

Supporting Information: Selective reduction of oxalic acid to glycolic acid at low temperature in a continuous flow process

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Abstract

Next to biomass, CO₂ is the only other promising carbon source to replace fossil feedstocks to produce chemicals and polymers. In a CO₂ fed chemical industry, new platform chemicals will arise. Oxalic acid derived from CO₂ based formate is one of them. It can be converted to a wide array of chemicals including ethylene glycol, or carboxylic acids such as glycolic acid. Glycolic acid is currently a fossil-based monomer used in the production of polyesters. Today the most common route from oxalic acid to glycolic acid proceeds via the oxalic acid di-esters as intermediates and thus requires multiple steps. Recently, we proved that the direct reduction of oxalic acid to glycolic acid at high yields is possible. In this work, we translate this process into a stable and continuous process in industrially relevant conditions. We lowered the reaction temperature by 25°C to 50°C, reduced the reaction time from hours to minutes and proved the catalyst stability over 100 hours using oxalic acid derived from CO₂. This research lays the foundation of an industrial continuous process for the direct reduction of oxalic acid to glycolic acid and closes a gap in the route from CO₂ to chemicals.

1 Complementary figures and tables to Main Article

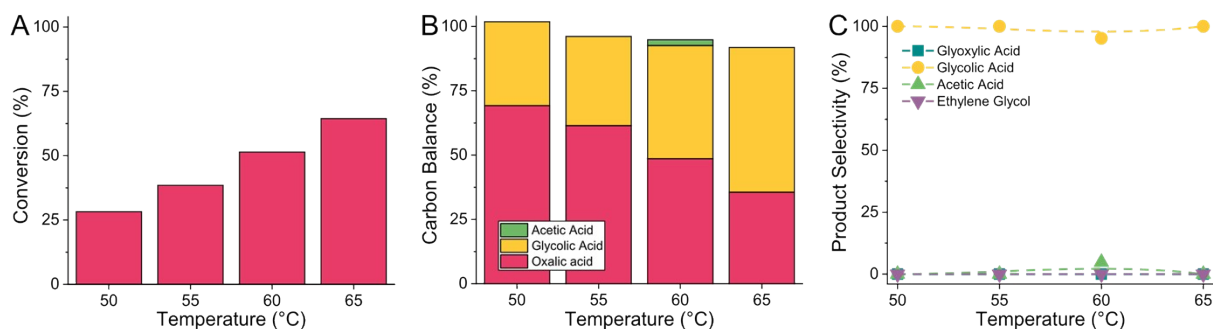


Figure S1 Results of SFU experiment of oxalic acid reduction for different temperatures. Conversion (A), Selectivity (B), and Carbon Balance (C) data as obtained by liquid chromatography (LC). Conditions during reactions: Temperature = 50-65 °C, Pressure = 60 bar, Feed = Oxalic Acid (5 wt.%) in water, Flow of Feed = 0.2 ml min⁻¹, Flow of Gas (H₂) = 200 ml min⁻¹. This reaction used a commercial catalyst provided by Johnson Matthey with the following characteristics (9.76 wt.% Ru/C, 0.5 wt.% moisture) as a catalyst.

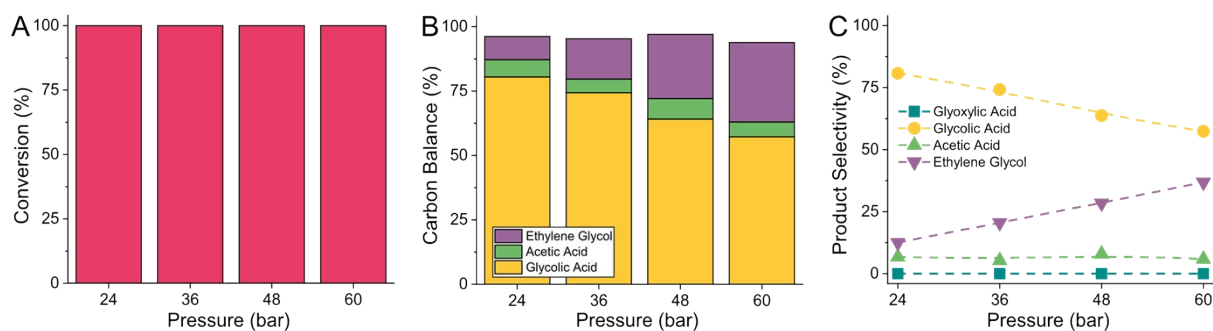


Figure S2 Results of SFU experiment of oxalic acid reduction for different pressures. Conversion (A), Selectivity (B), and Carbon Balance (C) data as obtained by liquid chromatography (LC). Conditions during reactions: Temperature = 80 °C, Pressure = 24-60 bar, Feed = Oxalic Acid (5 wt.%) in water, Flow of Feed = 0.1 ml min⁻¹, Flow of Gas (H₂) = 200 ml min⁻¹. This reaction used a commercial catalyst provided by Johnson Matthey with the following characteristics (9.76 wt.% Ru/C, 0.5 wt.% moisture) as a catalyst.

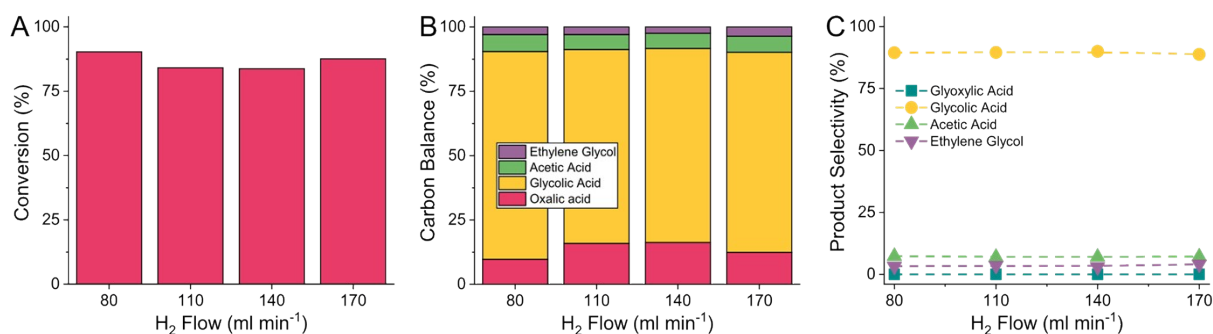


Figure S3 Results of SFU experiment of oxalic acid reduction for different hydrogen flow rates. Conversion (A), Selectivity (B), and Carbon Balance (C) data as obtained by liquid chromatography (LC). Conditions during reactions: Temperature = 70 °C, Pressure = 24 bar, Feed = Oxalic Acid (5 wt.%) in water, Flow of Feed = 0.1 ml min⁻¹, Flow of Gas (H₂) = 80-170 ml min⁻¹. This reaction used a commercial catalyst provided by Johnson Matthey with the following characteristics (9.76 wt.% Ru/C, 0.5 wt.% moisture) as a catalyst.

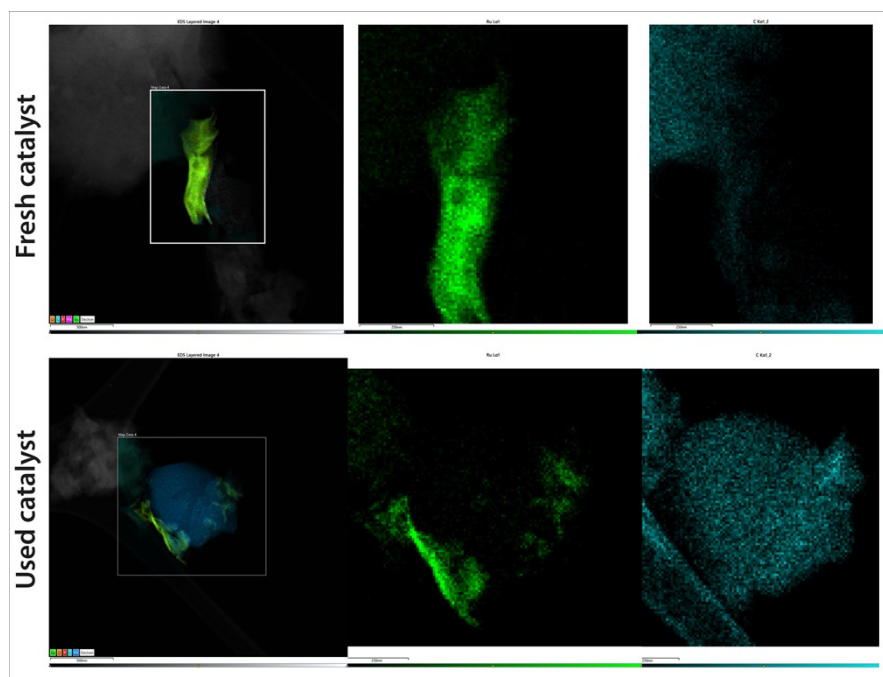


Figure S4 High-resolution tunnel electron microscope (HRTEM) images and elemental mapping with Energy-dispersive X-ray spectroscopy (HRTEM-EDS) of commercially available 9.78 wt.% Ru/C catalyst from Johnson Matthey before and after 100h use in trickle-bed flow reactor for reduction of oxalic acid to glycolic acid in absence of potassium.

2 Experimental details

2.1 Reactants

All additional reactants: Oxalic Acid ($C_2H_2O_4$), Glycolic Acid ($C_2H_4O_3$), Glyoxylic Acid ($C_2H_2O_3 \cdot H_2O$), Acetic Acid ($C_2H_4O_2$), and Ethylene Glycol ($C_2H_6O_2$) were obtained from commercial suppliers (Sigma-Aldrich®), dried and stored in a dry environment. Otherwise, the chemicals were not further processed. All water used during this work was filtered using a Millipore system.

2.2 Commercial Catalysts

We used a commercial catalyst with 9.76 wt.% Ruthenium on Carbon supplied by Johnson Matthey (ID: 110005, LOT M17160). The catalyst contained 0.5% moisture.

2.3 Catalyst Preparation and Reduction

We crushed the extrudates with a ceramic mortar and sieved the catalyst to obtain a mesh size between 105-200 μm . The particles were transferred to a ceramic crucible and transferred to a tubular furnace for reduction. In the furnace, the particles were treated with a gas mixture of 7% H_2 in N_2 with a flow rate of 100 $ml\ min^{-1}$. The temperature inside the furnace was increased with a ramp of 10 $K\ min^{-1}$ until it reached 350°C. This temperature was kept constant for 180 minutes. Upon completion of the reduction procedure, the temperature was slowly decreased, and the 7% H_2/N_2 mixture was flushed out with a flow of pure nitrogen.

2.4 Trickle-bed flow reactor

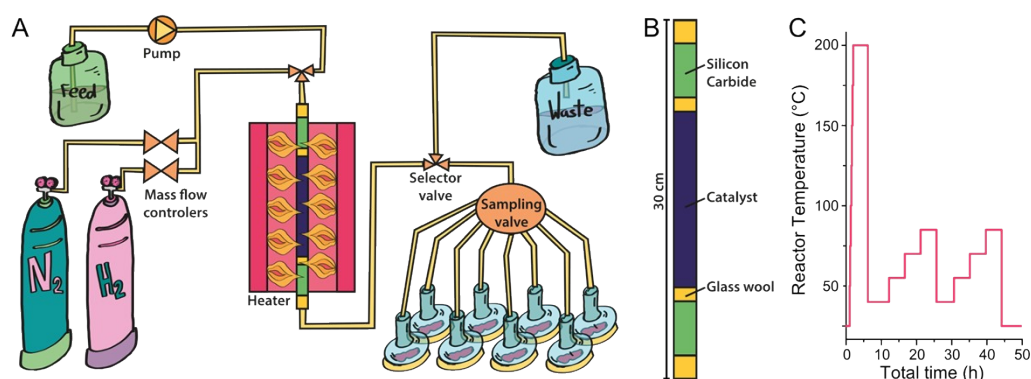


Figure S5 A) Schematic drawing of trickle-bed flow reactor system used for the development of Oxalic acid to Glycolic acid reduction reaction. The reactor itself is fed from an oxalic acid tank via an HPLC pump and the gas is fed individually via mass-flow controllers. After passing through the reactor, the exiting liquids and gases can either be directed to a waste container or a selector valve which allows the sequential collection of 8 samples over the time of an experiment. B) Packing of catalyst in the reactor. C) Exemplary test program here for reaction temperature starting with an in-situ pre-reduction at 200°C followed by two successive tests at four temperatures.

In this work, we used a trickle bed reactor system (Figure S5A). At the core is a 30 cm long reactor stainless-steel reactor, with a diameter of $\frac{1}{4}$ inch and a reactor volume of 5 ml. 1.82 ml of the reactor volume is within the isothermal zone of the system and loaded with a catalyst. The gas flow is controlled by 2 mass flow controllers (MFC's) for both nitrogen and hydrogen. The Nitrogen MFC is capable of a flow up to 1000 ml min^{-1} , whereas the Hydrogen MFC can go up to 200 ml min^{-1} . The pressure in the reactor is controlled by a pressure indicator, which puts pressure on a back pressure regulator located after the reactor to regulate the pressure inside the system.

The feed section consists of a Jasco HPLC pump. The flow rate range is between 0.1 and 5 ml min^{-1} . This system has a selector valve system with 8 separate sample vials, to collect products. During the experiments, the feed solution was heated and stirred continuously to ensure a homogeneous concentration of oxalic acid and prevent its precipitation.

A schematic drawing of the loaded reactor is shown in Figure S5B. Equilibration experiments were performed before this study on this reactor to determine that the isothermal zone lies between 9 and 20 cm from the bottom up. The catalyst was crushed with a ceramic mortar and sieved to obtain particles between 105 and $200 \mu\text{m}$. For each reactor loading, the maximum volume (1.82 ml) of catalyst was used to fill up the isothermal zone of the reactor. The remaining part of the reactor was filled up with layers of Silica Carbide (SiC) and Quartz wool. During some later experiments, powder catalyst was added instead of fixed particle size. When powder catalyst was used, the silica carbide was instead replaced by Zirblast.

Each experiment uses a different recipe, which for example, can have altering pressures, temperatures, or any other parameters we select beforehand. This procedure describes an example of a recipe in which we examined the effect of different temperatures (Figure S5C).

First, the reactor was loaded and installed in the unit. The reactant feed was added to an 800 ml bottle that was actively heated (40°C) and stirred during the reaction to create a homogeneously distributed concentration in the reactant. HPLC pumps were primed before the start of a reaction.

Before starting the experiment, we perform a 1 hour-long step of just nitrogen flow to blow out any potential liquids remaining within the system. First, we perform an in-situ pre-reduction on the catalyst for which we slowly increase the temperature to 200°C for 4 hours. During the heating, the pressure is increased to 50 bar and changed the gas from nitrogen to hydrogen. By slowly increasing the pressure, the chance of potential damage on the membrane of the backpressure regulator is

reduced. Slowly increasing the temperature prevents the temperature from rising significantly higher than the setpoint during the heating phase.

After the pre-reduction, the reactor is set to the desired reaction conditions. The temperature was cooled down to the desired temperature, which in this case was 40°C. The wait time (30 minutes for step 10) only starts when the desired conditions are reached. Cooling down from 200°C to the desired temperature can take multiple hours. When the reaction temperature is reached, we start the reactant feed flow with a flow of 1 ml min⁻¹ for 60 minutes. Initial flow is always at least 1 ml min⁻¹ to fill the system with the liquid. The liquid feed already goes through the entire system during this step, but the selector valve directs it towards the “waste” jerrycan.

Once the reactor is filled, we start the actual reaction. The reactant feed flow is decreased to 0.1 ml min⁻¹, the lowest possible flow in this system, and equilibrated for 3.5 hours. This step aims to avoid mixing of reactant feed that has been treated with different conditions (e.g., feed: 0.1 vs. 1 ml min⁻¹). After 3.5 hours we collect a sample for 1 hour. During this step, the feed which has reacted with the reactor is directed into one of the sample bottles by the selector valve. This liquid is the product that will be analysed by liquid chromatography eventually. The equilibration and sample step procedure repeat in total 8 times for the different selected conditions, which in this case is two series of a temperature range of 40, 55, 70, and 85°C. In the last step, the temperature is cooled down to 25°C, and all the other parameters are turned to 0.

After each experiment, we perform a cleaning procedure and replaced the feed with demineralized water in combination with a nitrogen flow. For the last steps of this recipe, only nitrogen is flowed through the system to flush out any liquids for a future experiment.

3 Blank experiments

We performed control experiments to exclude any possible reaction of the trickle bed reactor with the reactant feed. For the control experiments, we replaced the catalyst in the isothermal zone of the system with silica carbide. We loaded the reactor only with different layers of silica carbide and quartz wool, all of which we expected to be inert.

We observed near-zero conversion of oxalic acid during these reactions, as can be seen in Figure S6. The observed conversion lies within the margin of error of the analysis method. We did not observe any reaction products by liquid chromatography, visible in the carbon balance, shown in Figure S6B, which shows only oxalic acid. The different reactant feed flow rates (5 to 0.1 ml min⁻¹) examined during this experiment did not impact the yield, which we observed in the conversion and carbon balance data. We conclude that no oxalic acid converts in the absence of any catalyst. Therefore, any catalytic reactivity visible can be attributed to the catalyst.

In the second series of control experiments, we investigated the influence of hydrogen presence. In this experiment, we loaded the commercial catalyst (9.76 wt.% Ru/C, 0.5 wt.% moisture) in the isothermal zone of the reactor. Instead of a hydrogen flow, we examined different flows of nitrogen. The reaction conditions during this experiment. This experiment yielded no conversion or formation reaction products, as shown in Figure S7. We observed no reaction products as expected from the low conversion, which is also visible in the carbon balance that is equal to, or within the expected margin of error of 100%. We conclude that hydrogen is essential as a reactant in this reaction.

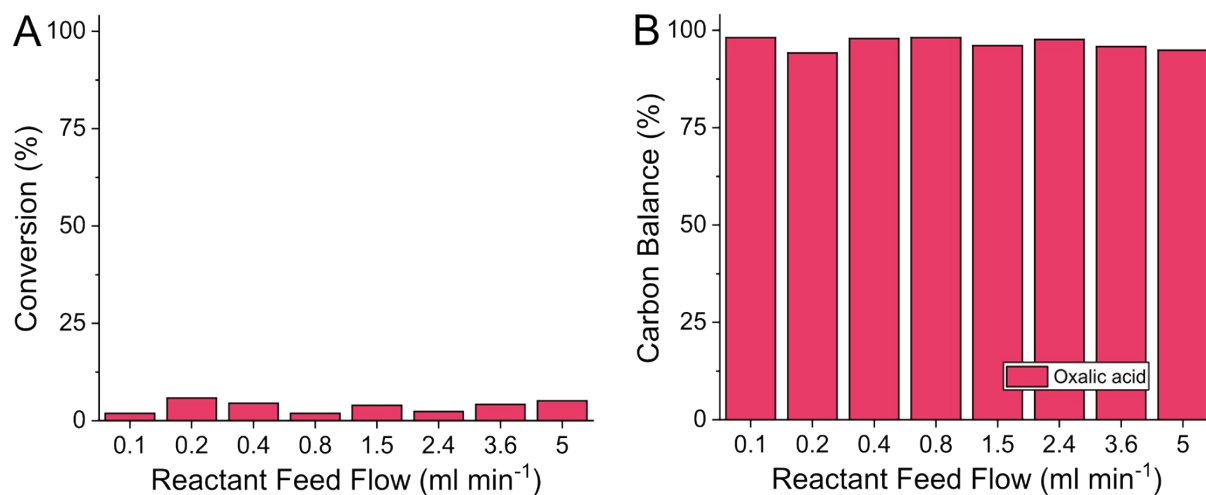


Figure S6 Results of SFU control experiment of oxalic acid in the absence of a catalyst. Conversion (A), Selectivity (B), and Carbon Balance (C) data as obtained by liquid chromatography (LC). Conditions during reactions: Temperature = 75°C, Pressure = 50 bar, Feed = Oxalic Acid (5 wt.%) in demineralized water, Flow of Feed = 5-0.1 ml min⁻¹, Flow of Gas (H₂) = 200 ml min⁻¹. No catalyst was loaded in the reactor for this experiment.

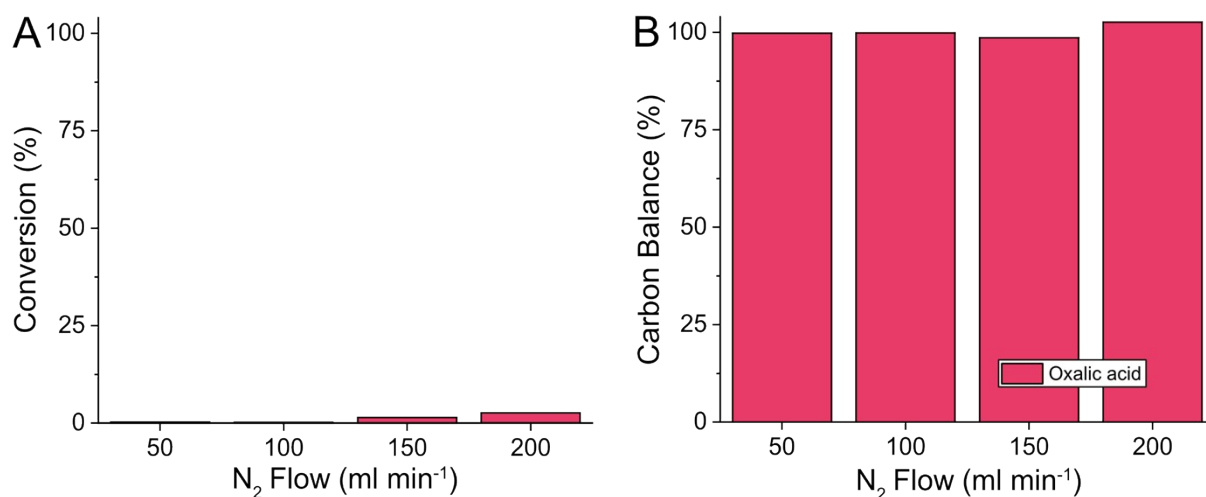


Figure S7 Results of SFU control experiment of oxalic acid in the absence of Hydrogen. Conversion (A), Selectivity (B), and Carbon Balance (C) data as obtained by liquid chromatography (LC). Conditions during reactions: Temperature = 75°C, Pressure = 50 bar, Feed = Oxalic Acid (5 wt.%) in demineralized water, Flow of Feed = 5-0.1 ml min⁻¹, Flow of Gas (N₂) = 200-4 ml min⁻¹. This reaction used a commercial catalyst provided by Johnson Matthey with the following characteristics (9.76 wt.% Ru/C, 0.5 wt.% moisture)) as a catalyst.

We investigated the effect of using glycolic acid dissolved in demineralized water as a feedstock in the trickle bed reactor. For most of the experiments performed, we used oxalic acid (5 wt.%) dissolved in demineralized water as a feed solution. Except for the experiments that used a ruthenium-tin catalyst, the formation of acetic acid occurred consistently, independent of the reaction conditions. The goal of this experiment was to investigate more into the formation of acetic acid. Santos et al.¹ report that acetic acid forms directly from oxalic acid, unlike ethylene glycol, which forms directly from glycolic acid. However, they do not report a mechanism for the formation of acetic acid or use different conditions during their reaction. We used the commercial catalyst from Johnson Matthey (9.76 wt.% Ru/C, 0.5 wt.% moisture) in this reaction. Only one temperature (70°C) and pressure (60 bar) were selected for this experiment since the main goal was only to investigate the formation of acetic acid, rather than optimization of the reaction. We observed no acetic acid formed during the reaction (Figure S8). This result confirms the earlier observation by Santos et al.¹ that acetic acid is a reaction product that forms from oxalic acid. We analysed eight samples since the concentration of acetic acid is often low and therefore can be under the detection limit. By having a significant number of samples,

we excluded this possibility. We still observed ethylene Glycol formation for all measured samples. This result is in line with all our earlier observations and the report of Santos et al.¹

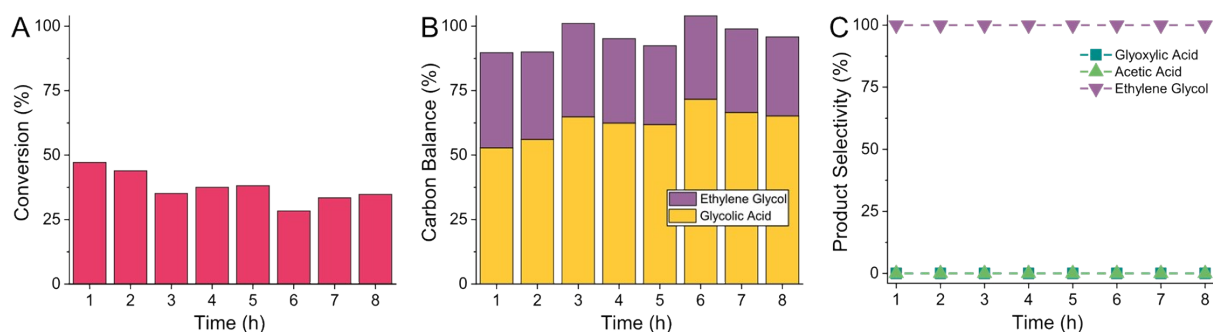


Figure S8 LGR63 Results of SFU experiment using glycolic acid as a feedstock. Conversion (A), Selectivity (B), and Carbon Balance (C) data as obtained by liquid chromatography (LC). Conditions during reactions: Temperature = 70°C, Pressure = 60 bar, Feed = Glycolic Acid (5 wt.%) in water, Flow of Feed = 0.1 ml min⁻¹, Flow of Gas (H₂) = 200 ml min⁻¹. This reaction used a commercial catalyst provided by Johnson Matthey with the following characteristics (9.76 wt.% Ru/C, 0.5 wt.%)

4 Catalyst Characterization

4.1 X-ray diffraction (XRD)

Before powder-XRD measurements, we crushed the catalysts using a ceramic mortar. Measurements were generally performed at an angle (2θ) of 3 to 90 degrees at a rate of 1 °/min and a step size of 0.05°. We used a MiniFlex-II diffractometer from Rigaku with a Cu Kα x-ray tube as a source. The X-ray tube was operated at 30kV and 15 mA. The received spectra were analysed and assigned using a spectral library within the PDXL software from Rigaku.

4.2 HRSTEM

High-Resolution Scanning Transmission Electron Microscopy (HRSTEM) images and chemical composition mapping with atomic resolution by Electron Energy Loss Spectroscopy (STEM-EELS) were taken using a High Angular Annular Dark Field detector (HAADF) in a probe-corrected FEI Titan 60-300 operated at 300 kV and equipped with a high brightness X-FEG and a CESCOR Cs-probe corrector allowing for the formation of an electron probe of mean size of 0.09 nm.

4.3 ICP-OES

We analysed liquid samples for the presence of Ru after performing a reaction in the trickle-flow reactor. The goal was to evaluate the potential leaching of and catalyst by oxalic acid. The spectra were measured in an Optical Emission Spectrometer Avio200 of PerkinElmer. An internal standard with a known concentration of Yttrium was used for correcting the ICP data.

5 Product analysis

5.1 Sample analysis - HPLC

The samples for analysis were prepared by diluting with demineralized water to a theoretical stock solution concentration of 0.67 mg stock mL⁻¹. High Performance Liquid Chromatography (HPLC) was used to determine oxalic acid, glycolic acid, glyoxylic acid, acetic acid, and ethylene glycol concentration. HPLC was performed on an Agilent 1260 Infinity II HPLC system for analysis of liquid samples, equipped with an autosampler, heated column compartment, diode-array detector (DAD) and refractive index detector (RID). The column was an Aminex HPX-87H (300 × 7.8 mm; dp 9 μm). 7 μL sample was injected and separated using 5 mM H₂SO₄ in MilliQ water (flow rate: 0.6 mL/min, 30 °C) as the mobile phase. All conditions are listed in the table below.

Table: Conditions used for liquid chromatography

Instrument	Shimadzu HPLC instrument with RID detection
Column	Aminex HPX-87H (300 × 7.8 mm; dp 9 μm)
Oven temperature	70 °C
Isocratic flow	0.6 mL/min
Mobile phase	0.005 M H ₂ SO ₄
Internal standard	Each analysis is started with a known standard and mixture
Sample preparation	Samples are diluted in demineralized water to theoretical stock solution concentration of 0.67 mg stock mL ⁻¹

5.2 Calculus

All presented values for conversion, selectivity, yield and carbon balance were calculated from the concentrations of each component in the product using the equations below:

$$\text{mol of product in original sample} = \text{concentration product (M)} \times \text{dilution coefficient} \quad (\text{Eq. S1})$$

$$\text{Conversion} = \frac{\text{mol product}}{\text{mol used oxalic acid}} \quad (\text{Eq. S2})$$

$$\text{Selectivity product} = \frac{\text{mol product}}{\text{mol used oxalic acid} - \text{mol unreacted oxalic acid}} \quad (\text{Eq. S3})$$

$$\text{Yield} = \text{Conversion} \times \text{Selectivity product} \times 100\% \quad (\text{Eq. S4})$$

$$\text{Carbon balance} = \frac{\text{sum (mol products)}}{\text{sum (mol products)} + \text{mol unreacted oxalic acid}} \quad (\text{Eq. S5})$$

6 Experiment details

6.1 Blank experiment with no catalyst

The goal of this experiment was to investigate if oxalic acid does react with the single flow unit, which includes the trickle bed reactor and all the other tubes. No catalyst was used during this reaction, and instead, a reactor was filled with silicon carbide and quartz wool. We investigated 8 different residence times which were achieved by changing the different flow rates from 5 to 0.1 ml min⁻¹ for this experiment. Additionally, 8 different hydrogen flow rates from 200 to 4 ml min⁻¹ were examined to keep the gas/liquid ratio constant at 40. The conditions during the experiment are shown in Table S1.

Table S1 Conditions of blank experiment without catalyst.

Sample	T (°C)	Pressure indicator (bar)	Pressure before Reactor (bar)	Pressure after Reactor (bar)	Pressure HPLC (bar)	Feed (ml min ⁻¹)	H ₂ Flow (ml min ⁻¹)	Ratio (gas/liq uid)	Time delta (s)	Sample Volume (ml)
1	75.0	50.0	50.2	50.1	112.2	5.0	200.0	40.0	110.0	9.2
2	75.0	50.0	49.8	49.9	110.4	3.6	144.0	40.0	301.0	18.1
3	75.0	50.0	49.6	49.6	107.8	2.4	96.0	40.0	410.0	16.4
4	75.0	50.0	49.4	49.4	106.0	1.5	60.0	40.0	520.0	13.0
5	75.0	50.0	49.3	49.3	105.6	0.8	32.0	40.0	930.0	12.4
6	75.0	50.0	48.2	48.2	105.5	0.4	16.0	40.0	1643.0	11.0

7	75.0	50.0	48.5	48.4	104.1	0.2	8.0	40.0	3176.0	10.6
8	75.0	50.0	47.3	47.3	100.5	0.1	4.0	39.9	6133.0	10.2

6.2 Blank experiment without hydrogen

The goal of this experiment was to investigate the need for hydrogen during the reaction. We used 927 mg of a Johnson Matthey (9.76 wt.% Ru/C, 0.5 wt.% moisture) during this experiment. We investigated 4 different nitrogen flow rates from 50 to 200 ml min⁻¹ in 2 subsequent series. The conditions during the experiment are shown in Table S2.

Table S2 Conditions during Blank experiment without hydrogen

Sample	T (°C)	Pressure indicator (bar)	Pressure before Reactor (bar)	Pressure after Reactor (bar)	Pressure HPLC (bar)	Feed (ml min ⁻¹)	H ₂ Flow (ml min ⁻¹)	Ratio (gas/liq uid)	Time delta (s)	Sample Volume (ml)
1	50.03	60.00	58.08	57.73	119.62	0.10	199.98	1999.84	3545.00	5.91
2	50.02	60.00	57.33	56.99	119.13	0.10	150.01	1500.14	3592.00	5.99
3	50.03	60.00	59.70	59.37	120.52	0.10	100.00	999.98	3545.00	5.91
4	50.03	60.00	56.19	55.88	116.52	0.10	49.97	499.69	3545.00	5.91
5	50.03	60.00	60.18	59.82	120.16	0.10	200.30	2003.00	3545.00	5.91
6	50.03	60.00	60.24	59.89	120.85	0.10	149.96	1499.60	3591.00	5.98
7	50.03	60.00	60.26	59.90	121.17	0.10	99.99	999.87	3591.00	5.98
8	50.03	60.00	60.29	59.93	122.70	0.10	49.83	498.25	3545.00	5.91

6.3 Glycolic Acid as a feedstock in combination with commercial catalyst

This experiment aimed to investigate the effect of using glycolic acid in demineralized water solution instead of the usual oxalic acid solution. We used 878 mg of a Johnson Matthey (9.76 wt.% Ru/C, 0.5 wt.% moisture) during this experiment. We investigated only one temperature: 70°C at different time intervals. The conditions during this experiment are shown in Table S3.

Table S3 Conditions during reduction of glycolic acid

Sample	T (°C)	Pressure indicator (bar)	Pressure before Reactor (bar)	Pressure after Reactor (bar)	Pressure HPLC (bar)	Feed (ml min ⁻¹)	H ₂ Flow (ml min ⁻¹)	Ratio (gas/liq uid)	Time delta (s)	Sample Volume (ml)
1	70.01	60.00	66.61	60.64	122.02	0.10	199.99	1999.94	5771.00	9.62
2	70.01	60.00	66.57	60.59	122.28	0.10	199.99	1999.93	7240.00	12.07
3	70.01	60.00	66.61	60.61	122.52	0.10	199.97	1999.72	7261.00	12.10
4	70.01	60.00	66.64	60.64	122.82	0.10	199.99	1999.92	7239.00	12.06
5	70.00	60.00	66.65	60.63	122.87	0.10	199.99	1999.93	7240.00	12.07
6	70.01	60.00	66.60	60.58	122.79	0.10	199.99	1999.92	7261.00	12.10
7	70.01	60.00	66.65	60.61	122.88	0.10	199.99	1999.94	7240.00	12.07
8	70.01	60.00	66.65	60.59	122.91	0.10	199.99	1999.94	7240.00	12.07

6.4 Temperature effects at 50 -100 °C

The goal of this experiment was to investigate the effect of different temperatures from 50-100 °C. To ensure repeatability, we split work into two experiments where we explore the temperature from 50-80°C in the first and 80-100 °C in the second experiment. We used 912 mg of a Johnson Matthey (9.76 wt.% Ru/C, 0.5 wt.% moisture) during this experiment. In the first experiment, we investigated 4 different temperatures, namely from 50 to 80 °C, in 2 subsequent series. The conditions during the experiment are shown in Table S4.

Table S4 Conditions during reduction of oxalic acid at 50 – 80 °C

Sample	T (°C)	Pressure indicator (bar)	Pressure before Reactor (bar)	Pressure after Reactor (bar)	Pressure HPLC (bar)	Feed (ml min ⁻¹)	H ₂ Flow (ml min ⁻¹)	Ratio (gas/liq uid)	Time delta (s)	Sample Volume (ml)
1	50.03	60.00	60.42	60.13	128.90	0.10	199.99	1999.92	3578.00	5.96
2	60.02	60.00	60.47	60.22	128.97	0.10	199.99	1999.92	3578.00	5.96
3	70.01	60.00	60.50	60.29	129.00	0.10	199.99	1999.92	3577.00	5.96
4	80.00	59.99	60.51	60.33	129.08	0.10	199.99	1999.93	3527.00	5.88
5	50.04	60.00	60.41	60.31	126.74	0.10	199.99	1999.95	3577.00	5.96
6	60.02	60.00	60.47	60.38	126.97	0.10	199.99	1999.93	3577.00	5.96
7	70.01	60.00	60.42	60.36	102.14	0.10	200.00	1999.95	3578.00	5.96
8	80.01	60.00	60.44	60.42	96.90	0.10	200.00	1999.98	3577.00	5.96

In the second experiment, we investigated 4 different temperatures: from 70 to 100 °C in 2 subsequent series. The conditions during the experiment are shown in Table S5. The first sample failed during this run due to technical errors, and therefore no data is reported.

Table S5 Conditions during reduction of oxalic acid at 80 – 100 °C

Sample	T (°C)	Pressure indicator (bar)	Pressure before Reactor (bar)	Pressure after Reactor (bar)	Pressure HPLC (bar)	Feed (ml min ⁻¹)	H ₂ Flow (ml min ⁻¹)	Ratio (gas/liq uid)	Time delta (s)	Sample Volume (ml)
1										
2	80.08	60.01	60.74	60.45	129.17	0.10	199.99	1999.93	3646.00	6.08
3	90.01	60.00	60.68	60.47	129.18	0.10	199.99	1999.94	3529.00	5.88
4	100.0	60.00	60.58	60.42	129.61	0.10	199.99	1999.93	3588.00	5.98
5	70.01	60.00	60.51	60.43	127.13	0.10	199.99	1999.93	3529.00	5.88
6	80.01	59.99	60.60	60.52	127.98	0.10	199.99	1999.91	3528.00	5.88
7	90.00	60.00	60.64	60.58	127.46	0.10	199.99	1999.93	3529.00	5.88
8	100.0	60.00	60.43	60.44	119.50	0.10	199.99	1999.92	3588.00	5.98

6.5 Temperature effects at 50 – 65 °C

The goal of this experiment was to investigate the effect of reaction temperature at higher flow speeds in the range of 50-65°C. We used 960 mg of a Johnson Matthey (9.76 wt.% Ru/C, 0.5 wt.% moisture) during this experiment. We investigated 4 different temperatures, namely from 50 to 65 °C, in 2 subsequent series. The conditions of this experiment are shown in Table S6.

Table S6 Conditions during reduction of oxalic acid at 50 – 65 °C

Sample	T (°C)	Pressure indicator (bar)	Pressure before Reactor (bar)	Pressure after Reactor (bar)	Pressure HPLC (bar)	Feed (ml min ⁻¹)	H ₂ Flow (ml min ⁻¹)	Ratio (gas/liq uid)	Time delta (s)	Sample Volume (ml)
1	50.02	60.00	57.89	57.38	121.82	0.20	200.00	999.98	1789.00	5.96
2	55.02	60.00	53.57	53.06	115.56	0.20	199.99	999.96	1788.00	5.96
3	60.02	60.00	57.44	56.94	118.29	0.20	200.00	1000.02	1807.00	6.02
4	65.01	60.00	58.12	57.63	120.03	0.20	200.00	1000.00	1789.00	5.96
5	50.03	60.00	60.57	60.10	123.23	0.20	199.99	999.93	1807.00	6.02
6	55.02	60.00	60.55	60.09	123.37	0.20	200.01	1000.04	1789.00	5.96
7	60.02	60.01	60.52	60.07	123.00	0.20	200.00	999.98	1789.00	5.96
8	65.01	60.00	60.57	60.13	123.18	0.20	199.99	999.93	1789.00	5.96

6.6 Pressure effects at 80°C and 24-60 bar

The goal of this experiment was to investigate the effect of different hydrogen pressures at 80 °C. We used 876 mg of a Johnson Matthey (9.76 wt.% Ru/C, 0.5 wt.% moisture) during this experiment. We investigated 4 different pressures: from 60 to 24 bar in 2 subsequent series. The conditions during the experiment are shown in Table S7.

Table S7 Conditions during reduction of oxalic acid at 80 °C and 60 to 24 bar.

Sample	T (°C)	Pressure indicator (bar)	Pressure before Reactor (bar)	Pressure after Reactor (bar)	Pressure HPLC (bar)	Feed (ml min ⁻¹)	H ₂ Flow (ml min ⁻¹)	Ratio (gas/liq uid)	Time delta (s)	Sample Volume (ml)
1	80.0	60.0	60.5	60.3	129.0	0.1	200.0	1999.9	3547.0	5.9
2	80.0	48.0	48.5	48.3	117.0	0.1	200.0	1999.9	3546.0	5.9
3	80.0	36.0	36.7	36.4	105.2	0.1	200.0	1999.9	3546.0	5.9
4	80.0	24.0	24.6	24.4	93.1	0.1	200.0	2000.2	3547.0	5.9
5	80.0	60.0	60.5	60.3	126.1	0.1	200.0	1999.9	3546.0	5.9
6	80.0	48.0	48.5	48.4	116.8	0.1	200.0	1999.9	3546.0	5.9
7	80.0	36.0	36.6	36.4	105.0	0.1	200.0	1999.9	3547.0	5.9
8	80.0	24.0	24.6	24.4	93.1	0.1	200.0	1999.9	3547.0	5.9

6.7 Pressure effects at 70°C and 10-25 bar

The goal of this experiment was to investigate the effect of different hydrogen pressures at 70 °C. We used 924 mg of a Johnson Matthey (9.76 wt.% Ru/C, 0.5 wt.% moisture) during this experiment. We

investigated 4 different pressures: from 25 to 10 bar in 2 subsequent series. The conditions during the experiment are shown in Table S8.

Table S8 Conditions during reduction of oxalic acid at 70°C and 60 to 24 bar

Sample	T (°C)	Pressure indicator (bar)	Pressure before Reactor (bar)	Pressure after Reactor (bar)	Pressure HPLC (bar)	Feed (ml min ⁻¹)	H ₂ Flow (ml min ⁻¹)	Ratio (gas/liq uid)	Time delta (s)	Sample Volume (ml)
1	70.01	25.00	24.79	24.49	89.71	0.10	199.99	1999.91	3560.00	5.93
2	70.01	19.99	20.50	20.23	87.00	0.10	199.97	1999.75	3559.00	5.93
3	70.01	15.00	15.54	15.28	82.48	0.10	199.99	1999.91	3559.00	5.93
4	70.01	9.99	10.54	10.29	77.98	0.10	199.99	1999.95	3559.00	5.93
5	70.01	25.00	25.48	25.23	89.03	0.10	199.99	1999.90	3504.00	5.84
6	70.00	20.00	20.49	20.26	86.76	0.10	200.00	1999.96	3559.00	5.93
7	70.01	15.00	15.48	15.26	82.29	0.10	200.00	1999.97	3559.00	5.93
8	70.01	10.02	10.55	10.32	77.88	0.10	199.99	1999.94	3560.00	5.93

6.8 Hydrogen flow effects at 80°C and 50 -200 ml min⁻¹

The goal of this experiment was to investigate the effect of different hydrogen flow rates at 80°C and 60 bar. We used 942 mg of a Johnson Matthey (9.76 wt.% Ru/C, 0.5 wt.% moisture) during this experiment. We investigated 4 different hydrogen flow rates: from 50 to 200 ml min⁻¹ in 2 subsequent series. The conditions during the experiment are shown in Table S9.

Table S9 Conditions during reduction of oxalic acid at 80°C and 50-200 ml min⁻¹ hydrogen flow

Sample	T (°C)	Pressure indicator (bar)	Pressure before Reactor (bar)	Pressure after Reactor (bar)	Pressure HPLC (bar)	Feed (ml min ⁻¹)	H ₂ Flow (ml min ⁻¹)	Ratio (gas/liq uid)	Time delta (s)	Sample Volume (ml)
1	80.01	60.00	60.31	60.24	125.94	0.10	49.99	499.93	3584.00	5.97
2	80.01	59.99	60.35	60.29	123.83	0.10	99.99	999.93	3584.00	5.97
3	80.01	60.00	60.18	60.13	125.03	0.10	149.99	1499.86	3526.00	5.88
4	80.00	59.99	60.43	60.35	125.10	0.10	199.99	1999.94	3526.00	5.88
5	80.00	60.00	60.41	60.35	127.00	0.10	50.00	499.95	3584.00	5.97
6	80.00	60.00	60.47	60.41	128.23	0.10	99.99	999.91	3526.00	5.88
7	80.00	60.01	60.39	60.33	127.84	0.10	149.99	1499.90	3526.00	5.88
8	80.00	60.00	60.42	60.36	128.03	0.10	199.99	1999.92	3584.00	5.97

6.9 Hydrogen flow effects at 80-170 ml min⁻¹

The goal of this experiment was to investigate the effect of different hydrogen flow rates at 70°C and 24 bar. We use 879 mg of a Johnson Matthey (9.76 wt.% Ru/C, 0.5 wt.% moisture) during this experiment. We investigated 4 different hydrogen flow rates: from 80 to 170 ml min⁻¹ in 2 subsequent series. The conditions during the experiment are shown in Table S10.

Table S10 Conditions during reduction of oxalic acid at 70°C and 80-170 ml min⁻¹ hydrogen flow

Sample	T (°C)	Pressure indicator (bar)	Pressure before Reactor (bar)	Pressure after Reactor (bar)	Pressure HPLC (bar)	Feed (ml min ⁻¹)	H ₂ Flow (ml min ⁻¹)	Ratio (gas/liq uid)	Time delta (s)	Sample Volume (ml)
1	70.01	24.00	24.85	24.54	89.72	0.10	79.99	799.90	3547.00	5.91
2	70.01	24.00	23.50	23.19	88.21	0.10	110.00	1099.99	3480.00	5.80
3	70.01	24.00	22.24	21.96	88.06	0.10	139.99	1399.90	3547.00	5.91
4	70.02	24.01	23.27	22.98	89.35	0.10	170.00	1699.96	3547.00	5.91
5	70.01	24.00	23.63	23.34	85.74	0.10	79.99	799.88	3547.00	5.91
6	70.01	23.99	22.24	21.95	85.76	0.10	109.99	1099.94	3547.00	5.91
7	70.01	24.00	20.55	20.28	84.17	0.10	139.98	1399.85	3547.00	5.91
8	70.01	24.00	24.25	23.99	86.85	0.10	169.99	1699.92	3547.00	5.91

6.10 Feed flow effects at 70 °C and 0.1-0.8 ml min⁻¹

This experiment aimed to investigate the effect of different residence times by changing the flow of reactant feed. We used 886 mg of a Johnson Matthey (9.76 wt.% Ru/C, 0.5 wt.% moisture) during this experiment. We investigated 4 reactant feed flows: from 0.8 to 0.1 ml min⁻¹ in 2 subsequent series. The conditions during the experiment are shown in Table S11.

Table S11 Conditions during reduction of oxalic acid at 70°C and 0.1-0.8 ml min⁻¹ oxalic acid flow

Sample	T (°C)	Pressure indicator (bar)	Pressure before Reactor (bar)	Pressure after Reactor (bar)	Pressure HPLC (bar)	Feed (ml min ⁻¹)	H ₂ Flow (ml min ⁻¹)	Ratio (gas/liq uid)	Time delta (s)	Sample Volume (ml)
1	70.01	59.93	60.47	60.23	128.91	0.80	199.99	249.99	456.00	6.08
2	70.01	60.00	60.45	60.22	126.60	0.40	199.99	499.97	867.00	5.78
3	70.02	60.00	60.40	60.20	127.00	0.20	200.00	999.97	1780.00	5.93
4	70.01	60.00	60.28	60.14	125.90	0.10	200.00	1999.95	3559.00	5.93
5	69.99	60.01	60.35	60.17	128.55	0.80	200.00	250.01	456.00	6.08
6	70.00	60.00	60.31	60.17	127.35	0.40	199.99	499.98	867.00	5.78
7	70.02	60.00	60.31	60.20	127.00	0.20	200.00	999.98	1734.00	5.78
8	70.01	60.00	60.22	60.13	125.06	0.10	199.99	1999.92	3559.00	5.93

6.11 100h experiments with feed from OCEAN process

The goal of this experiment was to investigate the long-term stability of the commercial catalyst with real feed from the OCEAN process. We used 943 mg of a Johnson Matthey (9.76 wt.% Ru/C, 0.5 wt.% moisture) during this experiment. The conditions during this experiment are shown in Table S12.

Table S12 Conditions during long-term reduction of oxalic acid obtained from OCEAN process

Sample	T (°C)	Pressure indicator (bar)	Pressure before Reactor (bar)	Pressure after Reactor (bar)	Pressure HPLC (bar)	Feed (ml min ⁻¹)	H ₂ Flow (ml min ⁻¹)	Ratio (gas/liq uid)	Time delta (s)	Sample Volume (ml)
1	50.03	60.00	70.15	60.53	121.17	0.10	200.00	1999.96	8921.00	14.87
2	50.03	60.00	70.30	60.60	121.67	0.10	199.99	1999.89	8921.00	14.87
3	50.03	60.00	70.65	60.78	121.67	0.10	199.99	1999.94	8921.00	14.87
4	50.03	60.00	70.73	60.69	121.01	0.10	199.99	1999.94	8921.00	14.87
5	50.03	60.00	70.83	60.62	121.57	0.10	199.99	1999.93	8921.00	14.87
6	50.04	60.00	71.00	60.61	121.08	0.10	199.99	1999.93	8921.00	14.87
7	50.03	60.00	71.14	60.60	120.93	0.10	199.99	1999.87	8921.00	14.87
8	50.03	60.00	71.27	60.56	120.92	0.10	199.99	1999.92	8814.00	14.69

6.12 100h experiments without the presence of potassium in feed

The goal of this experiment was to investigate the long-term stability of the commercial catalyst without the presence of potassium in 2.37 wt.%. The oxalic acid solution was prepared from commercial oxalic acid to mimic the concentration of the real feed. We did not remove the potassium from the real feed, due to the lack of availability of real feed. We used 934 mg of a Johnson Matthey (9.76 wt.% Ru/C, 0.5 wt.% moisture) during this experiment. The conditions during this experiment are shown in Table S13.

Table S13 Conditions during long-term reduction of oxalic acid obtained without potassium

Sample	T (°C)	Pressure indicator (bar)	Pressure before Reactor (bar)	Pressure after Reactor (bar)	Pressure HPLC (bar)	Feed (ml min ⁻¹)	H ₂ Flow (ml min ⁻¹)	Ratio (gas/liq uid)	Time delta (s)	Sample Volume (ml)
1	50.03	60.00	76.23	61.06	122.31	0.10	200.00	1999.96	8963.00	14.94
2	50.03	60.00	76.25	60.94	121.96	0.10	200.01	2000.07	8964.00	14.94
3	50.03	60.00	76.46	60.96	123.49	0.10	199.99	1999.91	8964.00	14.94
4	50.03	60.00	76.66	60.96	121.99	0.10	199.99	1999.95	8964.00	14.94
5	50.03	60.00	76.82	60.91	122.75	0.10	200.00	1999.98	8895.00	14.82
6	50.03	60.00	76.94	60.82	122.78	0.10	199.99	1999.89	3309.00	5.51

References

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