Catalysis Today 189 (2012) 111–116

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Design and performance of supported Lewis acid catalysts derived from metal contaminated biomass for Friedel–Crafts alkylation and acylation

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ARTICLE INFO

Article history:
Received 22 November 2011
Received in revised form 8 February 2012
Accepted 21 February 2012
Available online 22 March 2012

Keywords:
Supported Lewis acid catalysis
Metal hyperaccumulator plants
Friedel–Crafts reactions
Green chemistry

ABSTRACT

The main goal of this work was to prove the interest of metal hyperaccumulator plants in supported Lewis acid catalysis. Friedel–Crafts alkylation and acylation reveal the great catalytic activity of different plant extracts. This approach is a green solution with chemical benefits including high yield, excellent regioselectivity, small amounts of catalyst, mild conditions and concrete perspectives towards the depletion of mineral resources. The results also constitute an incentive for the development of phytoextraction programs on metal-bearing soils.

1. Introduction

Lewis acids play a central role in synthetic organic chemistry, especially in catalysis. Current interest in Green chemistry promotes the development of heterogeneous catalysis, including the use of supported Lewis acid catalysts [1]. The supported version is an attractive alternative to conventional methods; the potential of such systems is enormous and it is expected to bring numerous advantages: dispersion of moisture-sensitive Lewis acids on a support protects them from hydrolysis, manipulation is easier and deactivation by hydrolysis is avoided, chemo, regio and stereoselectivity can be optimized, work-up is a simple filtration and as a result treatment is simplified, wastes are minimized and Lewis acid catalyst recycling becomes possible [2].

In this communication, we report the preparation and use of supported Lewis acid catalysts, which derive from non-conventional biomass, i.e. metal hyperaccumulator species. These plants can accumulate metals above specific thresholds: 1000 mg kg^{-1} Co, Cu, Cr or Ni; or 10,000 mg kg^{-1} Mn or Zn. The discovery of these plants suggested using them for the remediation of heavy metal-contaminated soils [3–7]. However, no effective valorisation of this natural process has been developed so far, including in the field of chemistry [4]. Phytoextraction can constitute the starting point of an original and attractive approach to modern heterogeneous catalysis. Metal hyperaccumulator extracts allow the preparation of taylor-made polymetallic catalysts, which are multi-component chemical systems [8–11]. Specific interactions and cooperative effects can modulate the overall chemical behaviour of the catalysts. Indeed, it has been found that a combination of metal halides or metal oxides led to systems more active than the sum of individual components [12,13]. It has often revealed a synergetic effect, which improves the catalytic performance.

Taking advantage of our recent capacity to develop large-scale production of metallophyte species, we designed new catalysts resulting from the direct use of metallic cations derived from plants as "Lewis acid" catalysts in organic chemistry. The present work focuses on the study of novel polymetallic chloride catalysts derived from a series of metal hyperaccumulator plants (*Noccaea caerulescens*, *Anthyllis vulneraria*, *Psychotria douarrei* and *Geissois pruinosa*) containing varied but large percentages of Zn or Ni, deposited on a conventional support (montmorillonite K10) or mine wastes. The main goal of this work was to investigate the influence of mineral composition and support type on the catalytic activity through model reactions of industrial interest. Thus, the synthetic potential of these new systems is illustrated with one of the most important process in organic chemistry, the Friedel–Crafts alkylation and acylation.

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doi:10.1016/j.cattod.2012.02.044

2. Experimental

2.1. Catalysts preparation

Zn hyperaccumulators' leaves were collected from plants growing on the 'Les Avinières' mine site, Saint-Laurent-le-Minier, Gard, France. Ni hyperaccumulators' leaves were collected from plants growing in the Southern Province of New-Caledonia. Tailings were collected on the "Les Avinières" mine site. Leaves were harvested before flowering, air-dried and crushed. The obtained solid (150 g) was calcined at 400 °C for 5 h and the resulting powder (23.6 g) was added to 500 ml of a solution of hydrochloric acid (~1 M). The solution was heated at 60 °C and stirred for 2 h. The reaction mixture was then filtered on celite. The resulting solutions, composed of different metal chlorides, were then concentrated under vacuum and dry residues were stored in a stove at 90 °C: this temperature allowed conservation of the catalysts over several weeks without hydrolysis of the Lewis acids. Purification steps are not mandatory in our process and when required, partial purifications may be considered. The separation by ion exchange was found to be the most effective and rapid process when necessary. The acidic solution of the different solubilised metal chlorides was treated in order to remove undesired metals ions with exchange resin. Thus, the catalytic solution derived from *P. douarrei* was introduced at the top surface of the Dowex M4195 resin (about 60 g of resin per gram of solid). Operating conditions of purification were as follows: elution of alkali and alkaline earth metals with HCl at pH = 2.5 (3 ml/min); then elution of Ni (II) was performed with 12 M HCl. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was used to determine the composition of the various plant extracts obtained. Results are summarized in Table 1.

2.2. Mineral analysis of the catalysts

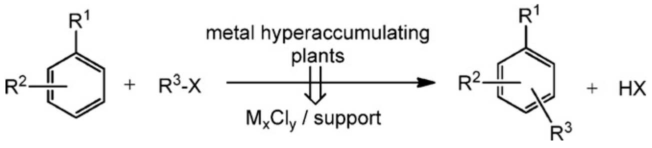
ICP-MS analyses were performed using the Metal Analysis of total dissolved solutes in 2.5% nitric acid. The dry samples were acidified with nitric acid 2.5%, stirred for 30 min and diluted to 0.05 g L^{-1}. Three blanks are recorded for each step (acidification and dilution) on a HR-ICP-MS Thermo Scientific Element XR.

Pulse polarography was performed according to Golimowski and Rubel [14].

2.3. Friedel–Crafts alkylation

Plant extracts were obtained through the process described above. Montmorillonite K10 was obtained from Alfa-Aesar. In a typical experiment, 200 mg montmorillonite K10 were placed in a porcelain mortar and air-dried. 150 mg plant extract were then added and mixed with montmorillonite K10 using a pestle to obtain a homogeneous powder. This powder was then put in a dry round-bottom flask in which 20 mmol arene and 1 mmol aryl or alkyl halide were then added. The aryl or alkyl halide/catalyst ratio is then 2.86×10^{-3} mol g^{-1}. The reaction mixture was left 1 h at ambient temperature under magnetic stirring and after 1 h the mixture is filtered, concentrated under reduced pressure and diluted in dichloromethane before GC–MS analysis. The analysis was also confirmed by ^{1}H NMR spectroscopy. NMR spectra were recorded on Bruker AC 300 (300 MHz) spectrometer using tetramethylsilane as internal standard and $CDCl_3$ as solvent.

Gas chromatography and mass spectrometry (GC–MS) analyses were performed using electronic impact ionization mode on a Varian Saturn 2000 ion trap instrument, interfaced with a Varian CP-3800 apparatus. The Varian CP-3800 was equipped with a 1079 split-splitless injector (206 °C) and a 30 m × 0.25 mm × 0.25 μm film thickness ID WCOT CPSil-8CB fused silica capillary column (Chrompack®, Bergen op Zoom, The Netherlands), with helium as carrier gas (1 ml/min), and programmed 2 min isothermal at 50 °C, then increasing from 50 °C to 220 °C at 4 °C/min. Mass spectra were recorded in electronic impact (EI) at 70 eV, and identified by comparison with data of the NIST 98 software library (Varian, Palo Alto, CA, USA) and by comparison of the retention time of the standard compounds.



Scheme 1. Friedel–Crafts alkylation catalysed by metal hyperaccumulator plants extracts.

2.4. Friedel–Crafts acylation

The green catalyst (1 g) was dried prior to the reaction and supported on montmorillonite K10 (1.5 g) in a typical procedure adapted from Gupta et al. [15]. Acid derivative (1.59 mmol) was added under N_2, at 70 °C, to 3 ml of anhydrous anisole with the supported catalyst. The mixture was stirred for 3, 6 or 15 h. The thick mixture is then filtered to recover the catalyst and washed with dichloromethane (20 ml). An internal standard (nitrobenzene, respectively 0.22 ml or 0.11 ml) was added to measure the progress of the reaction using GC–MS in the conditions stated before.

The products were confirmed by comparison of their technique data (IR, ^{1}H NMR, ^{13}C NMR) with those of authentic samples. IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer, in ATR mode.

2.5. Recycling of the catalysts

After completion of the reaction, the supported catalyst was filtered, washed twice with dichloromethane and easily dried by heating at 110 °C for 30 min. The solid residue was kept in a stove at 90 °C. It can be used as "green catalytic solid" under the same conditions and retained optimum activity until four cycles. The batch to batch variability of reagent was controlled by ICP-MS.

3. Results and discussion

3.1. Composition of the catalysts

The most noteworthy results are summarized in Table 1. Zn (II), Cd (II), Pb (II), Ni (II) result of heavy-metal hyperaccumulation capacities of metallophyte plant species while the other metal cations are present as they are essential for plant growth (Na (I), K (I), Ca (II), Mg (II), Fe (III), Cu (II), Mn (II)). Oxidation state of Fe (III) was confirmed by colorimetric reaction with ammonium thiocyanate [16]. Pulse polarographic analysis unequivocally confirmed this result and the concentration established using ICP-MS.

3.2. Friedel–Crafts alkylation

Experiments aimed at examining the possibility of catalysing Friedel–Crafts alkylation (Scheme 1) with these new green systems gave interesting results. Table 2 presents the data obtained. The results clearly show the interest of heterogeneous catalysis. If a catalyst derived from *N. caerulescens* is used in homogeneous phase, the reaction leads to the degradation of the expected product (entry 1). A mixture of Zn adducts difficult to identify and undesirable side-products was obtained. If the catalyst was dispersed on a solid, it promoted an efficient and unambiguous reaction. For the reaction of toluene with benzyl chloride, different supports were studied

Table 1
Mineral composition of different catalysts established by ICP-MS.

Catalyst	Concentration (ppm)									
	Mg	Al	Ca	Mn	Fe	Ni	Cu	Zn	Cd	Pb
N. caerulescens extract	15,921	10,904	100,641	594	48,322	584	409	**73,443**	4,475	20,320
A. vulneraria extract	35,876	6,015	168,579	862	14,888	2,734	2,460	**154,202**	533	11,700
N. caerulescens + *A. vulneraria* extract	28,202	14,878	134,925	936	27,275	2,985	523	**91,232**	4,845	29,249
P. douarrei extract	20,768	5,419	96,731	1,402	5,570	**80,153**	299	7,902	80	703
G. pruinosa extract	76,265	5,302	119,756	1,066	7,882	**73,868**	551	9,597	215	2,808

Bold indicates the metal of main interest for each plant extract.

(entries 5 and 6 in Table 2). Montmorillonite K10 (K10 in Table 2) and mine tailings from les Avinières (AS in Table 2) both gave an efficient heterogeneous catalyst as exemplifies Table 2. It should be noted that the ratio 0.15 g/0.20 g catalyst/support is the most efficient.

Generally, Lewis acid strength plays a decisive role in the catalysis of Electrophilic Aromatic Substitution (EAS). So, experiments using catalysts derived from different plants have been conducted. Table 2 illustrates these results. Lewis acid catalysis was observed with systems derived from *N. caerulescens*, *A. vulneraria*, *P. douarrei* and *G. pruinosa*, Zn hyperaccumulator plants extracts leading to the best catalysts (being strongest, quick and most efficient, entries 5–8, entries 13–18, entries 23–24 and 26–27). In comparison to earlier reports of supported catalysis [17], *N. caerulescens* and *A. vulneraria* extracts were more efficient and the reaction conditions were milder than those described in previously reported methods [17–19]. In particular, heating was not required to obtain good yields and short times of conversion.

The catalysts derived from Ni hyperaccumulator plants should be also noted (entries 10–11, entries 20–21). It is well known that $NiCl_2$ is a poor acid-catalyst in this reaction type and Ni catalysed Friedel–Crafts reaction are rarely described. Thus it should be noted with interest that *Psychotria douarrei* and *G. pruinosa* led to the expected products with satisfactory yields. These last results were better than commercial $NiCl_2$. In order to learn more about the results, it was of interest to determine the total number of Lewis acids of the green catalysts. As can be seen in Table 2, the mole ratio Ni/R_3X was three times lower with our systems, and 45% inferior with the sum Zn + Ni + Fe + Al. These results clearly indicate that the combination of Ni (II), Zn (II), Fe (III) and Al (III) cannot explain the observed yields. Cseri et al. [17] showed that the relative activities of various cation exchanged clays are significantly different from those of the corresponding Lewis acidic chloride derivatives in homogeneous phase: this is an effect that we also observed. In particular *P. goniocarpa* extracts, which contain high levels of Al(III) were unsuccessfully tested in Friedel–Crafts alkylations. It was also

Table 2
Friedel–Crafts alkylation catalysed by metal hyperaccumulator plants extract.

Entry	Catalyst	Support	Ratio M/R^3–X	Ratio (Zn + Ni + Fe + Al)/R^3-X	R^1	R^2	R^3	X	Time (25 °C)	Yield %	Regio isomers % o/m/p
1	None	None	–	–	Me	H	Bn	Cl	1 h	1	-
2	None	K10	–	–	Me	H	Bn	Cl	1 h	11	-
3	$ZnCl_2$	None	–	–	Me	H	Bn	Cl	1 h	2	-
4	$ZnCl_2$	K10[a]	Zn/R^3–X: 0.62	0.62	Me	H	Bn	Cl	1 h	100	18/0/82
5	*N. caerulescens* extract	K10[a]	Zn/R^3–X: 0.34	0.52	Me	H	Bn	Cl	1 h	100	18/0/82
6	*N. caerulescens* extract	AS[a]	Zn/R^3–X: 0.34	0.52	Me	H	Bn	Cl	1 h	100	18/0/82
7	*A. vulneraria* extract	K10[a]	Zn/R^3–X: 0.34	0.52	Me	H	Bn	Cl	1 h	100	18/0/82
8	*A. vulneraria* + *N. caerulescens extract*	K10[a]	Zn/R^3–X: 0.34	0.52	Me	H	Bn	Cl	1 h	100	18/0/82
9	$NiCl_2$	K10[a]	Ni/R^3–X: 0.62	0.62	Me	H	Bn	Cl	3 h	35	18/0/82
10	*P. douarrei extract*	K10[a]	Ni/R^3–X: 0.21	0.26	Me	H	Bn	Cl	3 h	40	18/0/82
11	*G. pruinosa extract*	K10[a]	Ni/R^3–X: 0.19	0.27	Me	H	Bn	Cl	3 h	50	18/0/82
12	$ZnCl_2$	K10[a]	Zn/R^3–X: 0.62	0.62	H	H	Bn	Cl	1 h	100	–
13	*A. vulneraria* + *N. caerulescens* extract	K10[a]	Zn/R^3–X: 0.34	0.52	H	H	Bn	Cl	1 h	88	–
14	*A. vulneraria* + *N. caerulescens* extract	K10[a]	Zn/R^3–X: 0.34	0.52	H	H	Bn	Cl	3 h	100	–
15	*N. caerulescens* extract	K10[a]	Zn/R^3–X: 0.34	0.52	OMe	H	Bn	Cl	1 h	100	15/0/85
16	*N. caerulescens* extract	K10[a]	Zn/R^3–X: 0.34	0.52	1-Me	4-Me	Bn	Cl	1 h	52	–
17	*N. caerulescens* extract	K10[a]	Zn/R^3–X: 0.34	0.52	1-Et	2-Et	Bn	Cl	14 h	89	31/0/69
18	*N. caerulescens* extract	K10[a]	Zn/R^3–X: 0.34	0.52	OMe	H	1-PhPr	1-Cl	14 h	31	30/0/70
19	$NiCl_2$	K10[a]	Ni/R^3–X: 0.62	0.62	H	H	Bn	Cl	24 h	10	–
20	*P. douarrei* extract	K10[a]	Ni/R^3–X: 0.21	0.26	H	H	Bn	Cl	24 h	16	–
21	*G. pruinosa* extract	K10[a]	Ni/R^3–X: 0.19	0.27	H	H	Bn	Cl	24 h	22	–
22	$ZnCl_2$	K10[a]	Zn/R^3–X: 0.62	0.62	Cl	H	Bn	Cl	1 h	100	35/0/65
23	*A. vulneraria* + *N. caerulescens* extract	K10[a]	Zn/R^3–X: 0.34	0.52	Cl	H	Bn	Cl	1 h	60	35/0/65
24	*A. vulneraria* + *N. caerulescens* extract	K10[a]	Zn/R^3–X: 0.34	0.52	Cl	H	Bn	Cl	7 h	80	35/0/65
25	$ZnCl_2$	K10[a]	Zn/R^3–X: 0.62	0.62	H	H	n-Pr	Br	5 h[c]	50	35/20/45 (*n*-Pr/*i*-Pr: 50/50)
26	*A. vulneraria* + *N. caerulescens* extract	K10[b]	Zn/R^3–X: 0.34	0.62	H	H	n-Pr	Br	6 h[c]	50	35/20/45 (*n*-Pr/*i*-Pr: 48/52)
27	*A. vulneraria* + *N. caerulescens* extract	K10[b]	Zn/R^3–X: 0.34	0.62	H	H	n-Pr	Br	10 h[c]	60	35/20/45 (*n*-Pr/*i*-Pr: 55/45)

[a] Catalyst/support: 150 mg/200 mg.
[b] Catalyst/support 300 mg/400 mg.
[c] *T* = 50 °C.

showed that acid treatments of clays were not sufficient to improve catalytic activity in Friedel–Crafts reactions [17]. Thus it may be concluded a synergetic effect between the present Lewis acids. The comparison between benzylation of toluene with green catalysts derived from *N. caerulescens* led to the same conclusions (ratio two times lower for Zn/R_3X and 8% inferior with the sum Zn + Ni + Fe + Al with better yields).

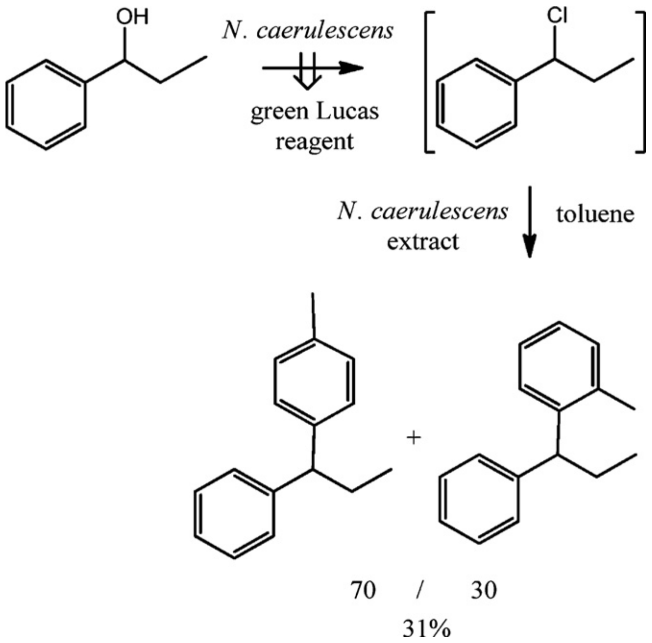
Under hyperaccumulator plants, Friedel–Crafts benzylation was possible with a number of nucleophilic substrates such as anisole, toluene, benzene and chlorobenzene. The EAS were carried out under both Zn and Ni hyperaccumulator plants. As expected, the best rate and yields were obtained using Zn hyperaccumulator plants. The reaction was satisfactory with deactivating substituent such as chloride atom if the catalyst derived from *N. caerulescens* or the mixture *N. caerulescens*–*A. vulneraria* (entries 23 and 24). The benzylation of 1,4-dimethyl- and 1,2-diethylbenzene was cleanly carried out with good yields (entries 16 and 17). The steric hindrance did not modify the efficiency of EAS and no polybenzylation was observed.

The synthetic value of the process is based on the variety of structures that can be introduced. Thus we studied the capacity of green catalysts to attach propyl group to toluene (entries 26–27). Zn hyperaccumulator plants gave the expected products with quantitative yields. A mixture of 6 isomeric products (2-, 3-, 4-Pr and 2-, 3-, 4-*i*Pr) was formed, because the propyl group arranged. However, no further substitution was observed.

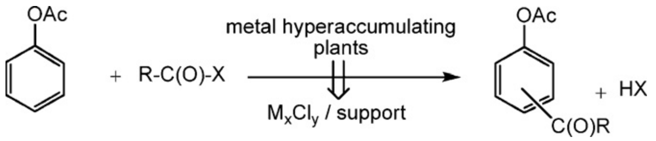
Particular interest lies in the possibility of using catalysts derived from metallophyte species in multi-step synthesis. 1-Chloro 1-phenyl propane being a useful starting material in EAS, has been the object of particular study. Under the conditions described by us [12,13] *N. caerulescens* was able to catalyse the chlorination of 1-phenyl 1-propanol (Scheme 2). As expected, the obtained chloride derivative was benzylated with the same catalyst in 31% yield over two steps (entry 18).

3.3. Friedel–Crafts acylation

We first studied the Friedel–Crafts acylation on model electrophilic compounds, anhydride acetic acid and propionyl chloride (Scheme 3 and Table 3).



Scheme 2. Preparation of 1-toluyl 1-phenyl propane in two steps catalysed by *N. caerulescens* extracts.



Scheme 3. Friedel–Crafts acylation catalysed by catalysts derived from metal hyperaccumulator plants.

A systematic search for the most efficient plants revealed that both Zn and Ni hyperaccumulator plants were excellent for this reaction (entries 11–17 and 22–23). Pleasingly, the efficiency of the catalysis was maintained with *P. douarrei*, under the established reaction conditions (raw or purified extracts, 6 h at 60 °C, catalyst/K10:1 g/1.5 g).

Table 3
Friedel–Crafts acylation catalysed by catalysts derived from metal hyperaccumulating plants at 60 °C.

Entry	Catalyst (1 g)	Support (1.5 g)	Ratio M/R^3–C(O)–X	Ratio (Zn + Ni + Fe + Al)/ R^3–C(O)–X	R	X	Time (h)	Yield %	Regio-isomer o/p
1	None	None	–	–	Ac	OAc	15	0	–
2	None	K10	–	–	Ac	OAc	15	0	–
3	None	AS	–	–	Ac	OAc	15	1	–
4	$ZnCl_2$	None	Zn/R^3–C(O)–X: 2.3	2.3	Ac	OAc	1	42	42/58
5	$ZnCl_2$	None	Zn/R^3–C(O)–X: 2.3	2.3	Ac	OAc	3	100	40/60
6	$ZnCl_2$	None	Zn/R^3–C(O)–X: 4.6	4.6	Ac	OAc	1	52	40/60
7	$ZnCl_2$	None	Zn/R^3–C(O)–X: 4.6	4.6	Ac	OAc	3	100	40/60
8	$ZnCl_2$	K10	Zn/R^3–C(O)–X: 4.6	4.6	Ac	OAc	3	79	3/97
9	$ZnCl_2$	K10	Zn/R^3–C(O)–X: 4.6	4.6	Ac	OAc	6	100	3/97
10	$ZnCl_2$	AS	Zn/R^3–C(O)–X: 2.3	2.3	Ac	OAc	15	100	2/98
11	*N. caerulescens* extract	K10	Zn/R^3–C(O)–X: 0.85	1.24	Ac	OAc	3	43	3/97
12	*N. caerulescens* extract	K10	Zn/R^3–C(O)–X: 0.85	1.24	Ac	OAc	6	100	3/97
13	*N. caerulescens* extract	K10	Zn/R^3–C(O)–X: 3.9	4.5	Ac	OAc	3	70	3/97
14	*N. caerulescens* extract	K10	Zn/R^3–C(O)–X: 3.9	4.5	Ac	OAc	6	100	3/97
15	*N. caerulescens* extract	AS	Zn/R^3–C(O)–X: 1.9	2.5	Ac	OAc	15	31	3/97
16	*N. caerulescens* extract	AS	Zn/R^3–C(O)–X: 3.9	4.5	Ac	OAc	15	100	3/97
17	*N. caerulescens* extract	K10	Zn/R^3–C(O)–X: 3.9	4.5	Pr	Cl	6	100	3/97
18	$NiCl_2$	None	Ni/R^3–C(O)–X: 4.8	4.8	Ac	OAc	6	44	40/60
19	$NiCl_2$	None	Ni/R^3–C(O)–X: 4.8	4.8	Ac	OAc	15	81	40/60
20	$NiCl_2$	K10	Ni/R^3–C(O)–X: 4.8	4.8	Ac	OAc	6	78	40/60
21	$NiCl_2$	K10	Ni/R^3–C(O)–X: 4.8	4.8	Ac	OAc	15	80	40/60
22	*P. douarrei* raw extract	K10	Ni/R^3–C(O)–X: 0.85	1.1	Ac	OAc	6	84	2/98
23	*P. douarrei* purified extract	K10	Ni/R^3–C(O)–X: 1.96	2.12	Ac	OAc	6	10	2/98

Table 4
State of the art acetylation of anisole.

Catalyst	Support	Time (h)	*T* (°C)	Yield %	Ref.
Ti (IV)	K-10	24	95	83	[20]
Cu (II)	K-10	24	95	32–47	[21]
Cr (III)	H-β zeolite	4	60	71	[22]
–	H-β zeolite	4	60	12	[23]
N. caerulescens extract	K-10	3	60	70	
N. caerulescens extract	K-10	6	60	100	
P. douarrei raw extract	K10	6	60	84	
P. douarrei purified extract	K10	6	60	10	

Varying the support, in the catalysis by Zn hyperaccumulator plant (*N. caerulescens*) with anisole as nucleophilic aromatic cycle, illustrates the interest of mine wastes. Tailings of the 'les Avinières' mine sites cleanly promoted the acylation of anisole by acetic anhydride (entries 10, 15 and 16). The reaction occurred without undergoing demethylation or rearrangement. It should be noted high *para* regioselectivity: only traces of the *ortho* acylation of anisole could be detected with GC–MS. This result is in agreement with the shape selectivity of zeolites (entries 11–14 [20–23]). Similar *para* selectivity was obtained with mine tailings (entries 10, 15 and 16).

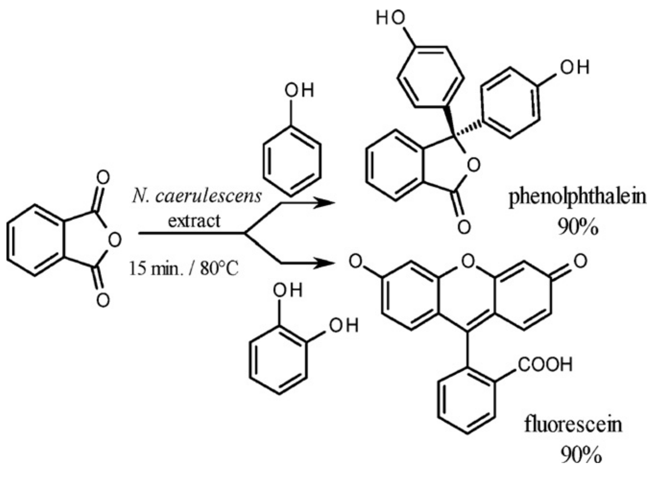
Reaction conditions are green: the acylating ability of vegetal drawn catalysts can be exploited at moderate temperature <70 °C. They are also compliant with industrial processes. The conditions were interesting, because methoxyacetophenone is a key intermediate for the synthesis of fragrances and a variety of pharmaceuticals, such as anti-bacterial, antiallergic, anti-inflammatory and anticancer compounds as well as an endothelin antagonist [24].

The classical aromatic acylation causes a general problem. It requires more than one molar equivalent of Lewis acid. This limitation was easily overcome with green catalysts, which do not form stable complexes with the resulting aryl ketones. So, in comparison to $NiCl_2$, *P. douarrei* was two times more efficient with four times less catalyst (entries 18 and 22).

As shown in Table 4, the comparison between the recently described methods reveals that the performances of our green catalysts are significantly higher for the acetylation of anisole.

To check the applicability of these catalysts, the reaction was extended to pronionyl chloride (entry 17). The reaction was quantitative after 3 h at 60 °C.

Herein we wish to demonstrate the flexibility offered with applications to green acylation of phenol and resorcinol to synthesise two common but useful aromatic structures, phenolphthalein and fluorescein (Scheme 4). Optimum results were obtained using *N. caerulescens* extract in homogeneous or heterogeneous catalysis at 80 °C in 15 min. Thus, phenolphthalein and fluorescein were furnished in excellent yields (90%).



Scheme 4. Synthesis of phenolphthalein and fluorescein catalysed by *N. caerulescens* extract.

Table 5
Reusability of supported plant extracts catalysts in Friedel–Crafts reactions.

Run	Benzylation of toluene	Acetylation of anisole	
	N. caerulescens extract yield (%)	*N. caerulescens* extract yield (%)	*P. douarrei* extract yield (%)
First	100	100	84
Second	95	100	85
Third	85	100	86
Fourth	83	100	83

3.4. Recycling of the catalysts

Reusing supported catalysts was studied for both Friedel–Crafts reactions through two model reactions, benzylation of toluene and acetylation of anisole. After the reactions supported catalysts were filtered, washed and dried. They were reused directly without purification and under the same conditions. As summarized in Table 5, they retained until four cycles, with only small or marginal decrease in catalytic activity. The batch to batch variability of reagent was controlled by ICP-MS; the mineral composition remained almost the same after four-run, which was illustrated with the compared amount of Zn (II) (from 21.96 mg for the first run to 21.56 mg for the fourth run).

4. Conclusion

The aim of this work was to prepare and to study novel Lewis acid catalysts based on using metal hyperaccumulator plants, which present an interest for the phytoremediation of mine sites. From these studies, it may be concluded that the new catalytic systems show a very interesting activity in Friedel–Crafts alkylation and acylation.

This approach is a green solution with chemical benefits: high yields, excellent regioselectivity, small amounts of catalyst, mild conditions and concrete perspectives towards 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 will continue to display very interesting properties for cutting-edge Green chemistry.

Acknowledgements

The authors gratefully acknowledge financial support from the Centre National de la Recherche Scientifique (CNRS), the PIR-CNRS-CEMAGREF INGECOTECH and the ANR (11ECOT01101) and two grants from the Ecole Polytechnique, Palaiseau and ADEME. They also thank Jacques Bessiere and Yves Pillet for the polarographic studies (UHP Nancy I), Bruno Buatois for the CEFE platform of chemical analysis, Eddy Petit (IEM/UM2 UMR 5635) for the NMR analysis and Rémi Freydier (Hydrosciences laboratory/AETE platform/UM2) for the ICP-MS analysis.

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