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Woody species: a new bio-based material for dual Ca/Mg catalysis with remarkable Lewis acidity properties

Pierre-Alexandre Deyris,^a Pauline Adler,^a Eddy Petit,^b Yves-Marie Legrand^b and Claude Grison^{a,*}

Advances in green catalysis have promoted the development of ecocatalysis encountered in most of the main transformations of organic chemistry. Taking advantage of the remarkable capacity of certain plants to hyperaccumulate transition metals into shoots or roots, we have addressed the direct use of metals derived from contaminated plant wastes as supported Lewis acid catalysts, coupling agents, oxidative and reducing catalysts in green chemistry. This approach constituted the first example of chemical catalyst based on phytotechnologies. Herein, we show that the concept can be extended to common and abundant plant species that are surprisingly appropriated for chemical catalysis. We present that willow, birch, plane and linden trees can be used to produce bio-based and original Lewis acid catalysts. The catalytic potential of these species will be illustrated through two representative transformations, acetalisation and oxidative esterification. Thanks to their original polymetallic composition, ecocatalysts provided better results compared to classical metal chlorides such as MgCl_2 , CaCl_2 or ZnCl_2 . This illustrates the interest of the ecocatalysis and is incorporated within the green and sustainable chemistry concept.

1. Introduction

Whereas the spread of metal pollutants in the environment continues, a series of novel approaches for the remediation and full-fledged ecological rehabilitation of contaminated soils and aquatic systems is developing^{1–3}. In order to give viable economic outlets for such ecological programs, metal-rich biomass can be turned into useful tools for sustainable chemistry^{3,4}. Taking advantage of the remarkable adaptive capacity of certain plants to bioconcentrate transition metals in their shoots or roots, our group has explored the direct use of metals derived from contaminated plant waste as green catalysts, also known as ecocatalysts^{3,4}. They were the first bio-sourced metallic catalysts. We have demonstrated that they can serve as efficient tools for valuable supported "Lewis acid" transformations^{4,5}. They are excellent promoters of cross-coupling transformations, such as Suzuki and Heck reactions^{6,7}, which are ligand-free and work with homeopathic amounts of Pd. Ecocatalysts also represent practical and elegant substitutes of conventional catalysts, enabling green

processes for difficult oxidation^{8,9} and reduction^{10,11} reactions with interesting regio- and chemoselectivities.

Ecocatalysts have attracted broad interest among researchers as they combine the merits of both sustainable catalysts and an ecological approach. They constitute the first practical chemical application of new phytoextraction and rhizofiltration technologies.

Recently, we reported extensive structural studies of a series of ecocatalysts in order to establish correlations between their structure and their catalytic properties¹². Fine studies revealed novel mixed salts such as CaMg_2Cl_6 ⁵, and KMgCl_3 ¹³. These unusual species were generated from physiological metallic elements of all plants. In this article, we postulate that these mixed salts play an important role in the catalytic process. For instance, KMgCl_3 has recently been demonstrated to show unique catalytic activity in Knoevenagel reactions, even better than that achieved with MgCl_2 ¹³. This suggests the interest of evaluating the synthetic potential of bio-based mixed salts of physiological origin.

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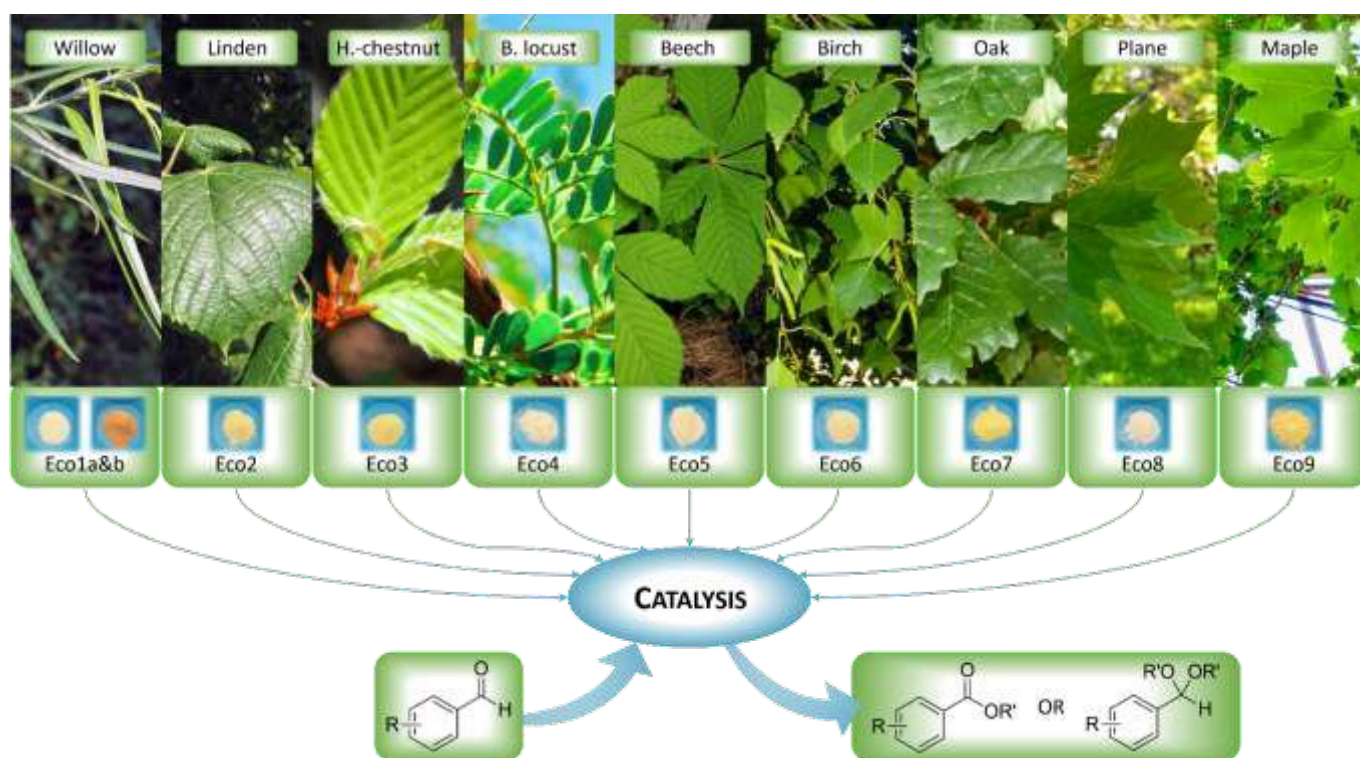


Figure 1 From leaves of common trees to chemical reactions

In this article, we wish to demonstrate that the ecocatalysis concept can be extended to common and abundant plant species that are not metallophytes but that are nevertheless surprisingly appropriate for chemical catalysis (Figure 1). We will show that willow (*Salix* x, Salicaceae), birch (*Betula* x, Betulaceae), beech (*Fagus* x, Fagaceae), plane (*Platanus* x, Platanaceae), maple (*Acer* x, Aceraceae), black locust (*Robinia pseudoacacia*, Fabaceae), oak (*Quercus* x, Fagaceae), horse-chestnut (*Aesculus hippocastanum*, Sapindaceae) and linden (*Tilia* x, Malvaceae) trees can be used to produce bio-based and novel Lewis acid catalysts. We will thoroughly characterise newly identified ecocatalysts via MP-AES, XRD, HR-STEM/EDX, IR, ESI-SM and DFT in order to elucidate their chemical compositions, structures and properties. We will illustrate the catalytic potential of these ecomaterials through two representative transformations, oxidative esterification and acetalisation reactions.

2. Results and discussion

2.1. Characterisation of ecocatalysts

In a first step, a thermal treatment was applied to the harvested biomass at 550 °C in order to destroy organic matter. In a second step, the resulting residues were treated with hydrochloric acid to convert metallic cations into metal chlorides. The reaction mixture was stirred for 3 h at 60 °C. The resulting aqueous solution, composed of different metal chlorides, was then concentrated under vacuum and dry residues were stored in a desiccator. Microwave Plasma Atomic Emission Spectroscopy (MP-AES) was used to

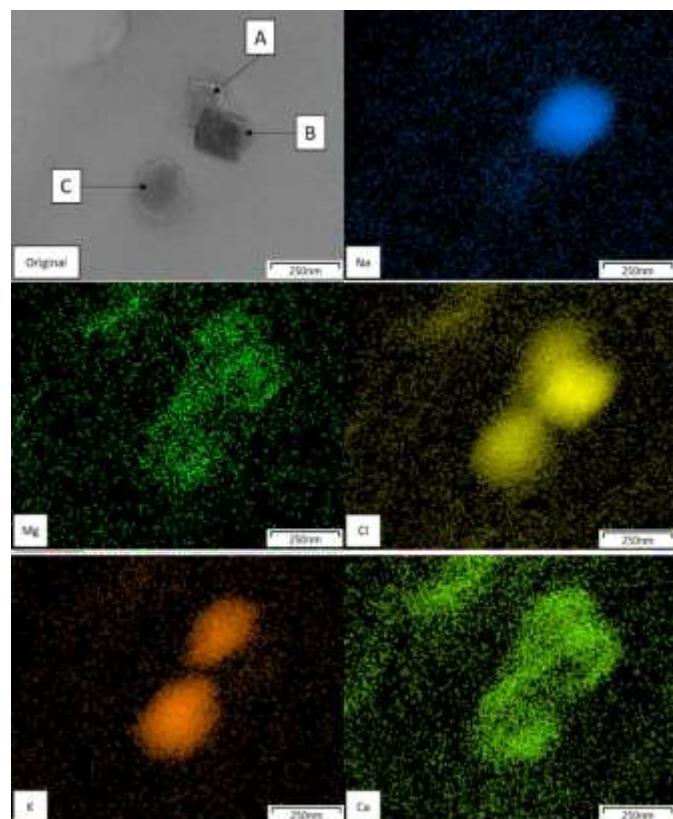
determine the composition of the various ecocatalysts. Results are summarised in Table 1. In all cases, the ecocatalysts obtained from different leaves of common trees appeared as a slightly yellow powder, probably because of the presence of trace amounts of Fe(III). MP-AES analyses showed the presence of varying concentrations of physiological metallic species coming directly from these plants. Each ecocatalyst contained high proportions of calcium and potassium, the most abundant cations in plant constituents. Interestingly, the concentration of magnesium ranged from 0.75 wt% for Eco10 to 2.75 wt% for Eco3. It should be noted that Eco1a&b possessed low but significant proportions of Zn. These data are in agreement with the ability of some willow species to accumulate high Zn concentration in aerial parts¹⁴. Complementary to XRPD analyses, direct mass injection analysis was performed (Supporting Information 3). Eco1a was dissolved in a highly concentrated solution of HCl in water (9 M) and filtered over Amberlist IRA 400 in order to separate alkali or alkaline earth metals from iron salts¹⁵. Then a sample was injected by diffusion in the mass detector in negative ESI. The presence of CaCl_3^- was confirmed and a new species composed of calcium and chlorine (Ca_2Cl_5^-) was observed. Moreover, the presence of MgCl_3^- probably showed the presence of KMgCl_3 , which was not detected in XRPD analysis. Eco1a was then studied by High Resolution Scanning Transmission Electron Microscopy (HR-STEM) coupled with Energy-Dispersive X-ray spectroscopy (EDX) in order to characterise the microstructural features of the ecocatalyst (Figure 2).

Table 1 Major cationic species determined by MP-AES analyses of catalysts (wt%). The Relative Standard Deviation percentage is written in brackets.

Ecocatalyst	Plant material	Acid	Ca	Fe	K	Mg	Zn
Eco1a	Willow	HCl	14.34 (\pm 0.57%)	0.11 (\pm 1.47%)	8.27 (\pm 1.15%)	2.04 (\pm 1.03%)	0.27 (\pm 8.04%)
Eco1b	Willow	HBr	7.51 (\pm 0.74%)	0.09 (\pm 1.86%)	6.72 (\pm 0.89%)	1.09 (\pm 0.37%)	0.15 (\pm 38.3%)
Eco2	Linden	HCl	16.18 (\pm 2.09%)	0.14 (\pm 2.02%)	2.73 (\pm 0.97%)	2.75 (\pm 1.15%)	0
Eco3	Horse Chestnut	HCl	14.72 (\pm 0.85%)	0.14 (\pm 2.80%)	8.72 (\pm 0.61%)	2.59 (\pm 1.27%)	0
Eco4	Black locust	HCl	19.32 (\pm 1.41%)	0.08 (\pm 7.26%)	2.92 (\pm 1.68%)	0.87 (\pm 0.84%)	0
Eco5	Beech	HCl	16.8 (\pm 0.96%)	0.11 (\pm 1.41%)	2.98 (\pm 0.50%)	2.32 (\pm 0.57%)	0
Eco6	Birch	HCl	17.31 (\pm 0.93%)	0.13 (\pm 3.71%)	4.64 (\pm 0.20%)	2.13 (\pm 0.54%)	0
Eco7	Oak	HCl	14.71 (\pm 0.44%)	0.22 (\pm 4.14%)	12.49 (\pm 0.71%)	1.19 (\pm 0.25%)	0
Eco8	Plane	HCl	19.75 (\pm 0.55%)	0.04 (\pm 13.63%)	7.04 (\pm 1.13%)	0.75 (\pm 1.87%)	0
Eco9	Maple	HCl	11.39 (\pm 2.48%)	0.32 (\pm 9.94%)	8.51 (\pm 0.39%)	0.97 (\pm 1.59%)	0

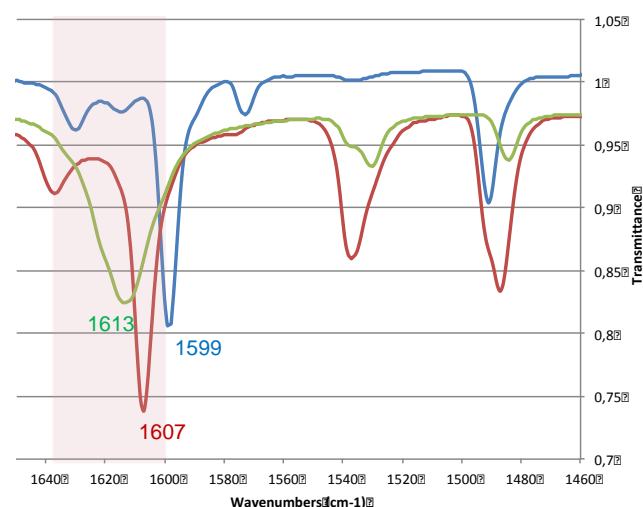
In the original picture, three crystalline species of about 200 nm length were clearly identified, namely A, B and C, which were surrounded by a very light halo (Figure 2, top left panel). The mapping process coupled with the crystal form indicated that B probably was NaCl. A and C seemed to correspond to KCl or KCaCl₃, consistent with XRPD and mass analyses. What really caught the eye in this picture was the composition of the halo. Indeed, it included neither potassium nor sodium but rather magnesium, calcium and chlorine. This composition strongly suggests the presence of CaMg₂Cl₆, which confirm the results of XRPD.

Figure 2 STEM-EDX mapping of Eco1a



Ammonia-temperature programmed desorption (NH₃-TPD) analysis was performed on Eco1a in order to evaluate the acidity on the surface of the catalyst (See Supporting Information 7). There was two parts on the curve. The first signal appeared at low temperature as a classical gaussian curve. It was attributed to weak acid sites. The second part was a flat signal between 220 and 280 °C. Eco1a is a polymetallic catalyst, which results from a combination of various pure metallic salts. This means that each pure metallic species, which presents an acid site, can interact with gaseous ammonia in various intensities. Thus, the flat non-gaussian signal could be rationalised with the successive desorptions of each acid sites occurring during the increase in temperature. In order to distinguish Lewis and Bronsted acid sites, the method using sorption/desorption of the pyridine coupled with infrared analyses was performed¹⁶.

Figure 3 FT-IR vibration bands comparison of adsorbed pyridine linked with CaMg₂Cl₆ (green), CaCl₂ (blue) and MgCl₂ (red).



FT-IR measurements of the absorbed pyridine on the surface of acidic solids were used to compare Lewis acidity and Brønsted acidity of ecocatalysts and of several pure salts contained by them. As shown in Supplementary Information 4, each species exhibited the presence of Lewis acid sites. After evaporation at 150 °C of Eco1a, we could observe that the Brønsted acid character was stronger than the Lewis acid one. After the ecocatalyst was heated at 450 °C, the IR pattern of Eco1a totally changed. The Lewis acid sites emerged while a large decrease of Brønsted acid sites was observed. This could be explained by the thermal decomposition of metal chlorides into oxides or hydroxides, which possess Lewis acid properties. Interestingly, the bromide form of Eco1a (Eco1b) possessed both Brønsted and Lewis acidities. However, Lewis acid bands of Eco1a had higher values than Eco1b, leading us to think that Eco1a could be a stronger Lewis acid than Eco1b. The XRPD studies of Eco1a highlighted the presence of simple metal chlorides such as CaCl_2 , but above all, the presence of mixed metal chlorides such as KCaCl_3 . These salts had a Lewis acid character without Brønsted acidity. The cases of MgCl_2 and KMgCl_3 are different. The first one possessed the same Brønsted acid band as Eco1a while the second did not show any acidic character. In view of the bands at 1616 and 1464 cm^{-1} (Supplementary Information 4), KMgCl_3 is a far better Lewis acid than other species. For comparison, FT-IR measurements of CaCl_2 , MgCl_2 and CaMg_2Cl_6 at 150 °C are presented in Figure 3. In view of the bands between 1599 and 1613 cm^{-1} , it was clear that CaMg_2Cl_6 was a better Lewis acid than CaCl_2 and MgCl_2 , confirming the interest of studying mixed salts.

The catalytic potential of ecocatalysts, and their specific Lewis acidity, suggested interesting opportunities for catalysis in organic synthesis. This view is supported by the study of molecular interactions with the $\text{C}=\text{O}$ bond of benzaldehyde, the substrate of targeted reactions (For more details, see Supporting Information 4). Spectra involving CaCl_2 and KCaCl_3 presented approximately the same vibration bands (Supplementary Information 4). Two bands corresponding to a $\text{C}=\text{O}$ vibration were observed for MgCl_2 , which were more shifted than those with calcium salts. This meant that $\text{C}=\text{O}-\text{Mg}$ interaction was stronger than $\text{C}=\text{O}-\text{Ca}$ interaction. This trend was confirmed with the spectrum involving the stronger Lewis acid KMgCl_3 , which showed very shifted $\text{C}=\text{O}$ stretching vibrations. CaMg_2Cl_6 presented a single signal, meaning that only one benzaldehyde- CaMg_2Cl_6 complex was formed. By comparison with KMgCl_3 , CaMg_2Cl_6 was more strongly associated with the benzaldehyde. Finally, Eco1a showed a broad signal between 1700 and 1600 cm^{-1} , which resulted from a succession of many interactions due to the polymetallic composition of the ecocatalyst. Regarding the position of the $\text{C}=\text{O}$ stretching vibration band, the conclusion was unambiguous: Eco1a possess a very strong Lewis acid character (Supplementary Information 4).

As a result, Lewis acidity of CaMg_2Cl_6 was shown to be stronger than for KMgCl_3 , which in turn seemed to be stronger than MgCl_2 . These outcomes were consistent with the pyridine FT-IR analyses. In conclusion, the presence of these mixed salts in

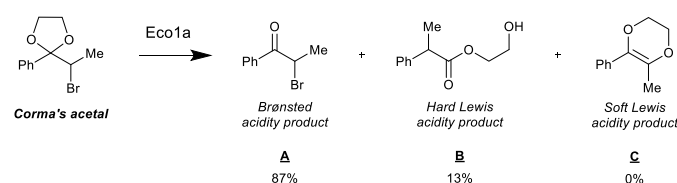
the ecocatalysts promotes an unusual Lewis acidity in organic synthesis with interesting potential for application.

Regarding these qualitative trends, we decided to perform Corma's experiment on the ecocatalyst Eco1a, in order to quantify Brønsted and hard and soft Lewis acid sites¹⁷. Corma's acetal was treated with Eco1a in 1,2-dichlorobenzene at 180 °C during 16 h (Scheme 1). The product **A**, resulting from Brønsted acid catalyst, was formed in 87% yield. The ester **B**, resulting from a hard Lewis acid activation, was obtained in 13% yield. No product **C** was observed, leading to the conclusion that the ecocatalysts do not present soft Lewis acid sites.

Furthermore, both catalysts MgCl_2 and CaCl_2 were not efficient enough to convert Corma's acetal. In conclusion these ecocatalyst present lots of Brønsted acid sites and small hard Lewis acidity.

Given the experimental differences of reactivity between CaCl_2 , MgCl_2 , and CaMg_2Cl_6 we decided to evaluate theoretically criteria indicating the reactivity of the metal hydrates. As previously mentioned¹³, Denmark¹⁸, Massa¹⁹ and other groups

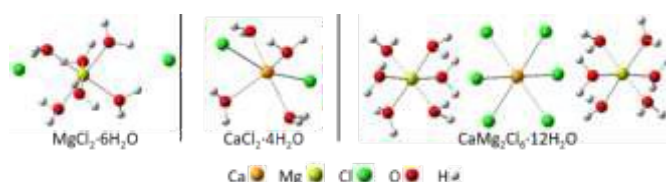
Scheme 1 Analysis of the acidic properties of the ecocatalyst by Corma's method.



Conditions: Eco1a (4.2 mol%), 1,2-dichlorobenzene (1 M), 180 °C, 16 h

supplemented the concepts introduced by Gutmann and a series of rules²⁰. These studies demonstrated that an acid-base adduct induced an increase in electron density in the acceptor fragment of the adduct. Accordingly, CaMg_2Cl_6 should be a better Lewis acid than CaCl_2 and MgCl_2 , which was supported by IR data. We performed DFT calculations to evaluate the electronic distribution when comparing those three chloride-based salt hydrates (Supporting Information 5). CaMg_2Cl_6 is a mixed salt where the calcium cation has a central position and is coordinated by chloride anions and surrounded by hydrated Mg cations, as depicted in Figure 4.

Figure 4 Optimised structures of three chloride-base hydrates using DFT calculations.



In the catalytic intermediary, the magnesium is very likely partially desolvated, while the central cation does not interact directly in the catalytic cycle but act as an electron sink (donor/acceptor). As shown in Table 2, the Mg centre is more

electropositive (1.566 for MK charge) in the case of CaMg_2Cl_6 than in MgCl_2 (1.332 for MK charge), thus has an increased acceptor effect towards the electron rich adduct. Meanwhile the calcium centre is accepting electrons from each side of the complex and this can be confirmed by the less electropositive character of Ca in the case of CaMg_2Cl_6 compared to CaCl_2 . This analysis is consistent of the nature of the charge (Mulliken, natural, MK). Using the Pearson acid-base concept²¹, the chemical hardness η and softness S were also estimated from the lowest unoccupied and highest occupied molecular orbital energies using the following formalisms²²: $\eta \sim E_{\text{LUMO}} - E_{\text{HOMO}}$ and $S = 1/\eta$. CaMg_2Cl_6 presents the softest character ($S=2.634$) and therefore the smallest HOMO-LUMO gap among the three species, which implies it can have its electron density exchanged more easily than the harder metal hydrates CaCl_2 ($S=2.559$) and MgCl_2 ($S=2.176$).

Table 2 Mulliken, natural and Merk-Kollman charges on cationic centres in CaCl_2 , MgCl_2 and CaMg_2Cl_6 , and molecular softness of the three hydrates obtained by DFT calculations.

Compound		$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$
Mulliken Charge^(a)	Ca	0.886	-	0.764
	Mg	-	0.764	0.788
Natural (NBO) Charge^(a)	Ca	1.268	-	0.611
	Mg	-	1.366	1.375
MK Charge^(a)	Ca	1.331	-	1.004
	Mg	-	1.332	1.566
$\eta^{(a,b)}$		0.3907	0.4595	0.3796
$S^{(a,b)}$		2.559	2.176	2.634

^a Using MPW1PW91/cc-PVTZ, implicit solvation: methanol, ^b chemical hardness η and softness S .

The evaluation of charges and softness has also been performed using a water implicit solvation as reported in Supporting Information 5; no significant variations were observed. These theoretical calculations fit very well with all the experimental data collected for this study and are very useful for the interpretation of the reactivity of these novel ecocatalysts.

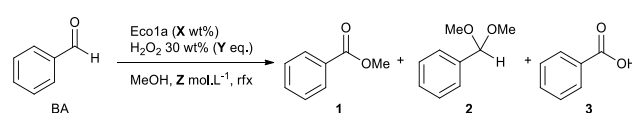
Like their transition metal-containing analogues, ecocatalysts obtained from common trees also possessed unique properties owing to their polymetallic compositions and differing ratios between all metal elements. The catalytic activity of the ecocatalysts was investigated with two model reactions, namely oxidative esterification and acetalisation reactions.

2.2. Oxidative esterification

Carboxylic esters constitute fundamental intermediates for the production of fragrances, flavours²³, biomedicines²⁴, biodegradable polymers²⁵ or biofuel²⁶. Over more than a century, Fischer and Speier synthesis²⁷ have seen many improvements and alternatives²⁸. Among these numerous methods, oxidative esterification is a one-pot preparation of

ester starting from an aldehyde²⁹. The assumed mechanism is based on two steps: the hemiacetalisation of aldehyde followed by the oxidation of the hemiacetal intermediate. This direct transformation is a significant reaction in green chemistry. Various metal-based catalysts have been used to perform this reaction, including rhenium³⁰, titanium³¹, cerium³², copper^{33,34}, zinc^{35,36}, calcium or magnesium³⁷ or iron³⁸ as a non-exhaustive list. Ionic liquids³⁹ can also be used, as well as supported Brønsted acids⁴⁰. Direct oxidative esterification of alcohols into esters is also possible but requires harsh conditions and/or expensive catalysts^{41–44}. Since then, the reaction has been extensively studied^{28,29} and appears to be a very interesting model to prove the efficiency of ecocatalysts. Regarding the presence of both Lewis and Brønsted acidities of non-accumulating plant-based ecocatalysts, they could act as efficient promoters of oxidative esterification reaction.

Table 3 Screening of conditions for the oxidative esterification reaction.



Entry	X (wt%)	Y (eq.)	Z (mol.L ⁻¹)	Conv (%)	1 (%)	2 (%)	3 (%)
1	16	1.1	0.41	95	64	13	18
2	16	2	0.41	98	79	2	17
3	16	3	0.41	99	77	1	22
4	16	4	0.41	>99	81	0	19
5	6	4	0.41	98	73	1	24
6	9	4	0.41	99	74	0	24
7	13	4	0.41	>99	72	0	28
8	19	4	0.41	>99	82	0	18
9	16	4	0.23	97	79	5	13
10	16	4	0.16	97	76	10	11
11	16	4	0.12	96	63	19	12
12	16	4	0.1	96	60	17	19

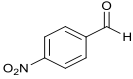
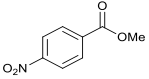
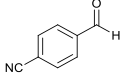
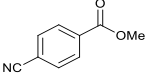
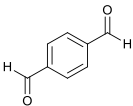
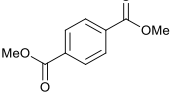
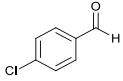
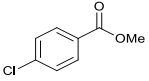
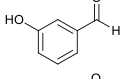
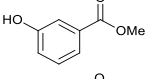
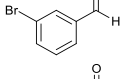
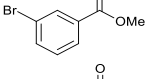
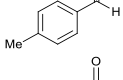
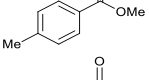
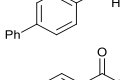
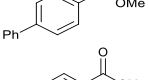
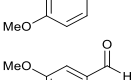
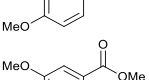
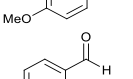
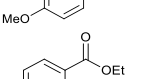
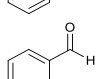
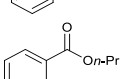
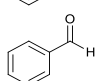
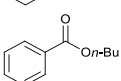
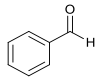
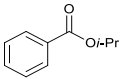
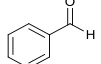
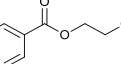
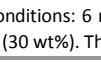
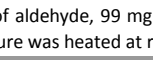
Benzaldehyde was put into a suspension of Eco1a in MeOH, to which was added a green oxidative reagent, aqueous H₂O₂. The reaction led to three different products, namely methyl benzoate **1**, dimethoxymethylbenzene **2** and benzoic acid **3** (Table 3). Pleasingly, all conversions were excellent (95-99%). We first investigated the influence of the quantity of hydrogen peroxide on the selectivity (Table 3, Entries 1-4). It should be noted that decreasing the amount of this oxidant led to incomplete conversion of the benzaldehyde, promoting the formation of acetal at the same time (Table 3, Entries 1-3). The use of 4 equivalents of hydrogen peroxide led to the best results by yielding ester **1** at 81% with quantitative conversion (Table 3, Entry 4). The effect of varying the amount of the catalyst was then studied (Table 3, entries 5-8). The best yield (82%) was obtained with a catalyst amount at 19 wt% (Table 3, entry 8). Decreasing catalyst amount to 13, 9 and 6 wt% led to slightly lower conversion and an almost 10% decline in yield of the ester **1** in favour of benzoic acid **3**. This result is surprising, because aqueous H₂O₂ has been considered to have a poor ability to oxidise aldehydes to carboxylic acids. During this

Two ecocatalysts obtained from willow and beech stood out from the crowd and provided total conversion of both benzaldehyde and acetal to only give methyl benzoate and benzoic acid. The selectivity ranged from 76% for Eco6&7 to 80% for Eco1a, making willow the best catalyst for this reaction. As indicated in MP AES analyses, 0.27 wt% of Zn was observed in Eco1a. In order to explain the high activity of Eco1a in oxidative esterification, we studied the activity of an ecocatalyst generated from Zn-accumulating species (Table 4, entry 22).

required to limit this side reaction and to promote the sequence hemiacetalisation/oxidation. CaMg_2Cl_6 was the most efficient pure salt. It provided a better conversion (up to 80%) and greater selectivity toward production of the ester. The combination of CaMg_2Cl_6 with HCl at pH = 5 gave a satisfactory conversion but lower selectivity than other pure salts. Despite the better conversion, the selectivity toward the ester remained practically the same compared to CaMg_2Cl_6 alone. To our knowledge, this is the first example that describes the Lewis acidity of CaMg_2Cl_6 . This mixed salt revealed an unexpected efficiency, exceeding that of simple calcium and magnesium salts. We can assume that the presence of

CaMg₂Cl₆ in the ecocatalysts explains their high efficiency. Upon optimising reaction conditions, we extended the scope of substrates to explore the versatility of ecocatalysts as illustrated in Table 5. The results clearly show the interest of ecocatalysis. Trials with activated aromatic aldehydes possessing electron-withdrawing groups such as -CN or -NO₂ provided total conversions but yields in ester were satisfactory (up to 60%). The only side product was the carboxylic acid, the formation of which a simple work-up allowed the separation of the diacid from the conditions with 65% (Table 5, entry 3). Optimised reaction conditions gave excellent conversion and good yields for deactivated aldehydes and are compatible with aryl halides or phenols (Table 5, entries 4-8). As expected, electron-rich aldehydes such as 4-methoxy- and 3,4-dimethoxybenzaldehyde did not reach total conversion

Table 5 Extension of the reaction to other aldehydes and alcohols.

$\text{R}^1\text{-C}_6\text{H}_4\text{-CHO} \xrightarrow[\text{R}^2\text{OH, 0.41 M, rfx}]{\text{Eco1a (16 wt\%)}, \text{H}_2\text{O}_2 \text{ (30 wt\%) (4.0 eq.)}} \text{R}^1\text{-C}_6\text{H}_4\text{-COOR}^2$				
Entry	Aldehyde	Ester	Conv. (%)	Isolated yield (%)
1			>99	43
2			>99	60
3			>99	65
4			>99	83
5			>99	82
6			>99	82
7			>99	75
8			>99	79
9			88	55
10			86	52
11			>99	58
12			>99	46
13			>99	62
14			>99	25
15			>99	73

Reaction conditions: 6 mmol of aldehyde, 99 mg of Eco1a, 12 mL of alcohol, 2.5 mL of H₂O₂ (30 wt%). The mixture was heated at reflux for 16 h.

and gave esters in moderate yields up to 55% (Table 5, entries 9 and 10).

In selecting suitable reaction conditions, several alcohols were investigated (Table 5, entries 11-15). Straight-chain alcohols were good nucleophiles (Table 5, entries 11-13). Selectivity decreased with bulky alcohols such as isopropanol (Table 5, entry 14). Interestingly, the use of ethylene glycol gave the

monoester with 73% yield (Table 5, entry 15). The direct, clean and green monoesterification of diol is interesting because it could avoid a delicate separation of monoesters from diesters and diols. The differences between conversions and isolated yields are explained by the formations of the corresponding carboxylic acids, which are eliminated by the basic work-up.

Several applications could be found, especially for a rapid synthesis of insect sex attractants or the preparation of polyesters and fungicides²⁵. Distinct advantages of this method are its simplicity, its efficiency and its use of renewable resources.

In addition to their simple and eco-friendly preparation, the performance of ecocatalysts allows performing oxidative esterification reaction up to large-scale synthesis. Moreover, these results show the advantages of polymetallic catalysts compared to monometallic ones, advantages first recognized by Corma and Garcia and substantiated by our previous work.^{6,46}

2.3. Acetalisation

Acetalisation and ketalisation are common and useful reactions, mostly used for protection strategy in carbohydrate chemistry or during synthetic processes of multifunctional molecules⁴⁷. Several solutions exist to switch this equilibrium, such as trapping the water formed during the reaction by using Dean-Stark apparatus, orthoformates or a catalytic membrane on a flow reactor⁵¹. Other methods involving metallic Lewis acids,^{52–61} cationic species such as aromatic tropylium cation⁶² or pyridinium salt derivatives⁶³ and supported materials,^{56,64} have been reported. It is also possible to conduct acetalisation reaction by using Eosin Y as a photocatalyst under green light.⁶⁵ Recently, Grabowski *et al.* reported the synthesis of acetals under basic conditions in order to preserve acid-sensitive groups.⁶⁶

Encouraged by the previous results with oxidative esterification reaction, we studied the acetalisation of benzaldehyde under optimised conditions (Table 6). First reactions were performed using benzaldehyde and 16 wt% of ecocatalysts in MeOH at 25 °C. Conversions were excellent with ecocatalysts and reached up to 93% in the case of Eco9 (Table 6, entries 1-10). As expected, pH seemed to play a key role in the reaction. HCl and FeCl₃ (pH = 5) gave good results with respectively 78% and 85% yield (Table 6, entries 18-19). In the case of ecocatalysts, the pH value was measured at 5 (except for Eco1b, which was controlled at 6) and yields were between 78 and 93%. Interestingly, experiments with thermally activated Eco1a and Eco1b (Table 6, entries 11 and 12) exhibited a neutral pH. The resulting Eco1a and Eco1b completely lost their catalytic activity. However, the Brønsted acidity of a catalyst is not the only parameter of the reaction. At pH = 6, MgCl₂ gave only 15% yield (Table 6, entry 13). Moreover, the use of KMgCl₃, which is a better Lewis acid than MgCl₂, provided 23% yield at pH=7. CaCl₂ and KCaCl₃ were poor promoters of acetalisation, whereas CaMg₂Cl₆ yield 69% of acetal at pH=7 (Table 6, entry 17).

Table 6 GC-MS yields and pH measures of acetalisation reactions as a function of the catalysts.

Entry	Plant material	Catalyst	BA ^f (%)	Acetal (%)	pH
1	Willow	Eco1a ^a	8%	92%	5
2	Willow	Eco1b ^a	10%	90%	6
3	Linden	Eco2 ^a	22%	78%	5
4	Horse chestnut	Eco3 ^a	9%	91%	5
5	Black locust	Eco4 ^a	15%	85%	5
6	Beech	Eco5 ^a	10%	90%	5
7	Birch	Eco6 ^a	8%	92%	5
8	Oak	Eco7 ^a	12%	88%	5
9	Plane	Eco8 ^a	11%	89%	5
10	Maple	Eco9 ^a	7%	93%	5
11	Willow	Eco1a ^b	100%	0%	7
12	Willow	Eco1b ^b	100%	0%	7
13	-	MgCl ₂ ^c	85%	15%	6
14	-	KMgCl ₃ ^c	77%	23%	7
15	-	CaCl ₂ ^d	92%	8%	7
16	-	KCaCl ₃ ^d	95%	5%	7
17	-	FeCl ₃ ^e	15%	85%	5
18	-	CaMg ₂ Cl ₆ ^c	31%	69%	7
19	-	HCl to pH = 5	22%	78%	5
20	-	CaMg ₂ Cl ₆ at pH=5 ^c	11%	89%	5

Classical catalysts (entries 13-20) were added to obtain the same amount of metal than in Eco1a. Reaction conditions: Benzaldehyde (636 mg, 6 mmol), catalyst, MeOH (12 mL), 1 h at r.t.. ^a 16 wt% of ecocatalyst. ^b Catalysts were heated at 450 °C for 5 min. ^c 1.4 mol%. ^d 5.9 mol%. ^e 0.03 mol%. ^f BA: benzaldehyde

Moreover, at the same pH, most of the ecocatalysts work better than Brønsted acid catalysis alone (Table 6, entry 19). These results lead us to think that synergetic dual Lewis-Brønsted catalysis (Lewis or Brønsted) could explain the very good conversions obtained with ecocatalysts. The excellent result using CaMg₂Cl₆ at pH = 5 (89%) confirmed this explanation. This conclusion was consistent with results reported by Shi and Houk^{67,68}. We can consider that specific interactions and cooperative effects can modulate the overall chemical behaviour of the catalysts.

Finally, the ecocatalysts were the best promoters of acetalisation. They exhibited the best combination of metal halides and led to more active systems than the sum of individual components. In other terms, extracts of common tree species allowed the preparation of tailor-made polymetallic catalysts, improving their catalytic performances compared to monometallic ones. In a context of growing environmental consciousness, it is gratifying to be able to propose novel catalysts that combine efficiency, use of renewable resources and eco-friendly processes. These considerations all suggest a promising life-cycle analysis.

3. Conclusions

The aim of this work was to produce and study novel Lewis acid catalysts originated from common tree species. The synthetic potential of these new systems was illustrated with two important processes in organic chemistry, oxidative esterification and acetalisation reactions. Reaction conditions were devised that gave economic, technical and environmental advantages. From these studies, it might be concluded that the new biosourced catalytic systems showed very interesting activity. We described the unusual structure and composition of these novel ecocatalysts. CaMg_2Cl_6 , a mixed salt whose production in this system was unexpected, was identified by XRPD analyses first and then confirmed by HR-STEM-EDX studies. Its catalytic potential and its specific Lewis acidity are promising. These results suggest new opportunities for sustainable catalysis in organic synthesis. The approach illustrated in this study is a green solution with chemical and environmental benefits: high yields, good selectivity, requirement for only small amounts of catalyst, mild conditions and concrete perspectives for facing the exhaustion of mineral resources. Further experimentation would be required in order to fully determine the potential of these new plant-based catalysts, but there is no doubt that they display very interesting properties for cutting-edge green chemistry.

4. Experimental section

4.1. Preparation of ecocatalysts

All the leaves were first oven-dried at 40 °C for two days and then coarsely crushed and homogenised. A sample of approximately 50 g of leaves of each species underwent a controlled thermal treatment at 550 °C for 4 hours (6 h for leaves of plane tree) to form residues. These residues (\approx 5 g) were then suspended in a solution of acid (hydrochloric at 37% or hydrobromic at 48%) in water (50 mL). The mixture was heated at 60 °C for 3 h and then cooled and filtered on a previously washed celite pad in order to remove the insoluble material. The filtrate was evaporated under vacuum until it yielded a slightly yellow powder (\approx 5.7 g). The catalyst was crushed using a mortar in order to homogenise the powder, which was then stored at 90 °C for two days. The catalysts were stored in an anhydrous environment.

4.2. Preparation of mixed salts

The procedure described by Poddar *et al.*⁶⁹ was applied to synthesise KMgCl_3 and extended to the synthesis of KCaCl_3 . KCl (7.46 g; 100 mmol) was dissolved in pure water (30 mL). A solution of MgCl_2 (9.52 g; 100 mmol) or a solution of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (18.3 g; 100 mmol) in pure water (respectively 80 mL and 25 mL) was added. The mixture was stirred and then heated under vacuum to give a white crystalline hygroscopic powder. The salt was quickly crushed with a mortar and stored in an anhydrous environment.

The procedure described by Erd *et al.*⁷⁰ led us to obtain CaMg_2Cl_6 salt. Dry CaCl_2 (200 mg, 1.8 mmol) and dry MgCl_2

(240 mg, 2.52 mmol) were dissolved in 560 μL of pure water. The mixture was stirred at 80 °C until complete dissolution of the solids. The solution was cooled and kept 2 days at 5 °C. The crystals formed were dried on filter-paper and stored in an anhydrous environment.

4.3. General procedure for acetalisation reactions

In a 25 mL round-bottom flask equipped with a magnetic stirrer and a cooler, were added the catalyst (99 mg), the benzaldehyde (636 mg, 6 mmol) and the biphenyl (208 mg, 1.35 mmol, 1.35 eq.), followed by the alcohol (12 mL). The mixture was stirred at room temperature for 1 h. Then a sample was collected to perform GC-MS analyses.

4.4. General procedure for oxidative esterification reaction

In a 25 mL round-bottom flask equipped with a magnetic stirrer and a cooler, were added the catalyst (99 mg) and the aldehyde (6 mmol), followed by the alcohol (12 mL). The mixture was stirred at room temperature for 1 h. Hydrogen peroxide 30 wt% in water (2.5 mL; 24 mmol; 4.0 eq.) was added and the resulting mixture was heated at reflux for 16 h. The reaction medium was left to cool to room temperature. A sample was collected to perform quantitative GC-MS analyses. Treatment: the solution was diluted in Et_2O (50 mL) and washed two times with a saturated aqueous solution of sodium hydrogenocarbonate. The aqueous phases were brought together and extracted with 25 mL of Et_2O . The organic phases were combined, dried on MgSO_4 , filtered and then evaporated to give the product.

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Conflicts of interest

Authors assure that there are no conflicts to declare.

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