# Supported-metal catalysts in upgrading lignin to aromatics by oxidative depolymerization

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## **Supporting information**

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## 1. General information

Nuclear magnetic resonance spectroscopy

NMR analyses were performed with a Bruker AVANCE III 400MHz spectrometer equipped with a BBFO probe (Z gradient). HSQC NMR analyses, the acquisitions were realized at 50 °C (hsqcedetgpsp.3; 48 scans). Lignin samples (*c.a.* 50 mg) were dissolved in 600 mg of DMSO-d<sup>6</sup>.

The characterization and quantification of hydroxyl groups in lignin were made using previously developed methods[1-3]. For this analysis, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) is used as a phosphytilation agent to quantify the different OH groups (phenol, aliphatic, carboxylic). Samples were accurately weighted (*c.a.* 30 mg) and solubilized in 0.5 mL of a solution of cyclohexanol (3.95 mg/g<sub>solution</sub> - internal standard) in pyridine and DMF (v/v: 1/1). Once dissolved, 200 mg of CDCl<sub>3</sub> were added before introducing 100 mg of TMDP. The product of the reaction of TMDP with water ( $\delta = 132.2$  ppm) was used to calibrate the chemical shifts.

Inductively Coupled Plasma (ICP)

The metal content in the prepared catalysts were analyzed by the analytical service of the IRCELYON with the help of an ICP-OES (Activa from Horiba Jobin Yvon). Samples were dissolved and mineralized by a treatment of HCl/HNO<sub>3</sub>, followed by complete water evaporation before heating further the residue in HCl or HNO<sub>3</sub>.

X-Ray diffraction (XRD)

Powder X-ray diffraction patterns were obtained with a Bruker D5005 using a radiation Cu-K $\alpha$  ( $\lambda = 1.054184$ A°).

BET Surface area measurements

Nitrogen adsorption–desorption isotherms at 77 K were measured using a Micromeritics ASAP 2010M physisorption analyzer. The samples were evacuated at 160°C for 24 h before the measurements. Specific surface areas were calculated following the BET procedure. Pore size distribution was obtained by using the BJH pore analysis applied to the desorption branch of the nitrogen adsorption/desorption isotherm.

## 2. Catalyst characterization

### 2.1. Determination of % metal deposited and surface area analysis

Table S1: Percentage of metal on each catalyst and BET surface area determination

Catalyst	% Metal/catalyst <sup>a</sup>	$S_{BET} \left(m^2/g\right)$
Au/TiO <sub>2</sub>	1	40
Pt/TiO <sub>2</sub>	$3,56^{b}$	90

<sup>a</sup>Analyzed by ICP; <sup>b</sup>targeted: 3.5%

#### 2.2. XRD Analysis



Figure S1: XRD Diffractogram of Au/TiO<sub>2</sub> (top) and Pt/TiO<sub>2</sub> (bottom) before and after lignin oxidative depolymerization (Conditions: T: 150°C, Pair: 20 bar, C<sub>NaOH</sub>: 10g/L, 5h)

## 3. Lignin catalytic oxidative depolymerization



#### 3.1. Degradation of vanillin by Au/TiO<sub>2</sub> and Pt/TiO<sub>2</sub>



## **3.2.** Evaluation of TiO<sub>2</sub> on lignin oxidative depolymerization



**Figure S3:** Influence of air pressure on **Kraft** lignin conversion and yields of the main aromatic compounds. Conditions: 1h, P<sub>air</sub>: 20 bar, C<sub>lignin</sub>: 5g/L, C<sub>NaOH</sub>: 10g/L

### 3.3. HSQC NMR Spectroscopy

#### 3.3.1. HSQC NMR Spectra



Figure S4: HSQC NMR structural identification



Figure S5: HSQC NMR spectra of Kraft, EOL-Ab and EOL-As lignins



Figure S6: HSQC NMR spectra of the "precipitate" obtained after Kraft lignin oxidation (Oxygenated aliphatic region [left] and aromatic region [right]) versus time



**Figure S7**: HSQC NMR spectra of the "precipitate" obtained after **EOL-Ab** lignin oxidation (Oxygenated aliphatic region [left] and aromatic region [right]) *versus* time



Figure S8: HSQC NMR spectra of the "precipitate" obtained after EOL-As lignin oxidation (Oxygenated aliphatic region [left] and aromatic region [right]) *versus* time

#### 3.3.2. Quantitative determination of the number of linkages in lignins

Quantitative determination of the number of  $\beta$ -O-4 linkages  $N_{\beta}$  was determined using the methodology reported by R.-C. Sun and co-workers[4]. It gives the number of  $\beta$ -O-4,  $\beta$ - $\beta$  and  $\beta$ -5 linkages per 100 Aromatic Units using the aromatic units  $I_{Ar}$  as internal standard. The following equation was used:

$$N_{\beta}(\%) = 100 \times \frac{I_{\beta}}{I_{Ar}}$$

with  $I_{\beta}$  = integral value of the  $\alpha$ -position of the  $\beta$ -O-4,  $\beta$ - $\beta$  and  $\beta$ -5 linkages;  $I_{Ar} = I_{G_2}$  for softwood lignin (**Kraft, EOL-Ab**);  $I_{Ar} = 0.5I_{S_{2,6}}$  for hardwood lignin (**EOL-As**);  $I_{G_2}$  and  $I_{S_{2,6}}$  = integral value of G<sub>2</sub> units and S<sub>2,6</sub> units (including S and S'), resp.



Figure S9: Semi-quantitative analyses of the ratio of inter-units β-O-4 (●), β-β (■) and β-5
(♦) bonds in Kraft, EOL-Ab and EOL-As lignin upon the reaction time.
(Expressed per 100 aromatic units)

## 4. Development of a kinetic model representing lignin oxidative depolymerization

As a reminder, the conditions used were the following: T: 150°C,  $P_{air}$ : 20 bar,  $C_{NaOH}$ : 10 g/L, 1 h, Pt/TiO<sub>2</sub>:  $m_{Pt}/m_{Lignin} = 0.1\%_{wt}$ 

#### 4.1. Development of the first two kinetic models



**Figure S10**: Representation of **EOL-As** lignin oxidative depolymerization predicted by model I (left) and model II (right). Data: (—) model, (•) experimental



## 4.2. Representation of lignin oxidative depolymerization kinetics by model III

Figure S11: Evolution of the three fractions (left) and the yields of aromatics (right) versus time for Kraft (top), EOL-As (middle) and EOL-As (bottom) lignin oxidation. Data: (—) model, ( $\bullet$ ) experimental



**Figure S12**: Evolution of the three fractions (left) and the yields of aromatics (right) *versus* time for **Kraft** (top), **EOL-As** (middle) and **EOL-As** (bottom) lignin oxidation with Pt/TiO<sub>2</sub>. Data: (—) model, ( $\bullet$ ) experimental

## 5. References

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