# Electronic Supplementary Information (ESI)

## Selective deoxygenation of lignin during catalytic fast pyrolysis

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# Content

## Experimental section

### Fast pyrolysis procedure

The non continuous fast pyrolysis experiments were conducted by means of a platinum coil pyrolyzer (5150, CDS Analytical). The probe was a computer-controlled, resistively heated element (up to 20 °C/ms), which held an open ended quartz reactor with an approximate volume of 0.6 mL. The pyrolysis temperature was 650 °C and the reaction time of 60 s. Before pyrolysis, lignin was ground and sieved (< 200 mesh, 75 μm). Lignin and the catalysts were physically mixed to give a weight ratio of 1:4. The usual amount of loaded lignin was 1.5 mg with 6 mg catalyst. The powdered samples were weighed and introduced into the reactor packed with loose quartz wool; during pyrolysis, the vapours flowed from the open end of the quartz tube into a larger cavity, the pyrolysis interface, by a helium carrier gas stream before entering into the gas chromatograph.

### GC/MS analysis

The carrier gas stream containing the pyrolysis products was directly injected into an Agilent 7890A gas chromatograph (GC) system through the pyrolysis interface and transfer line, both of which were heated to 300 °C. The GC was equipped with a thermal conductivity detector and an Agilent 5975C mass spectrometer (MS) detector. The oven was programmed to start at 40 °C, remained stable for 5 min and increased at 10 °C per minute to a final temperature of 260 °C, maintained for 25 min. The injector temperature was 300 °C and a split ratio of 50:1 was applied. The GC separation of pyrolysis vapours in the condensable gas range was done with a HP-5MS column (30 m × 0.25 mm × 0.25 μm) with helium as carrier gas (1.1 mL/min). Peak identification was achieved by means of the NIST08 mass spectrum library. Pyrolysis vapours, comprising condensable gases such as water and pyrolytic oil, were classified as ‘liquid’. More than 100 compounds were detected. These products were classified according to seven categories and ‘unidentified’.

The analysis of non-condensable gas range products was done simultaneously in the same equipment using Agilent Plot/Q and molecular sieve capillary columns (both 30 m × 0.53 mm). To quantify permanent gas yields, calibration curves were produced using a standard gas mixture of CO, $CO_2$, $CH_4$ and $C_2$~$C_3$ (containing $C_2H_4$, $C_2H_6$, $C_3H_6$ and $C_3H_8$) in He (Messer AG, Switzerland). The residue formed in pyrolysis was classified as “solid”. Ash remained after pyrolysis in addition to coke/char. The yield of solid implies the amount of solid left after pyrolysis and was determined gravimetrically. The liquid yield was calculated as remaining after quantification of the gases and solids.

By calibrating the most abundant and representative compounds, vanillin, guaiacol, 4-allyl-methoxy-phenol and phenol, the mass balance of the liquid fraction was estimated in a pyrolysis experiment without catalyst at 500 °C. Those compounds represent well the observed variety of products in chemical structure, relative abundance and molar weight. All other reaction conditions remained the same except the pyrolysis temperature to ensure inertness of the internal standard. Their detected mass made up to 32 % of the total assumed liquid fraction and 50% of the total peak area in the GC/MS analysis. Extrapolation of those model compounds to the non-calibrated liquid fraction by assuming a similar ratio of peak area to mass for all other detected compounds, but not quantified compounds fulfilled the mass balance to 82 wt% together with solid and gas fractions. If one assumes that the missing part is made up of 15 to 30 wt% water formed during pyrolysis[1], which was observed, but not quantified, and that only volatile products with a boiling point lower than 300 °C are injected into GC/MS (temperature of the interface and connecting lines), this is in good correlation to the results and makes the mass balance well acceptable. Quantification of the aromatic products at catalytic fast pyrolysis of lignin and H-ZSM5(25) resulted in a mass balance, which is up to 75.9 ± 3.8 wt% fulfilled. The difference can be explained by the higher production of water due to acid catalysed deoxygenation reaction. Additionally the mass balance of the catalysed pyrolysis has to be treated with care, as no internal standard was usable at pyrolysis conditions. Table S1 shows a detailed mass balance of the described experiment. All reactions were performed at least in duplicate and reproduced within 95 %.

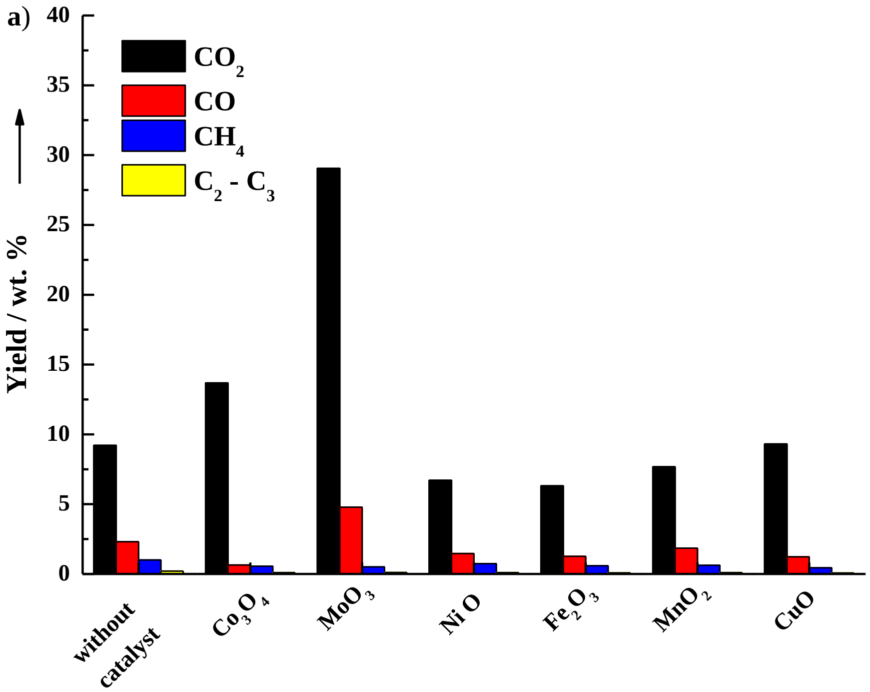
## Materials

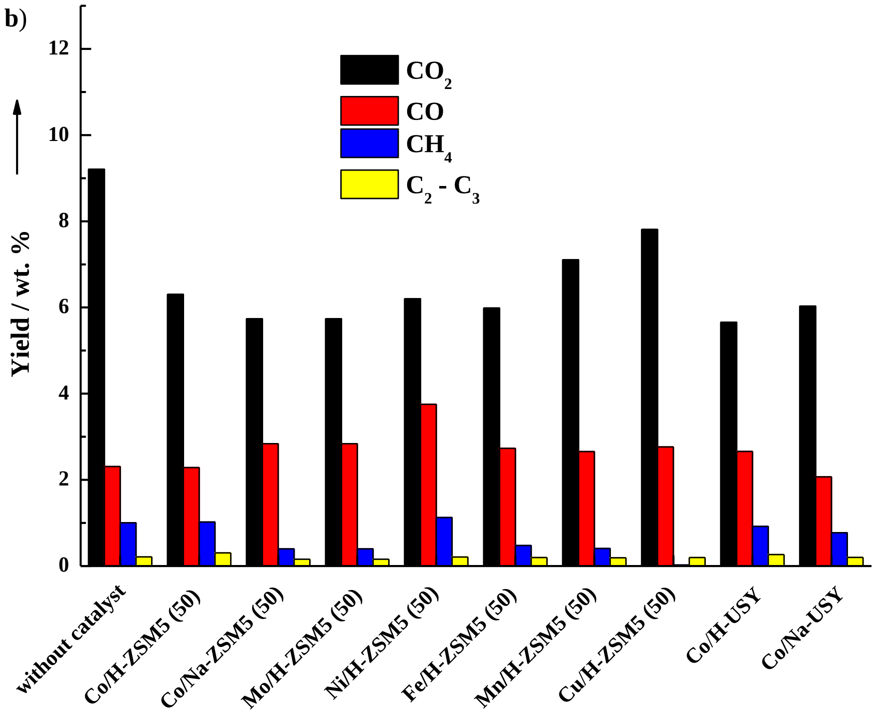
The starting materials were alkaline lignin from TCI Europe with weight composition of C : H : O : S : N ratio 49 : 5 : 37 : 3.8 : 0; the lignin contained about 5 wt% of ash; the elemental composition and ash content were determined by elemental analysis; zeolite H-USY was commercial zeolite (Zeochem AG, Switzerland) with Si/Al = 7, fully ion exchanged, 0.2 wt% of $Na_2O$. Silicalite was synthesized using an established method.[1] Amorphous silica-alumina (ASA) was obtained from Shell. Transition metal nitrates were analytical grade (Fluka).

## Catalyst pretreatment and characterization

Prior to pyrolysis, the zeolite was calcined in air at 550 °C for 5 h at a heating rate of 5 °C/min. Transition metal oxides were obtained by calcination of the metal nitrates in air at 550 °C for 5 h. The zeolite-supported transition metal catalysts were synthesized wetness impregnation. The content of the supported transition metal was 5 wt.% (metal basis). After impregnation, the samples were dried at 80 °C overnight and then calcined in air at 550 °C for 5 h. The surface area and pore structure were determined by means of low-temperature nitrogen adsorption (-196 °C) by physisorption (Tristar 3000, Micromeritics). Before the analysis, the samples were outgassed at 200 °C for 5 h under vacuum. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method based on adsorption data. Pore volume was determined from the amount of the nitrogen adsorbed at $P/P_0=0.99$. Transmission electron microscopy (TEM) images and energy dispersive X-ray (EDX) spectra of the samples were taken by a Tecnai F30 ST microscope (FEG, 300 kV). X-ray diffraction (XRD) patterns were recorded on a STOE STADI-P2 diffractometer in transmission mode (flat sample holder, Ge-monochromator, $CuK_{\alpha1}$ radiation) equipped with a position-sensitive detector with a resolution of ~ 0.01° in 2θ. Transition metal loading of the zeolites, dissolved in a mixture of $HNO_3$ and HF, and their silica to alumina ratio has been obtained by flame atomic absorption spectroscopy (AAS) .

Solid state $^{13}$C-NMR of the lignin sample before an after pyrolysis was taken with a Bruker Avance 400 MHz spectrometer at a resonance frequency of 100.5 MHz by using a 4 mm probe. In the experiment a spinning rate of approximately 10 kHz was used.


a)
Yield / wt. %
0
5
10
15
20
25
30
35
40
$CO_2$
CO
$CH_4$
$C_2$ - $C_3$
without catalyst
$Co_3O_4$
$MoO_3$
Ni O
$Fe_2O_3$
$MnO_2$
CuO


b)
Yield / wt. %
0
2
4
6
8
10
12
$CO_2$
CO
$CH_4$
$C_2$ - $C_3$
without catalyst
Co/H-ZSM5 (50)
Co/Na-ZSM5 (50)
Mo/H-ZSM5 (50)
Ni/H-ZSM5 (50)
Fe/H-ZSM5 (50)
Mn/H-ZSM5 (50)
Cu/H-ZSM5 (50)
Co/H-USY
Co/Na-USY

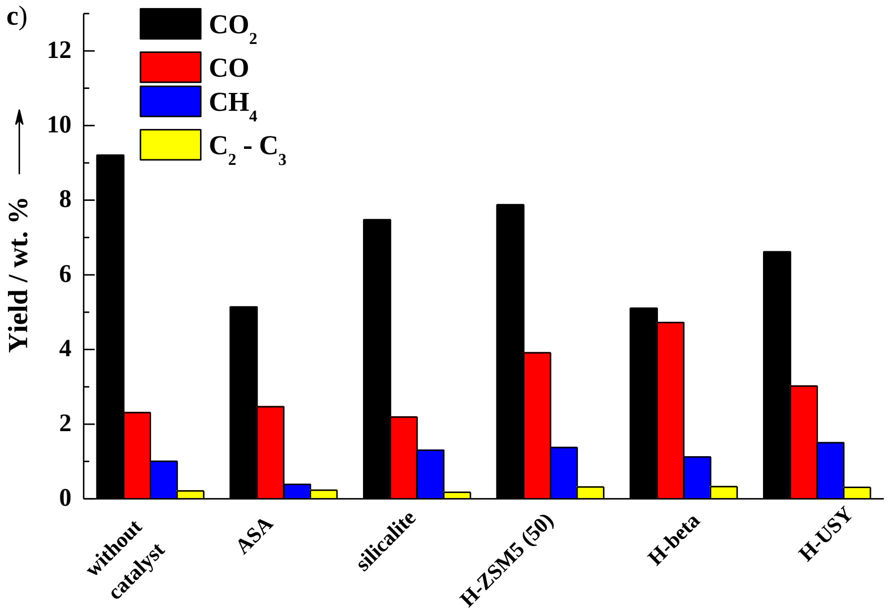


**Figure S1.** Gaseous product distribution during lignin non-catalytic/catalytic fast pyrolysis at 80 wt% of catalyst loading: a) over transition metal oxide catalysts; b) over zeolite-supported transition metal catalysts; c) over alumina silicates (data in Ref.[2]).

| | |
|---|---|
| Kraft lignin 1.5-2.5 mg<br>Solid residues [wt%] | 49.8 ± 2.1 |
| Gas [wt%] | 6.11 ± 0.1 |
| Liquid detected [wt%] [a] | 13.34 ± 0.4 |
| Liquid extrapolated [wt%] [b] | 24.96 ± 0.7 |
| Total detected [wt%] | 81.87 ± 2.9 |
| Missing (includes water and higher boiling liquids)[c] | 18.13 ± 2.9 |

**Table S1.** Mass balance of sample pyrolysis (at 500 °C without catalyst, same conditions as above); [a] as liquid the following model compounds have been quantified with an internal standard: Phenol, Guaiacol, Vanillin and 4-allyl-methoxy-phenol; [b] Extrapolation by assuming a similar ratio of peak area to mass for all other detected compounds. The detected molecules contribute to ~50% of the total peak area in the GC/MS measurement; [c] 16-20 wt% of missing or not detected compounds include water (10-30 wt%)[1] and compounds with a higher boiling point than 300°C and thus not injected into the GC/MS-system.

| H-ZSM5(25) 80wt% with 1.1-1.5 mg of kraft lignin | |
|---|---|
| Solid residues [wt%] | 35.4 ± 0.9 |
| Gas [wt%] | 9.7 ± 0.3 |
| Liquid detected [wt%] [a] | 5.4 ± 0.8 |
| Liquid extrapolated [wt%] [b] | 30.8 ± 3.8 |
| Total detected [wt%] | 75.9 ± 5.0 |
| Missing (includes water and higher boiling liquids)[c] | 24.1 ± 5.0 |

**Table S2.** Mass balance of catalytic fast pyrolysis without internal standard at 650 °C using a blank H-ZSM5(25) catalyst. Detected compounds are: Benzene, toluene, naphthalene and phenol and represent 15 % of the total peak area in the GC/MS. Reproducibility is reduced due to the missing internal standard, which cannot be used in catalytic fast pyrolysis conditions.

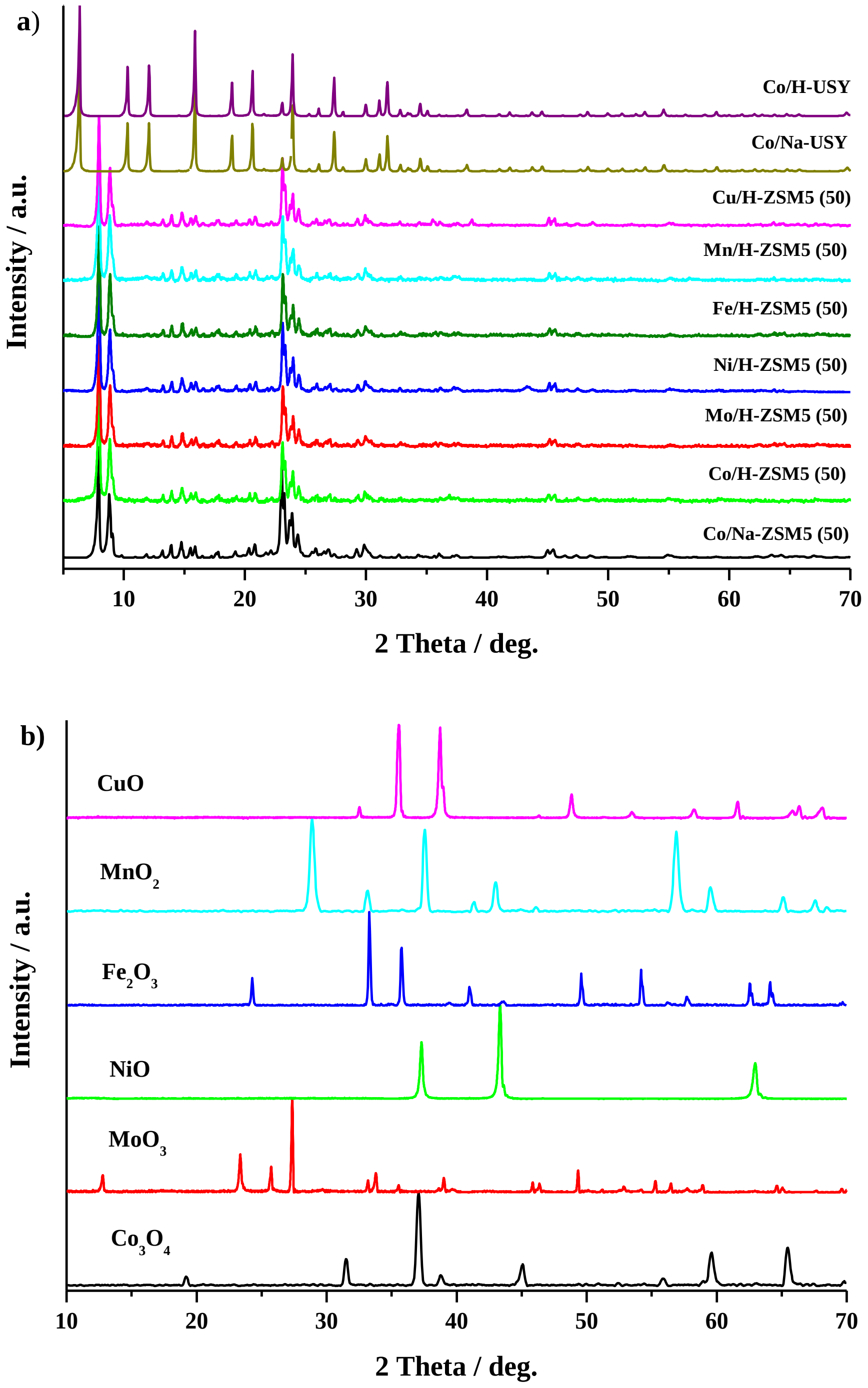


**Figure S2.** XRD patterns of the catalysts. a) zeolite-supported transition metal catalysts; b) transition metal oxide catalysts.

XRD patterns show that addition of metal does not induce any obvious change in the crystal structure or crystallinity of the ZSM-5 and USY zeolites (Figure S2a). An obvious feature is that no metal oxide crystal phase appears. The phase of transition metal oxide is confirmed by comparing the patterns with ICSD (inorganic crystal structure database) (Figure S2b). The average particle size of cobalt oxide is around 35 nm calculated by Scherrer equation from (311) reflection peak ($2\theta = 36.9$ °) of the XRD pattern.

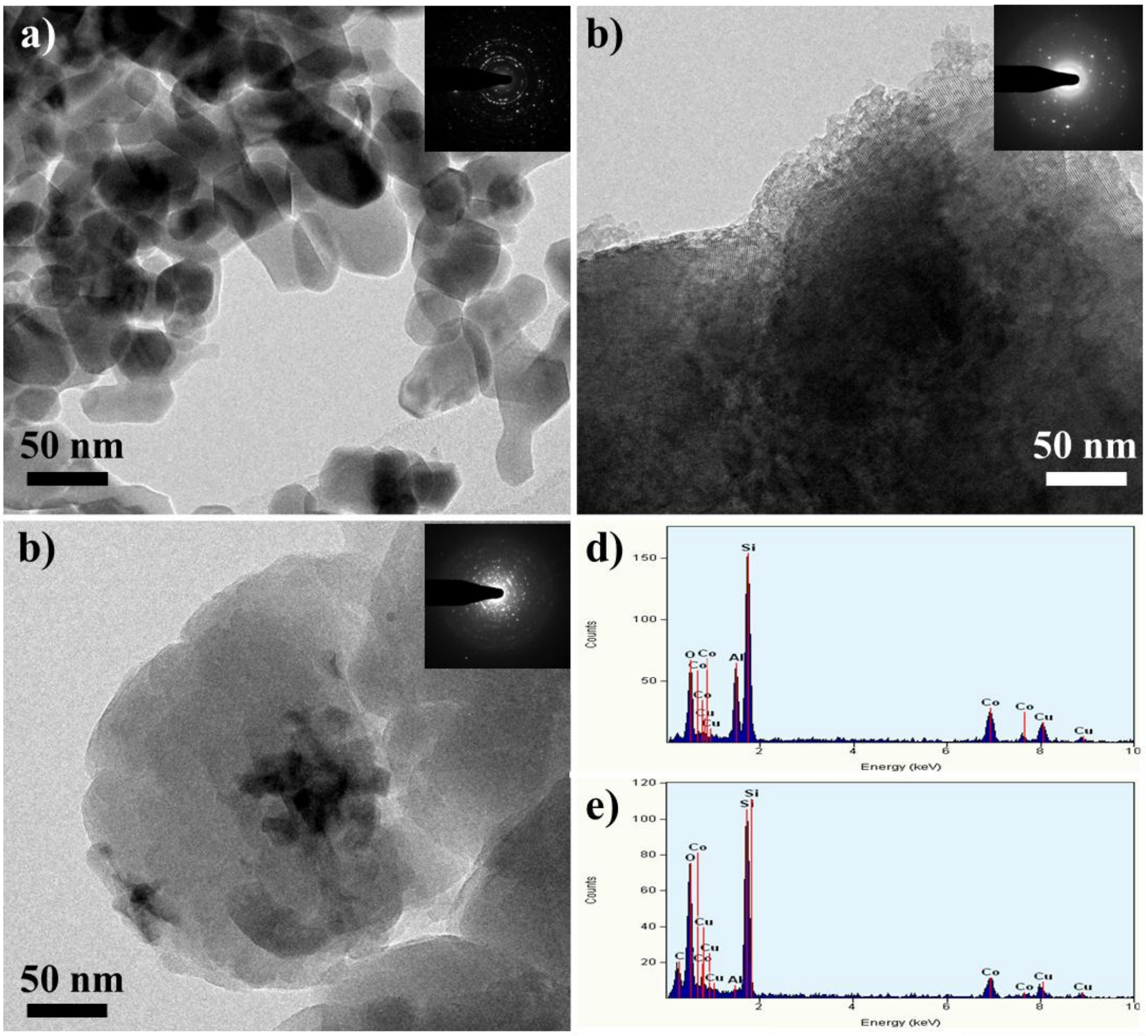


**Figure S3.** TEM images and EDX spectra of selected samples: a) $Co_3O_4$; b) Co/H-USY; c) Co/H-ZSM5; d) Co/H-USY; e) Co/H-ZSM5. Insert: selected area electron diffraction pattern.

The TEM image of the selected cobalt oxide reveals particles from 20 to 50 nm (Figure S3a), in egreement with the average particle size obtained from XRD. EDX spectra confirm presence of cobalt species in the zeolite-supported cobalt catalysts (Figure S3d and e), however, no large particles are visible (Figure S3b and c); probably because the metal particles are well dispersed on the surface of the zeolites or in the form of cations cooperating in the framework.

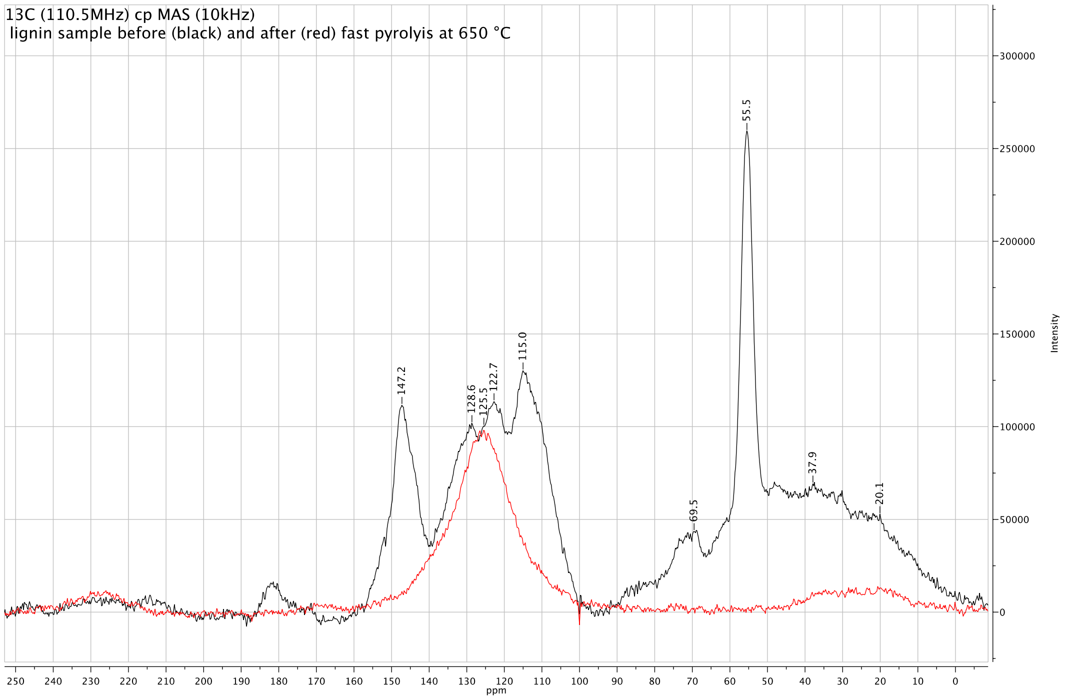


Figure **S4**. Solid state $^{13}$C-NMR. Black: unreacted kraft-lignin and red: solid residues after pyrolysis at 650 °C. Visible typical peaks of the lignin sample: $^{13}$C NMR (101 MHz) δ 147.24, 128.61, 122.73, 115.02, 69.53, 55.46, 37.90, 20.07. The solid residues only show a broad peak at 125 ppm.

## References

1 N. Ren, Z.-J. Yang, X.-C. Lv, J. Shi, Y.-H. Zhang and Y. Tang, *Microporous Mesoporous Mater.*, 2010, **131**, 103-114.

2 Z. Ma, E. Troussard and J. A. van Bokhoven, *Appl. Catal. A*, 2012, **423-424**, 130-136.