Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 402–404

Gasification of hydrolysis lignin with CO_2 in the presence of Fe and Co compounds

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Hydrolysis lignin was used as an initial carbon-containing material. Elemental analysis of the initial lignin is carried out. The results (weight percent) are shown in Table S1.

Table S1. Elementary analysis of initial lignin*

	C, %	O, %	H, %	N, %	S, %	Ash, %
Mass content	52,82	31,91	5,34	0,36	0,18	9,41

Hydrolysis lignin was used. The BET equation was used to determine the specific surface area of the material (163.8 $m^2 g^{-1}$). Elemental analysis of the initial lignin was performed (Table S1). For the preparation of metal-containing samples Fe/lignin and Co/lignin, the method of incipient wetness impregnation with aqueous solutions of $Fe(NO_3)_3*9H_2O$ and $Co(NO_3)_2*6H_2O$ was used. After impregnation, the samples were dried for 24 hours at 100 °C. Samples with a mass content of the supported metal of 1,3,5,7% by mass were prepared.

The powder X-ray diffraction pattern was obtained using a Rigaku IV Ultra instrument with CuKα radiation. The samples were examined in the 2θ = 15–60° region at a rate of 1 degree per minute.

Catalytic tests were carried out in a quartz flow reactor with an internal diameter of 8 mm. The sample loading was 1 g. The CO_2 flow rate was 30 ml min^{-1} with a total pressure of 1 atm. A Bronkhorst EL-FLOW SELECT F-111B gas flow controller was used to determine the gas flow rate. The temperature increased at a constant rate: 600 °C $hour^{-1}$ in the range from 100 to 850 °C. In the course of the reaction, the analysis of the gas products was carried out using a gas chromatograph "Chromatek Crystal 5000" with thermal conductivity detectors, columns M ss316 3m * 2mm, Hayesep Q 80/100 mesh, and CaA molecular sieves. The ratios of amounts of

* Elemental analysis was performed using a PerkinElmer 2400 Series II CHNOS analyzer. The sample weight was 50 mg.

substances were determined from the data of gas chromatography by the method of absolute calibration. Basic parameters of providing the process presented in the table below:

Parameter	**Description**
CO_2 pressure	1 bar
Test protocol	temperature ramp up from 25°C up to 800°C with rate 600°/hour
Flow settings CO_2 inlet	470.7 $hour^{-1}$
WHSV for 1% wt. of metal	353,6 $hour^{-1}$
WHSV for 3% wt. of metal	117,9 $hour^{-1}$
WHSV for 5% wt. of metal	70,7 $hour^{-1}$
WHSV for 7% wt. of metal	50,5 $hour^{-1}$
Analytical methods	Gas chromatography for gaseous products. SEM-EDX and XRD analysis for solid remains.

The microscopic and EDX study was carried out with a LEO EVO 50 XVP electron microscope equipped with an INCA-Energy 450 energy-dispersive analyzer. For the study, less than 1 mg of the sample was applied to a conductive tape and placed in a microscope chamber. The chamber was evacuated to a residual pressure of 10–6 Torr. The energy of primary electrons was 3–10 keV, the current varied in the range of 2–40 pA. The focal length of the electron beam was varied from 5 to 15 mm.

Micrographs were taken using a scanning electron microscope of the initial sample of lignin, as well as samples with supported catalysts (7% by weight), and the EDX-analysis of the samples was studied. The EDX-analysis of the samples confirmed the presence of silicon, probably in the composition of quartz.

According to the EDX-analysis data for the Fe(7%)/lignin sample, the metal content by weight was 6.53%. The closeness of the average value of the content of iron on the surface and a small standard deviation (2.17) indicate the uniformity of the distribution of iron over the surface of the sample. The mass content of cobalt in the Co(7%)/lignin sample was 7.75% according to the EDX data. The standard deviation of the mass content of cobalt on the surface was 4.17. Mapping was also performed for carbon (Ka1,2) silicon (Ka1), cobalt (Ka1) for the Co(7%)/lignin sample. The mapping shows reasonably good uniformity in the distribution of cobalt over the lignin surface. A Fe(7%)/lignin sample was mapped to carbon (Ka1,2), sulfur (Ka1), iron (Ka1). The mapping shows excellent uniformity of the deposition of iron compounds over the lignin surface.

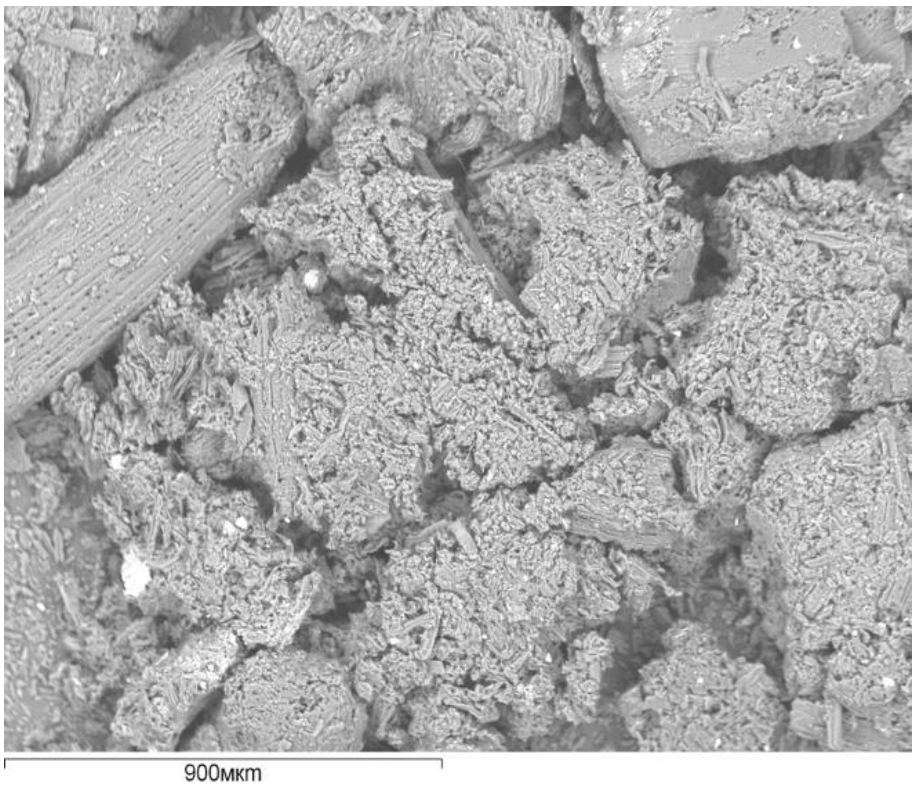

Figure S1. SEM images of the initial hydrolysis lignin.

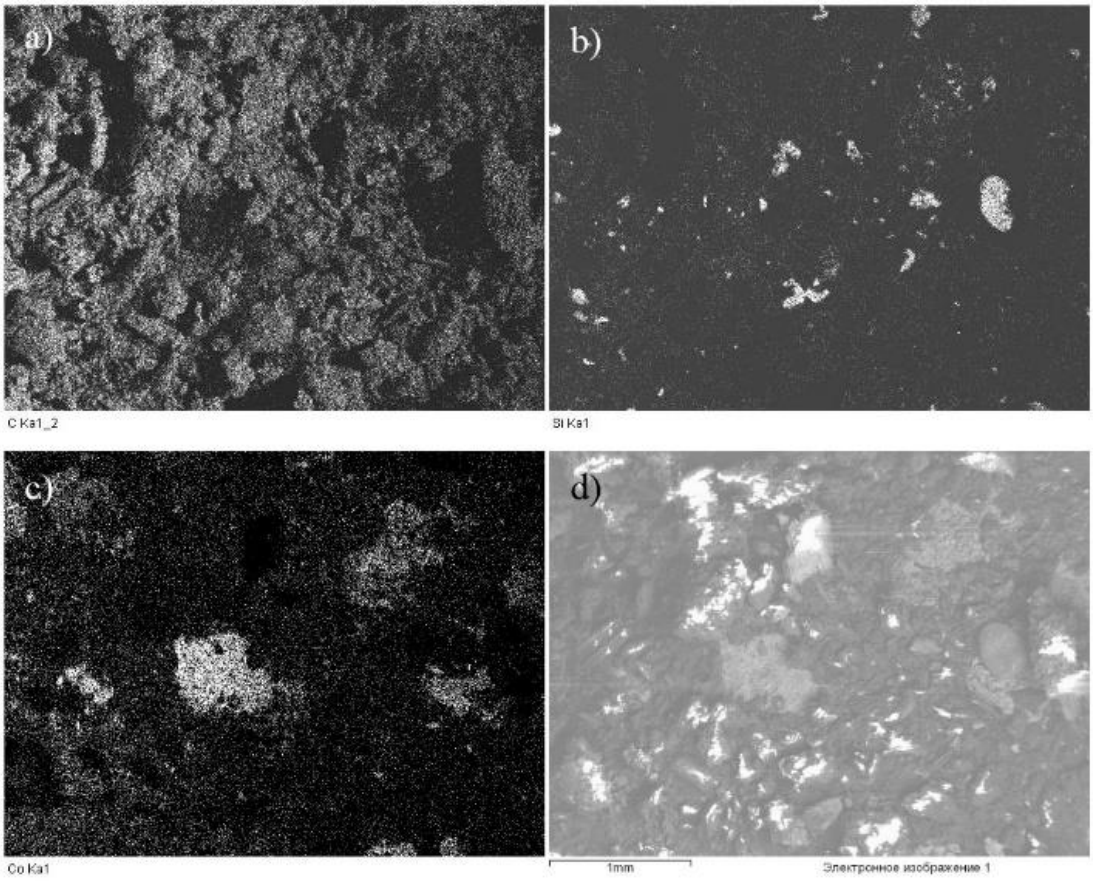

Figure S2. The results of EDX mapping for the sample Co(7%)/lignin: a) carbon; b) silicon; c) cobalt; d) general view of the surface of the Co(7%)/lignin sample.

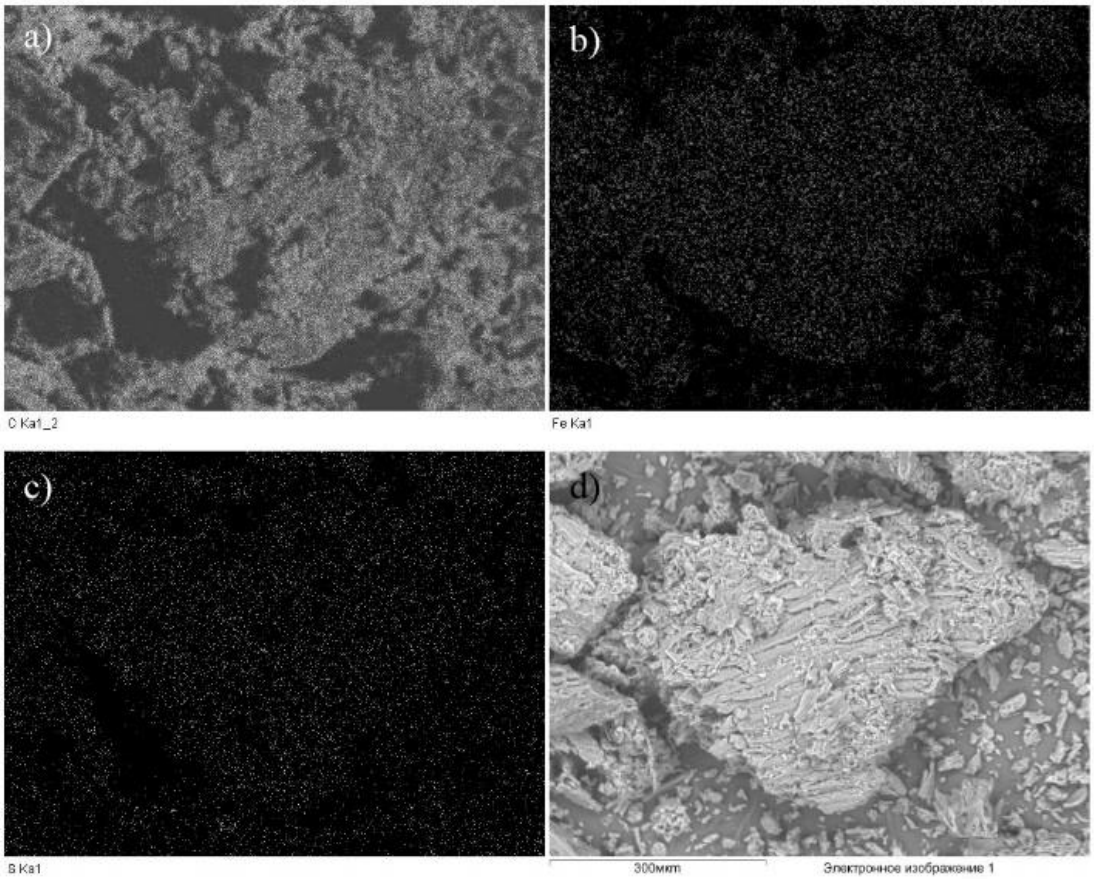

Figure S3. The results of EDX mapping for the sample Fe(7%)/lignin: a) carbon; b) iron; c) sulfur; d) general view of the sample surface of Fe(7%)/lignin.