catalysed by Manganese(III) Tetra-Aryl Porphyrins. *J. Chem. Soc., Chem. Commun.* **1989**, 779−780.
(68) Banfi, S.; Legramandi, F.; Montanari, F.; Pozzi, G.; Quici, S. Biomimetic Models of Cytochrome P-450. A Doubly Tailed Manganese(III)−Tetraaryl Porphyrin; an Extremely Efficient Catalyst for Hydrocarbon Oxygenations Promoted by 30% H2O2. *J. Chem. Soc., Chem. Commun.* **1991**, 1285−1287.
(69) Maraval, V.; Ancel, J.-E.; Meunier, B. Manganese(III) Porphyrin Catalysts for the Oxidation of Terpene Derivatives: A Comparative Study. *J. Catal.* **2002**, *206*, 349−357.
(70) Martins, R. R. L.; Neves, M. G. P. M. S.; Silvestre, A. J. D.; Simões, M. M. Q.; Silva, A. M. S.; Tomé, A. C.; Cavaleiro, J. A. S.; Tagliatesta, P.; Crestini, C. Oxidation of Unsaturated Monoterpenes with Hydrogen Peroxide Catalysed by Manganese(III) Porphyrin Complexes. *J. Mol. Catal. A: Chem.* **2001**, *172*, 33−42.
(71) Berkessel, A.; Frauenkron, M.; Schwenkreis, T.; Steinmetz, A.; Baum, G.; Fenske, D. Pentacoordinated Manganese(III) Dihydrosalen Complexes as Biomimetic Oxidation Catalysts. *J. Mol. Catal. A: Chem.* **1996**, *113*, 321−342.
(72) Pietikäinen, P. Convenient Asymmetric (Salen)Mn(III)-Catalyzed Epoxidation of Unfunctionalized Alkenes with Hydrogen Peroxide Using Carboxylate Salt Cocatalysts. *Tetrahedron* **1998**, *54*, 4319−4326.
(73) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. Enantioselective Epoxidation of Unfunctionalized Olefins Catalyzed by Salen Manganese Complexes. *J. Am. Chem. Soc.* **1990**, *112*, 2801−2803.
(74) Katsuki, T. Mn-Salen Catalyst, Competitor of Enzymes, for Asymmetric Epoxidation. *J. Mol. Catal. A: Chem.* **1996**, *113*, 87−107.
(75) Ito, Y. N.; Katsuki, T. What Is the Origin of Highly Asymmetric Induction by a Chiral (Salen)Manganese(III) Complex? Design of a Conformationally Fixed Complex and Its Application to Asymmetric Epoxidation of 2, 2-Dimethylchromenes. *Tetrahedron Lett.* **1998**, *39*, 4325−4328.
(76) Serra, A. C.; Marçalo, E. C.; Gonsalves, A. D. A View on the Mechanism of Metalloporphyrin Degradation in Hydrogen Peroxide Epoxidation Reactions. *J. Mol. Catal. A: Chem.* **2004**, *215*, 17−21.
(77) Zammataro, A.; Gangemi, C. M. A.; Pappalardo, A.; Toscano, R. M.; Puglisi, R.; Nicotra, G.; Fragalà, M. E.; Tuccitto, N.; Sfrazzetto, G. T. Covalently Functionalized Carbon Nanoparticles with a Chiral Mn-Salen: A New Nanocatalyst for Enantioselective Epoxidation of Alkenes. *Chem. Commun.* **2019**, *55*, 5255−5258.
(78) Martinez-Lorente, M. A.; Battioni, P.; Kleemiss, W.; Bartoli, J. F.; Mansuy, D. Manganese Porphyrins Covalently Bound to Silica and Montmorillonite K10 as Efficient Catalysts for Alkene and Alkane Oxidation by Hydrogen Peroxide. *J. Mol. Catal. A: Chem.* **1996**, *113*, 343−353.
(79) Doro, F. G.; Smith, J. R. L.; Ferreira, A. G.; Assis, M. D. Oxidation of Alkanes and Alkenes by Iodosylbenzene and Hydrogen Peroxide Catalysed by Halogenated Manganese Porphyrins in Homogeneous Solution and Covalently Bound to Silica. *J. Mol. Catal. A: Chem.* **2000**, *164*, 97−108.
(80) Beigi, M.; Roller, S.; Haag, R.; Liese, A. Polyglycerol-Supported Co- and Mn-Salen Complexes as Efficient and Recyclable Homogeneous Catalysts for the Hydrolytic Kinetic Resolution of Terminal Epoxides and Asymmetric Olefin Epoxidation. *Eur. J. Org. Chem.* **2008**, *2008*, 2135−2141.
(81) Arpe, H.-J. *Industrial Organic Chemistry*, 5th Completely Revised Edition; Wiley-VCH Verlag GmnH & Co. KGaA: Weinheim, Germany, 2016.
(82) Lane, B. S.; Vogt, M.; DeRose, V. J.; Burgess, K. Manganese-Catalyzed Epoxidations of Alkenes in Bicarbonate Solutions. *J. Am. Chem. Soc.* **2002**, *124*, 11946−11954.
(83) Lane, B. S.; Burgess, K. A Cheap, Catalytic, Scalable, and Environmentally Benign Method for Alkene Epoxidations. *J. Am. Chem. Soc.* **2001**, *123*, 2933−2934.
(84) Bauer, K.; Garbe, D.; Surburg, H. Single Fragrance and Flavor Materials. In *Common Fragrance and Flavor Materials*; John Wiley & Sons, Ltd, 2001; pp 7−165.
(85) Wender, P. A.; Mucciaro, T. P. A New and Practical Approach to the Synthesis of Taxol and Taxol Analogs: The Pinene Path. *J. Am. Chem. Soc.* **1992**, *114*, 5878−5879.
(86) Mimoun, H. Catalytic Opportunities in the Flavor and Fragrance Industry. *CHIMIA* **1996**, *50*, 620−625.
(87) Hölderich, W. F.; Röseler, J.; Heitmann, G.; Liebens, A. T. The Use of Zeolites in the Synthesis of Fine and Intermediate Chemicals. *Catal. Today* **1997**, *37*, 353−366.
(88) Wilson, K.; Rénson, A.; Clark, J. H. Novel Heterogeneous Zinc Triflate Catalysts for the Rearrangement of α-Pinene Oxide. *Catal. Lett.* **1999**, *61*, 51−55.
(89) Kaminska, J.; Schwegler, M. A.; Hoefnagel, A. J.; van Bekkum, H. The Isomerization of α-Pinene Oxide with Brønsted and Lewis Acids. *Recl. Trav. Chim. Pays-Bas* **1992**, *111*, 432−437.
(90) Bleier, D. B.; Elrod, M. J. Kinetics and Thermodynamics of Atmospherically Relevant Aqueous Phase Reactions of α-Pinene Oxide. *J. Phys. Chem. A* **2013**, *117*, 4223−4232.
(91) Stekrova, M.; Kumar, N.; Aho, A.; Sinev, I.; Grünert, W.; Dahl, J.; Roine, J.; Arzumanov, S. S.; Mäki-Arvela, P.; Murzin, D. Y. Isomerization of α-Pinene Oxide Using Fe-Supported Catalysts: Selective Synthesis of Campholenic Aldehyde. *Appl. Catal., A* **2014**, *470*, 162−176.
(92) Qi, B.; Lu, X.-H.; Zhou, D.; Xia, Q.-H.; Tang, Z.-R.; Fang, S.-Y.; Pang, T.; Dong, Y.-L. Catalytic Epoxidation of Alkenes with 30% H2O2 over Mn2+-Exchanged Zeolites. *J. Mol. Catal. A: Chem.* **2010**, *322*, 73−79.
(93) Fraile, J. M.; Garcı′a, J. I.; Mayoral, J. A.; Vispe, E. Optimization of Cyclohexene Epoxidation with Dilute Hydrogen Peroxide and Silica-Supported Titanium Catalysts. *Appl. Catal., A* **2003**, *245*, 363−376.
(94) Timofeeva, M. N.; Kholdeeva, O. A.; Jhung, S. H.; Chang, J.-S. Titanium and Cerium-Containing Mesoporous Silicate Materials as Catalysts for Oxidative Cleavage of Cyclohexene with H2O2: A Comparative Study of Catalytic Activity and Stability. *Appl. Catal., A* **2008**, *345*, 195−200.

(95) Murphy, E. F.; Mallat, T.; Baiker, A. Allylic Oxofunctionalization of Cyclic Olefins with Homogeneous and Heterogeneous Catalysts. *Catal. Today* **2000**, *57*, 115−126.
(96) Menini, L.; Pereira, M. C.; Parreira, L. A.; Fabris, J. D.; Gusevskaya, E. V. Cobalt- and Manganese-Substituted Ferrites as Efficient Single-Site Heterogeneous Catalysts for Aerobic Oxidation of Monoterpenic Alkenes Under Solvent-Free Conditions. *J. Catal.* **2008**, *254*, 355−364.
(97) Yao, H.; Richardson, D. E. Epoxidation of Alkenes with Bicarbonate-Activated Hydrogen Peroxide. *J. Am. Chem. Soc.* **2000**, *122*, 3220−3221.
(98) Frank, W. C. Surprising Stereoselectivity in the Payne Epoxidation of Terpinen-4-Ol with Acetonitrile/Hydrogen Peroxide. *Tetrahedron: Asymmetry* **1998**, *9*, 3745−3749.
(99) Cahiez, G.; Alami, M.; Taylor, R. J. K.; Reid, M.; Foot, J. S. Manganese Dioxide. In *Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons, Ltd: Chichester, 2004.
(100) Raupp, Y. S.; Yildiz, C.; Kleist, W.; Meier, M. A. R. Aerobic Oxidation of α-Pinene Catalyzed by Homogeneous and MOF-Based Mn Catalysts. *Appl. Catal., A* **2017**, *546*, 1−6.
(101) Patil, M. V.; Yadav, M. K.; Jasra, R. V. Catalytic Epoxidation of α-Pinene with Molecular Oxygen Using Cobalt(II)-Exchanged Zeolite Y-Based Heterogeneous Catalysts. *J. Mol. Catal. A: Chem.* **2007**, *277*, 72−80.
(102) Parrino, F.; Fidalgo, A.; Palmisano, L.; Ilharco, L. M.; Pagliaro, M.; Ciriminna, R. Polymers of Limonene Oxide and Carbon Dioxide: Polycarbonates of the Solar Economy. *ACS Omega* **2018**, *3*, 4884−4890.
(103) Couture, G.; Granado, L.; Fanget, F.; Boutevin, B.; Caillol, S. Limonene-Based Epoxy: Anhydride Thermoset Reaction Study. *Molecules* **2018**, *23*, 2739.
(104) Bähr, M.; Bitto, A.; Mülhaupt, R. Cyclic Limonene Dicarbonate as a New Monomer for Non-Isocyanate Oligo- and Polyurethanes (NIPU) Based upon Terpenes. *Green Chem.* **2012**, *14*, 1447−1454.
(105) Longo, J. M.; Sanford, M. J.; Coates, G. W. Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides with Discrete Metal Complexes: Structure−Property Relationships. *Chem. Rev.* **2016**, *116*, 15167−15197.
(106) Childers, M. I.; Longo, J. M.; Van Zee, N. J.; LaPointe, A. M.; Coates, G. W. Stereoselective Epoxide Polymerization and Copolymerization. *Chem. Rev.* **2014**, *114*, 8129−8152.
(107) Klein, E.; Farnow, H.; Rojahn, W. Die Chemie der Linalooloxide. *Justus Liebigs Ann. Chem.* **1964**, *675*, 73−82.
(108) Bihanic, C.; Stanovych, A.; Pelissier, F.; Grison, C. Putting Waste to Work: The Demonstrative Example of Pyrite Quarry Effluents Turned into Green Oxidative Catalysts. *ACS Sustainable Chem. Eng.* **2019**, *7*, 6223−6233.
(109) Raguso, R.; Pichersky, E. New Perspectives in Pollination Biology: Floral Fragrances. A Day in the Life of a Linalool Molecule: Chemical Communication in a Plant-Pollinator System. Part 1: Linalool Biosynthesis in Flowering Plants. *Plant Species Biol.* **1999**, *14*, 95−120.
(110) Buisman, G. J. H. Biodegradable Binders and Cross-Linking Agents from Renewable Resources. *Surf. Coat. Int.* **1999**, *82*, 127.
(111) Adhvaryu, A.; Erhan, S. Z. Epoxidized Soybean Oil as a Potential Source of High-Temperature Lubricants. *Ind. Crops Prod.* **2002**, *15*, 247−254.
(112) Joseph, R.; Madhusoodhanan, K. N.; Alex, R.; Varghese, S.; George, K. E.; Kuriakose, B. Studies on Epoxidised Rubber Seed Oil as Secondary Plasticiser/Stabiliser for Polyvinyl Chloride. *Plast., Rubber Compos.* **2004**, *33*, 217−222.
(113) Sheldon, R. A.; Wallau, M.; Arends, I. W. C. E.; Schuchardt, U. Heterogeneous Catalysts for Liquid-Phase Oxidations: Philosophers' Stones or Trojan Horses? *Acc. Chem. Res.* **1998**, *31*, 485−493.
(114) Robert, C.; De Montigny, F.; Thomas, C. M. Tandem Synthesis of Alternating Polyesters from Renewable Resources. *Nat. Commun.* **2011**, *2*, No. 586.