

**Adsorption-catalytic removal of diclofenac from water
by a carbon-supported palladium catalyst**

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1. Experimental part

Catalyst preparation

The granules of a support were moistened with distilled water, and a calculated amount of palladium nitrate solution (Aurat, Russia) was added. The material was stirred for 1 h at room temperature, then the water was evaporated by heating to 60°C, and then the material was dried in an oven at 150°C for 1 h. The dried catalyst was calcined in air under a static atmosphere (heated to 400°C for 4 h and maintained at 400°C for 5 h).

Catalyst reduction before testing.

The catalyst was grounded to approx. 60 mesh and reduced at 30°C in a catalytic reactor (a jacketed three-necked flask with a reflux condenser, hydrogen supply system, and magnetic stirring) at 30°C for 2 h with H₂ feed (0.6 L·h⁻¹). The catalyst was reduced both in a dry atmosphere and as a suspension in 15 ml of distilled water. After reduction in water, the catalyst was allowed to settle, the water was removed with a pipette, and then the DCF solution was loaded into the reactor. After dry reduction, the DCF solution was added immediately. High-temperature reduction was performed at 300°C for 2 h in a tube furnace with a pure hydrogen feed (0.6 L·h⁻¹), followed by cooling and passivation by passing 2 L of nitrogen containing small amounts of oxygen.

Water cleaning from diclofenac (DCF) by adsorption-hydrodechlorination method

The catalysts were tested in HDC at 30°C in a 30 mL glass reactor. The reactor was a three-necked jacketed flask equipped with a hydrogen supply system, a reflux condenser, and a sampling septum. 0.05 g of Pd/ACF grounded to approx. 60 mesh was used in each experiment. After catalyst reduction, 15 mL of an aqueous solution of DCF (sodium salt, Sigma-Aldrich, USA) with a concentration of 150 mg·L⁻¹ (0.507 mmol·L⁻¹) was added to the reactor. Magnetic stirring was applied, and samples were collected at specified intervals with a syringe fitted with a long needle. The collected samples were centrifuged for 30 s (2000 rpm) to precipitate the catalyst and analyzed by HPLC on an Agilent 1100 chromatograph (Agilent Technologies Inc., USA) with a Zorbax SB-C18 column. A mixture of acetonitrile and 0.1 M aqueous formic acid in a 1:1 (v/v) ratio was used as the eluent. The column temperature was 35°C, and the operating pressure was approximately 120 bar. An UV spectrometer with a wavelength of 278 nm served as the detector. The retention times of the reaction products were: 4.5 min for sodium 2-(2-anilinophenyl)acetate (APA), 6.5 min for sodium 2-[2-(2-chloroanilino)phenyl]acetate (CIAPA), and 7.5 min for DCF.

Apparent TOF values were calculated on the base of HDC results for the first 10 min of reaction using the formula:

$$TOF = \frac{X_{DCF} \cdot v_0(DCF)}{v(Pd) \cdot \Delta t},$$

where X_{DCF} – conversion of DCF after 10 min of the reaction (%), $\Delta t = 0.17$ h, $v_0(DCF) = 0.507 \text{ mmol} \cdot \text{L}^{-1} \cdot 0.015 \text{ L} = 7.6 \cdot 10^{-3} \text{ mmol}$; $v(Pd) = 0.125 \cdot 10^{-3} \text{ g} : 106 \text{ g} \cdot \text{mol}^{-1} = 1.17 \cdot 10^{-5} \text{ mmol}$ (molar Pd loading in the reactor).

$$v_0(DCF) = 0.507 \frac{\text{mmol}}{\text{L}} \cdot 0.015 \text{ L} = 0.0076 \text{ mmol}$$

$$m(Pd) = \frac{0.05 \text{ g}}{100} \cdot 0.25 = 0.000125 \text{ g} = 0.125 \text{ mg}$$

$$v(Pd) = 0.125 \cdot 10^{-3} \text{ g} : 106 \frac{\text{g}}{\text{mol}} = 1.17 \cdot 10^{-6} \text{ mol} = 1.17 \cdot 10^{-3} \text{ mmol}$$

Effective mass activity (EMA) was calculated as follows:

$$EMA = \frac{\Delta m_{DCF}}{\Delta t \cdot m_{Pd}},$$

where Δm_{DCF} – decrease in DCF amount in 15 ml of reaction medium (mg), $\Delta t = 0.17$ h, m_{Pd} – Pd loading in the weighted portion of catalyst in the reactor (0.125 mg).

Atomic Absorption Spectroscopy (AAS)

Metal content in the catalysts was measured by atomic absorption spectroscopy on an iCE 3000 series spectrometer (Thermo Scientific, USA) with acetylene-air flame atomization. To prepare a sample for analysis, a weighed portion of catalyst was burned in air for 1 hour at 1000°C, followed by dissolution of the ash in aqua regia at reflux. The resulting solution was diluted to the concentration recommended by the instrument manufacturer. Calibration curves were plotted with a series of standard solutions of palladium nitrate.

X-ray diffraction analysis (XRD)

Diffraction patterns were recorded on a Rigaku Ultima IV powder diffractometer (Rigaku, Japan) (CuK α radiation, 1.5418 Å). The 2 θ angle range was from 10° to 80° with a 0.02° increment. The JCPDS PDF-1 (ICDD) database was used for phase identification.

Low-Temperature N₂ Adsorption-Desorption

Low-temperature nitrogen adsorption-desorption isotherms were recorded at 77 K on an Autosorb-1 instrument (Quantachrome, USA). Before analysis the samples were degassed in vacuum at 200°C for 7 h. The specific surface areas of ACF and Pd/ACF were calculated by the BET method while micropore volumes and pore size distributions were determined using the QSDFT method (slit pore, equilibrium model).

Raman Spectroscopy

The Raman spectra were measured on a LabRAM HR 800 UV instrument (Horiba JobinYvon, Japan) using an argon laser with a wavelength of 514 nm.

Transmission Electron Microscopy with Energy-Dispersive X-ray Analysis (TEM-EDX)

TEM images were recorded on a JEOL2100F/Cs instrument (JEOL, Japan) at accelerating voltage of 200 keV.

Temperature-programmed reduction (TPR)

The TPR profiles were recorded on a USGA-101 gas chemisorption analyzer (UNISIT, Russia). in a 5% H₂ + 95% Ar flow in the temperature range from 30 to 400°C (heating rate of 10°C·min⁻¹). Approximately 0.05 g of the sample was measured. The sample was preliminary treated in argon (30 mL·min⁻¹) at 30°C for 30 min.

X-ray Photoelectron Spectroscopy (XPS)

The XPS spectra were acquired on an Axis Ultra DLD spectrometer (Kratos Analytical, UK) with a monochromatic AlK_α radiation source (hν = 1486.7 eV, 150 W). The pass energies of the analyser were 160 eV for survey spectra and 40 eV for high resolution scans. The binding energy scale of the spectrometer was preliminarily calibrated using the positions of the peaks for the Au 4f_{7/2} (83.96 eV), Ag 3d_{5/2} (368.21 eV) and Cu 2p_{3/2} (932.62 eV) core levels of pure metallic gold, silver, and copper. The powder samples were fixed on a holder using a double-sided nonconductive adhesive tape. The Kratos charge neutralizer system was used, and the spectra were charge-corrected to give the C1s peak a binding energy of 284.5 eV typical for sp²-carbon. Along with ex-situ reduced at 30 °C powder catalysts (the spectra of Pd/ACF-30dr and Pd/ACF-30wr), a whole catalyst granule was used to produce the spectra of unreduced catalyst. Then the granule was reduced in the catalytic cell of the spectrometer (5vol.% H₂/95 vol.% Ar, 300 °C, 2h, 5 °C·min⁻¹) to obtain the spectra for Pd/ACF-300dr.

2. Experimental data

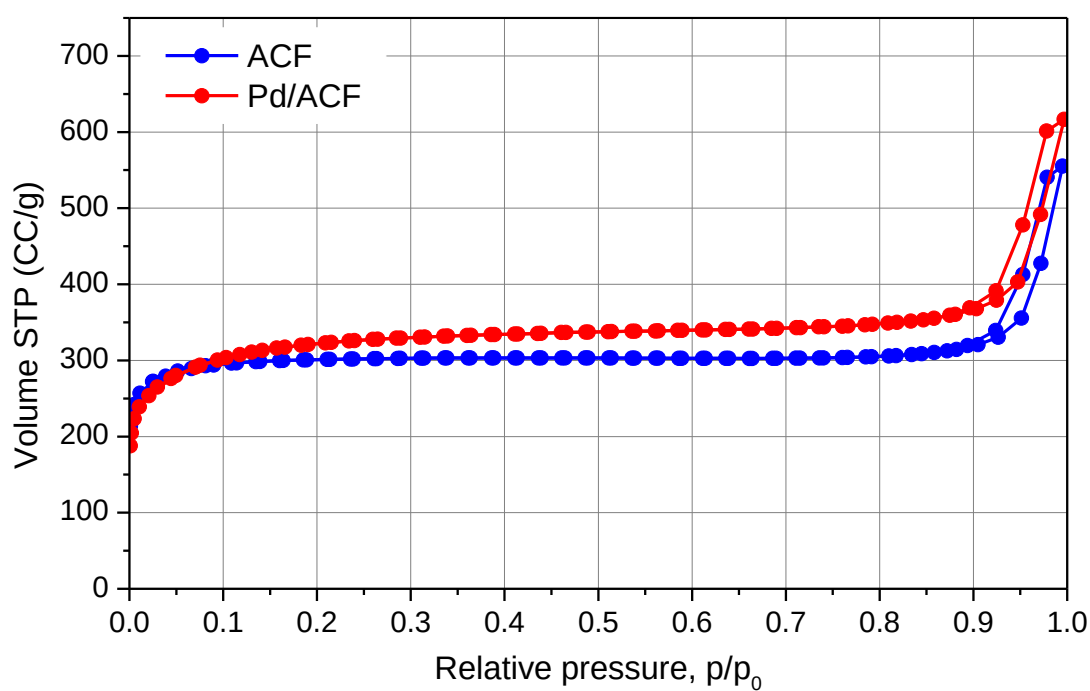


Figure S1 Low-temperature nitrogen physisorption isotherms of ACF and Pd/ACF.

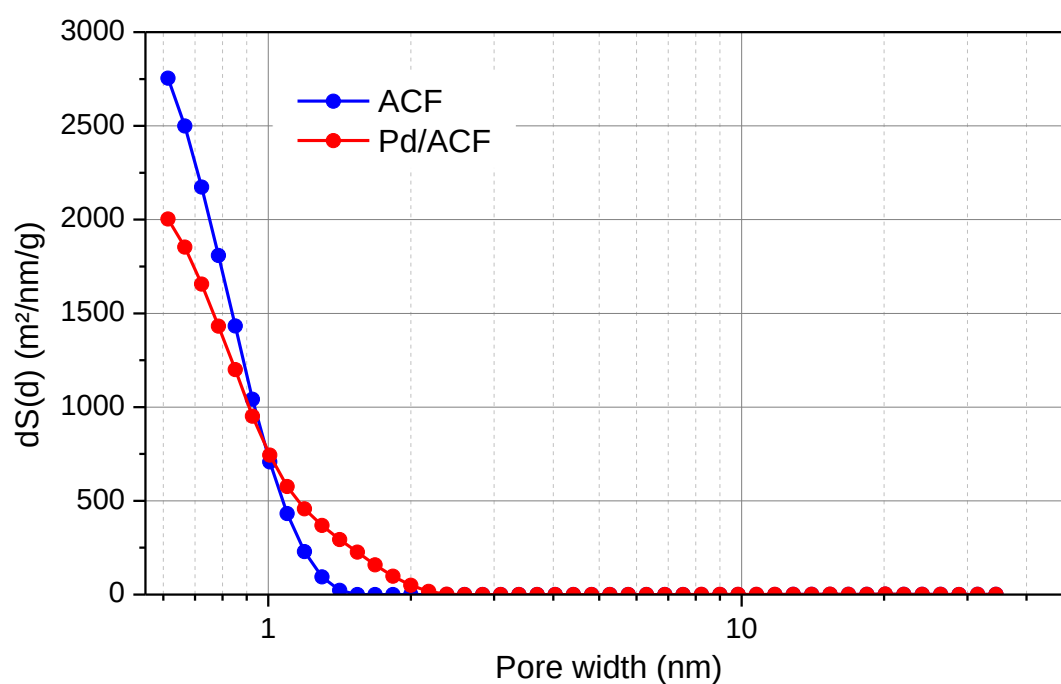


Figure S2 Pore size distributions in ACF and Pd/ACF calculated from physisorption isotherms by QSDFT method (slit pore, equilibrium model).

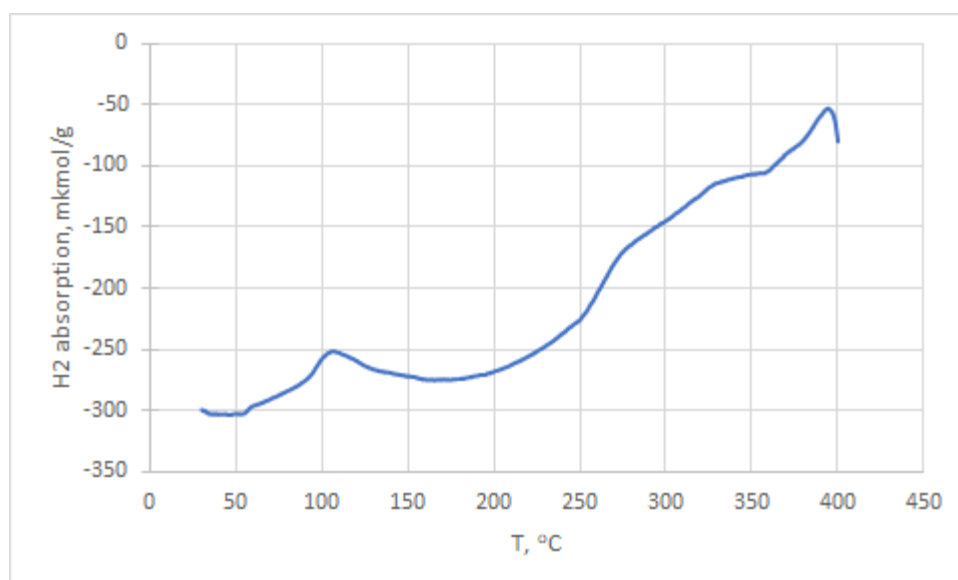


Figure S3 TPR profile of Pd/ACF.

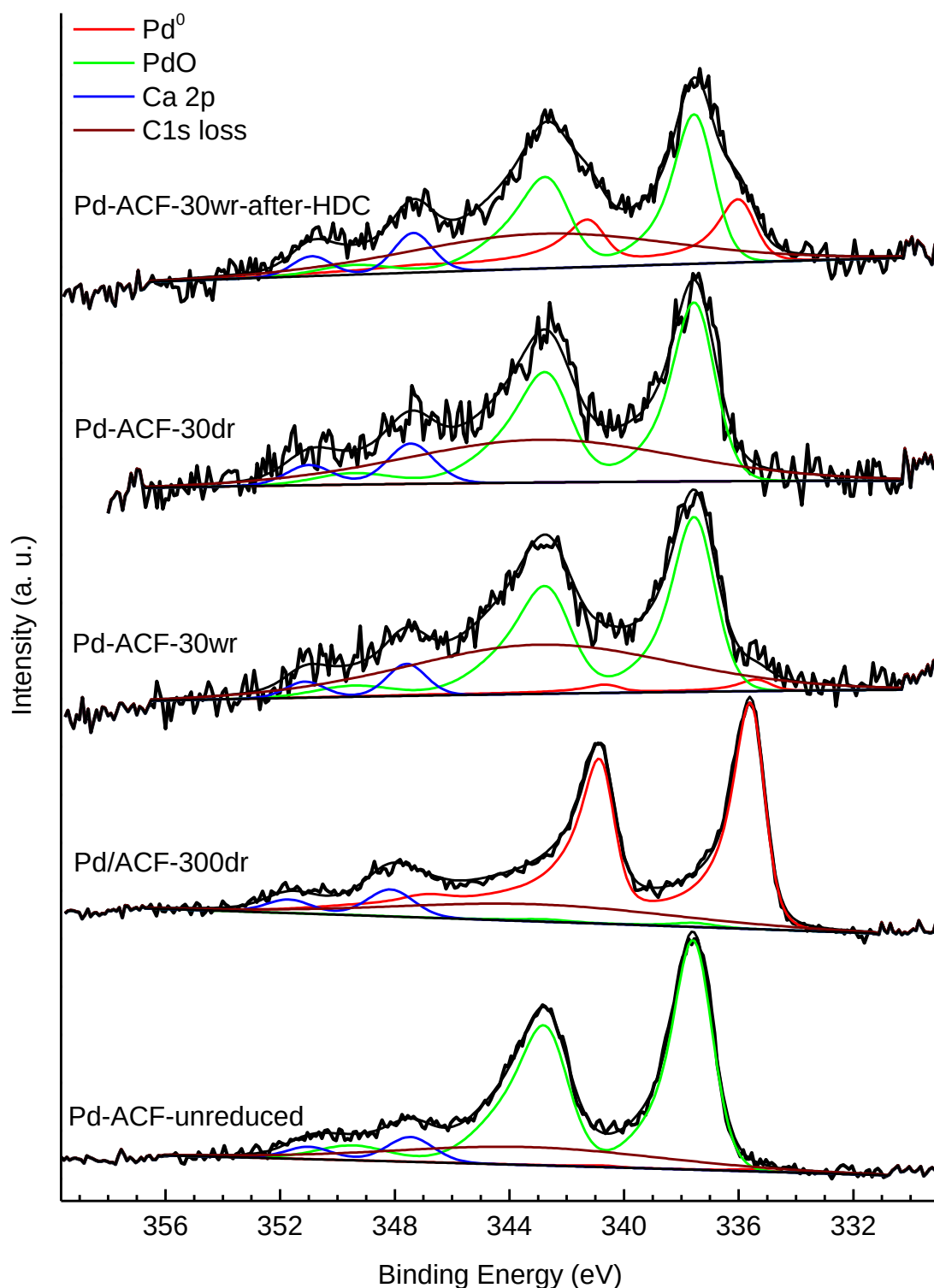


Figure S4. Pd3d XPS spectra of unreduced, reduced and used Pd/ACF catalyst. Reduction at 300°C was performed in-situ in the catalytic cell of the spectrometer. The spectra of unreduced and reduced at 300°C catalyst were recorded for a large granule, while other spectra – for ground powders.

A large catalyst granule was used to produce spectra of unreduced catalyst; then it was treated at 300°C in the catalytic cell of the XPS spectrometer in a H₂/Ar (5:95, vol.) flow. The spectra of the samples reduced at 30°C in dry and wet conditions were obtained using grinded granules of the catalyst. The powdered sample was reduced ex-situ at 30°C in the catalytic batch reactor

under the same conditions as before the catalytic test with a subsequent drying under H_2 flow in the case of wet treatment. The grinded catalyst Pd/ACF-30wr after catalytic test in HDC was dried under H_2 flow to record the spectrum of the used catalyst.

The signal-to-noise ratios in the spectra of unreduced and reduced at 300°C catalyst are much higher than those in the spectra of catalysts reduced at 30°C . This results from a core-shell nature of the catalyst granules. Their surface is enriched with palladium, which led to a more intense Pd3d signal in the surface sensitive XPS analysis. The palladium content on the surface of ground powders decreases leading to a lower signal-to-noise ratio in Pd 3d spectra.

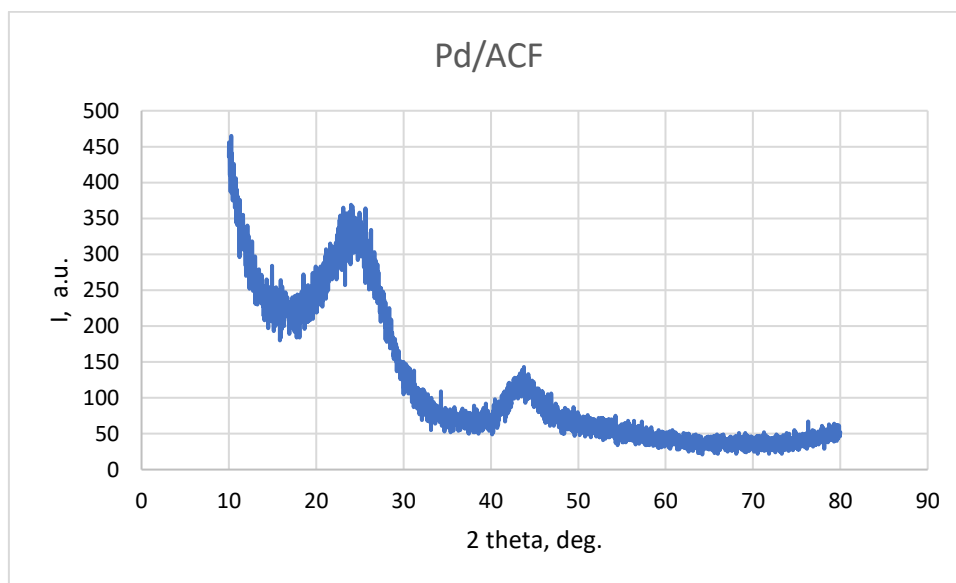


Figure S5 XRD profile of Pd/ACF.

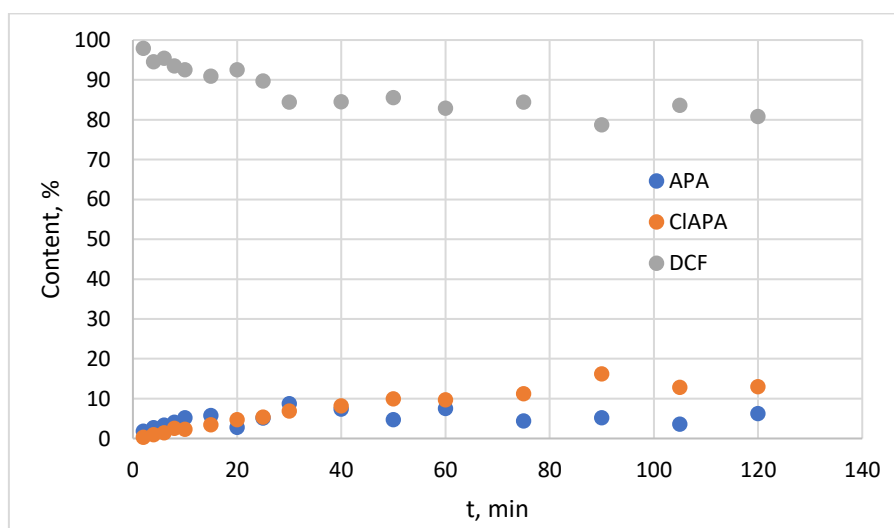


Figure S6. Relative contents of DCF and products of its HDC in water over Pd/ACF-30dr.

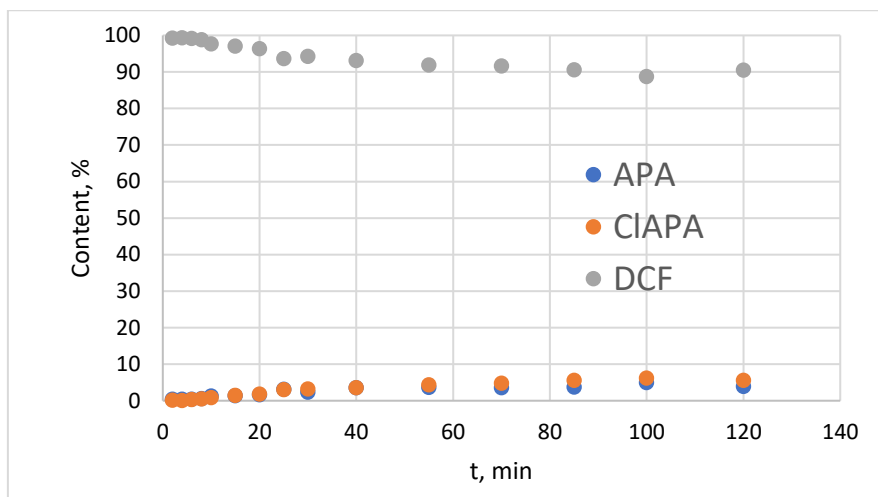


Figure S7 Relative contents of DCF and products of its HDC in water over Pd/ACF-300dr.

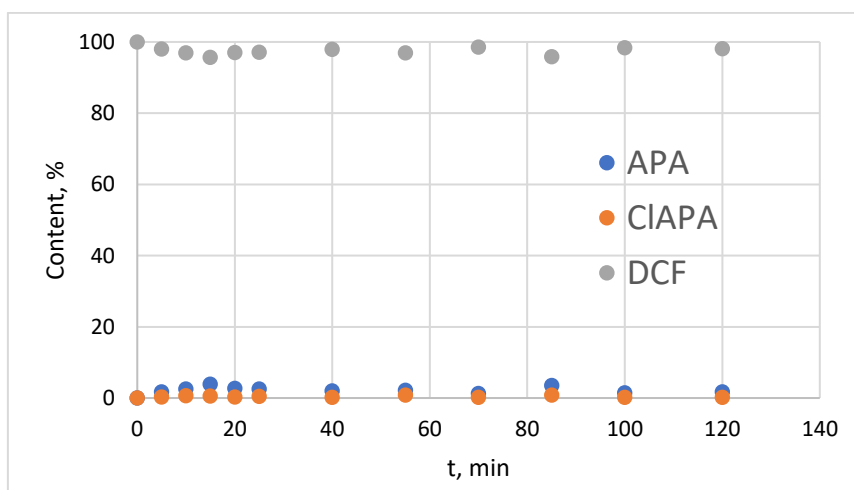


Figure S8 Relative contents of DCF and products of its HDC in water over pure ACF support.