

Effect of Temperature on the Hydrotreatment of Sewage Sludge-Derived Pyrolysis Oil and Behavior of Ni-Based Catalyst

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Experimental Procedures

Analysis of reaction products

GC-TCD/FID analysis of gas phase

The gas-phase products were analyzed using GC Chromos GCh 1000 equipped with two columns (3 m×2 mm i.d.) packed with silochrome and activated carbon. A thermal conductivity detector (TCD) and a flame ionization detector (FID) were used for the registration of respective column eluents. The injector temperature was set at 100 °C; the detector temperature—at 150 °C. The oven temperature was kept at 40 °C for 5 min, then increased to 120 at 20 °C/min, and kept at this temperature for 5 min. Argon was used as the carrier gas.

Hydrogen consumption (calculation procedure)

The amount of hydrogen consumed in each experimentation and reflecting the catalyst activity was estimated according to the procedure reported previously [1]. It is based on pressure and temperature recordings and gas-phase composition data before and after the reaction. The volume of the gas phase during the reaction is assumed constant and the ideal gas law is applied in these calculations. The following expressions were used for calculation of the initial amount of H₂ in the reactor (Ex. 1), the residual amount of hydrogen after the process (Ex. 2), and hydrogen uptake related to the amount of Py-SS (Ex. 3):

$$n_{\text{H}_2(\text{initial})} = \frac{p_{\text{rt}}^{\text{init}} \cdot V_{\text{gas}}}{R \cdot T_{\text{rt}}^{\text{init}}} \quad (\text{Ex. 1})$$

$$n_{\text{H}_2(\text{residual})} = \varphi_{\text{H}_2} \cdot \frac{p_{\text{rt}}^{\text{fin}} \cdot V_{\text{gas}}}{R \cdot T_{\text{rt}}^{\text{fin}}} \quad (\text{Ex. 2})$$

$$\text{H}_2 \text{ uptake} = \frac{(n_{\text{H}_2(\text{initial})} - n_{\text{H}_2(\text{residual})}) \cdot 24.436}{m_{\text{Py-SS}}} \quad (\text{Ex. 3})$$

Ex. 1 (before the reaction): $n_{\text{H}_2(\text{initial})}$ is the amount of hydrogen (in moles) placed into the reactor free volume V_{gas} (L) not occupied by the liquid matter, $p_{\text{rt}}^{\text{init}}$ —initial pressure (atm) of hydrogen in the reactor at room temperature $T_{\text{rt}}^{\text{init}}$ (K), R —the gas constant (0.082 L·atm/mol·K).

Ex. 2 (after the reaction): $n_{H_2(\text{residual})}$ is the amount of hydrogen (in moles) remaining in the gas phase after the reaction, T_{rt}^{fin} —final temperature after cooling the reactor (K), p_{rt}^{fin} —the pressure of gaseous phase (atm) and φ_{H_2} —hydrogen mole fraction determined by gas chromatography (GC-TPD), after cooling the reactor to room temperature.

Ex. 3: H_2 uptake is the amount of hydrogen consumed during hydrotreatment of Py-SS, expressed in normal liters per kg of feed, 24.436—the molar volume (L) of any gas at normal conditions (298 K, 1 atm), m_{Py-SS} —initial loading of pyrolysis liquid into the reactor.

H_2 uptake was corrected taking into account the formation of light hydrocarbons in the gas phase. The adverse reactions leading to the formation of such products consume hydrogen and contribute to unwanted carbon loss. The following expression (Ex. 4) was applied in these calculations, assuming that all hydrogen atoms in gas products are from the H_2 phase:

$$H_2 \text{ uptake} = \frac{(n_{H_2(\text{initial})} - n_{H_2(\text{residual})}) \cdot 24.436}{m_{Py-SS}} - \frac{n_{H(\text{gas prod})} \cdot 24.436}{2 \cdot m_{Py-SS}} \quad (\text{Ex. 4})$$

where $n_{H(\text{gas prod})}$ —the number of hydrogen atoms (in moles) calculated for light hydrocarbons C1–C4 by Ex. 5:

$$n_{H(\text{gas prod})} = \sum_i \varphi_i \cdot N_{H(i)} \cdot \frac{p_{rt}^{\text{fin}} \cdot V_{\text{gas}}}{R \cdot T_{rt}^{\text{fin}}} \quad (\text{Ex. 5})$$

φ_i —mole fraction of i -product determined by GC-FID, $N_{H(i)}$ —the number of hydrogen atoms in i -product, for example, eight hydrogen atoms in propane molecule (C_3H_8).

Ultimate analysis (CHNS-O)

The elemental CHNS-O analysis of the Py-SS and the product oils was performed by using an Elemental Vario EL Cube analyzer (Elementar Analysensysteme GmbH, Germany). The amount of oxygen was calculated by difference ($O\% = 100 - C - H - N - S$). All measurements were carried out at least in triplicate and average values are reported.

Conradson carbon residue analysis (CCR)

Conradson Carbon Residue (ASTM D189) is intended to provide an indication of the thermal stability of Py-SS and hydrotreatment products based on relative coke-forming propensities. The CCR is calculated from the residual mass of coke (wt. %) being formed after evaporation of volatile components and pyrolysis of relatively non-volatile components in the analyzed sample, which undergo partial degradation during atmospheric distillation. All analyses were carried out in triplicate.

Water content

The water content in the Py-SS and organic-phase products was determined by Karl Fischer titration using Metrohm 870 Titrino Plus equipment. About 0.1 g of sample was placed by a syringe into a closed glass vessel containing the Hydranal Working medium K solvent (Riedel de Haen, Germany). The titration procedure was performed using AKVA M-Composite Titrant 2MN (LLC Akvometriya, Russia) as a titration reagent. Each sample was analyzed at least three times and the average value is reported.

X-Ray fluorescence analysis

The sulfur content of the pyrolysis liquid and the product oils were measured on a Lab-X 3500SCI energy dispersive X-ray fluorescence analyzer (Oxford Instruments, United Kingdom). Inorganic impurities in the pyrolysis oil were determined using X-Ray fluorescence spectrometer ARL Perform'X (Thermo Fisher Scientific, USA) equipped with Rh anode as an X-ray source. The mass percentage of elements was estimated using UniQuant software. Before analysis, the liquid sample (12 ml) was placed into a plastic cuvette covered with a 6 μm polypropylene film. The cuvette was put into the spectrometer chamber filled with helium, and measurements were conducted.

Density

The density of initial feed Py-SS and organic liquids after the hydrotreatment process was determined using a Densito 30PX densimeter (Mettler Toledo, Switzerland) via the ASTM D 4052 procedure.

Gas chromatography—mass spectrometry (GC–MS)

GC–MS analyses of the pyrolysis liquid and the product oils were performed using GC system Agilent 7000B equipped with a triple quadrupole detector. Chromatographic separations were performed using a self-designed capillary column based on N-propyl-6-methyl-quinolinium (10 m length, 0.25 mm i.d., and 0.2 μm film thickness) [2]. Helium was used as the carrier gas with a constant flow rate of 0.9 ml/min. Before the injection, each sample was dissolved in acetone. The samples (1 μL) were injected into the gas chromatograph under split conditions, the split ratio being 50:1. The injector temperature was 300 °C. The oven temperature increased from 70 °C to 280 °C at a rate of 7 °C/min. The temperature of EI source was 230 °C, the electronic ionization energy of 70 eV, and the scanning range (m/z) from 40 to 500. Data were acquired and processed using MassHunter B7.02 software. The compounds were identified by comparing mass spectra with the NIST11 mass spectra data library. Calibration was not carried out, since a large number of compounds and functionalities were present in the samples. The percentage of the components was calculated from respective peak areas divided by the total ion chromatogram (TIC). This approach of peak area normalization does not provide the real concentration of compounds but serves for a general comparison of samples.

Catalyst characterization

X-Ray fluorescence analysis (XRF)

The elemental composition of catalyst was determined using X-Ray fluorescence spectrometer ARL Advant'X 2247 (Thermo Fisher Scientific, USA) equipped with Rh anode as an X-ray source. The mass percentage of elements was estimated using QuantAS software. Before analysis, the catalyst powder was mixed with cellulose (weight ratio 1:1) to obtain the volume necessary to fill in the sample holder, which was then placed into a cassette covered with a Spectrolene Six film. The cassette was put into the spectrometer chamber filled with helium, and measurements were conducted.

Nitrogen physisorption

Nitrogen physisorption analyses were carried out at the liquid nitrogen temperature using an ASAP-2400 automated volumetric adsorption analyzer (Micromeritics Instrument. Corp., USA). Before analysis, the samples were de-gassed at 150 °C and pressure 0.13 Pa for 4 hours. The resulting adsorption isotherms were used to calculate the specific surface area A_{BET} , the total pore volume V_{Σ}

(from ultimate adsorption at a relative pressure of $P/P_0 = 1$), the micropore volume $V_{\text{micropore}}$, and the mean pore size $\langle d \rangle$.

Temperature-programmed reduction (TPR)

Catalyst sample (0.1 g) was placed in a U-tube quartz reactor and treated in 10 vol. % of H_2 balanced in argon (90 vol. %) at a flow rate of 20 ml/min and a constant heating rate of 10 °C/min up to 950 °C. The hydrogen concentration in the outlet stream during the reduction was measured by TCD.

In situ X-ray photoelectron spectroscopy (XPS)

The chemical composition of the catalyst surface was studied by the X-ray photoelectron spectroscopy (XPS) using a photoelectron spectrometer (SPECs Surface Nano Analysis GmbH, Germany). The spectrometer was equipped with a hemispherical analyzer PHOIBOS-150, an X-ray monochromator FOCUS-500, an X-ray source XR-50M with a double Al/Ag anode, and a high-pressure cell (0.2 L volume) allowing the heating of the samples in gas mixtures at pressures up to 5 bars. To register the XPS spectra, the monochromated radiation $\text{AlK}\alpha$ ($h\nu = 1486.74$ eV) was used. The scale of binding energies (E_{BE}) was calibrated by the internal standard method using the $\text{Si}2p$ line ($E_{\text{BE}} = 103.30$ eV) of silicon. The relative concentrations of the elements were determined based on integral intensities of XPS lines considering the photoionization cross-sections [3]. For the detailed analysis, the spectra deconvolution was used. After the subtraction of background by the Shirley method [4], the experimental curves were deconvoluted using the CasaXPS software [5] into several lines corresponding to the photoemission of atoms in the different chemical surrounding. A convolution of the Gauss and Lorentz functions was used for the approximation of each peak by a symmetric function.

The catalyst NiCuMo-P-SiO_2 was studied in a pre-reduced form (see Section 2.2) after an additional reduction in H_2 in a high-pressure cell of the XPS spectrometer at a temperature of 450 °C ($\text{NiCuMo-P-SiO}_2\text{-R}$). Reductive treatment of the catalyst in the high-pressure cell of the XPS spectrometer was carried out as follows: 1) evacuation to ultra-high vacuum (10^{-7} mbar), hydrogen inlet (1.3 bar), 2) heating up to 450 °C for 10 minutes, processing at 450 °C for 30 minutes, 3) cooling down to room temperature in vacuum. After reduction, the catalyst was transferred to the analyzer chamber of the spectrometer without contact with air followed by spectra recording.

In situ XANES/EXAFS

X-ray absorption spectra at the K-edges of Ni, Cu, and Mo were obtained at the Structural Materials Science beamline at the Kurchatov Synchrotron Radiation Source (National Research Center “Kurchatov Institute”, Moscow, Russia). The station characteristics are described in detail elsewhere [6]. The electron beam energy in the storage ring was 2.5 GeV at current in the range from 50 to 150 mA. Monochromatization of synchrotron radiation was provided using Si (111) and Si (220) single crystals in the form of a monoblock with a notch “Butterfly” mounted on a goniometric head. The Si (111) monochromator was used to obtain spectra at the K-edges of Cu and Ni, and Si (220) monochromator—at the Mo K-edge. All X-ray absorption spectra were obtained in a pass-through geometry. To perform the absorption studies, powder samples were mixed with amorphous BN and pressed into thin self-supported pellets. For in situ experiments, the pellets were placed into a high-temperature chamber and heated up to 400 °C in a flow of 10% H_2 in nitrogen. At these conditions, each sample was treated for 20 min. Simultaneously, with the spectrum of the analyzed sample, the absorption spectra of several reference samples (metallic Ni, Cu, or Mo) were recorded for calibration.

Before and after passing through the sample, the intensity of the X-ray beam was measured using two ionization chambers equipped with Keithley 6487 digital picoamperemeters (Keithley Instruments LLC, USA). The obtained spectra were processed using standard procedures for extracting the background, normalization to the value of the K-edge jump, and extracting atomic absorption. For further Fourier transformation of obtained EXAFS spectra, the IFEFFIT software was applied [7]. The threshold ionization energy E_0 was defined from the maximum of the first derivative of the K-edge.

X-Ray diffraction analysis

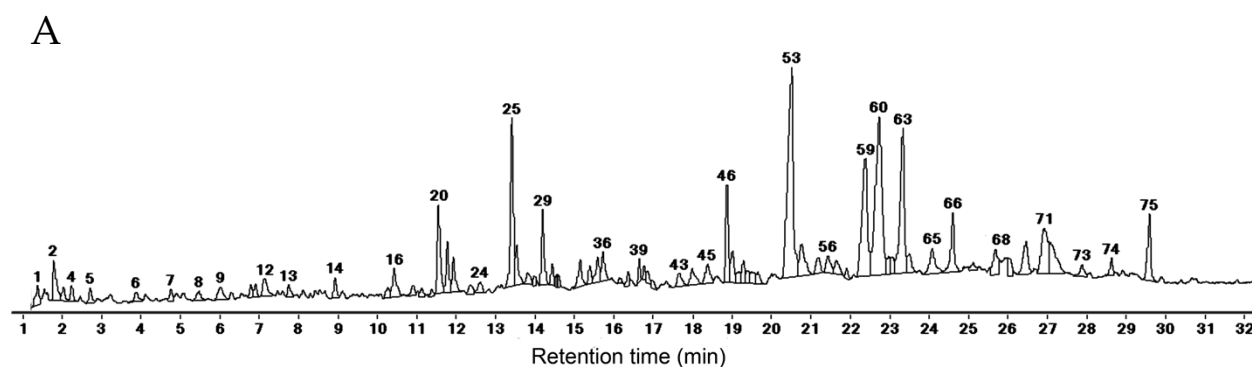
X-ray diffraction (XRD) studies were performed on an ARL X'TRA (Thermo Scientific, Switzerland) using the monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 0.1542 \text{ nm}$). X-ray diffraction patterns were recorded in a step scan mode in the 2θ range from 15 to 80° with the step of 0.05° and accumulation time 3 s in each point. The lattice parameters and the phase ratios were defined by the Rietveld method [8].

High-resolution transition electron microscopy (HRTEM)

High-resolution transmission electron microscopy (HRTEM) studies were performed on a JEM-2010 (JEOL, Japan) electron microscope with a resolution of 0.14 nm and an accelerating voltage of 200 kV . The samples for the TEM study were prepared by the ultrasonic dispersing in ethanol and consequent deposition of the suspension upon a "holey" carbon film supported on a copper grid. Local elemental analysis was performed with the EDX method on an energy-dispersive X-ray Phoenix spectrometer equipped with a Si(Li) detector with an energy resolution of 130 eV .

CHNS-analysis of spent catalysts

The elemental CHNS analysis of the spent catalyst was performed by using an Elemental Vario EL Cube analyzer (Elementar Analysensysteme GmbH, Germany). All measurements were carried out at least in triplicate and average values are reported.



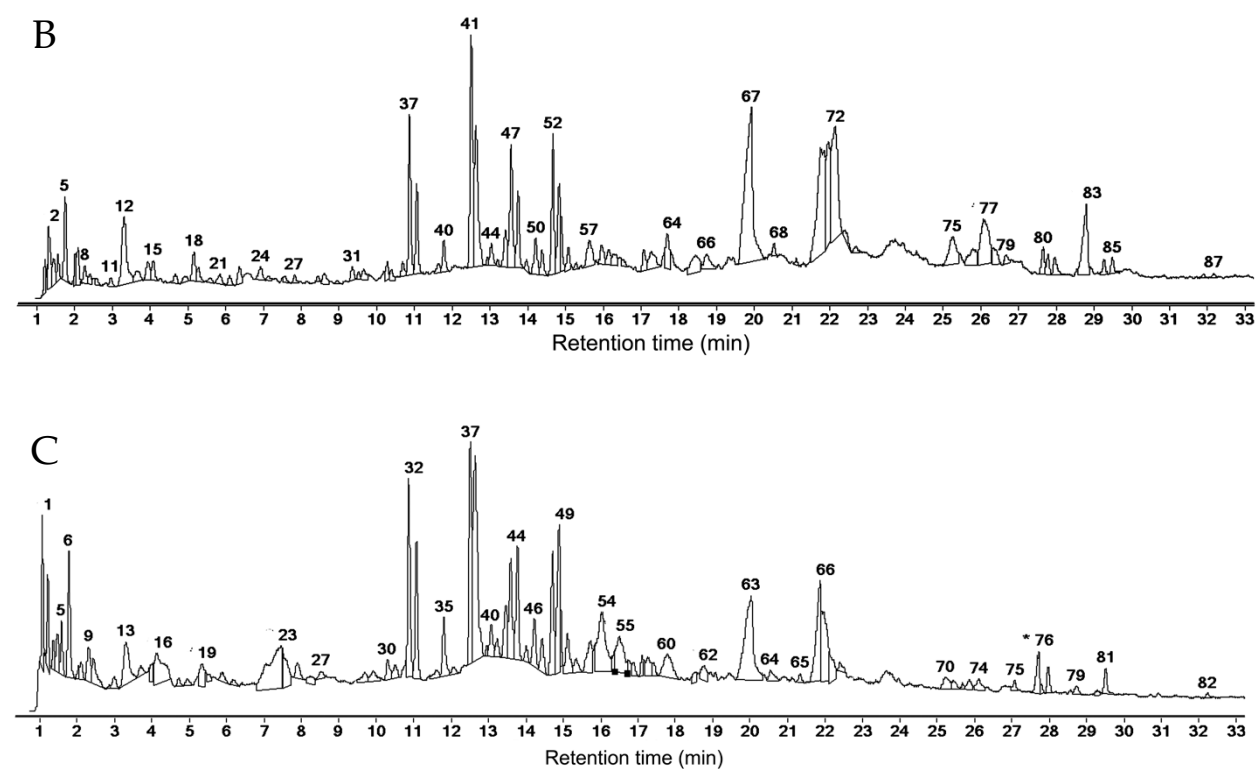


Figure S1. Total ion chromatograms: (A) of sewage sludge pyrolysis oil Py-SS (TIC1), (B) of OP obtained after Py-SS hydrotreatment at 350 °C (TIC2), (C) of OP obtained after Py-SS hydrotreatment at 390 °C (TIC3). Peak assignment is provided in the original paper, Table 4.

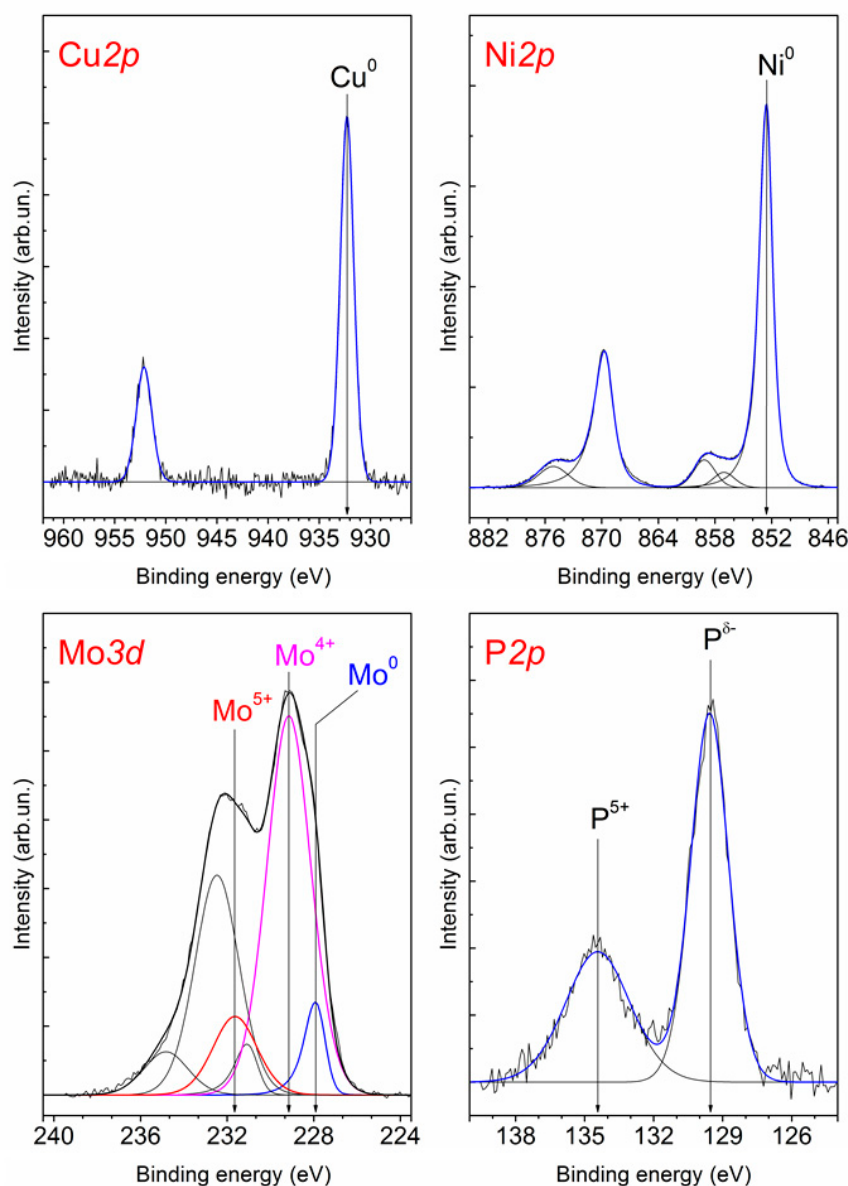


Figure S2. The Ni2p, Cu2p, Mo3d, and P2p core-level spectra of the reduced NiCuMo-P-SiO₂-R catalyst.

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