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Depolymerization of hydrolysis lignin over Ca- or Mg-containing catalysts supported on alumina: IR analysis of products separated by benzene extraction

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1. Properties of the parent hydrolysis lignin.

In this work, hydrolysis lignin produced by the "Fuel and Technology Complex" company, Republic of Belarus (technical conditions TU BY 490822905.001-2015) was used. It was the waste product of furfural production from oak and elm wood at the Rechitsa Pilot Hydrolysis Plant. The elemental composition of this material was determined on the Perkin Elmer 2400 CHN analyzer (Perkin Elmer, USA), the results are presented in Table S1.

Table S1 – The elemental composition of the initial hydrolysis lignin

Element	C	H	N	S	O	Ash	Total
Content, wt%	52.95	5.34	0.36	0.18	31.77	9.41	100.00
Ratio element : carbon	1.0000	1.2090	0.0057	0.0013	0.4500	—	—

Differential thermogravimetric analysis (DTA) of the parent hydrolysis lignin.

The TG-DTA method was used for the investigation of parent hydrolysis lignin decomposition.

Combined TG–DTG–DTA analysis was done on “Derivatograph-C” (MOM Co.) under static conditions on air or helium with a linear heating program (10◦/min) up to 900 ◦C.

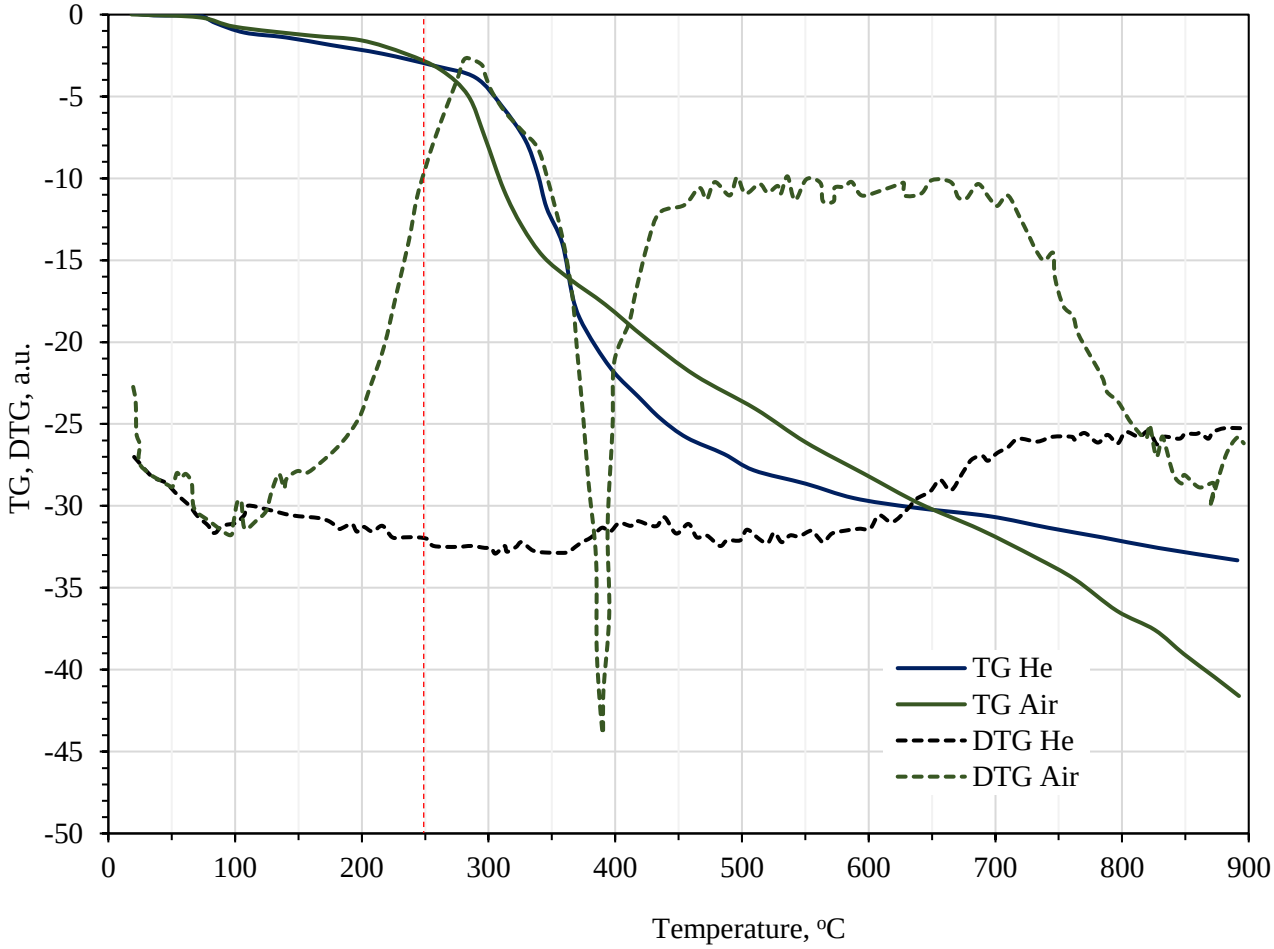


Figure S1. DTA of the parent lignin in an air flow and helium flow.

2. Properties of the catalysts

BET analysis of the catalysts

The porous parameters of the catalysts were determined by N_2 adsorption − desorption analysis at 77 K using Micromeritics ASAP 2020 Plus system.

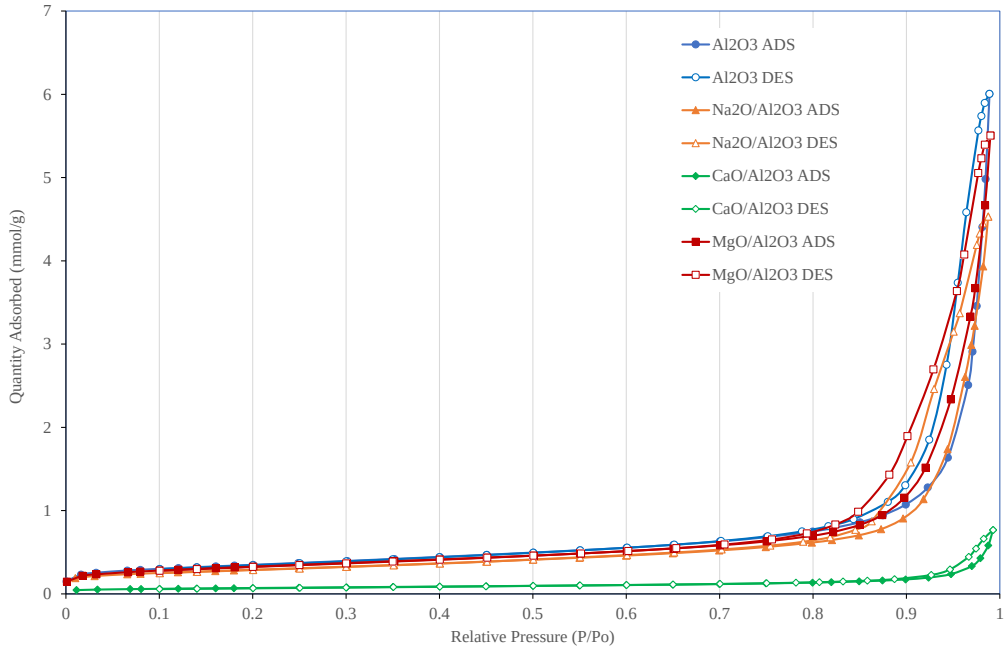


Figure S2. N_2 adsorption and desorption isotherms.

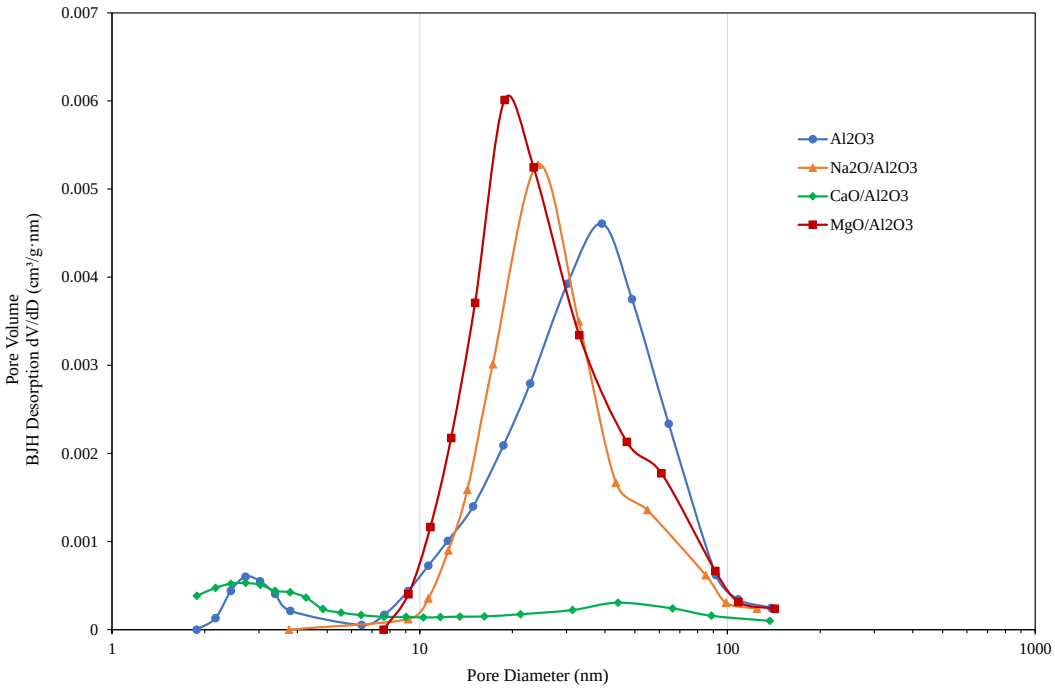


Figure S3. The BJH desorption pore distribution (see average values in Table S2)

XRD analysis of the catalysts

The phase composition of the materials was studied by X-ray diffraction (XRD) analysis. X-ray diffraction patterns were recorded using an ARL X'TRA diffractometer (Thermo Fisher Scientific) with CuKα radiation (40 kV, 40 mA) with a scanning rate of 1.2° per minute over the scanning range of $5 < 2\theta < 70°$.

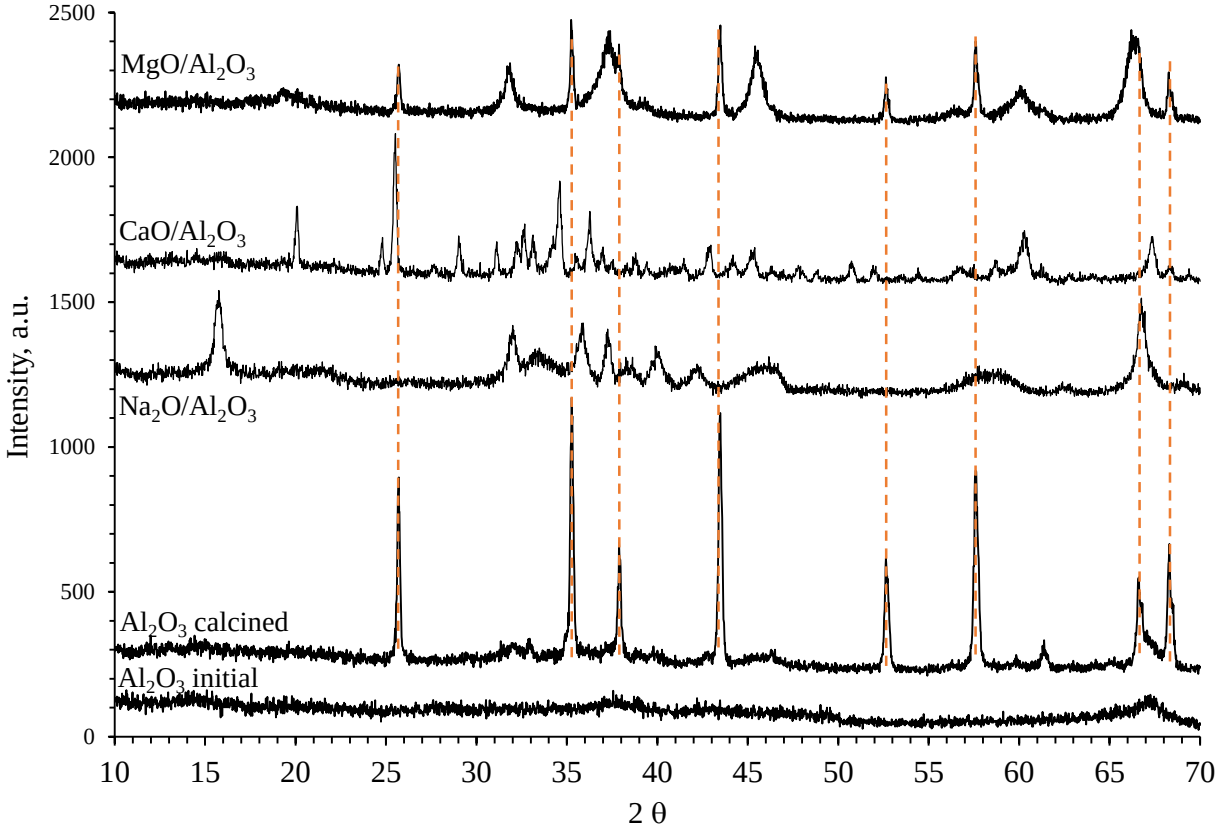


Figure S4. Survey of XRD patterns of the catalysts used in the present study. Vertical orange lines correspond to main Corundum reflexes (PDF#10-0173).

Table S2. Catalyst solid phases found by XRD (see Fig. S4 — S8)

#	Sample	Phase 1	Phase 2	Surface area, m^2/g	Desorption average pore diameter (4V/A by BET), nm	Supported metal content, m_{met}/m_{cat}, %
1	Initial A204 (γ–Al_2O_3)	Not detected	Not detected	204	8	0
2	Calcined Al_2O_3	Corundum **(α-Al_2O_3)** PDF#10-0173	Not detected	27	29	0
3	Na_2O/Al_2O_3	**$NaAl_7O_{11}$** PDF#21-1095	**$NaAl_5O_8$** PDF#19-1173	22	27	5.2 %
4	CaO/Al_2O_3	**$CaAl_4O_7$** PDF#23-1037	**$CaAl_{12}O_{19}$** PDF#38-0470	6	16	9.0 %
5	MgO/Al_2O_3	**$Mg_{0.388}Al_{2.408}O_4$** PDF#48-0528	Corundum **(α-Al_2O_3)** PDF#10-0173	26	28	5.5 %

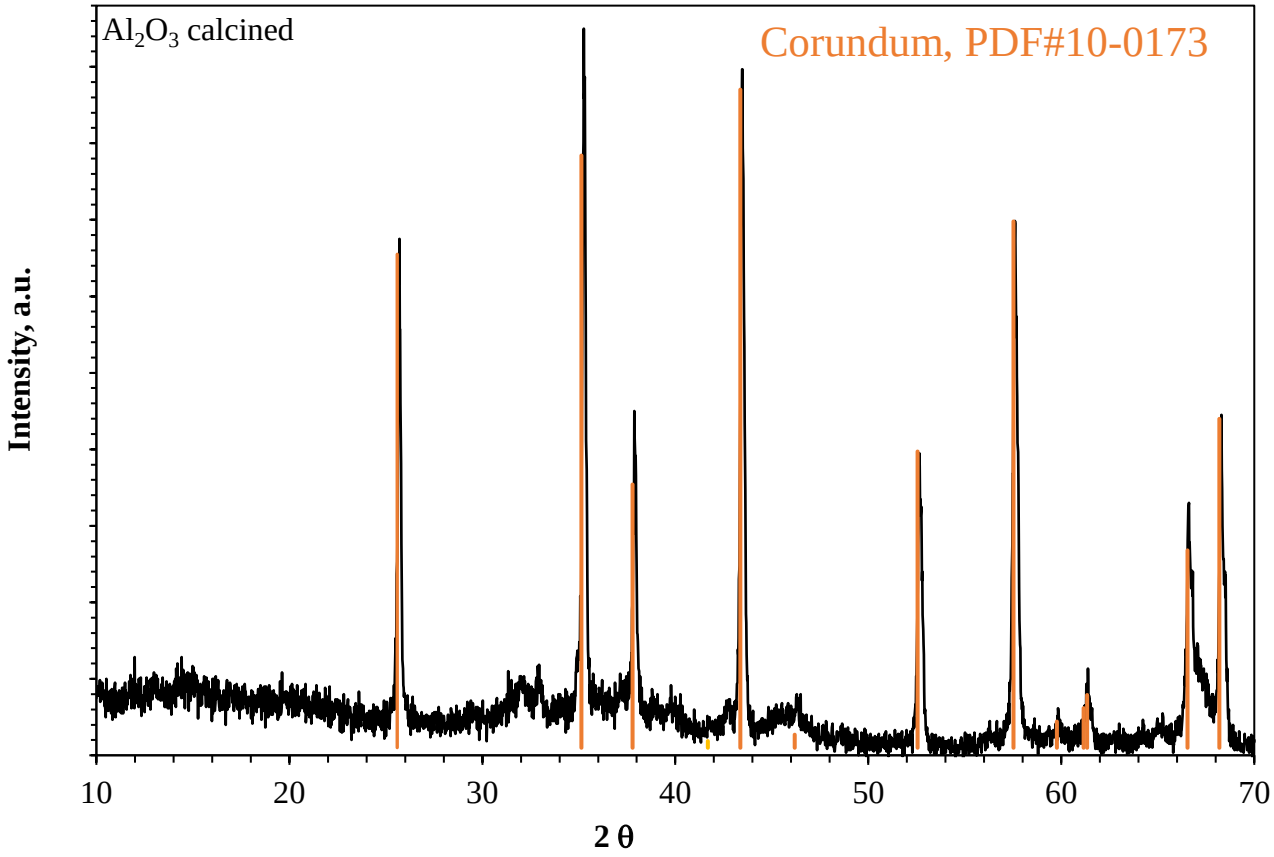


Figure S5. Comparison of the XRD patterns of the A-204 calcined at 1000ºC with PDF#10-0173

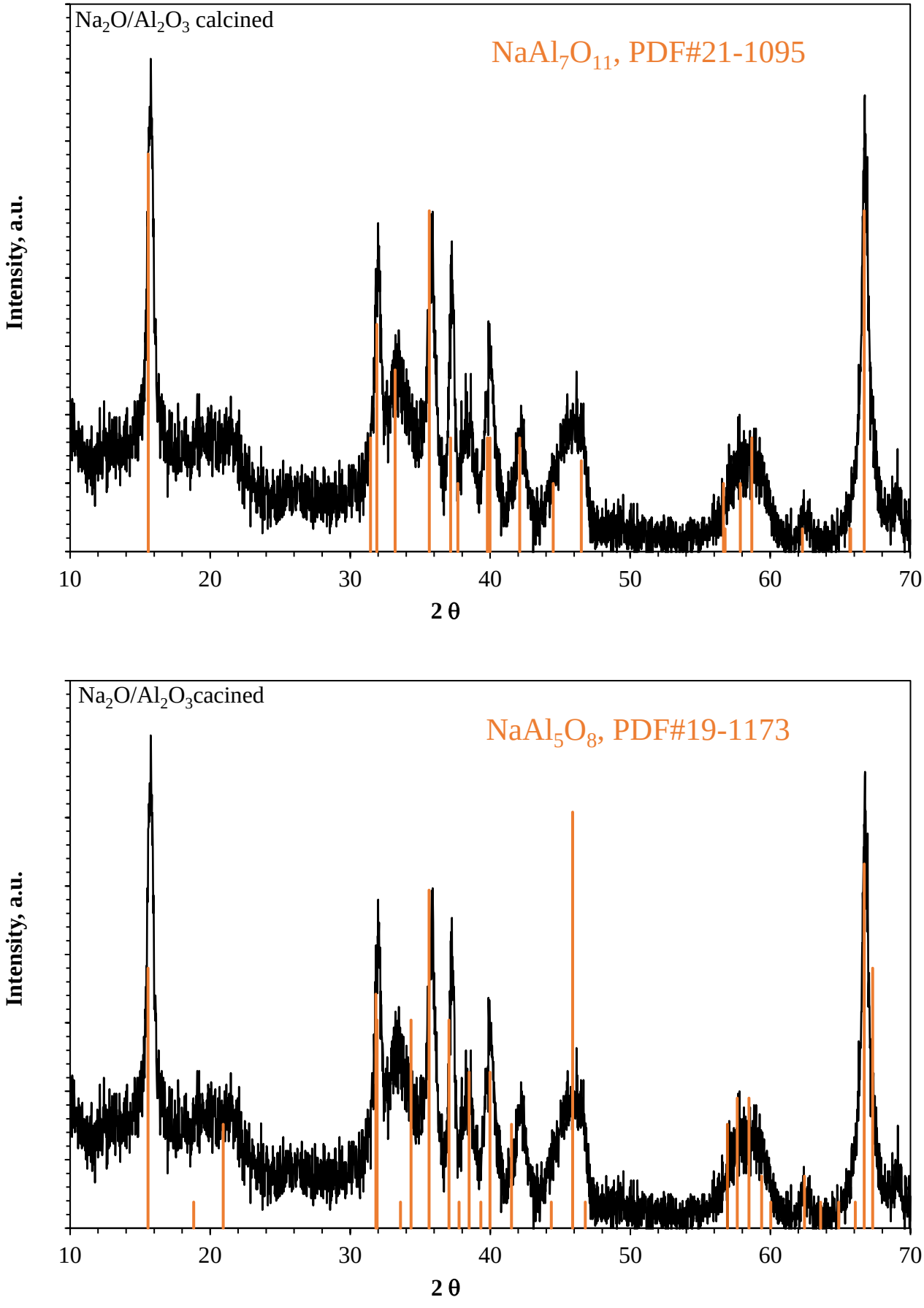


Figure S6. Comparison of the XRD patterns of the Na_2O/Al_2O_3 with PDF#21-1095 and PDF#19-1173

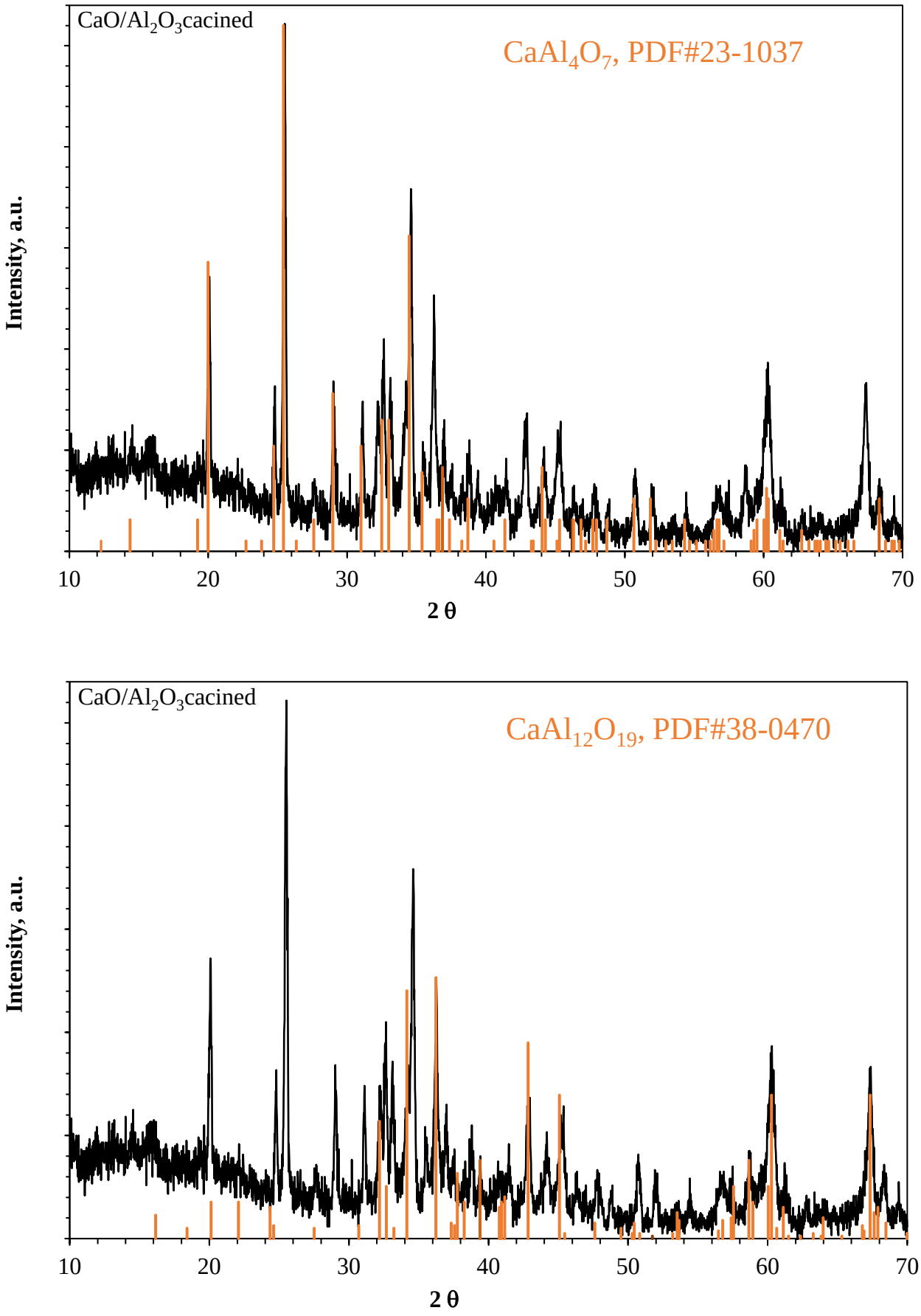


Figure S7. Comparison of the XRD patterns of the CaO/Al_2O_3 with PDF#23-1037 and PDF#38-0470

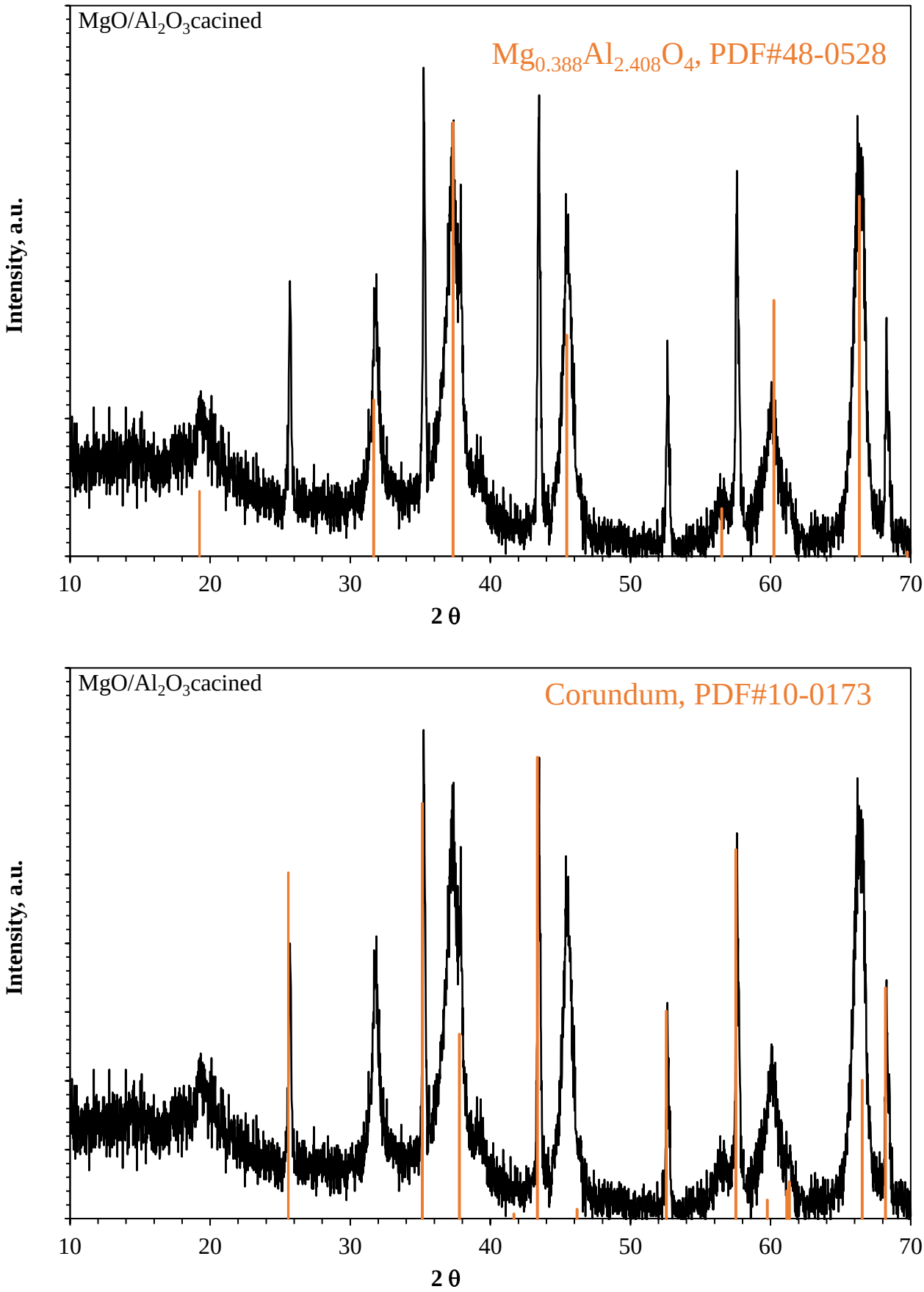


Figure S8. Comparison of the XRD patterns of the MgO/Al_2O_3 with PDF#48-0528 and PDF#10-1073

3. Mass balance discrepancy

Average mass balance discrepancy (ΔM) for experiments in presented study is: $\Delta M = 17 \pm 4\%wt$.

$\Delta M = 100 * (M_{LL}-(M_{WP}+M_{BP}+M_R))/M_{LL}$

where:

M_{LL} — mass of Lignin Loaded;

M_{WP} — mass of Water Phase solids;

M_{BP} — mass of Benzene Phase solids;

M_R — mass of Residual in the reactor.

The mass balance discrepancy includes losses caused by presence of gaseous products, volatile products evaporated during solvents removal and small solid particles deposited on filter during samples filtration.

4. FTIR-spectroscopy details

Transmission IR spectra were measured at room temperature using a Protege 460 spectrometer (NICOLET, USA) with a resolution of 4 cm^{-1}. To achieve a satisfactory signal-to-noise ratio, 128 spectra were accumulated. The samples of dissolved lignin with a volume of 0.1 mL were applied by an automatic pipette to a KRS-5 glass disk having a thickness of 3 mm and fitted with a holder (2 cm^2 window) and dried at 60 °C. To exclude the background, a spectrum of the KRS-5 glass disk in the holder without the applied sample was registered. Additionally, the baseline was corrected using the intensity of transmitted light in the regions of 3660, 2450, 1900, 700 cm^{-1}.

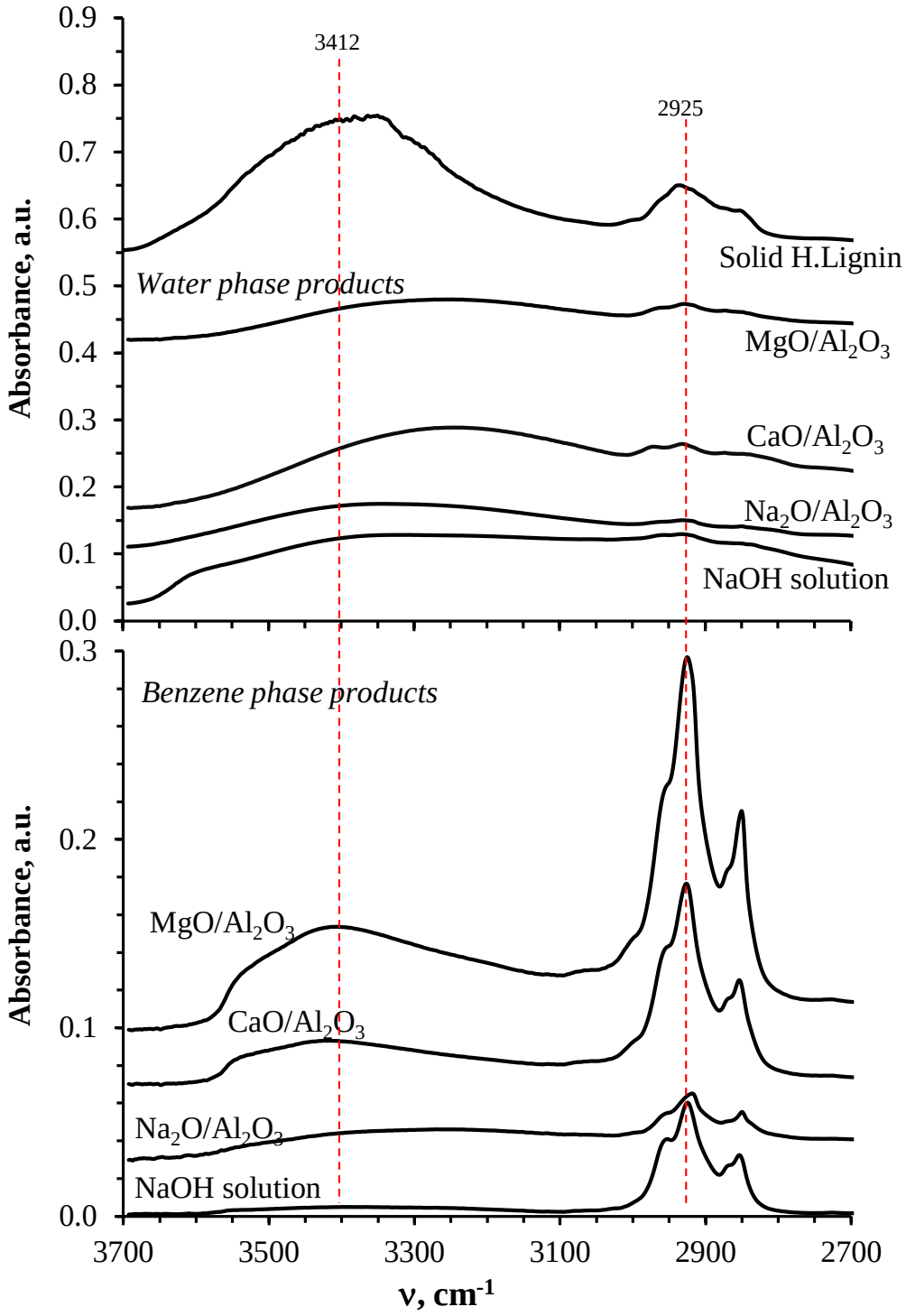


Figure S9. FTIR spectra (range 3700 — 2700 cm^{-1}) of the hydrolysis lignin conversion products. The top part corresponds to water phase products, the bottom part corresponds to benzene phase products.

Comparison of the IR spectra of obtained products with database and literature spectra.

Water-phase products

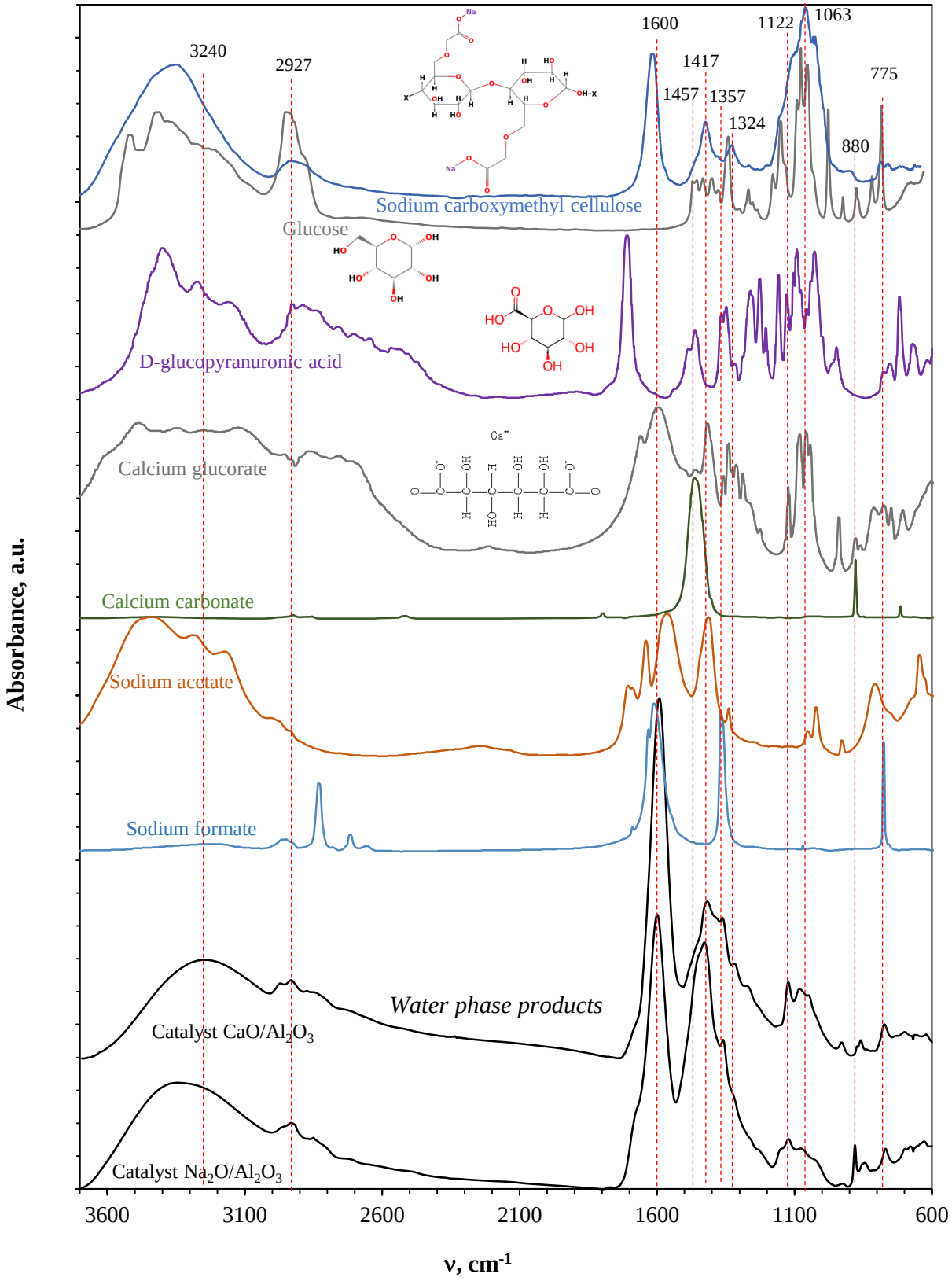


Figure S10. Comparison of the FTIR spectra of water-phase products with spectra of substances found in the spectral database.

Benzene-phase products

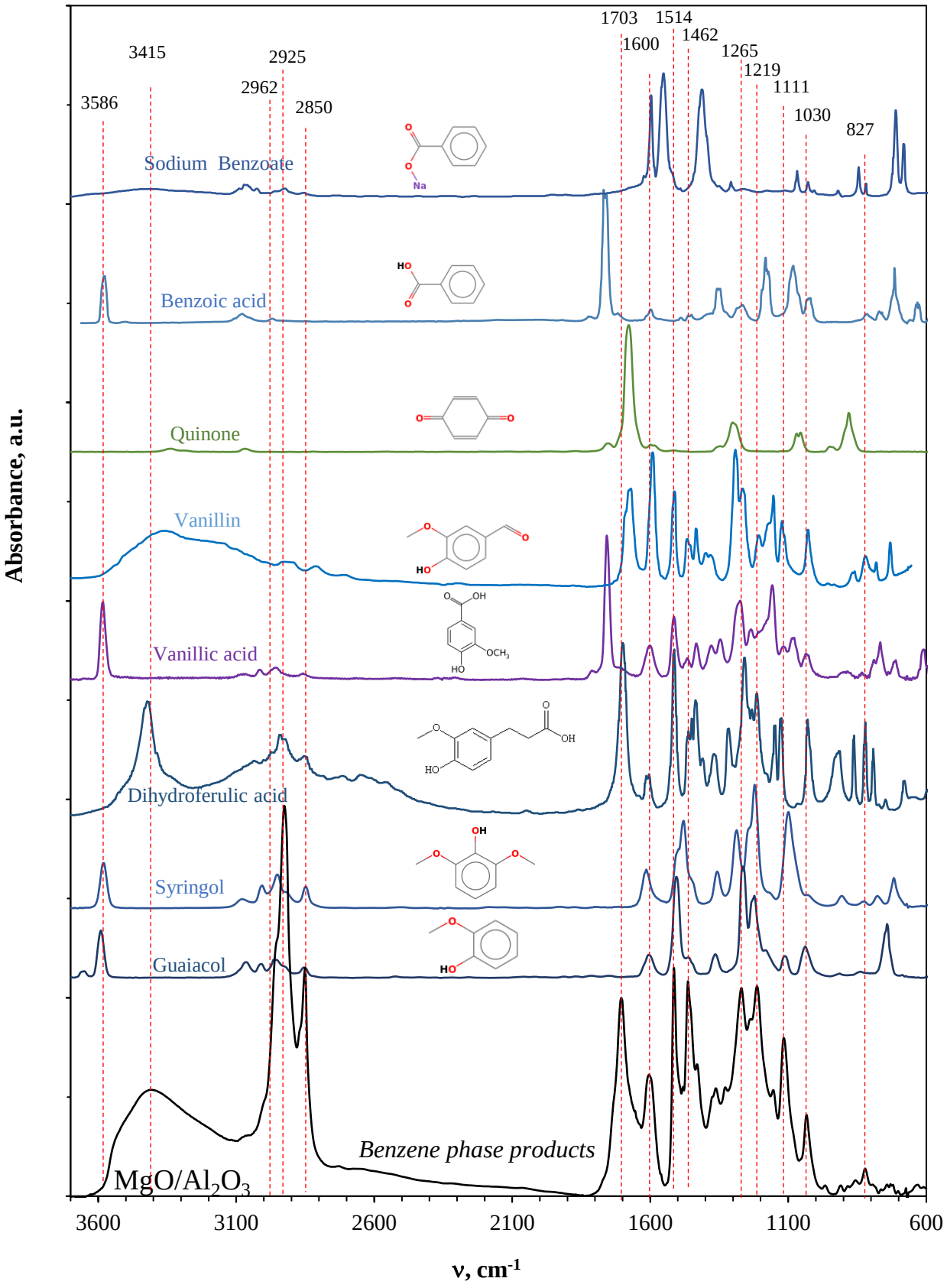


Figure S11. Comparison of the FTIR spectra of benzene-phase products with spectra of substances found in the spectral database.

Simulation of the FTIR spectra of obtained products by linear combination of spectra available in the spectral database

The simulated IR spectra were found as a linear combination of the spectra of the basic substances with coefficients proportional to the concentrations of the components in the mixture. The coefficients were determined by the least squares method, the optimized function was the sum of the quadratic deviations of the intensities of the simulated spectrum from the experimentally measured one in the range of wave numbers 1800 — 970 cm^{-1}. The region of stretching vibrations of the C-H and O-H groups (3800 — 2700 cm^{-1}) was not taken into account.

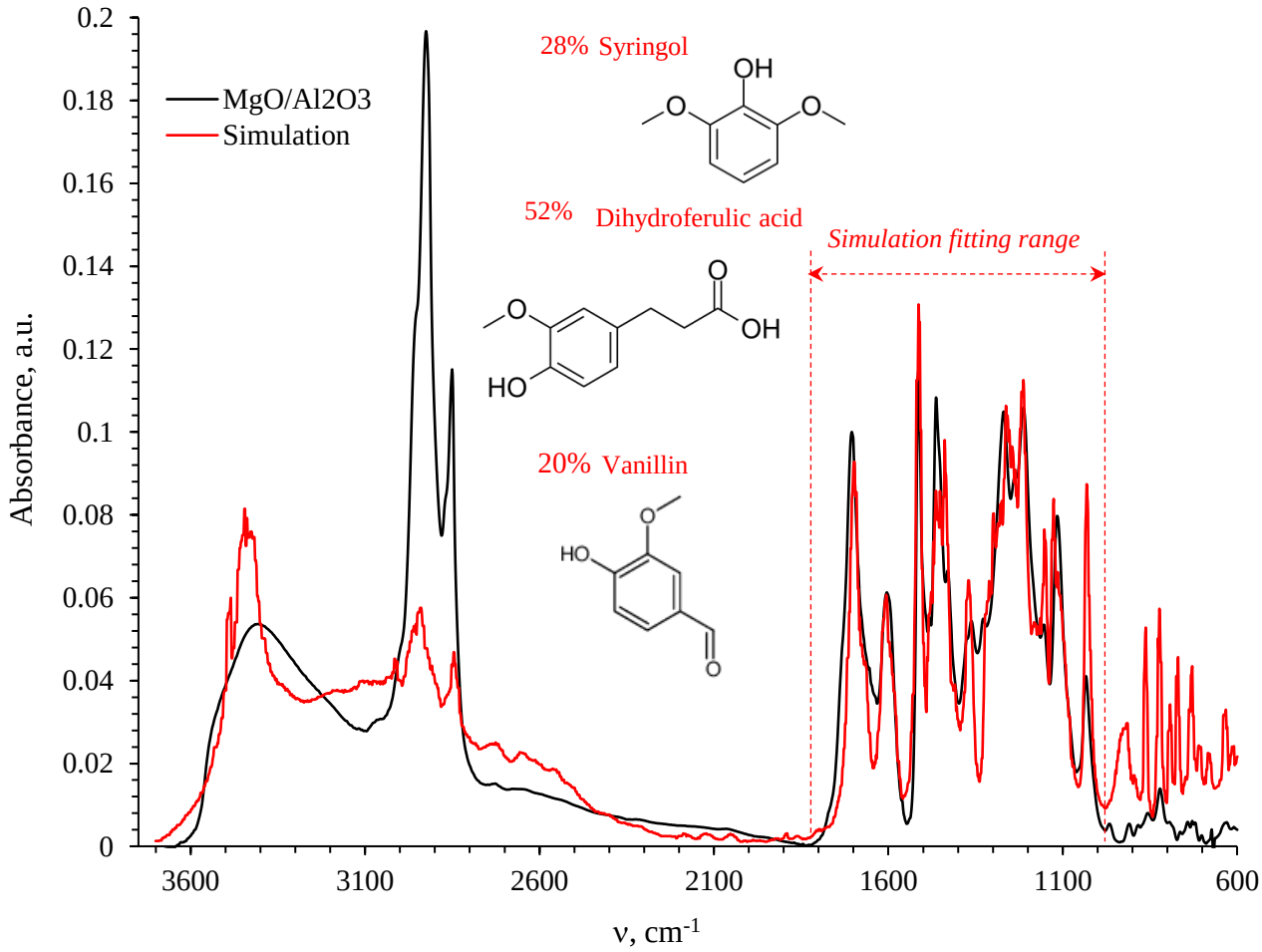


Figure S12. Comparison of the FTIR spectra of benzene-phase products with simulated spectra.

Comparison of the FTIR spectra of the obtained product with literature data

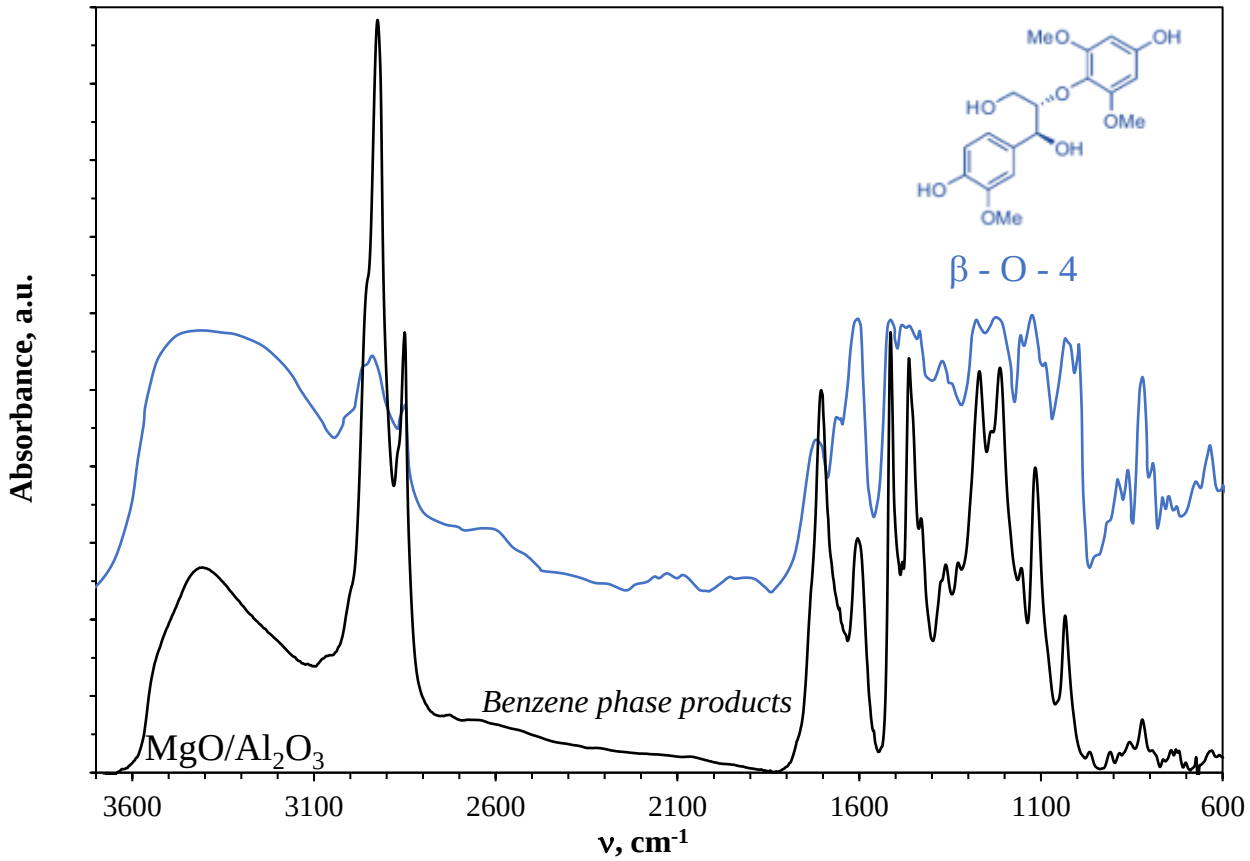


Figure S13. Comparison of the experimental FTIR spectra of benzene-phase products for the MgO/Al_2O_3 catalyst with experimental spectra of the dimeric lignin fragment (lignan).