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

### Supporting information

Pierre-Alexandre Deyris<sup>a</sup>, Pauline Adler<sup>a</sup>, Eddy Petit<sup>b</sup>, Yves-Marie Legrand<sup>b</sup>, Claude Grison<sup>a</sup>,\*

- <sup>a</sup> Laboratoire de Chimie Bio-inspirée et d'Innovations Écologiques, ChimEco, UMR 5021 CNRS Université de Montpellier, Cap Delta, 1682 Rue de la Valsière, 34790 Grabels, France
- <sup>b</sup> IEM, Université de Montpellier, CNRS, ENSCM, Montpellier, France

### SI1 Reagents and instruments

All the biomasses were harvested between August and October 2017. Leaves of linden, beech, birch, horse-chestnut and oak were collected in the area of Nancy (Grand Est region, France). Leaves of willow were harvested in the Picardie region, France. Leaves of black locust, plane tree and maple were collected in the area of Montpellier (Occitanie region, France). All reagents and solvents used in this work were purchased from commercial sources. Aldehydes were previously washed with a saturated aqueous solution of sodium bicarbonate and stored under argon in order to remove any carboxylic acid traces. Analyses of composition of catalysts were performed on Agilent MP-AES 420. The samples were digested in 10 mL of reversed aqua regia (1:2 hydrochloric acid (37%): nitric acid (65%)) under a microwave-assisted digestion (Multiwave-Go Anton Paar) with the following program: 20–165°C in 20 min and then 10 min isothermal at 165 °C. Samples were filtered and then diluted to 0.4 mg/L in 1% aqueous nitric acid.

Pyridine desorption infrared analyses were conducted using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Samples (10 mg) were suspended on  $CH_2Cl_2$  (2 mL) and 100  $\mu$ L of pyridine were added. The suspension was stirred for 1 min and the solvent was then removed under reduce pressure at room temperature. A first IR analysis was then conducted before drying the sample under vacuum at 150 °C for 25 min. A second IR analysis was then performed. The studies of benzaldehyde-salts interactions were recorded on the same spectrometer. 10 mg of each salt was suspended in a solution of benzaldehyde (50  $\mu$ L) in 2 mL of  $CH_2Cl_2$ ). The suspension was stirred for 1 min and was put under vacuum at 150 °C for 1 h before analyses were performed.

Gas chromatography analyses were performed using a Thermo Scientific Trace 1300 device equipped with an EI ionization source and an ISQ-QD detector. The reactions were monitored by using biphenyl as internal standard and SIM methods for the calibration.

 $^{1}$ H NMR and  $^{13}$ C NMR spectra were recorded on a Bruker 300 AVANCE fitted with a dual  $^{1}$ H/ $^{13}$ C-gradient Z probe at 300 and 75 MHz respectively and using solvent as internal standard (7.26 ppm for  $^{1}$ H and 77.00 ppm for  $^{13}$ C for CDCl<sub>3</sub>).

X-Ray Diffraction (XRPD) analyses were performed on a Bruker diffractometer (D8 advance, with a Cu K $\alpha$  radiation,  $\lambda$  = 1.54086 Å) equipped with a Lynxeyes detector.

Mass analyses were made on a Waters Quattro Micro mass spectrometer equipped with ESI. The detection conditions were: capillary potential 3.5 kV, cone potential 30 V, source temperature 100 °C, desolvation temperature 200°C, cone gas flow 50 l/h, and desolvation gas flow 200 l/h. Nitrogen is the nebulizer gas. The triple quadrupole MS was operated in scanning mode with compounds being ionized in the negative electrospray ionization mode.

Transmission Electron Microscopy / Energy Dispersive X-Ray (TEM/EDX) analyses were recorded on a Jeol 2200 FS which possessed an EDX-SDD Jeol detector (30 mm<sup>2</sup> - 129 eV).

 $NH_3$ -TPD analyses were recorded on a Micromeritics' Autochem 2910 device. Samples were cleaned and degassed at 200 °C under helium flow (30 mL/min). The temperature was cooled to 100 °C, then the adsorption of  $NH_3$  (100%) was realised for 30 min at 30 mL/min. Next, a helium flow at 30 mL/min replaced the ammoniac one for one hour at 100 °C in order to remove the physisorbed ammoniac molecules. Once the baseline of the signal is stabilised, the experiments were recorded at a constant helium flow (30 mL/min) and with a temperature gradient set at 10 °C/min.

### SI2 XRPD analyses

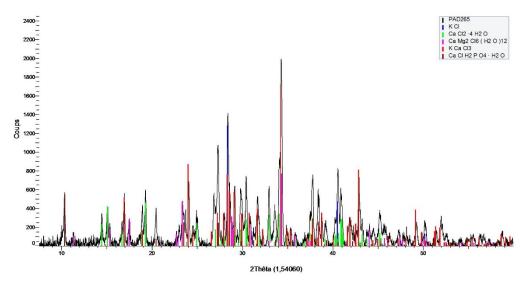


Figure 1: XRPD spectrum of Eco1a.

## SI3 Mass analyses

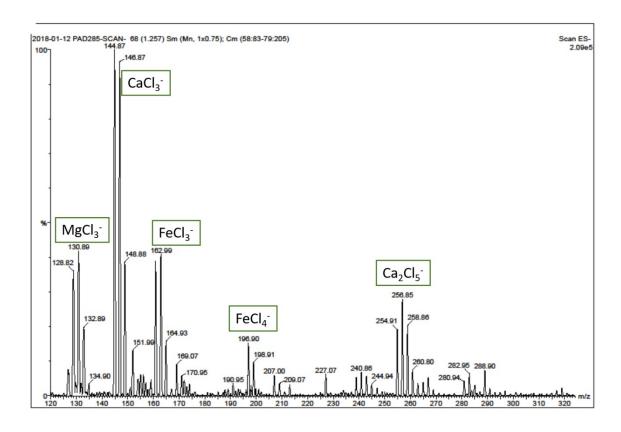


Figure 2: Mass analysis of Eco1a dissolved in 9 M hydrochloric acid.

### SI4 FT-IR analyses

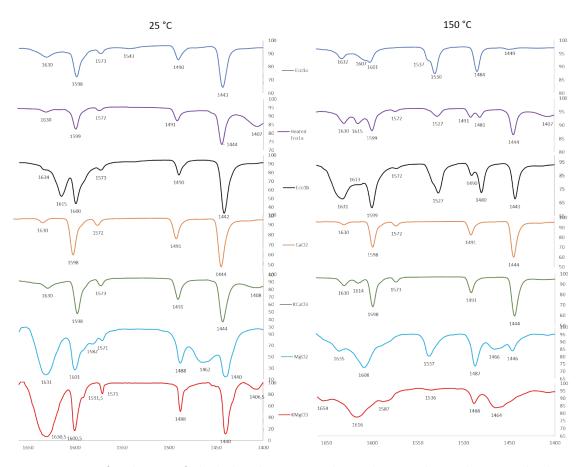


Figure 3: Infrared spectra of adsorbed pyridine on ecocatalysts and on several pure salts contained in them.

By studying the bands between 1660 and 1400 cm<sup>-1</sup>, Brønsted and Lewis acidities of each ecocatalysts could be compared to pure metal chloride salts. <sup>1,2</sup> Bands in the range of 1440 – 1460 cm<sup>-1</sup> and 1633 – 1595 cm<sup>-1</sup> are attributed to  $\nu_{\text{C-C=N}}$ , the stretching vibrations of Lewis acid coordinated pyridine. On the other hand, vibration bands between 1540 and 1500 cm<sup>-1</sup> correspond to protonated pyridine and thus Brønsted acid sites. These spectra were first recorded after evaporation of the solvent at 25 °C (Figure 3, left column).

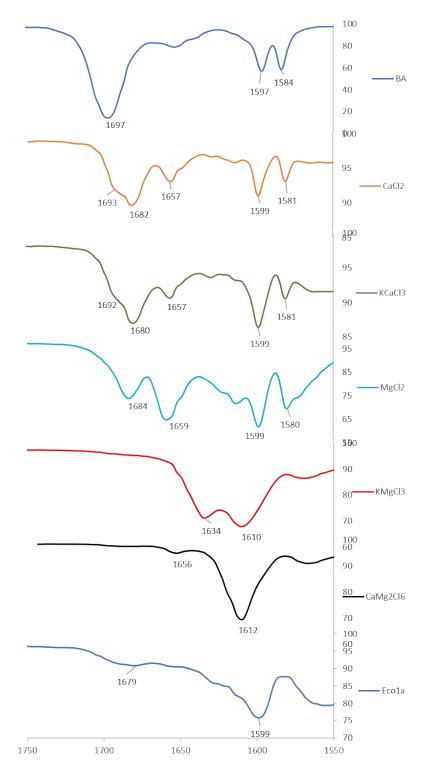


Figure 4: Infrared spectra showing the shifts of adsorbed benzaldehyde on several solid species. BA corresponds to benzaldehyde.

The stretching vibration of the carbonyl group of the benzaldehyde  $v_{C=0}$  occurred at 1697 cm<sup>-1</sup> while bands at 1597 and 1584 are attributed to C-C stretching vibrations of the aromatic ring<sup>3</sup>. Spectra involving CaCl<sub>2</sub> and KCaCl<sub>3</sub> presented approximately the same vibration bands. Two bands corresponding to a C=O vibration were detected at 1693-2 and 1682-0 cm<sup>-1</sup> and could be attributed to two benzaldehyde-Ca complexes. Two bands at 1684 and 1659 cm<sup>-1</sup> were observed for MgCl<sub>2</sub> which were more shifted than those with calcium salts. This meant that C=O-Mg interaction was stronger than C=O-Ca interaction. This trend was confirmed with the spectrum involving the stronger

Lewis acid  $KMgCl_3$  which showed very shifted C=O stretching vibrations at 1634 and 1610 cm<sup>-1</sup> with almost the same intensity.  $CaMg_2Cl_6$  presented a single signal at 1612 cm<sup>-1</sup>, which meant 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<sup>-1</sup>, which resulted from a succession of many interactions due to the polymetallic composition of the ecocatalyst. The conclusion regarding the band at 1599 cm<sup>-1</sup> was ambiguous. On the one hand, it could be attributed to a very strong Lewis acid character. But on the other hand, the band could be assimilated to a signal of aromatic stretching vibration due to its switched position.

#### SI5 DFT calculations

The initial conformation of the metal hydrates was taken from the crystal structures found in crystallographic database. The optimization and single point energy were performed using the generalized gradient approximation (GGA) with the PW1PW91 functional and the polarized triple zeta basis set<sup>4</sup> in the Gaussian09 computational package<sup>5</sup>. Explicit water molecules from the crystal structures were kept while using an additional implicit solvation. This combination of method/base is known to be particularly efficient for the alkaline earth metals.<sup>6</sup> Three different models have been applied to determine partial atomic charge: Mulliken<sup>7</sup>, Natural Bond Orbital<sup>8</sup> and Merz-Singh-Kollman (MK)<sup>9</sup>. Chemical hardness ② and softness S have been calculated using HOMO and LUMO energies<sup>10</sup>.

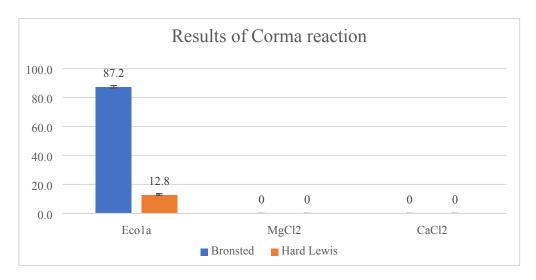
	Mulliken Charge <sup>(1)</sup>		Natural (NBO) Charge <sup>(1)</sup>		MK Charge <sup>(1)</sup>		ŋ <sup>(1,2)</sup>	S <sup>(1,2)</sup>
Compound	Ca	Mg	Ca	Mg	Ca	Mg		
CaCl₂·4H₂O	0.893	-	1.269	-	1.327	-	0.3918	2.552
MgCl <sub>2</sub> ·6H <sub>2</sub> O	-	0.766	-	1.367	-	1.345	0.4636	2.157
CaMg <sub>2</sub> Cl <sub>6</sub> ·12H <sub>2</sub> O	0.761	0.792	0.610	1.376	0.991	1.581	0.3791	2.638

Table 1: Mulliken, natural and Merk-Kollman charges on cationic centers in  $CaCl_2$ ,  $MgCl_2$  and  $CaMg_2Cl_6$ , and molecular softness of the three hydrates obtained by DFT calculations. (1)Using MPW1PW91/cc-PVTZ, implicit solvation: water, (2)chemical hardness  $\square$  and softness S

### SI6 Corma's acetal reaction

Scheme 1 : Possibles products formed during the reaction of Corma's acetal.

Corma's acetal is a compound (Scheme 1), which can react in several ways in function of the presence of different acidities (Bronsted, hard or soft Lewis). Lewis). Ketone  $\underline{\mathbf{A}}$  can be formed by hydrolysis in presence of Bronsted acid. While  $\underline{\mathbf{B}}$  is the product of rearrangement in presence of hard Lewis acidity,  $\underline{\mathbf{C}}$  is observed with soft Lewis acidity. Several catalysts have been tested in order to determine the proportion and the nature of acidic sites. The results are summarised in the following figure.



First of all, results showed that  $MgCl_2$  and  $CaCl_2$  were not efficient enough to convert Corma's acetal. We can observe that Eco1a possessed a huge proportion of Bronsted acid sites (87%) and only 13% of hard Lewis sites. There was no traces of rearrangement's product  $\underline{\mathbf{c}}$ , that indicates Eco1a ecocatalyst did not exhibit soft Lewis acid character.

### SI7 NH<sub>3</sub>-TPD analysis of Eco1a

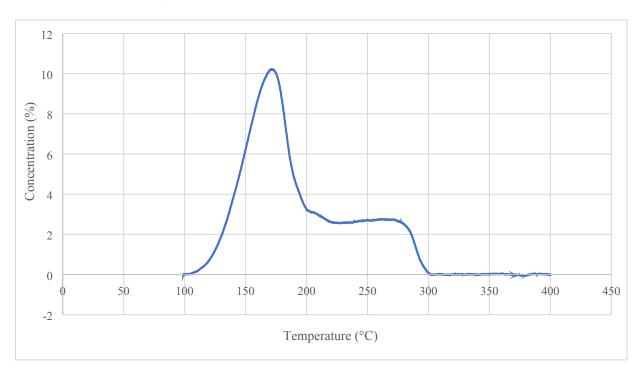


Figure 5: NH<sub>3</sub>-TPD analysis of Eco1a

This figure describes the desorption of ammonia in function of the temperature. The first observation was that the ecocatalyst Eco1a possessed acidic characters. The first well-defined signal at 170 °C represented weak acid sites but what is interesting in this graph is the flat signal between 220 and 280 °C. Eco1a is polymetallic catalyst, which results from a combination of various pure metallic salts. This means that each pure metallic species, which own an acid site, can interact with gaseous ammonia in various intensities. Thus, it could be rational to think that during the increase in temperature, successive desorptions of each acid sites can form a flat non-gaussian signal like we observed in the Figure 5. This hypothesis is supported by the FT-IR analysis of pyridine desorption of

Eco1a (Figure 3) but mostly by its interaction with benzaldehyde (Figure 4, bottom spectra). Indeed, the signal between 1700 and 1600 cm<sup>-1</sup> is broad, not well-defined and also result from the polymetallic composition.

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