

## Supplementary information - Oxalic acid hydrogenation to glycolic acid: heterogeneous catalysts screening

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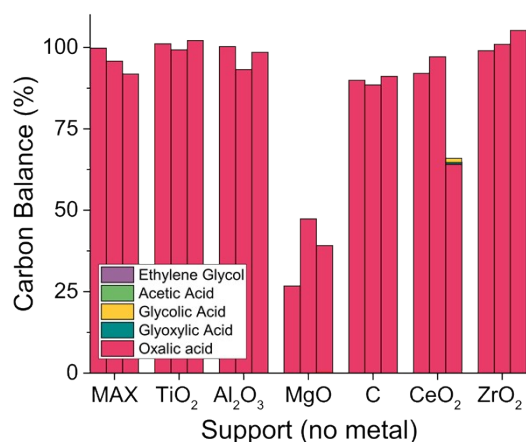
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### Abstract

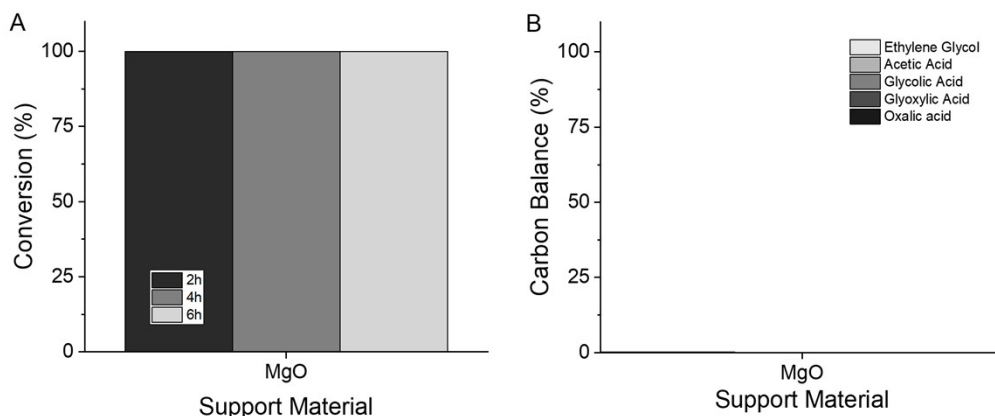
To meet our ambitions of a future circular economy and drastically reduce CO<sub>2</sub> emissions, we need to make use of CO<sub>2</sub> as a feedstock. Turning CO<sub>2</sub> into monomers to produce sustainable plastics is an attractive option for this purpose. It can be achieved by electrochemical reduction of CO<sub>2</sub> to formic acid derivatives, that can subsequently be converted into oxalic acid. Oxalic acid can be a monomer itself and it is a potential new platform chemical for material production, as useful monomers such as glycolic acid and ethylene glycol can be derived from it. Today the most common route from oxalic acid to glycolic acid requires multiple steps as it proceeds via oxalic acid di-esters as intermediates. In this work, we aim to avoid the extra reaction step of esterification. We explore the direct conversion of oxalic acid to glycolic acid in a two-step approach. In the first step, we define the ideal reaction conditions and test commercially available catalysts. We show that the reduction of oxalic acid can be performed at much lower temperatures and glycolic acid yields higher than those reported previously can be obtained. In the second step, we explore the design principles required for ideal catalysts which avoid the formation of acetic acid and ethylene glycol as side products. We show that ruthenium is the most active metal for the reaction and that carbon appears the most suitable support for these catalysts. By adding tin as a promotor, we could increase the selectivity and yield further whilst maintaining high activity of the resulting catalyst. This research lays the foundation for the efficient direct reduction of oxalic acid to glycolic acid and defines the design parameters for even better catalysts and the ideal process and conditions.

## 1 Complementary figures and tables to Main Article

### 1.1 Supports



**Figure S1** Carbon balance of Batchington experiment with only support material in the presence of oxalic acid. All data were obtained by liquid chromatography (LC). Conditions during reactions: Temperature = 75 °C, Pressure = 80 bar, Substrate = Oxalic Acid (5 wt.%) in demineralized water (2 mL), Catalyst/Support Loading = 50 mg, Time = 2, 4 and 6 hours

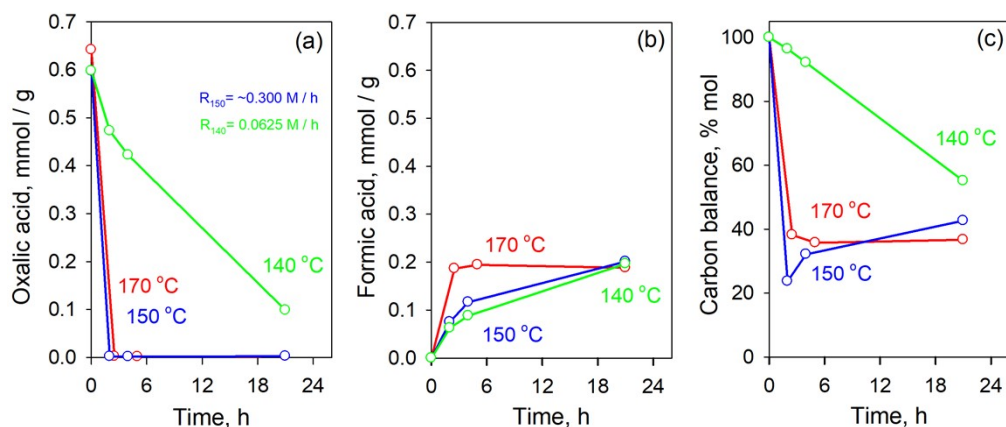


**Figure S2** Results of control experiment which examined the adsorption of oxalic acid by MgO. Conversion (A) and Carbon Balance (B) data as obtained by liquid chromatography (LC). Oxalic Acid (5 wt.%) solution in demineralized water was added to a MgO support. The concentration of oxalic and possible reaction products was measured by LC for different time intervals.

## 1.2 Initial screening of reaction products and oxalic acid decomposition

**Table S1** Catalytic decomposition of oxalic acid in absence of catalyst: All reactions were performed in 100 mL Hastelloy reactor without liner. Substrate: 5 wt.% aqueous oxalic acid (41.58 g, 23.1 mmol oxalic acid), temperature 170 °C, 150 °C and 140 °C, Pressure (H<sub>2</sub>) 70 bar, reaction time 24 h.

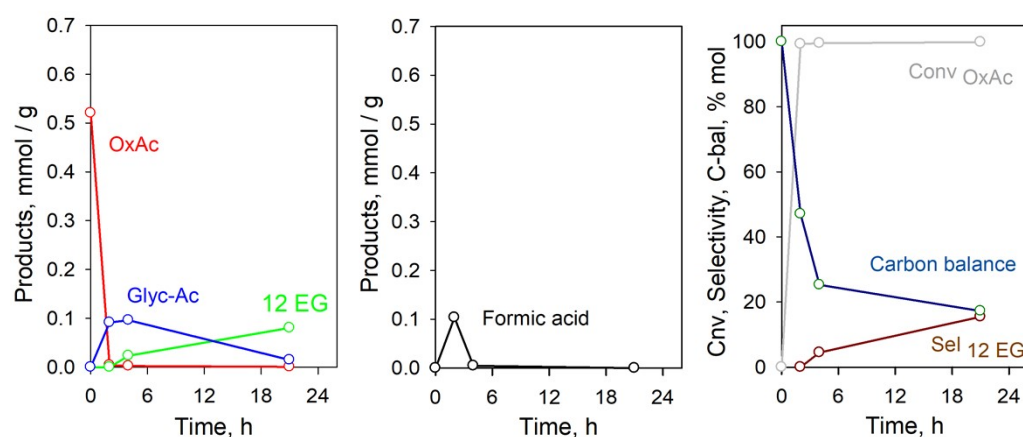
Temperature (°C)	Concentration, mmol/g							Conversion (%)	Carbon balance (%)
	Glyoxylic Acid	Glyoxylic aldehyde	Glycolic acid	Glycolic Aldehyde	Ethylene glycol	Unknown	Formic acid		
170	0.00	0.00	0.00	0.00	0.00	0.01	0.19	99.6	36.6
150	0.00	0.00	0.00	0.00	0.00	0.03	0.21	98.8	46.3
140	0.00	0.00	0.00	0.00	0.00	0.01	0.20	84.1	53.7



**Figure S3** Thermal decomposition of oxalic acid (without catalyst) at different temperatures in 100 mL Hastelloy reactor. Reaction conditions: T=170 °C, 150 °C and 140 °C. Pressure (H<sub>2</sub>) = 70 bar, feed 5 wt.% aqueous oxalic acid 41.5 g (23 mmol oxalic acid), stir rate 800 RPM. The GC-MS analysis of the gas phase revealed the presence of only CO<sub>2</sub>.

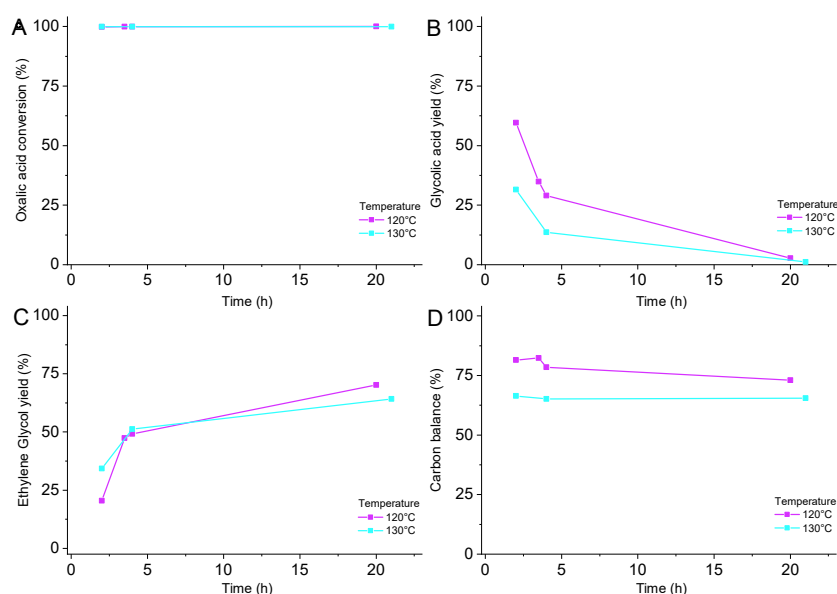
**Table S2** Thermal decomposition of oxalic acid with a 5 wt.% Ru/C (Johnson Matthey, C4198) catalyst: All reactions were performed in 100 mL Hastelloy reactor without liner. Substrate: 5 wt.% aqueous oxalic acid (41.58 g, 23.1 mmol oxalic acid), Catalyst weight 0.3 g, Temperature 170 °C, Pressure (H<sub>2</sub>) 100 bar, reaction time 24 h. Catalyst reduced in a tube with gaseous hydrogen.

Time (h)	Concentration, mmol/g								Conversion (%)	Carbon balance (%)
	Oxalic acid	Glyoxylic Acid	Glyoxylic aldehyde	Glycolic acid	Glycolic Aldehyde	Ethylene glycol	Unknown	Formic acid		
0	0.52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100
2	0.00	0.00	0.00	0.07	0.00	0.00	0.06	0.10	99.3	43.6
4	0.00	0.00	0.00	0.08	0.00	0.02	0.01	0.00	99.5	21.1
21	0.00	0.00	0.00	0.01	0.00	0.08	0.00	0.00	99.9	16.7

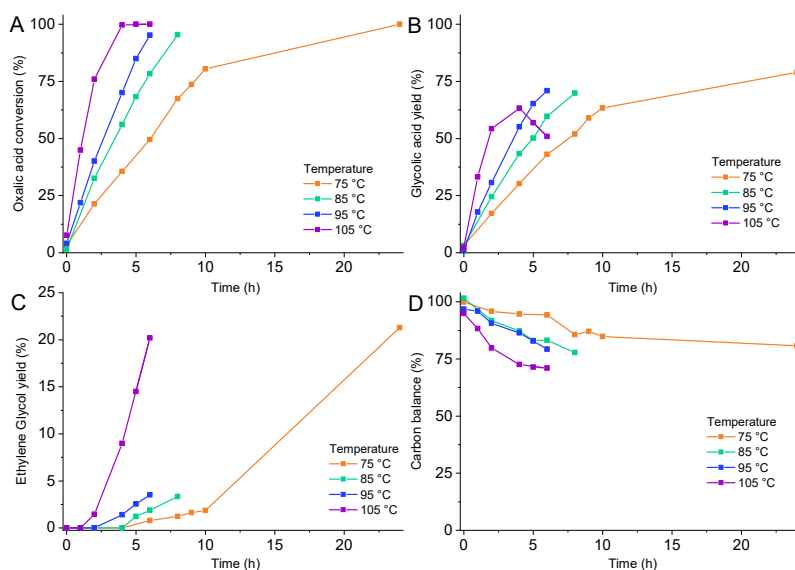


**Figure S4** Thermal decomposition of oxalic acid with a 5 wt.% Ru/C (Johnson Matthey, C4198) catalyst at different temperatures in 100 mL Hastelloy reactor. Reaction conditions: T=170 °C, 150 °C and 140 °C. Pressure (H<sub>2</sub>) = 100 bar, feed 5 wt.% aqueous oxalic acid 41.5 g (23 mmol oxalic acid), stir rate 800 rpm. Comment: The GC-MS analysis of the gas phase shows the presence of CO<sub>2</sub>, CH<sub>3</sub>OH, HCHO, CH<sub>4</sub> and C<sub>2</sub>-C<sub>6</sub> hydrocarbons.

### 1.3 Reaction temperature and time

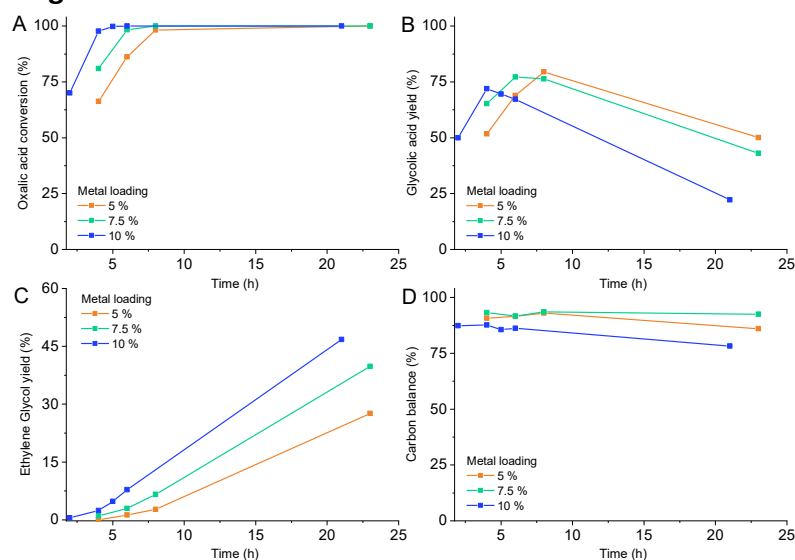


**Figure S5** Influence of reaction temperature in reduction of 5% oxalic acid in aqueous feed on A) oxalic acid conversion, B) Glycolic acid yield, C) Ethylene Glycol yield, and D) Carbon balance. All reactions were performed using a 100 mL all Hastelloy reactor filled with 0.275g (0.45g for 75°C) of 5 wt.% Ru / C (JM, Type 5R600) catalyst, reduced at 250°C no pre-reduction in the reactor; Substrate = 41.5 g of 5 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure (H<sub>2</sub>) = 100 bar; Temperature = 120 °C – 130 °C; Reaction time = 21 hours.



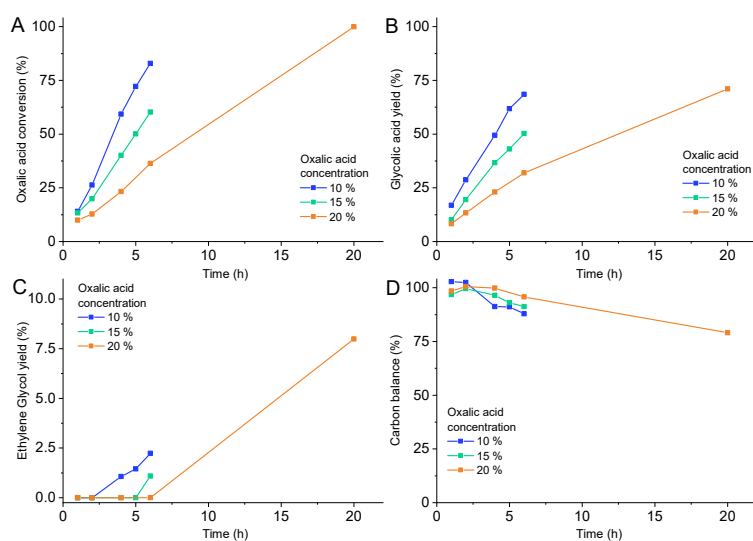
**Figure S6** Influence of reaction temperature in reduction of 10% oxalic acid in aqueous feed on A) oxalic acid conversion, B) Glycolic acid yield, C) Ethylene Glycol yield, and D) Carbon balance. All reactions were performed using a 100 mL all Hastelloy reactor filled with 0.7885g of 5 wt.% Ru / C (JM, Type 5R600) catalyst reduced at 300 °C then pre-reduced in the reactor at 100 °C; Substrate = 41.5 g of 10 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure ( $H_2$ ) = 100 bar; Temperature = 75 °C – 105 °C; Reaction time = 21 hours.

#### 1.4 Metal loading



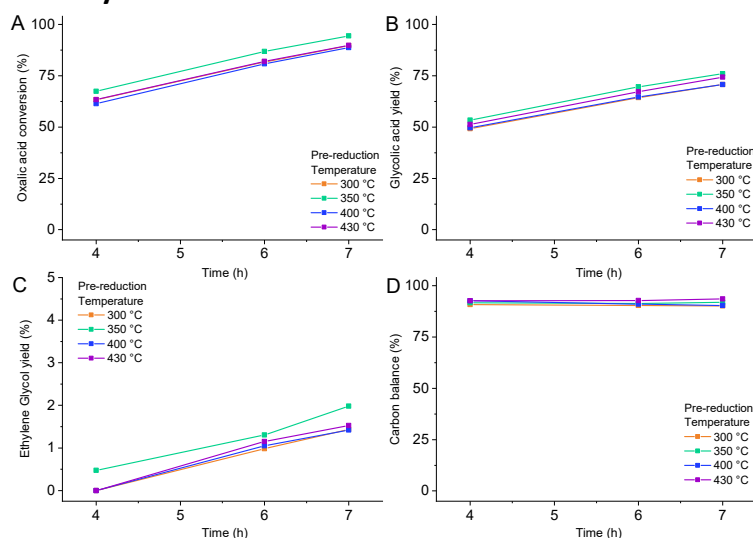
**Figure S7** Influence of metal loading in reduction of 25% oxalic acid in aqueous feed on A) oxalic acid conversion, B) Glycolic acid yield, C) Ethylene Glycol yield, and D) Carbon balance. All reactions were performed using a 100 mL all Hastelloy reactor filled with 1.125 g of 5 WT.% Ru / C (JM, Type 5R600), 7.5% Ru / C (JM, Type D102023-7.5), 10% Ru / C (JM, Type D101023-10), reduced at 300 °C then pre-reduced in the reactor at 100 °C; Substrate = 41.5 g of 25 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure ( $H_2$ ) = 100 bar  $H_2$ ; Temperature = 75 °C; Reaction time = 23 hours.

## 1.5 Reactant concentration



**Figure S8** Influence of oxalic acid concentration in aqueous feed on A) oxalic acid conversion, B) Glycolic acid yield, C) Ethylene Glycol yield, and D) Carbon balance. All reactions were performed using a 100 mL all Hastelloy reactor charged with 0.546 g of 5% Ru / C (JM, Type 5R600), reduced at 300 °C then pre-reduced in the reactor at 100 °C; Substrate = 41.5 g of 10-20 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure (H<sub>2</sub>) = 100 bar; Temperature = 75 °C; Reaction time = 20 hours.

## 1.6 Reduction of catalyst



**Figure S9** Influence of catalyst pre-reduction temperature on the A) oxalic acid conversion, B) Glycolic acid yield, C) Ethylene Glycol yield, and D) Carbon balance. All reactions were performed using a 100 mL all Hastelloy reactor charged with 0.546 g of 5 wt.% Ru/C (JM, Type 5R600), reduced at 300-430 °C then pre-reduced in the reactor at 100 °C; Substrate = 41.5 g of 25 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure (H<sub>2</sub>) = 100 bar; Temperature = 75 °C; Reaction time = 7 hours.

## 2 Experimental details

### 2.1 Catalyst Supports

All catalyst support materials: Carbon (NORIT SX 1 G), Ti<sub>2</sub>Al<sub>2</sub>C (MAX-Phase) Titania (TiO<sub>2</sub>), Alumina (γ-Al<sub>2</sub>O<sub>3</sub>), Magnesium Oxide (MgO), Cerium Oxide (CeO<sub>2</sub>), Zirconia (ZrO<sub>2</sub>), and TASC-Max Phase

(Ti<sub>3</sub>(Al<sub>0.8</sub>Sn<sub>0.2</sub>)<sub>2</sub>) were obtained from commercial suppliers (Sigma-Aldrich®), dried and stored in a dry environment. Otherwise, the chemicals were not further processed.

## 2.2 Metal Precursors

All metal precursors used at the University of Amsterdam and Avantium were obtained from commercial suppliers (Sigma-Aldrich®) and dried and stored in a dry environment and not further processed. Copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O), Zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), Magnesium nitrate (Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), Indium oxide (In(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O), Ruthenium nitrosyl nitrate (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>), Ammonium heptamolybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>), Cobalt chloride (CoCl<sub>2</sub>·6H<sub>2</sub>O), Tin Chloride (SnCl<sub>2</sub>·2H<sub>2</sub>O), Ruthenium chloride (RuCl<sub>3</sub>·xH<sub>2</sub>O), Nickel chloride (NiCl<sub>2</sub>·6H<sub>2</sub>O), Iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), Ammonium perrhenate (NH<sub>4</sub>ReO<sub>4</sub>), Nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), Copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), Cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), (Benzene)ruthenium dichloride dimer (C<sub>12</sub>H<sub>12</sub>Cl<sub>4</sub>Ru<sub>2</sub>).

The metal precursors used at Seton Hall University were obtained from various commercial suppliers indicated in brackets. They were dried and stored in a dry environment and not further processed. Ruthenium nitrosyl nitrate (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>) (Alfa-Aesar), HReO<sub>4</sub> (Sigma-Aldrich), Pd(NO<sub>3</sub>)<sub>2</sub> (Johnson Matthey), AgNO<sub>3</sub> (Fisher Scientific), SnCl<sub>4</sub>·H<sub>2</sub>O, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, HAuCl<sub>4</sub>·xH<sub>2</sub>O, RuCl<sub>3</sub> (Strem Chemicals)

## 2.3 Reagents

All additional reactants: Oxalic Acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>), Glycolic Acid (C<sub>2</sub>H<sub>4</sub>O<sub>3</sub>), Glyoxylic Acid (C<sub>2</sub>H<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O), Acetic Acid (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>), Ethylene Glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>), Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), Ammonium Hydroxide (NH<sub>4</sub>OH), Ethanol (C<sub>2</sub>H<sub>5</sub>OH), Sodium borohydride (NaBH<sub>4</sub>), Dopamine (C<sub>8</sub>H<sub>11</sub>NO<sub>2</sub>), Tris-HCl (C<sub>4</sub>H<sub>11</sub>NO<sub>3</sub>·HCl), Melamine (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>), Sodium Citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O) 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.

## 2.4 Commercial Catalysts

All commercial catalysts are listed in the table below and were purchased directly from the manufacturer. All catalysts were stored in a dry environment. Otherwise, the catalysts were not used for further processing.

**Table S3** Commercial catalysts used for the oxalic acid reduction reaction

Catalyst	Type	Lot	% H <sub>2</sub> O	Supplier
5 wt.% Ru / C	D101023-5	C4198	57.15	Johnson Matthey
5 wt.% Ru / C		F14X032	57.1	Alfa-Aesar
5 wt.% Ru / Al <sub>2</sub> O <sub>3</sub>	Degussa H213R/D	10714KY	--	Sigma Aldrich
5 wt.% Pd / C	A405028-5	C8738	58.37	Johnson Matthey
5 wt.% Ru / C	D101002-5	C-11266		Johnson Matthey
5 wt.% Ru / C	5R600	C-12052		Johnson Matthey
7.5 wt.% Ru / C	D102023-7.5	C-11106		Johnson Matthey
10 wt.% Ru / C	D101023-10	C-11309		Johnson Matthey
5 wt.% Ru / Al <sub>2</sub> O <sub>3</sub>	D302011-5	C-12053		Johnson Matthey
5 wt.% Ru / C	Type 619	M11099		Alfa-Aesar
5 wt.% Ru / C		H30Z004		Alfa-Aesar
10 wt.% Ru / C		C09Y010		Alfa-Aesar
7.5 wt.% Ru / C		C-12136		Johnson Matthey
7.5 wt.% Ru / C		C-12137		Johnson Matthey

## 3 Catalyst Synthesis

### 3.1 Catalyst Synthesis – CuMg/ZnO

We based the synthesis of CuMg/ZnO on a procedure described by Kong et al. 2017.<sup>1</sup> First; we dissolved the metal precursors: copper chloride ( $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ; 0.36 g, 1.65 mmol), zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ; 0.58 g, 1.98 mmol) and magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ; 0.10 g, 0.38 mmol) together in demineralized water (3.8 mL). In addition, sodium carbonate ( $\text{Na}_2\text{CO}_3$ ; 0.41 g) was dissolved in demineralized water (3.8 mL) and added dropwise to the solution of dissolved metal precursors. The metal precursor and sodium carbonate mixture were stirred for 1 week at 75°C. After this period, a blue solid was filtrated out of the mixture through a vacuum filtration procedure and washed with demineralized water. The precipitate was dried at room temperature for 6 hours, the blue solid was then crushed to a powder with a pestle and mortar. The powder was calcined at 400°C for 4 hours with a ramp of 25 K min<sup>-1</sup> under a flow of 100 mL min<sup>-1</sup> H<sub>2</sub>/N<sub>2</sub> (7%). The catalyst that was obtained after the calcination had turned black. The catalyst was reduced through the procedure described in the chapter catalyst reduction below.

### 3.2 Catalyst Synthesis – In<sub>2</sub>O<sub>3</sub>

The synthesis of In<sub>2</sub>O<sub>3</sub> was based on the procedure described by Frei et al. 2018.<sup>2</sup> First; we dissolved the metal precursor indium nitrate ( $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ; 2.76 g, 7.2 mmol) in a liquid mixture of demineralized water and ethanol (11.2/32.8 mL) under stirring. In addition, we added dissolved (in demineralized water) ammonium hydroxide (NH<sub>4</sub>OH (25 wt.%); 3.6 mL) to a solution of ethanol (10.8 mL) in a separate flask. The ammonium hydroxide solution was added dropwise to the indium oxide solution. White crystals started forming immediately upon the addition of the first droplets of ammonium hydroxide. Ammonium hydroxide was added until we reached pH=9. The temperature of the solution was increased to 80 °C after the addition of all ammonium hydroxide, and the mixture was stirred for 20 minutes. During the heating to 80°C, the white crystals dissolved in the solution. After 20 minutes, the solution was cooled down again, and a vacuum filtration procedure was followed to filter out the white catalyst. The catalyst was first dried at 50°C for 4 hours and subsequently calcined at 300 °C for 3 hours in the air.

### 3.3 Catalyst Synthesis – NiFe/C

The synthesis of NiFe/C was based on the procedure described by Kong et al. 2018.<sup>6</sup> We dissolved Oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ; 1.2706 g, 10 mmol) and melamine ( $\text{C}_3\text{H}_6\text{N}_6$ ; 0.63 g, 5 mmol) in demineralized water (20 mL). The solution was refluxed at 70°C for 6 hours. Subsequently, the metal precursors iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ; 0.76 g, 1.85 mmol) and nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ; 0.90 g, 3.8 mmol) were dissolved in demineralized water and added to the refluxed solution. The new mixture was stirred for another 12 hours at room temperature. A green powder was obtained through vacuum filtration. The green powder was dried at 70°C for 12 hours. The catalyst was calcined at 800°C for 2 hours under a flow of N<sub>2</sub> with a ramp of 10 K min<sup>-1</sup>. The catalyst was reduced through the procedure described in the chapter catalyst reduction below.

### 3.4 Catalyst Synthesis – Ru(dimer)/C

The synthesis of Ru(dimer)/C was based on a procedure developed by Laan, P. from the Van 't Hoff Institute for Molecular Sciences (HIMS). We synthesized ruthenium on carbon support using a dimeric ruthenium precursor, namely (benzene)ruthenium dichloride dimer ( $\text{C}_{12}\text{H}_{12}\text{Cl}_4\text{Ru}_2$ ; 0.0133 g, 0.25 mmol). The metal precursor was dissolved in chloroform ( $\text{CHCl}_3$ ; 16 mL) and added dropwise to a mixture of Carbon (NORIT SX 1 G; 1.00 g) in chloroform ( $\text{CHCl}_3$ ; 60 mL). The mixture was stirred for 16 hours, after which the solvent chloroform was removed by rotary evaporation. The catalyst was dried in a vacuum oven at 50°C for 16 hours. The catalyst was reduced through the procedure described in the chapter catalyst reduction below.

### 3.5 Catalyst Synthesis – Polymeric Catalysts

We dissolved Tris-HCl ( $C_4H_{11}NO_3$ ; 0.394 g, 1.58 mmol) in demineralized water (250 mL). The support ( $C/Al_2O_3$ ; 0.25 g) was added to the Tris-HCl solution in addition to dopamine ( $C_8H_{11}NO_2$ ; 0.25 g, 2.57 mmol). The mixture was stirred for 16 hours as well as briefly sonicated. Dissolved ruthenium chloride in demineralized water ( $RuCl_3 \cdot xH_2O$ ; 50 mL, 0.24 mmol) was added to the mixture after 16 hours. In addition, sodium borohydride ( $NaBH_4(0.1M)$ ; 50 mL) was added dropwise to the suspension. After 24 hours of additional stirring, the solid catalyst was extracted from the suspension through a vacuum filtration procedure. The catalyst was dried in a vacuum oven.

### 3.6 Catalyst synthesis – incipient wet impregnation

Ruthenium was deposited on different commercially available types of carbon using an incipient wetness impregnation. For the impregnation, first the precursor  $Ru(NO)(NO_3)_3$  was added to a defined amount of demineralized water to reach the equivalent of 5wt.% of Ruthenium on carbon. Table S4 provides the specific carbons used as the catalyst support, along with the pore volume, determined in our Lab for each carbon. After dissolving the Ruthenium precursor, the carbon was added to the solution and stirred until all the water was absorbed by the pores of the catalyst. The wetted support is stirred occasionally for the next two hours and the beaker is transferred into a vacuum oven. The oven is evacuated to 22" Hg and the temperature slowly raised to 110 °C and held at that set overnight. The catalyst was then fully dried in an oven at 160 °C and then reduced and calcined in a tubular furnace at 350 °C for 3 hours in a nitrogen atmosphere.

Commercially available carbon supports were used to prepare the catalysts.

**Table S4** List of Carbon supports, source of support and amount of water per g support used for preparation.

Carbon support	Source of support	Amount of water/ g support
SX-Plus	NORIT	2.0 mL
R1 Extra	NORIT	1.2 mL
PICATAL	PICATAL	0.6 mL
RO-0.8	NORIT	1.2 mL
ROW-0.8	NORIT	1.6 mL
FISHER	FISHER chemicals	1.1 mL
DARCO G60	NORIT	1.8 mL

### 3.7 Catalyst Synthesis – Wet-Impregnation

The procedure for this synthesis was similar for each metal, with the only difference being the different metal precursors and quantities used. We used the different metal precursors shown previously during this synthesis. Support: Carbon (NORIT SX 1 G; 0.95 g) was added to a 25 mL round bottom flask together with a stirring bean. Demineralized water (10 mL) was added to this round bottom flask while active stirring was activated. A metal precursor was dissolved in demineralized water, which was slowly added to the stirred support mixture. The reaction temperature was gradually increased to 80°C. The reaction mixture was kept under these conditions until all the water had evaporated. In case the water had not evaporated, the temperature was increased more until all water evaporated. The solid catalyst was collected from the round bottom flask and dried at 160°C for 3.5 hours. The catalyst was reduced through the procedure described in the chapter catalyst reduction below.

### 3.8 Catalyst synthesis bi-metallic ruthenium catalysts

The section describes the performance of the series of bimetallic catalysts made by the same procedure as described 3.10 for the singular 5% Ru/Carbon catalyst. Here, instead of using a single impregnation solution of  $Ru(NO)(NO_3)_3$ , a mixture of two salts (Table of salts for alternative metals is shown below) was dissolved in the same volume of water to make the combined precursor solution.



**Table S5:** List of metal precursors used for preparation and source of precursors.

Metal precursor	Source of precursor
Ru(NO)(NO <sub>3</sub> ) <sub>3</sub>	Alfa-Aesar
HReO <sub>4</sub>	Aldrich
Pd(NO <sub>3</sub> ) <sub>2</sub>	Johson-Mathey
AgNO <sub>3</sub>	Fisher Scientific
SnCl <sub>4</sub> *H <sub>2</sub> O	Strem Chemicals
H <sub>2</sub> PtCl <sub>6</sub> .6H <sub>2</sub> O	Strem Chemicals
HAuCl <sub>4</sub> .xH <sub>2</sub> O	Strem Chemicals
RuCl <sub>3</sub>	Strem Chemicals

### 3.9 Catalyst Synthesis – Reduction

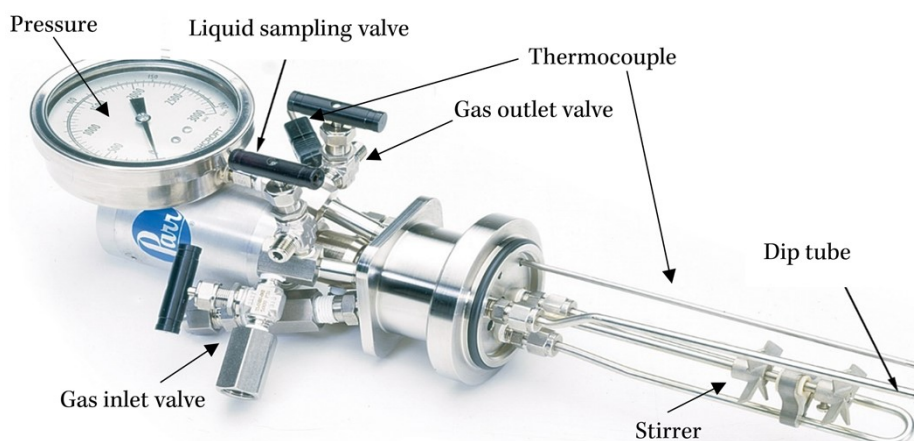
Catalysts were reduced in a tubular furnace. The catalyst particles were crushed with a ceramic mortar to a fine powder, which was added to a crucible. The powder was treated with a gas mixture of 7% H<sub>2</sub> in N<sub>2</sub> with a flow rate of 100 mL min<sup>-1</sup>. The temperature inside the furnace was increased with a ramp of 10 K min<sup>-1</sup> until it reached 300-450°C with 350°C being used most. This temperature was kept constant for 180 minutes. Upon completion of the reduction procedure, the temperature was slowly decreased, and the 7% H<sub>2</sub>/N<sub>2</sub> mixture was flushed out with a flow of pure nitrogen.

## 4 Reactors and general operation procedure

In this work, we used two different reactor set-ups depending on where the work was performed. At the Augustine Labs at Seton Hall University, we used a single 100 mL Hastelloy batch reactor from Parr. For the work carried out at the University of Amsterdam, we used a Batchington reactor system from Avantium, which allows us to perform up to 36 reactions in parallel.<sup>8</sup>

### 4.1 Hastelloy reactor

Preliminary hydrogenation condition optimizations were carried out in an in-house assembled reactor system. This enables to continuously monitor the hydrogen uptake rate and consists of a standard 100 mL stainless steel autoclave. The reactor is designed to allow the entire vessel to be removed from its stand for charging or product recovery. With an internal magnetic rotor, the reaction mixture can be stirred at predetermined stirring rate. The reactor has a total of three ports as shown in Figure S10.



**Figure S10** Reactor head used for initial screening reactions

Those are used as the gas inlet, for liquid sampling and to release gas. In case of extensive pressure build-up, a safety rupture disc is in place. The pressure can be measured with the pressure gauge on top of the reactor head and the temperature inside the reactor can be measured with a thermocouple

that reaches into the liquid section. In the case of exothermic reactions, a cooling loop also allows reducing the temperature by pumping cold liquid through.

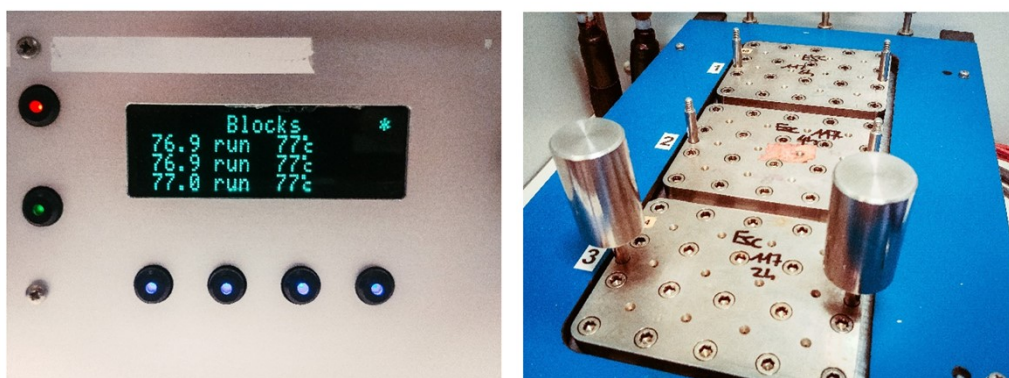
The consumption of hydrogen during the reaction in the Hastelloy reactor was monitored as follows: The reactor itself is connected to a High-Pressure Volumetric system which enables us to continuously monitor either gas absorption or gas evolution rate of the reaction. For reactions associated with gas adsorption, the reactor pressure is accurately monitored and controlled by a sensing module. The module is divided into three sections for feed high-pressure supply and low-pressure supply. The supply lines for reactant gases ( $H_2$  or  $O_2$ ), inert gases and vacuum lines are in the feed section. The high-pressure section consists of a forward pressure regulator, a pressure transducer and a calibrated volume reservoir. The low-pressure section is in line with the reactor and its pressure is monitored by a pressure transducer. For reactions such as hydrogenation, oxidation or hydroformylation, the gas consumption in the reactor section leads to a continuous pressure drop in the calibrated reservoir. The pressure in the calibrated reservoir and in the reactor, the reaction temperature and the reaction time are continuously monitored by computer and recorded at pre-set pressure drop increments of usually 1 psi. From the pressure drop and the volume of the reservoir, the amount of consumed gas is calculated and saved as an ASCII file.

A typical reaction in the Hastelloy reactor for catalyst testing was performed as follows: As a first step, the metal on the already reduced catalyst is preactivated to its active form. For a typical experiment, the reactor was charged with e.g., 130 mg of 5% Ru/C catalyst in 40 mL deionized water. The closed system then was purged 5 times with argon followed by 5 purges with hydrogen. A hydrogen pressure of 800 psi was established, and the reactor heated to the desired reaction temperature. This reduction step was carried out for 2-3 hours at a stirring rate of 200-400 RPM. After cooling the reactor down to ambient temperature, the water in the reactor was siphoned out through the dip tube. A 2mm stainless steel fritted filter prevents the reduced catalyst powder to leave the reactor.

Once the reduced catalyst is ready, the reactant can be charged into the reactor. For a typical experiment, 41.5 g of aqueous oxalic acid solution are added using a gas-tight syringe. To avoid the introduction of oxygen to the reactor reactant solution is purged with inert gas for at least 30 minutes before reaction. The reactor is flushed 5 times with hydrogen and pressurized to 800 psi. Over 1 hour the reactor is heated to the desired reaction temperature while stirring at a rate of 200 rpm. When the reaction temperature is reached, the pressure is adjusted to the desired value, the stirring rate is increased to 800-900 rpm and the hydrogen uptake monitoring started. In the first 6 hours, samples are taken every two hours then the hydrogenation was continued for another 21 hours without taking samples.

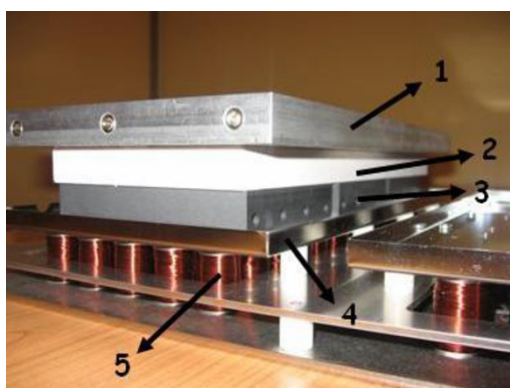
#### **4.2 Batchington reactor for quick catalyst screening**

For catalyst screening, a quick catalyst screening system (BATCHINGTON) developed by Avantium Technologies was used.<sup>8</sup> This system allows to perform up to 36 reactions in parallel when operated for the same time or for 12 reactions in parallel when three different reaction times are of interest. The whole system is shown in Figure S11:



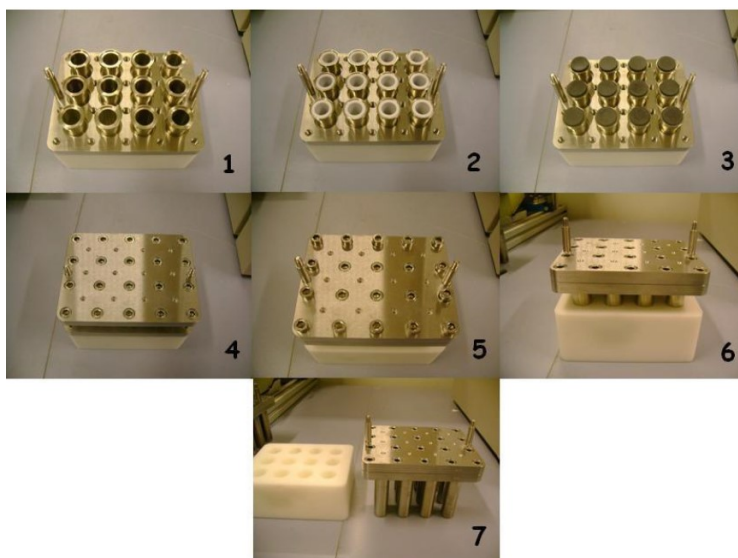
**Figure S11** BATCHINGTON system developed by Avantium. On the left, the temperature and stirring control boxes are shown. On the right, the heating blocks are shown.

The system consists of a temperature-controlled heating and stirring block which can be operated at a wide temperature and stirring range in constant conditions. It fits three reactor assemblies which all contain 12 individual reactors. The reactor assemblies can be inserted or removed from the system individually e.g., at different times. The schematics of the heating block are shown in Figure S12:



**Figure S12** Inside of a BATCHINGTON heating block. 1) Fluid Heated aluminium top plate; 2) Insulation layer; 3) Electrically heated graphite block; 4) Aluminium base plate; 5) Induction coils for stirring

The individual reactors are made from stainless steel and covered with a Teflon liner. The reactor assembly is shown in Figure S13:



**Figure S13** Reactor assembly for BATCHINGTON system in seven steps: 1) The 12 individual reactors are placed in the bottom plate; 2) Teflon liners are added to the reactors – the reactors are then filled with catalyst and reactant 3) Septa are placed on the reactor; 4) The top-plate is added to close the reactor; 5) 20 screws are used to seal the reactor; 6) The screws are equally tightened with 5nm; 7) Fill the reactor with the reactant gas.

A typical reaction in the Batchington reactor for catalyst testing was performed as follows: To compare the performance of the synthesized catalyst for the reduction of oxalic acid, we used tantalum reactors. These reactors were equipped with Teflon liners that were inserted in the reactors. Pre-reduced catalyst ( $50 \pm 2.5$  mg) was loaded into individual reactors, after which the reactors were stored for 16 hours. The reactors were closed from the top to prevent air from leaking in and oxidizing the catalysts during the reactor storing step. After 16 hours, we added stirring beans to the individual reactors. 2 mL of a stock solution of oxalic acid (5 wt.%) in demineralized water was transferred to the individual reactors with a Gilson Pipetman Concept, motorized air-displacement pipette. Septa were placed on the individual reactors. The reactor lid was attached in a 'criss-cross' tightening sequence starting from the middle. A torque wrench (5 N m) was used to create an equal distribution of force among the different screws. The reactors were flushed 3 times with  $N_2$  (10 bar) and 3 times with  $H_2$  (10 bar). The reactors are filled with Hydrogen once before the reaction. This filling is performed at room temperature in a specially build system. To account for the pressure, increase with increasing temperature, the required pressure at room temperature is calculated and added to the reactors. In our case we aimed for 100 bar hydrogen at reaction conditions therefore we filled the reactors with 79 bar hydrogen at room temperature.

To perform the reaction, the BATCHINGTON system is first calibrated for the desired temperature. This is done using thermocouples for each of the 12 reactors and three blocks. The mean deviation



between the individual reactors is 1°C and the maximum deviation is 1.5°C. The required settings are then applied one hour before the reaction is started to have the system in equilibrium. At the reaction start, all three reactor assemblies are inserted into the heating block. In this research project, we performed the reaction for 2, 4 and 6 hours. This means we removed the first reactor assembly after two hours, the second after four and the last block after six hours. Once removed from the heating block, the reaction was quenched by dropping the reactor assemblies in an ice bath. After cooling down, the reactor assemblies were depressurized by carefully opening the screws and slowly letting the remaining pressurized gas escape. The catalyst in the reactor was separated by centrifugation. Each sample was then removed from the reactor with a syringe and needle. The remaining catalyst particles still present in the liquid were filtered with a screw-on filter for the syringe as shown in Figure S14.

**Figure S14** Work-up of samples: On the left is shown how the samples are removed from the reactors using a syringe and needle. Followed is filtration with a screw-on filter as shown on the right.

### 4.3 Reaction conditions for carboxylic acid reduction catalysts test

We tested the in-house prepared catalysts reported for carboxylic acid reduction including polymeric ruthenium catalysts in carbon and Al<sub>2</sub>O<sub>3</sub>, ruthenium dimers on carbon, Ti<sub>3</sub>C<sub>2</sub> and Ti<sub>2</sub>C MXenes, CuMg on carbon, In<sub>2</sub>O<sub>3</sub>, and NiFe on carbon in the Batchington reactor system at Avantium.<sup>8</sup> We prepared the reactors as described in S.I. 4.2 and tested the catalysts under the following conditions:

*Temperature = 75°C, Pressure = 80 bar H<sub>2</sub>, Substrate = Oxalic Acid (5 wt.%) in demineralized water (2 mL), Catalyst/Support Loading = 50 mg (pre-reduced in H<sub>2</sub> ex-situ at 350°C for 3 h and in-situ at 200°C for 2 h), Stir rate = 800 rpm, Time = 2, 4 and 6 hours.*

After the reaction, the samples were filtered with a syringe filter as described in S.I. 4.2 and measured using LC as described in S.I. 5.6.

### 4.4 Reaction conditions for an active metal test

We tested in-house made catalysts with different active metals including ruthenium, scandium, nickel, copper, cobalt, platinum, palladium, and rhenium in the Batchington reactor system at Avantium.<sup>8</sup> We prepared the reactors as described in S.I. 4.2 and tested the catalysts under the following conditions:

*Temperature = 75°C, Pressure = 80 bar H<sub>2</sub>, Substrate = Oxalic Acid (5 wt.%) in demineralized water (2 mL), Catalyst/Support Loading = 50 mg (pre-reduced in H<sub>2</sub> ex-situ at 350°C for 3 h and in-situ at 200°C for 2 h), Stir rate = 800 rpm, Time = 2, 4 and 6 hours. For the palladium catalyst, all reaction times are 6h but temperatures have been varied from 75 °C, 100 °C and 125 °C.*

After the reaction, the samples were filtered with a syringe filter as described in S.I. 4.2 and measured using LC as described in S.I. 5.6.

#### 4.5 Reaction conditions for the carbon support test

We tested in-house made ruthenium catalyst using eight different commercial carbon supports including carbon supplied by Norit Co. (SX Plus, R1 extra, RO-0.8, ROW-0.8, DARCO G60), Pica USA (PICATAL) and Fisher chemicals (FISHER) in the 100 mL Hastelloy reactor at Seton Hall University. The reactor and catalyst were prepared as described in S.I. 4.1 and the catalysts were tested under the following conditions:

*Catalyst = 1.175g of catalyst reduced at 300 °C for 3h then pre-reduced in the reactor at 100 °C; Substrate = 41.5 g of 10 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure = 100 bar H<sub>2</sub>; Temperature = 75 °C; Reaction time = 21 hours.*

In the 100 mL, we took samples every hour for the first 6 hours. The samples were diluted, and an internal standard was added before measuring them in the LC following the procedure in S.I. 5.6.

#### 4.6 Reaction conditions for metal oxide and MAX phase support test

We tested in-house made ruthenium catalysts prepared on seven different supports including carbon, MAX phase, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, CeO<sub>2</sub> and ZeO<sub>2</sub> in the Batchington reactor system at Avantium.<sup>8</sup> We prepared the reactors as described in S.I. 4.2 and tested the catalysts under the following conditions:

*Temperature = 75°C, Pressure = 80 bar H<sub>2</sub>, Substrate = Oxalic Acid (5 wt.%) in demineralized water (2 mL), Catalyst/Support Loading = 50 mg (pre-reduced in H<sub>2</sub> ex-situ at 350°C for 3 h and in-situ at 200°C for 2 h), Stir rate = 800 rpm, Time = 2, 4 and 6 hours.*

After the reaction, the samples were filtered with a syringe filter as described in S.I. 4.2 and measured using LC as described in S.I. 5.6.

#### 4.7 Reaction conditions for commercial catalyst test

We tested in-house made ruthenium catalyst using eight different commercial carbon supports in the 100 mL Hastelloy reactor at Seton Hall University. The reactor and catalyst were prepared as described in S.I. 4.1 and the catalysts were tested under the following conditions:

*Catalyst = 1.175g of catalyst reduced at 300 °C for 3h then pre-reduced in the reactor at 100 °C; Substrate = 41.5 g of 10 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure = 100 bar H<sub>2</sub>; Temperature = 75 °C; Reaction time = 21 hours.*

In the 100 mL, we took samples every hour for the first 6 hours. The samples were diluted, and an internal standard was added before measuring them in the LC following the procedure in S.I. 5.6.

#### 4.8 Reaction conditions for thermal stability test

We performed two tests of thermal stability of oxalic acid in the absence of catalyst at Seton Hall University using the 100 mL Hastelloy reactor. Initially, we used three temperatures from 140 °C to 170 °C with exact conditions:

*No catalyst; Temperature = 170 °C, 150 °C and 140 °C. Pressure (H<sub>2</sub>) = 70 bar, feed 5 wt.% aqueous oxalic acid 41.5 g (23 mmol oxalic acid), stir rate 800 RPM.*

In a second test we tested the thermal decomposition of oxalic acid with a 5 wt.% Ru/C (Johnson Matthey, C4198) catalyst at different temperatures in a 100 mL Hastelloy reactor using the following conditions:

*No catalyst; Temperature = 170 °C, 150 °C and 140 °C. Pressure (H<sub>2</sub>) = 100 bar, feed 5 wt.% aqueous oxalic acid 41.5 g (23 mmol oxalic acid), stir rate 800 rpm.*

For both experiments, the product composition was analysed by HPLC (S.I. 5.6) and a sample from the gas phase (at 21 h reaction time) was analysed qualitatively by GC-MS (S.I. 5.5).

#### **4.9 Reaction conditions for reaction temperature tests**

After testing the thermal stability, we investigated the ideal reaction temperature for the oxalic acid reduction in presence of a Ru/C catalyst in different temperature ranges in the 100 mL Hastelloy reactor at Seton Hall University. The first test covered a temperature range from 75-130 °C and the following conditions:

*Catalyst = 0.275g (0.45g for 75°C) of 5 wt.% Ru/C (JM, Type 5R600) catalyst, reduced at 250°C no pre-reduction in the reactor; Substrate = 41.5 g of 5 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure = 100 bar H<sub>2</sub>; Temperature = 75 °C – 130 °C; Reaction time = 21 hours.*

The second test covered at a temperature range of 75 – 105°C, higher oxalic acid concentration and catalyst loading:

*Substrate = 41.5 g of 10 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure = 100 bar H<sub>2</sub>; Temperature = 75 °C – 105 °C; Reaction time = 21 hours.*

For both experiments, samples were taken every hour for the first 6 hours and then two samples were taken at 20 and 21 hours. The samples were diluted, and an internal standard was added. Analysis was performed using the HPLC protocol found in S.I. 5.6.

#### **4.10 Reaction conditions for hydrogen pressure test**

We tested the influence of hydrogen pressure on oxalic acid reduction with a commercial catalyst in the 100 mL Hastelloy reactor at Seton Hall University. The reactor and catalyst were prepared as described in S.I. 4.1 and the catalysts were tested under the following conditions:

*Catalyst = 1.125g of 5 wt.% Ru/C (JM, Type 5R600) reduced at 300 °C for 3h then pre-reduced in the reactor at 100 °C; Substrate = 41.5 g of 25 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure = 50 - 135 bar H<sub>2</sub> or 40 bar Argon; Temperature = 75 °C; Reaction time = 21 hours.*

We took samples every hour for the first 6 hours. The samples were diluted, and an internal standard was added before measuring them in the LC following the procedure in S.I. 5.6.

#### **4.11 Reaction conditions during Metal loading testing**

We tested the influence of metal loading on the catalyst with three different commercial catalysts in the 100 mL Hastelloy reactor at Seton Hall University. The reactor and catalyst were prepared as described in S.I. 4.1 and the catalysts were tested under the following conditions:

*Catalyst = 1.125 g of 5 wt.% Ru/C (JM, Type 5R600), 7.5 wt.% Ru/C (JM, Type D102023-7.5), 10 wt.% Ru/C (JM, Type D101023-10), reduced at 300 °C then pre-reduced in the reactor at 100 °C; Substrate = 41.5 g of 25 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure = 100 bar H<sub>2</sub>; Temperature = 75 °C; Reaction time = 23 hours.*

We took samples every hour for the first 6 hours and after 21, 22 and 23 hours. The samples were diluted, and an internal standard was added before measuring them in the LC following the procedure in S.I. 5.6.

#### 4.12 Reaction conditions during reactant concentration testing

We tested the influence of oxalic acid concentration on the catalyst commercial catalyst in the 100 mL Hastelloy reactor at Seton Hall University. The reactor and catalyst were prepared as described in S.I. 4.1 and the catalysts were tested under the following conditions:

*Catalyst = 0.546 g of 5 wt.% Ru/C (JM, Type 5R600), reduced at 300 °C then pre-reduced in the reactor at 100 °C; Substrate = 41.5 g of 10-20 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure = 100 bar H<sub>2</sub>; Temperature = 75 °C; Reaction time = 20 hours.*

We took samples every hour for the first 6 hours and after 21, 22 and 23 hours. The samples were diluted, and an internal standard was added before measuring them in the LC following the procedure in S.I. 5.6.

Due to the limited solubility of oxalic acid, we decided to use oxalic acid concentrations of 5 wt.% for the catalyst screening. Higher concentrations and the potential of oxalic acid precipitation make accurate product analysis challenging in the high-throughput Batchington system.<sup>8</sup>

#### 4.13 Reaction conditions during catalyst reduction tests

We tested the influence of oxalic acid concentration on the catalyst commercial catalyst in the 100 mL Hastelloy reactor at Seton Hall University. The reactor and catalyst were prepared as described in S.I. 4.1 and the catalysts were tested under the following conditions:

*Catalyst = 0.546 g of 5 wt.% Ru/C (JM, Type 5R600), reduced at 300-430 °C then pre-reduced in the reactor at 100 °C; Substrate = 41.5 g of 25 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure = 100 bar H<sub>2</sub>; Temperature = 75 °C; Reaction time = 7 hours.*

We took samples at 4, 6 and 7 hours. The samples were diluted, and an internal standard was added before measuring them in the LC following the procedure in S.I. 5.6.

#### 4.14 Reaction conditions during bimetallic-catalyst tests

We tested in-house made bi-metallic ruthenium on carbon catalysts for which we added silver (Ag), palladium (Pd), Rhenium (Re), Platinum (Pt), Gold (Au), Tin (Sn), Antimony (Sb) or Bismuth (Bi) as second metal. We the catalysts in the 100 mL Hastelloy reactor at Seton Hall University. The reactor and catalyst were prepared as described in S.I. 4.1 and the catalysts were tested under the following conditions:

*Catalyst = 2 g of catalyst, reduced at 300 °C then pre-reduced in the reactor at 100 °C; Substrate = 41.5 g of 10 wt.% aqueous oxalic acid; Stir rate = 400 rpm; Pressure = 100 bar H<sub>2</sub>; Temperature = 75 °C; Reaction time = 6 hours.*

We took samples every hour for the first 6 hours. The samples were diluted, and an internal standard was added before measuring them in the LC following the procedure in S.I. 5.6.

## 5 Product analysis

### 5.1 Analysis of samples from Hastelloy experiments

For the initial experiments, all products were analysed with gas chromatography for the volatile components (GC) and high-pressure liquid chromatography (HPLC) for the obtained liquids. Later, we only analysed the obtained liquids.



## 5.2 Analysis of liquid samples from Batchington experiments

For the product analysis, we used liquid chromatography. Samples were prepared by diluting stock solutions to concentrations of 0.67 mg stock mL<sup>-1</sup> in demineralized water. An Agilent Technologies 1260 Infinity II was used to measure the concentration of oxalic acid, glycolic acid, glyoxylic acid, acetic acid, and ethylene glycol.

To confirm the results by a second method we used quantitative liquid phase IR measurements in random order. The results for both methods agreed.

## 5.3 Liquid cell infrared spectroscopy

We used a SmartSeal liquid cell from PIKE technologies with CaF<sub>2</sub> windows and a cavity thickness of 0.025 mm. The spectra were recorded with a Varian 660-IR spectrometer. The exact analysis theory, procedure and calculations are described in the supporting information of chapter 3 (S3.2.1 and S3.2.2)

## 5.4 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:

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

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

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

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

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

## 5.5 Gas chromatography

At Seton Hall University a gas chromatograph from Hewlett Packard was used to analyse the gases produced during the reaction. The exact conditions are listed in Table S6.

**Table S6:** Conditions used for gas chromatography at Seton Hall university

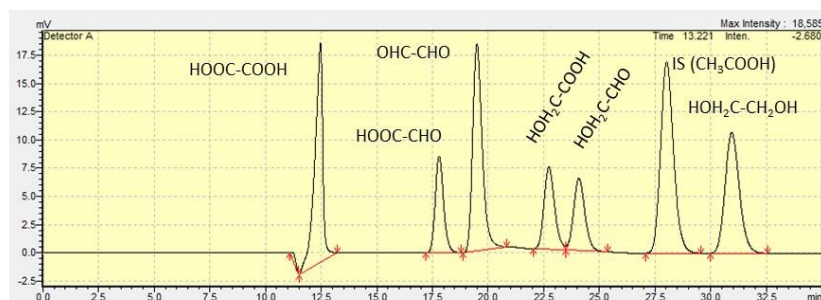
Instrument	HP 5890 with FID detector and an electronic integration
Column	Capillary column RTX-1701, 30 m x 0.32 mm ID x 1.50 m (RESTEK).
Split vent:	20 mL/min
Airflow:	300 mL/min
Hydrogen flow:	30ml/min
Head pressure:	15 psi
Signal range:	7
Injection volume	0.5mkl
Temperature program:	
Initial temperature:	60 °C, hold 1 min, ramp 15 °C/min to 90 °C, hold 2 min,
Program A:	ramp 20°C/min to 200°C hold 6min.
Injection and detector temp:	200 °C and 220 °C
Internal standard:	Diethylene glycol Dimethyl ether (DEG-DME, Diglyme) in water ( 0.100 g/g)

## 5.6 Liquid chromatography

At Seton Hall University the samples were prepared by diluting the samples in the mobile phase and adding internal standards. A Shimadzu HPLC instrument with RID detection was used to measure the concentration of oxalic acid, glycolic acid, glyoxylic acid, acetic acid, and ethylene glycol. The exact conditions are listed in Table S7. An example chromatogram is shown in Figure S15.

**Table S7:** Conditions used for liquid chromatography at Seton Hall University

Instrument	Shimadzu HPLC instrument with RID detection
Column	BIO-RAD, Aminex HPX-87H column, 300X7.8 mm
Oven temperature	70 °C
Isocratic flow	0.3 mL/min
Mobile phase	0.005 M H <sub>2</sub> SO <sub>4</sub>
Internal standard	The acetic acid in the mobile phase (~100 mg/mL)
Sample preparation	100 µl of the reaction solution, 50 µl of internal standard and makeup to 1 mL with the mobile phase.



**Figure S15** Exemplary HPLC trace of a standard mixture of components of interest recorded by RI detection.

At the University of Amsterdam (use of Batchington), the samples were prepared by diluting the samples in demineralized water to a theoretical stock solutions concentration of 0.67 mg stock mL<sup>-1</sup>. 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 H<sub>2</sub>SO<sub>4</sub> in MilliQ water (flow rate: 0.6 mL/min, 30 °C) as the mobile phase. All conditions are listed in Table S8.

**Table S8:** Conditions used for liquid chromatography at Seton Hall University

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 <sub>2</sub> SO <sub>4</sub>
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 <sup>-1</sup>

## 5.7 Inductively coupled plasma optical emission spectroscopy

We analysed liquid samples for the presence of Cr, Fe, Ni, Zn, Mo, and Ru after performing a reaction in the Teflon lined Batchington reactor. The goal was to evaluate the potential leaching of the reactor material and catalyst by oxalic acid. The goal was to evaluate the potential leaching of ruthenium from the 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.

## 6 Catalyst Characterization

### 6.1 X-ray diffraction (XRD)

Before powder-XRD measurements, we crushed the catalysts using a ceramic mortar. Measurements were generally performed at an angle ( $2\theta$ ) of 3 to 90 degrees at a rate of  $1^\circ/\text{min}$  and a step size of  $0.05^\circ$ . We used a MiniFlex-II diffractometer from Rigaku with a Cu  $K\alpha$  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.

### 6.2 Adsorption measurements after Brunauer-Emmett-Teller (BET)

Physical adsorption measurements were performed using a BELSORP-Max II. A flow of  $N_2$  was used adsorptive to determine the pore volume and surface of a measured catalyst. The samples were pre-treated in a vacuum at  $200^\circ\text{C}$  for 6 hours. The adsorption temperature was 77 K.

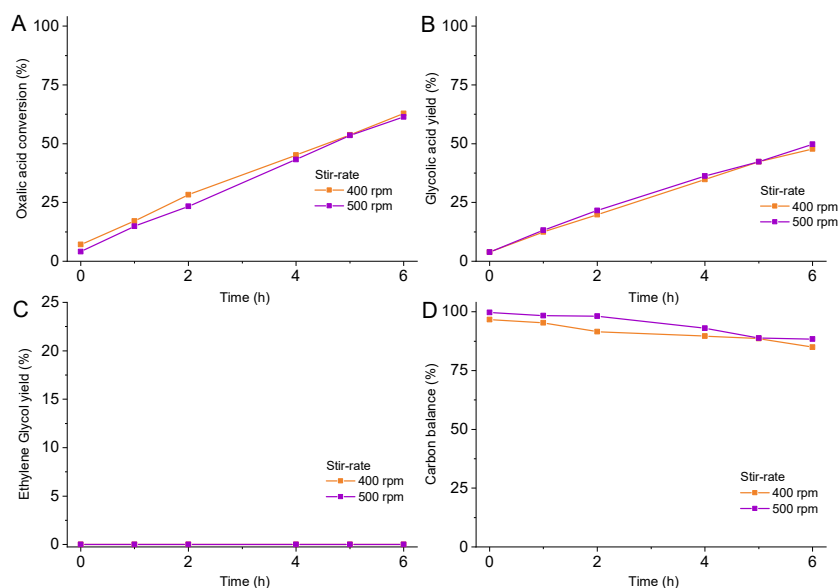
## 7 Control experiments

### 7.1 Reactor materials

As oxalic acid is a good complexing agent, it can potentially leach metals from the reactor components or the catalyst. To get an idea for leaching, we analysed the reaction solution after reaction of 25 wt% OA in water in a Hastelloy reactor for 2 hours at  $65^\circ\text{C}$  with ICP-OES. We observed strong leaching of chrome, iron, and nickel but no leaching of ruthenium from the catalyst. To study the effect of these metals in the solutions we added three times the amount found in the leaching experiments of Cr, Fe, Ni to the starting solution. We noticed inhibition of the initial reaction rate by 10-15 %. To prevent leaching, we tested non-metallic liners for the Hastelloy reactor and avoided any metal parts contacting the reaction solution. We compared the performance of the reactor with and without Teflon and glass liners and found better catalyst stability with liners. We performed the reaction six times consecutively with the same solvent to amplify the potential effect of leaching. For each of the six reactions, we added fresh reactant solution but kept the catalyst in the reactor. The Teflon liners worked best to preserve the catalytic activity as the high over-reduction to ethylene glycol. Metal ions from the reactor corrosion at ppm levels (Ni, Cr, Mo) might be inhibiting the catalyst performance and only Teflon liners provide adequate protection. We subsequently replaced all remaining Hastelloy parts from contact with the reactant and replaced the impeller with a Teflon coated magnetic stirring bean. These latter changes did not show any significant difference in reactor performance.

### 7.2 Mass-transfer limitations

Before testing various catalysts, we tested various stirring rates from 100 to 500 rpm for the 100 mL Hastelloy and 400 to 1000 rpm for the 2 mL tantalum Batchington reactors to avoid mistaking mass-transfer limitations for differences in catalytic activity. The different ranges were based on previous experience with the reactor systems and are not similar as the stir rate is directly related to the reactor design and layout. We settled on using the stirring rate above the rate at which we did not see any improvement anymore which was 400 rpm for the Hastelloy and 800 rpm for the Batchington reactors. The example in Figure S16 shows that no improvement is gained at stir-rates above 300 rpm and therefore mass-transfer limitations could be excluded. Overall, we see that the stir rate influenced the overall conversion but the selectivity towards glycolic acid (85-90 %) and the production of acetic acid (10-15 %) was unaffected.



**Figure S16:** Influence of stir-rate in reduction of 10 wt.% oxalic acid in aqueous feed on A) oxalic acid conversion, B) Glycolic acid yield, C) Ethylene Glycol yield, and D) Carbon balance. All reactions were performed using a 100 mL all Hastelloy reactor filled with 1.125g of 5 wt.% Ru / C (JM, Type 5R600) catalyst, reduced at 300 °C then pre-reduced in the reactor at 100 °C; Feed: 10 wt.% aqueous oxalic acid; Stir rate: 300 rpm and 400 rpm; Pressure: 100 bar H<sub>2</sub>; Temperature 75 °C

### 7.3 Support Adsorption – Magnesium Oxide (MgO)

Since BATCHINGTON experiments with magnesium oxide supports showed low carbon balances, we experimented to determine if the adsorption of oxalic acid by the support was happening. Magnesium Oxide (MgO; 0.25 g) was dissolved in oxalic acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>; 10 mL; 5 wt.%) in a round bottom flask. The solution was stirred for 6 hours. At time intervals of 2-, 4-, and 6-hours a liquid sample was removed from the solution. The samples was then filtered using a syringe M-filter and analyzed with HPLC.

### 7.4 Teflon Liner Adsorption

A control experiment was performed to examine if the Teflon liners used during BATCHINGTON reactions adsorbed oxalic acid or any of the potential reaction products. Solutions were prepared of the following chemicals in demineralized water: Oxalic Acid (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>; 50 g l<sup>-1</sup>), Glycolic Acid (C<sub>2</sub>H<sub>4</sub>O<sub>3</sub>; 42.2 g l<sup>-1</sup>), Glyoxylic Acid (C<sub>2</sub>H<sub>2</sub>O<sub>3</sub>.H<sub>2</sub>O; 41.1 g l<sup>-1</sup>), Acetic Acid (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>; 33.4 g l<sup>-1</sup>), Ethylene Glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>; 34.5 g l<sup>-1</sup>). Two milliliters of each solution was transferred to a separate Teflon liner. At time intervals of 2-, 4-, and 6-hours liquid sample was removed from the different solutions and measured using LC.

### 7.5 Syringe M-Filter control

To examine if the filter we used during the preparation of HPLC samples did not block oxalic acid or any other reaction products aside from the solid catalyst, a control experiment was performed.

## 8 Cost price estimation

For the analysis of the cost price of each of the pathways we have used the steps shown in Figure S17 to calculate an overall price. The aim was to replace the fossil-based feedstocks with CO<sub>2</sub> and water based feedstock with energy provided by renewable electricity.

The cost price was estimated from the energy cost, processing fee for each step and the feedstock cost. In our case we assume a free feedstock cost for water and CO<sub>2</sub> used in this process to simplify the approach.

This leaves us with the estimation of the cost price consisting of:

$$\text{Cost price} = \frac{\text{Energy input per ton of product}}{\text{Power efficiency} \times \text{Process efficiency}} + \text{Processing feed} \times \text{Number of Steps}$$

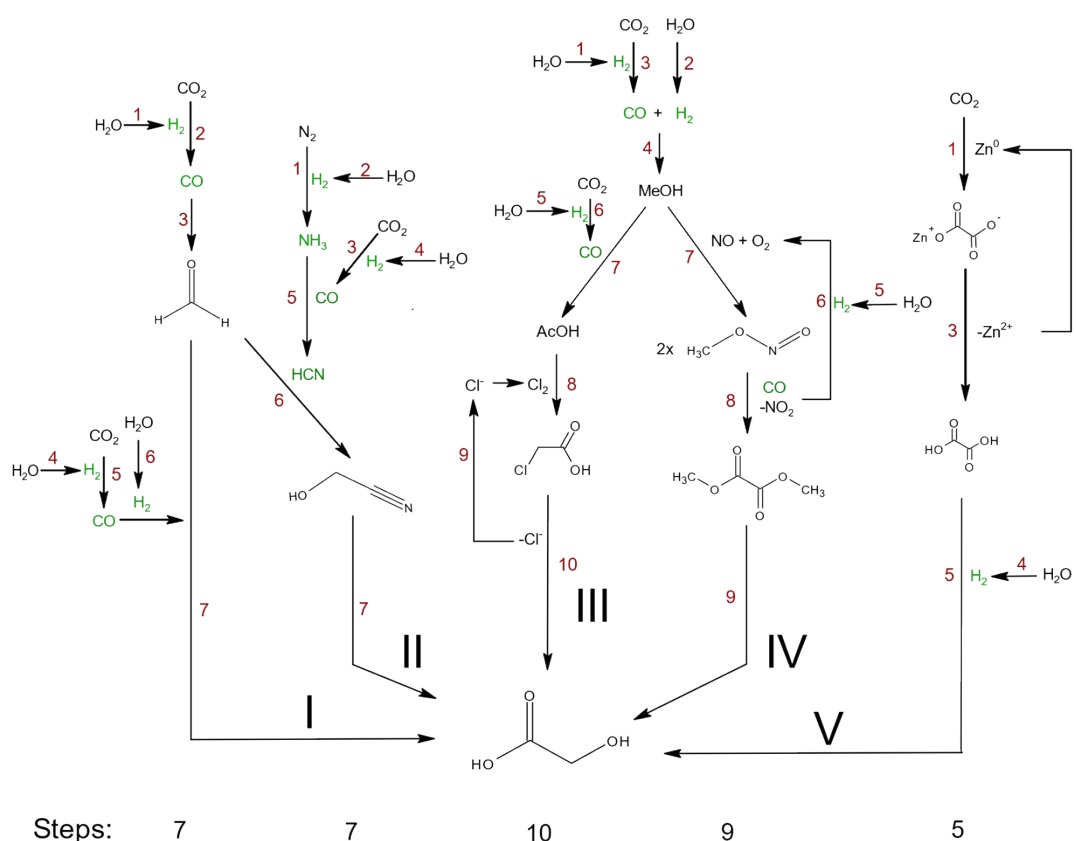
The process efficiency was calculated from the Yield per step and number of steps:

$$\text{Process efficiency} = \text{Yield per step}^{\text{Number of steps}}$$

The requires energy input was calculated from the standard reaction enthalpy with:

$$\text{Energy input per ton} = \frac{\Delta_{\text{rxn}}H}{\text{Molar mass product}}$$

We assumed 50 \$/ MWH for electricity based on average prices in the EU from 2015-2021; a yield per step of 98%; A power efficiency of 50% for a mature process and used the standard enthalpy of reaction for the formation of glycolic acid from 2 CO<sub>2</sub> and 2 H<sub>2</sub>O molecules with Δ<sub>rxn</sub>H of 775.7 kJ/mol



**Figure S17** Overview of routes and steps required to produce Glycolic acid from CO<sub>2</sub> and water following I: Carbonylation of formaldehyde, II: Glyconitrile route, III: Chloroacetic acid route IV: Methyl glycolate route, V: Oxalic acid hydrogenation. Each step in the routes is indicated by a red coloured number.

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