SUPPLEMENTARY INFORMATION

SI.1 | Experimental

SI.2 | Liquid-phase reaction

Materials

The reactant solutions were prepared by 5% ethanol (absolute, 100%, VWR chemicals) or acetaldehyde (anhydrous, ≥99.5%, Sial) diluted in distilled water, unless otherwise specified.

The catalyst used in the acetaldehyde and ethanol oxidation was the commercial 1%Au/TiO_2 AURO*lite*™ from Strem chemicals, inc. The properties of the catalyst are presented on previous work.[1] The catalyst grain size in the catalyst bed was 125-250 μm. The fixed-bed during the 'blank' tests in the flow reactor was SiC (abcr, medium, 120 grid); no solids were added in the batch system.

The radical scavenger, 2,6-Di-tert-butyl-4-methylphenol (BHT, ≥99.0%, Sigma-Aldrich) was added in the 'blank' tests in the batch system in a molar ratio with acetaldehyde of at least 1.5:1.

Flow reactor

The continuous flow experiments were tested in a custom-made trickle-flow reactor. Oxygen was supplied from a mass flow controller by Bronkhorst, calibrated for oxygen flow at 20 bar. The liquid was introduced with a KNAUER AZURA® P 4.1S high-pressure liquid chronography pump, equipped with a titanium 10 ml pump head. Spring check valves by Swagelok prevented backflow. The two phases were met and introduced to the reactor via Swagelok 1/8" stainless steel tubing. Before entering the reactor, the reactant stream was preheated at about 393 K. The catalyst bed (150 ± 0.1 mg catalyst diluted 1:1 with SiC) was fixed with quartz wool inside a 4 mm inner diameter stainless steel tube (reactor); The bed was stabilised in the middle of the heating zone by a hollow stainless steel rod of ca. 1.5 outer diameter, which ensured a constant height and minimum back pressure (maximum 0.2 bar). A custom-made metal plate heater heated the reactor. An Equilibar® U3L Series precision back-pressure regulator, equipt with a PTFE glass laminated diaphragm, maintained the pressure of the system. The back-pressure regulator was controlled by a Bronkhorst process pressure controller EL-PRESS P-802CV. The flows, temperature of the heater, and the pressure of the back pressure regulator were all recorded and controlled via a custom-made LabVIEW™program. The temperature of the catalyst bed was recorded with a K-type thermocouple. The system pressure was also recorded before the reactor with a Keller Digital Manometer dV-2 PS. The product stream was cooled down below 280 K by a dry ice-water bath and introduced to a 25 mL two-neck pear-shaped flask, which allowed the separation of gas and liquid. The liquid sample was collected for analysis into a 2 mL vial and sealed.

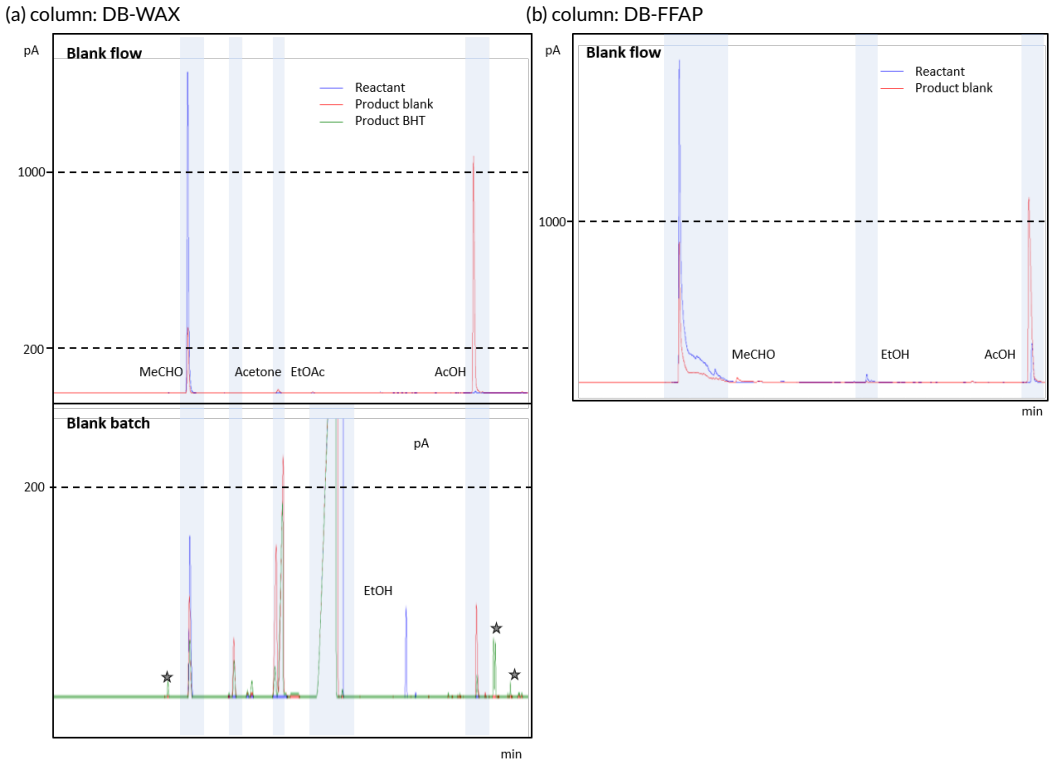
Batch reactor

The batch experiments were conducted in a series of Berghof BR-25 autoclaves, as reported elsewhere.[1] In the 'blank' tests, the acetaldehyde solution was placed in an empty Teflon™ coated reactor. Then, a magnetic stirrer was added, and the autoclave was closed and sealed with the help of a Teflon™ O-ring. After that, oxygen was introduced until the pressure reached to 15 bar. Each reactor was stirred and heated with a Heidolph MR3002 apparatus, which was controlled by a BTC-3000 Berghof controller. At the end of the reaction, the autoclaves were cooled below 280 K before the pressure was released. The liquid sample was collected for analysis into a 2 mL vial and sealed.

Product analysis

The liquid products were analysed off-line by an Agilent 7890A gas chromatographer (GC) equipped with a flame ionisation detector (FID). During the analysis, 0.5 μL of sample was injected at 343 K and carried in a 2 mL/min helium flow through the column DB-WAX. The temperature of the column was constant at 313 K for 2 min and was then heated at 8 K/min up to 409 K. The FID was fed by 30 mL/min hydrogen mixed in 400 mL/min air at 573 K. The molar concentration of each component was determined using linear regression of calibration standards. The quantification of the compounds was used to determine the ethanol conversion and the product selectivity. The reactant concentration taken into account was that determined by GC analysis of the used reactant solution; it was compared with the theoretical concentration.

SI.3 | Product analysis



SUPPLEMENTARY FIGURE 1 Chromatographs of representative samples. a) Analysed in DB-WAX after a blank test in flow (top) and in batch (bottom). b) Analysed in a DB-FFAP after blank test in flow. The tests in the presence of the scavenger BHT is shown in green. Additional, unidentified peaks are marked with start. Acetone is used to clean the sampling needle.

Test	Concentration (mol/L)					
	MeCHO in	MeCHO out	EtOH in	EtOH out	AcOH in	AcOH out
flow / MeCHO (a-top)	1.09	0.16	0	0	0.01	0.66
flow / EtOH	0.00	0.00	0.99	0.92	0.01	0.00
batch / N2 - MeCHO	1.23	0.86	0.00	0.00	0.00	0.02
batch / MeCHO-H2O-EtOH (a-botom)	1.59	0.95	n/a	n/a	0.00	0.54
batch / BHT (a-botom)	1.59	0.64	n/a	n/a	0.00	0.09

SUPPLEMENTARY TABLE 1 Concentration of reactant and product of representative reaction conditions. The consecrations are defined by the GC analysis as shown in supplementary figure 1.

SI.4 | Evaporation of acetaldehyde

Acetaldehyde is a very volatile compound, with a boiling point of about 293 K. The 5%MeCHO-H_2O (0.2 mol%) mixture, used in this study, has a boiling point of about 296 K. To minimise evaporation during handling, sampling, and analysis, we took the following measures:

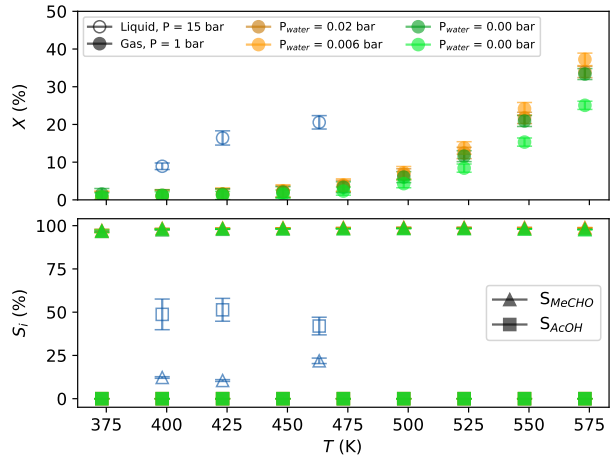
- The acetaldehyde and the equipment used to prepare the reaction solutions were cooled with dry ice before use.
- The product stream in the flow was continuously cooled before sampling.
- The batch reactors were cooled in an ice bath below 280 K before opened.
- The liquid samples were collected and introduced in sealed GC vials with the help of a one-use syringe and needle.

Nonetheless, we observed significant evaporation, which contributes to the increase of the apparent conversion. For example, when there is no reaction, when operating under nitrogen (supplementary table 1), the evaporation at 423 K and 15 bar (supplementary table 1) was about 30%. We expect similar evaporation level in the flow system when assuming that the converted acetaldehyde forms only liquid products and no combustion is possible under those conditions. The evaporation level does not affect the reaction kinetics: evaporation during the preparation of the reactant mixture is taken into account in the calculations, by analysing each reactant mixture and both the batch and flow reactors are leak-tested before each measurement. However, we expect high evaporation of acetaldehyde during cooling and sampling. That effect influenced the apparent conversion but not the concentration of the non-volatile products, such as acetic acid.

Reactor	Res. time (min)	Source	*T* (K)	*p* (bar)	AcOH Yield (%)
Flow No.1	empty tube	1%MeCHO/dist. H_2O	373	15	3.5
Flow No.1	empty tube	1%MeCHO/dist. H_2O	423	15	26.3
Flow No.5	1 (0.15 g SiC)	5%MeCHO/dist. H_2O	423	15	48.9
Flow No.5	2 (0.3 g SiC)	5%MeCHO/dist. H_2O	424	15	77
Batch No.24	120	5%MeCHO/dist. H_2O	373	15	76
Batch No.22	240	5%MeCHO/dist. H_2O	423	15	93
Flow No.5	2 (0.3 g SiC)	5%MeCHO/H_2O (Fisher, W6-121)	423	15	81.0

SUPPLEMENTARY TABLE 2 Acetaldehyde oxidation operating in various reactors and by using alternate regent sources

SI.5 | Gas and liquid phase oxidation



SUPPLEMENTARY FIGURE 2 The catalytic behaviour of liquid phase The effect of temperature on the oxidation of different ethanol concentration mixtures and pressures. Top: Ethanol conversion of 5% EtOH/H_2O at 15.0 bar and 28 and 100% at 1.0 bar. Bottom: Selectivity of acetaldehyde (squares) and acetic acid (triangles).

Experimental conditions of gas-phase experiments

Reactor

The gas-phase measurements were performed in a continuous-flow fixed-bed quartz reactor under ambient pressure. All the gases used were from Messer at 99.999% purity. About 2 mg of catalyst were mixed with quartz sand to a total of 20 mg catalyst bed. Prior to each reaction, the catalyst bed was pre-treated in two steps: First, it was oxidised at 673 K, heating step 10 K/min, for 30 minutes under a 50 mL/min flow of 20%O_2/He. Then it was cooled down to 573 K, where it was reduced for 30 minutes under a 50 mL/min flow of 5% H_2. The reactions wed performed as discribed in table 3.1.

Product analysis

The product stream was on-line analysed in an Agilent 7890A GC, equipped with an FID and a TCD detector. During the analysis, 1000 μL of sample were introduced at 383 K. The inlet was operated in splitless mode. Carrier gas (He) flow on column was kept at 6 mL with the following method: 313 K for 4.5 minutes. followed a rapid heating (100 K/min.) to 473 K which was kept for 11 minutes. The FID Detector was set at 523 K with a 40 mL/min H_2 and 400 mL/min air flow. The TCD was set at 493 K with a 20 mL/min reference flow. The molar concentration of each component was determined using linear regression of calibration standards.

REFERENCES

[1] Mostrou S, Sipcz T, Nagl A, Fdi B, Darvas F, Föttinger K, et al. Catalytic oxidation of aqueous bioethanol: An efficient upgrade from batch to flow. React Chem Eng 2018 oct;3(5):781–789. http://xlink.rsc.org/?DOI=C8RE00054A.

Conditions	O_2 flow (mL/min)	EtOH flow (mL/min)	H_2O flow (mL/min)	Total flow (mL/min)	*T* Saturator (K)
3.1	0.55	0.52	-	49.57	294
3.2	0.55	0.51	0.30	51.32	280
3.3	0.55	0.52	0.98	50.55	294

SUPPLEMENTARY TABLE 3 Gas flows and saturator temperature at the different reaction conditions of the gas ethanol oxidation.