

Supporting information

Continuous flow oxidation of HMF using supported AuPd-alloys

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Experimental

Materials and Chemicals

All chemicals were used without further purification. Palladium(II) chloride and Activated charcoal NORIT® Type ROX 0.8 (denoted as ROX; LOT 1383179) was received from FLUKA. Synthetic air (20.5 ± 0.5% O₂ in N₂) was obtained from AirLiquide. 2,5-furandicarboxylic acid (98%) (FDCA), sulfuric acid (50% v/v aq. soln.), hydrogen tetrachloroaurate(III) trihydrate and Zirconium(IV) oxide were purchased from Alfa Aesar. Sodium borohydride was purchased from Merck Millipore. 5-(hydroxymethyl)furan-2-carboxylic acid (HFCA), 5-formyl-2-furancarboxylic acid (FFCA) and 2,5-diformylfuran (DFF) were received from TCI. Potassium hydroxide was received from VWR chemicals. 5-(hydroxymethyl)furfural (≥99%) (HMF), poly(vinyl alcohol) (PVA; M_w =9000-10000), hydrochloric acid (36%) were purchased from Sigma-Aldrich. Sodium carbonate was obtained from Roth. Titanium(IV) oxide (P25) was purchased from Acros Organics.

Catalyst synthesis

AuPd-alloyed particles with an intended ratio of 52:48 were prepared according to a method previously published by our group. In brief, PdCl₂ ($m = 0.0222$ g) and HAuCl₄·3 H₂O ($m = 0.0533$ mg) were dissolved in diluted HCl (3 mL conc. HCl in 77 mL H₂O) for about 3 h. Afterwards, 620 mL H₂O and poly(vinylalcohol) (PVA; $m(\text{Au+Pd}):m(\text{PVA}) = 1:0.95$; $m = 37.8$ mg) were added. The solution was stirred for 10 min and then a diluted NaBH₄ ($n(\text{NaBH}_4):n(\text{Au+Pd}) = 4:1$; $m = 39.4$ mg) solution was added. After further stirring for 30 min, the pH of the solution was adjusted by addition of either 50 vol.% H₂SO₄ or KOH (AC-ROX: pH=13, ZrO₂: pH=1, TiO₂: pH=1). Then, the support material ($m = 1.96$ g) was added to the solution corresponding to a AuPd-loading of 2 wt.%. The catalyst was further stirred overnight before filtering the catalyst off the solution. The catalyst was thoroughly washed with 500 mL H₂O and dried at 65 °C overnight.

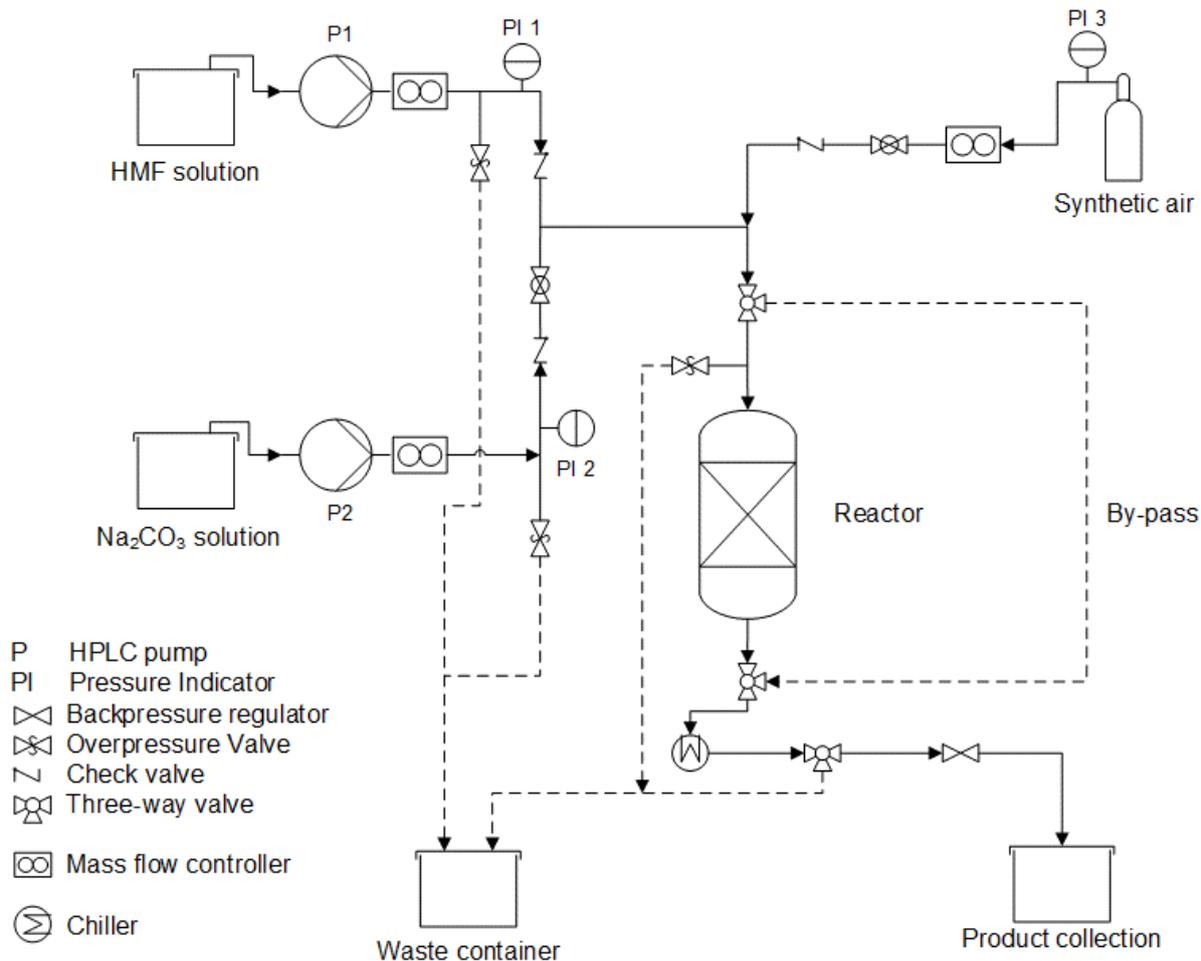
Adsorption of HMF, DFF, and FFCA on the support materials

The adsorption of HMF, DFF, and FFCA on the support materials was studied by adding 100 mg of the support to a 10 mL 0.01 M solution of either HMF, DFF, or FFCA in water. For activated carbon ROX, a concentration of 0.02 M was chosen due to the better adsorption properties. The compounds were adsorbed on the surface of the supports for about 5 h by stirring the suspension at room temperature. After filtering off the support materials, a sample for HPLC analysis was taken. The concentration at the end of the adsorption experiment was compared with the initial solution to determine the amount of adsorbed compound.

Continuous flow oxidation setup

Continuous flow oxidation of HMF was carried out in an in-house built reaction setup (Scheme S1 and Figure S1). The setup allowed for pressures up to 75 bar (limited by backpressure regulator) and was predominantly built with stainless-steel pipes. The flow of each reactant (aqueous HMF-solution and aqueous Na₂CO₃-solution) was controlled separately by a HPLC-pump (flusys WADOSE-LITE-HP-40-PE-I-S-C) with a peek-based pump head connected with a Bronkhorst MINI CORI-FLOW (M12-RGD-11-O-H). The flow-range was 0.02 to 0.4 mL min⁻¹. Synthetic air was dosed with a Bronkhorst EL-FLOW (F-221M-RGD-22-W) mass flow controller with a flow range of 12 to 600 mLn min⁻¹. First, both liquid streams were mixed prior to mixing with the airflow. Mixing was performed using a T-piece and a 0.5 micron stainless-steel filter. The mixed stream then passed through a tubular reactor prepared from stainless-steel with an outer-diameter of 3/8-inch. The reactor was heated with a tubular oven from HTM Reetz (LK 1100-15-300-1-V) equipped with an alumina (C610) isolation fitting to the outer-diameter of the reactor to ensure sufficient heat transfer. The oven temperature was controlled by a thermocouple (Type N), which was mounted in the catalyst bed. The product stream continued to a chiller, made from a 1/16-inch metal tube in a water bath. A backpressure regulator cartridge controlled the pressure of the setup (Upchurch Scientific gold coated SS-needle back pressure regulator cartridge) at the specified reaction pressure. The product solution was collected at the outlet.

The reactor was filled by putting two layers of a metal mesh with a glass wool plug on top at the bottom of the reactor. Atop silicon carbide (0.5 mm) was filled in the reactor until the start of the isothermal zone of the oven (Figure S2). The temperature profile of the reactor was measured with an external setpoint of 220 °C by moving a thermocouple inside the tubular reactor without any flow and measuring the temperature at every point after a few minutes of equilibration. The catalyst was filled above the silicon carbide. A sieve fraction of 200-450 μm was used for the catalyst. The reactor was mounted in a way that the stream was flowing downwards.



Scheme S1: Schematic flow diagram of the reaction setup for the continuous-flow oxidation of HMF.

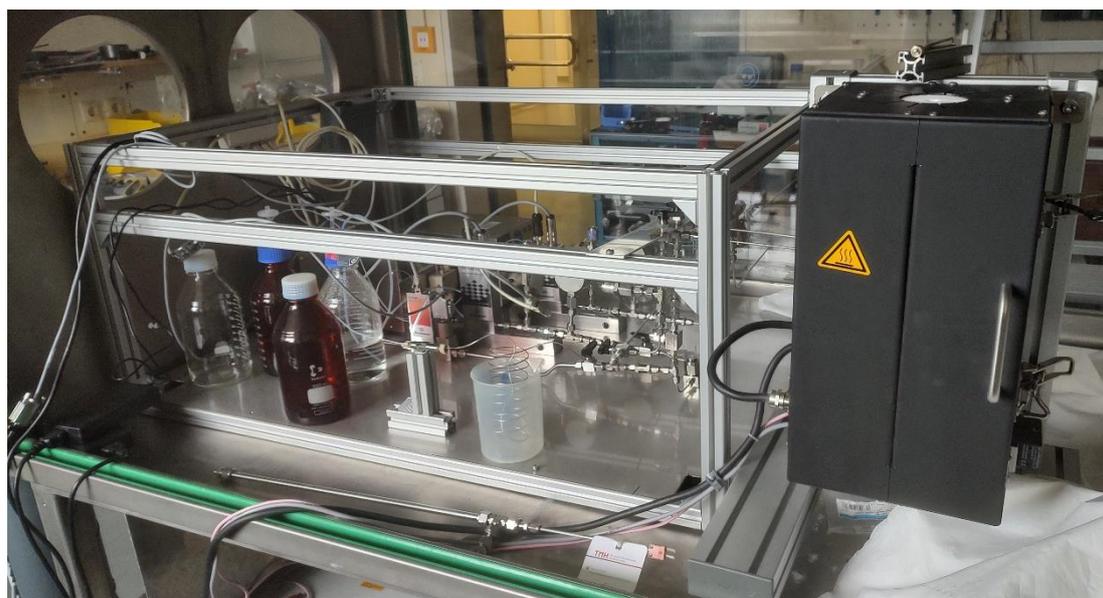


Figure S1: Picture of the continuous-flow oxidation setup with the oven on the right.

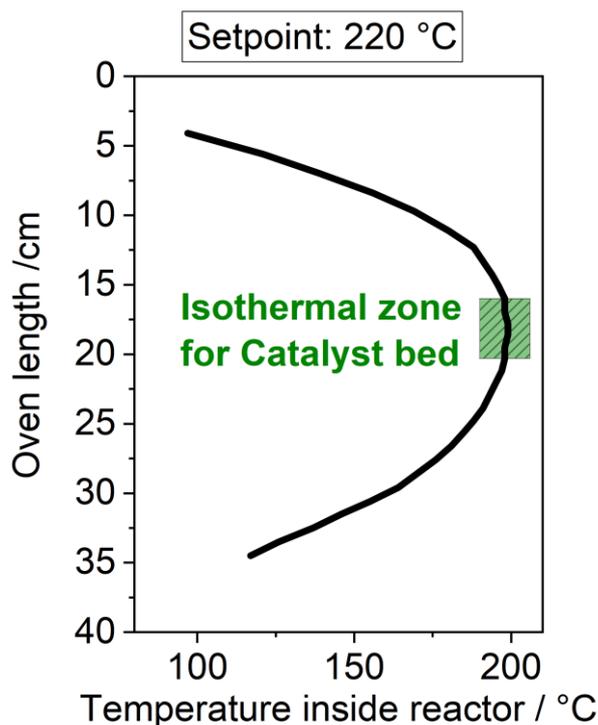


Figure S2: Temperature profile inside the tubular reactor.

Oxidation of HMF in batch reactor

All prepared catalysts were additionally tested in the batch oxidation of HMF in powder form in in-house built stainless-steel autoclaves. The autoclaves were equipped with polytetrafluoroethylene (PTFE) inlets (total volume of 50 mL) with a stirring bar for mixing of the solution (1400 rpm). 75.8 mg of catalyst (M:HMF 1:92, based on intended Metal loading of 2 wt.%) and 10 mL of aqueous HMF-solution (0.1 M) were filled in the reactor. The autoclaves were closed with a torque wrench and purged three times with synthetic air. Then they were pressurized at 15 bar with synthetic air and heated to 100 °C. After reaching the reaction temperature, the reaction was continued for 5 h. Afterwards, they were cooled down in an ice-bath, and they were depressurized after reaching room temperature. To calculate conversion and yields, 20 μ L samples were taken before and after the reaction for HPLC analysis.

High-performance liquid chromatography (HPLC)

For determination of conversion, yields and selectivities, a sample of the initial reaction mixture and samples of the product mixture were measured with HPLC. Segregation of the different compounds was achieved using a Bio-Rad Aminex HPX-87H column operated at 25 °C with a flow rate of 0.65 mL min⁻¹. 0.004 M H₂SO₄ was used as eluent.

Quantification of the compounds was performed using preliminary calibration curves (4 points) for a UV-Vis detector. The concentration of the initial HMF-solution measured in by-pass was used for the calculations as $t=0$.

$$X = \left(1 - \frac{n_{\text{HMF}, t}}{n_{\text{HMF}, t=0}}\right) \times 100\%$$

$$Y = \frac{n_{m, t}}{n_{\text{HMF}, t=0}} \times 100\%$$

$$\text{C-balance} = \left(\frac{Y_{\text{HFCA}}}{X} + \frac{Y_{\text{DFP}}}{X} + \frac{Y_{\text{FFCA}}}{X} + \frac{Y_{\text{FDCA}}}{X}\right) \times 100\%$$

Additional characterization and testing results

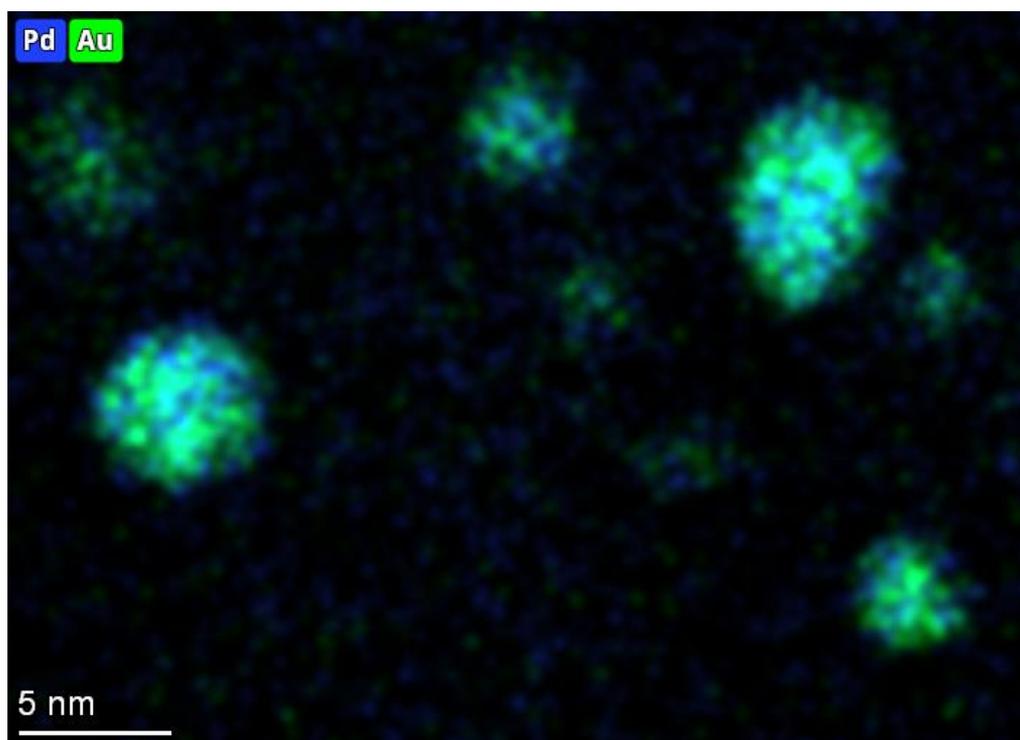


Figure S3: Energy dispersive X-ray mapping of AuPd/TiO₂ (blue: Pd, green: Au).

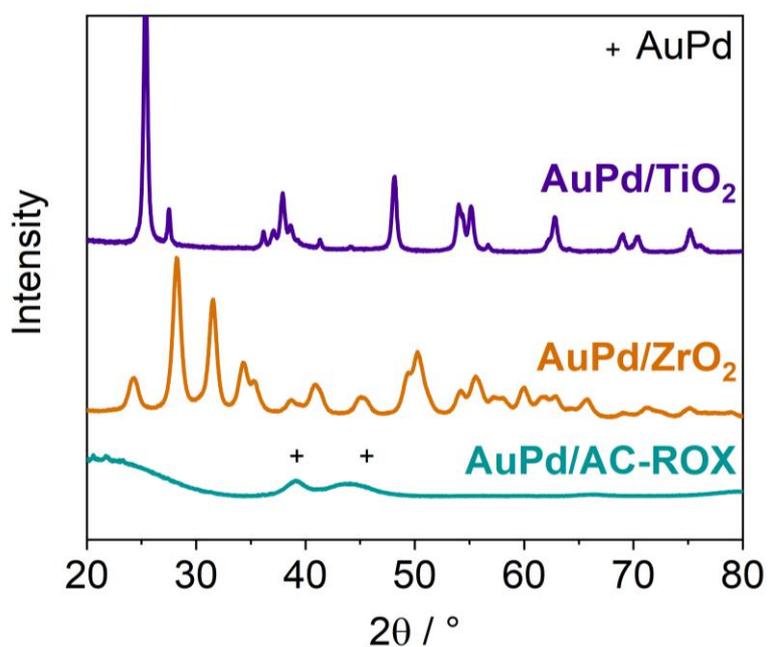


Figure S4: X-ray patterns of AuPd/TiO₂, AuPd/ZrO₂ and AuPd/AC-ROX. AuPd reference (+) is shown from ICSD collection code 58571.

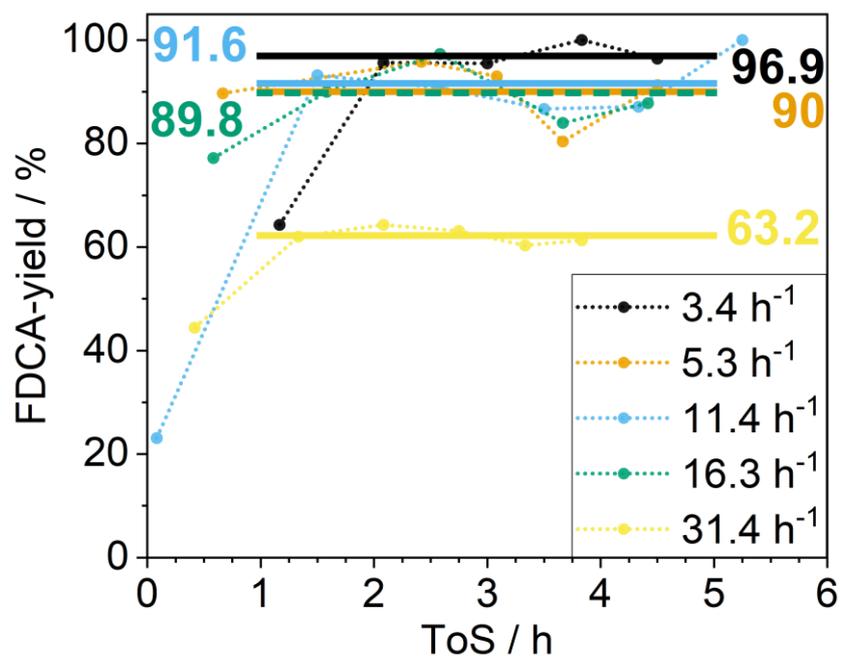


Figure S5: Influence of the LHSV on the FDCA yield with AuPd/AC-ROX in the continuous flow oxidation of HMF (0.1 M HMF, 6 eq. Na₂CO₃, 60 ± 10 bar, Air-flow: 20 mL min⁻¹).

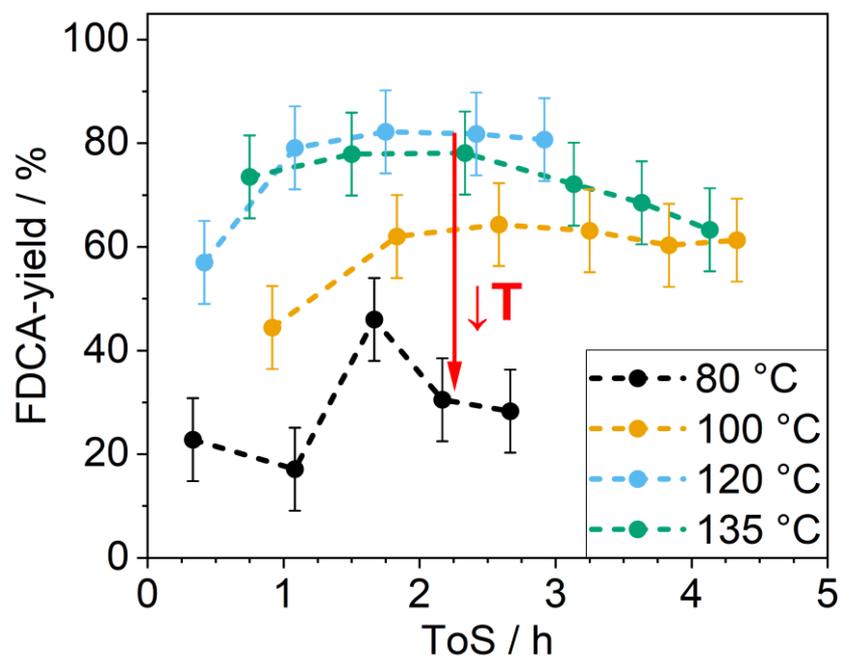


Figure S6: Temperature influence on the continuous flow oxidation of HMF with AuPd/AC-ROX (0.1 M HMF, 6 eq. Na₂CO₃, 55 ± 5 bar, Liquid-Flow: 0.22 mL min⁻¹, Air-flow: 20 mL min⁻¹, LHSV: 31.4 min⁻¹).

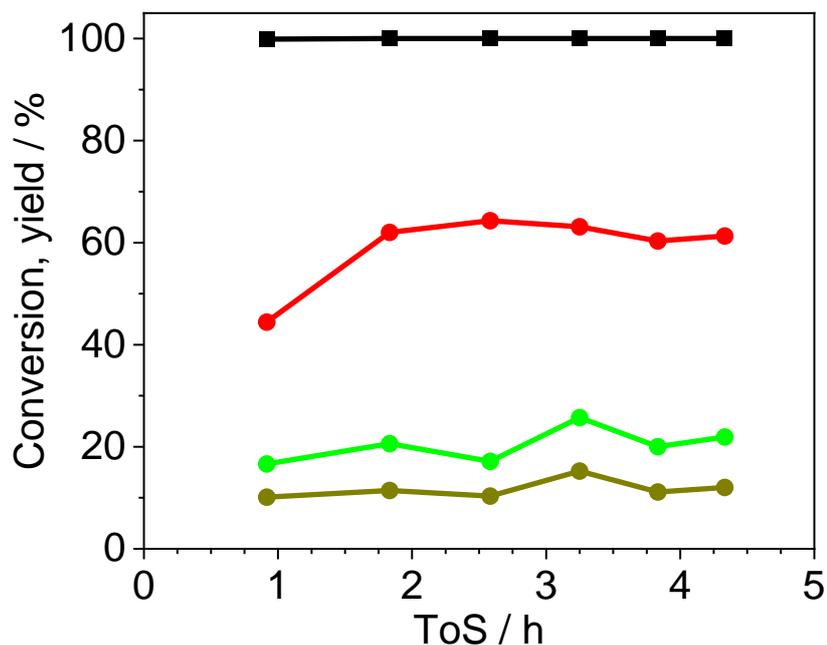


Figure S7: Continuous flow oxidation of HMF with AuPd/AC-ROX at 100 °C (0.1 M HMF, 6 eq. Na₂CO₃, 55 ± 5 bar, Liquid-Flow: 0.22 mL min⁻¹, Air-flow: 20 mL min⁻¹, LHSV: 31.4 min⁻¹).

Table S1: Average daily FDCA yields during the continuous oxidation of HMF with AuPd/AC-ROX (0.1 M HMF, 6 eq. Na₂CO₃, 58 ± 5 bar, Liquid-Flow: 0.22 mL min⁻¹, Air-flow: 20 mL min⁻¹, LHSV: 19.6 min⁻¹).

| Day | FDCA yield / % | FFCA yield / % | HFCA yield / % |
|-----|----------------|----------------|----------------|
| 2 | 74 | 3 | 12 |
| 3 | 72 | 3 | 14 |
| 4 | 78 | 4 | 14 |
| 5 | 77 | 3 | 13 |

Adsorption of HMF and its oxidation products on the support materials

Table S2: Quantification of HMF, DFF, and FFCA adsorption for AC-ROX, TiO₂, and ZrO₂ (room temperature, atmospheric pressure, 5 h for equilibration).

| Support | HMF adsorption ^[a] / mmol g ⁻¹ | DFF adsorption ^[a] / mmol g ⁻¹ | FFCA adsorption ^[a] / mmol g ⁻¹ |
|-----------------------|---|---|--|
| AC-ROX ^[b] | 1.43 | 1.95 | 1.88 |
| TiO ₂ | 0 | 0.04 | 0.17 |
| ZrO ₂ | 0 | 0.03 | 0.45 |

[a] substrate 0.01 M, 100 mg support, V=10 mL, [b] substrate 0.02 M

Characterization of spent catalyst

To determine the adsorption properties of the spent catalyst after the oxidation of HMF in continuous flow (0.1 M HMF, 6 eq. Na₂CO₃, 100 °C, 67 ± 5 bar, LHSV: 31.4 min⁻¹, 6 h time on stream), an experiment with AuPd/AC-ROX in a sieve fraction of 200-300 μm was performed. The smaller sieve fraction allowed for a separation of the catalyst from SiC (~500 μm) by sieving, which was used to maintain the catalyst bed in the isothermal zone of the reactor. After the experiment, the catalyst was flushed with distilled water for washing before being removed from the reactor and dried. The adsorption capacity of the spent catalyst for HMF and FFCA was tested by stirring the catalyst in 0.02 M solutions of each substrate, similarly to the adsorption experiments with the bare support materials (Table S3). We observed, that reactants from the oxidation experiment were still adsorbed on the surface of the catalyst even after washing and were exchanged with the respective substrate (HMF or FFCA) during the adsorption experiment. Interestingly, the adsorption capacity for FFCA was decreased by far in comparison to the initial support material, while the capacity for HMF varied only slightly (87%) from the initial activated carbon. Thus, a high capacity for the adsorption of HMF was preserved in the spent catalyst, facilitating the oxidation of HMF.

In addition, XRD of the spent catalyst was measured. The diffractogram showed a broad reflection at 38.97°, which is specific for the AuPd alloy. The position of the reflection was only slightly (<0.1°) shifted in comparison to the fresh catalyst. Only one reflection was observed and no indications of a phase segregation of the alloy were found. The full width at half maximum decreased slightly compared to the fresh catalyst, suggesting that the particles might sinter slightly during operation in the first hours. Nevertheless, the alloy shows a good stability in the process, in agreement with

the long-term study, which gave a stable FDCA yield over 90 h ToS. Thus, any sintering is not the major cause of deactivation.

Table S3: Quantification of HMF and FFCA adsorption on a spent AuPd/AC-ROX catalyst (200-300 μm sieve fraction, room temperature, atmospheric pressure, 5 h for equilibration, substrate 0.02 M, 30 mg catalyst, 3 mL H_2O).

| Experiment | HMF / mmol g^{-1} | FFCA / mmol g^{-1} |
|--|----------------------------|-----------------------------|
| Corrected adsorption on spent catalyst | 1.25 | 0.60 |

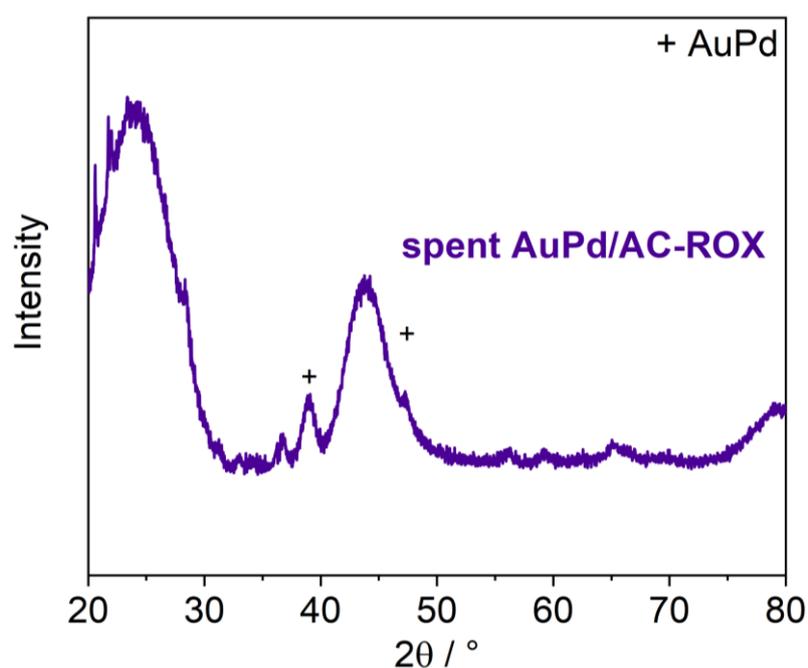


Figure S8: X-ray pattern of spent AuPd/AC-ROX after the oxidation of HMF in continuous flow (0.1 M HMF, 6 eq. Na_2CO_3 , 100 $^\circ\text{C}$, 67 ± 5 bar, LHSV: 31.4 min^{-1} , 6 h time on stream). AuPd reference (+) is shown from ICSD collection code 58571.

Investigation of mass transport limitations:

To determine if external mass transport limitations were limiting the reaction kinetics, the reaction was performed three times under the same reaction conditions (0.1 M HMF, 6 eq. Na_2CO_3 , 55 ± 5 bar, 100 $^\circ\text{C}$) with AuPd/AC-ROX and the same sieve fraction. However, the liquid flow, air flow and catalyst mass were increased proportionally (1.) Liquid-Flow: 0.22 mL min^{-1} , Air-flow: 20 mL min^{-1} , Catalyst mass: 120 mg; 2.) Liquid-Flow: 0.28 mL min^{-1} , Air-flow: 25 mL min^{-1} , catalyst mass: 153 mg; 3.) Liquid-Flow: 0.34 mL min^{-1} , Air-flow: 31 mL min^{-1} , catalyst mass: 185 mg). In this way, we could ensure the same LHSV of 31.4 min^{-1} for all three reactions (Figure S5).

We observed a decrease of the average FDCA-yield over multiple hours with increasing catalyst bed length. Interestingly, also the fluctuations caused by pulsing of the high-pressure pump were enhanced. However, the deviation between the reaction with a liquid-flow of 0.22 mL min^{-1} and 0.28 mL min^{-1} was small with just 2.8%. Hence, the external transport limitations were decreasing with shorter catalyst bed length. All reactions shown for the continuous flow oxidation of HMF were performed in a range of 0.1 to 0.22 mL min^{-1} where no major limitations by external transport could be observed.

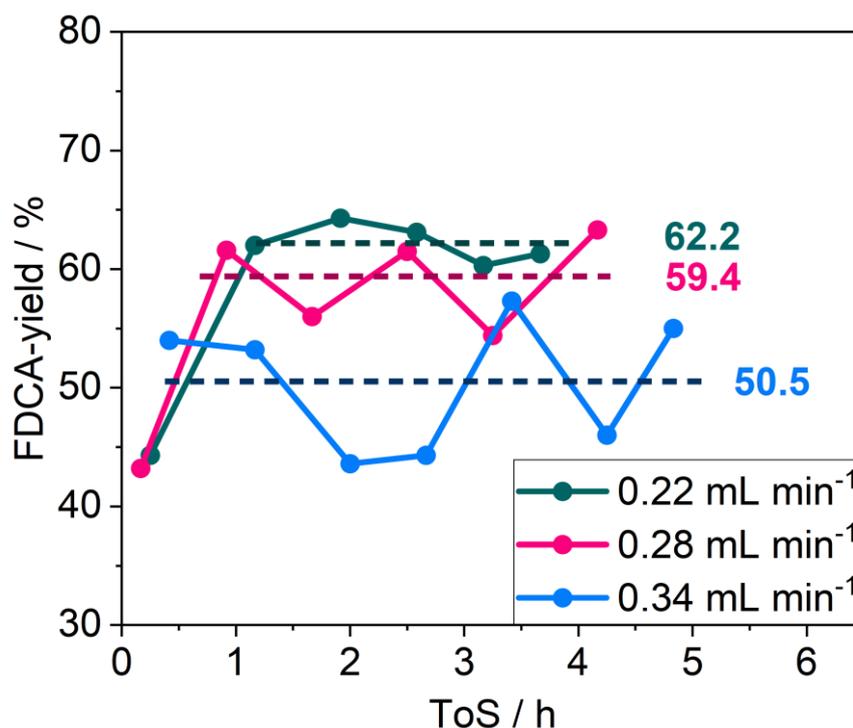


Figure S9: Continuous flow oxidation of HMF with AuPd/AC-ROX at different liquid-flow rates (0.1 M HMF, 6 eq. Na_2CO_3 , $100 \text{ }^\circ\text{C}$, $55 \pm 5 \text{ bar}$, LHSV: 31.4 min^{-1}). The air-flow and the catalyst mass were adjusted to keep a LHSV of 31.4 min^{-1} .